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ABSTRACT BOOK

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Introduction

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How to Use the Abstract Book

Refer to the Table of Contents to determine page numbers on which specific session abstracts begin. At the beginning of each session are headings that list session title, location and session chair. Starting times for presentations and paper numbers precede each paper title. The Author Index lists each author and the page number on which their abstract can be found.

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SII: Glass Physics

SIII: Glass Technology and Manufacturing

SIV: Emerging Applications of Glass

Monday, June 10, 2019

Opening Session

Room: Grand Ballroom A (mezzanine)
Session Chairs: Alicia Durán, Instituto de Ceramica y Vidrio (CSIC); Richard Brow, Missouri S&T; Liping Huang, Rensselaer Polytechnic Institute

9:45 AM

(ICG-PL-001-2019) The 2018 V. Gottardi Prize: Multicomponent Photonic Glasses and Fibers

S. Zhou*[1]

1. South China University of Technology, School of Materials Science and Engineering, China

Multicomponent glasses and fibers are considered to be the fundamental building blocks of the next-generation fiber photonics. In this talk, the recent progress in designs, fabrications and applications of selected materials for multicomponent optical glasses and fibers is introduced. In the first part of the talk, the typical microstructures represented by topological features, heterogeneities and locally crystallized domains are discussed. The preliminary results about the relation between the glass microstructure and its optical properties are introduced. In the second part, glasses and glass-ceramics with various optical functions, including photons generation, manipulation and detection are highlighted.

10:15 AM

(ICG-PL-002-2019) The 2019 V. Gottardi Prize: Toward intrinsic damage resistance and ductility in oxide glasses

M. Smedskjaer*[1]

1. Aalborg University, Department of Chemistry and Bioscience, Denmark

10:45 AM

(ICG-PL-003-2019) Woldemar A. Weyl International Glass Science Award: Metal-organic framework liquids, glasses and blends

T. Bennett*[1]

1. Cambridge University, United Kingdom

Crystalline solids dominate the field of metal–organic frameworks (MOFs), which are highly porous materials formed from the linking of metal nodes with organic linkers. In this family, which number of 70,000 structures, access to the liquid and glass states of matter are usually prohibited by relatively low temperatures of thermal decomposition. Recently, the group has demonstrated the melting three dimensional MOFs belonging to the zeolitic imidazolate framework (ZIF) family, of chemical composition $Zn(Im)_2$ ($Im - C_3H_3N_2$]. Cooling of these ZIF liquids yields glasses, which are chemically and structurally distinct from existing categories of melt-quenched glasses, and retain the basic metal–ligand connectivity of their parent crystalline frameworks. They possess continuous random networks, and may be thought of, using the data currently available to us, as hybrid equivalents of silica glass. These new families of metal-organic framework materials, called MOF-glasses and MOF-liquids, provide new opportunities to combine glass science with MOF chemistry. Examples of this, including the mixing together to MOF liquids to form MOF-blends, crystal-glass MOF composites and flux melted glasses are presented here.

11:30 AM

(ICG-PL-004-2019) George W. Morey Award: The architectured glass

H. Jain*[1]

1. Lehigh University, International Materials Institute for New Functionality in Glass, USA

Glass is most widely known to consumers as a transparent, hard solid; to artists and manufacturers as the material that can be formed into most complex shapes by a variety of thermal processes; and to glass scientists as an ever-relaxing metastable material. A combination of these unique characteristics offers opportunities to selectively design i.e. architecture the structure, hence the properties, of glass, which would be nearly impossible to accomplish in any other class of material. Furthermore, an architectured glass can exhibit active functionality in an otherwise inactive matrix. Such developments pave the way for transforming microelectronic chip into an integrated photonic chip made of optical circuits with multiple functionalities; for a novel grayscale photoresist; for lab-on-a-chip with multiple diagnostic tools; etc. We will explore the development of this paradigm for expanding the application space of glass, based on the fundamental understanding of the structural evolution under external stimuli (light, electron beam, temperature, electric field, mechanical stress). Examples from author's lab as well as from the literature will show that a stimulus can drive the structure toward the most stable single crystal state, or a less stable state with electronic and atomic defects, thus allowing a great degree of freedom for tuning the properties, even in opposite directions. Prospects of architectured glass for the future will be presented.

12:00 PM

(ICG-PL-005-2019) Stookey Lecture of Discovery: Formation of glass and ceramics by chemical polymerization and its effects on properties

B. Yoldas*[1]

1. Carnegie Mellon University, Dept. of Chemical Engineering, USA

Almost any type of oxide glass or ceramics can be made by non-thermal chemical reactions of metal organic compounds. At the heart of this process is the capability of metal alkoxides to form oxide networks by hydrolytic poly-condensation reactions at room temperature. This condensates then can be reduced to pure oxides around 500°C. The morphology and the stoichiometry of the resultant networks are subject to significant manipulation which allows one to introduce a spectrum of configuration variation. These variations show a surprising stability at high temperatures and a significant effects on the thermoplastic and photonic properties. In this presentation, the genesis and nature of the differences between the chemical and thermal formation of oxide networks as well as their effects on properties will be discussed.

SI: Glass Structure and Chemistry

Session 4: Chalcogenide Glass Structure and Chemistry I

Room: Arlington (mezzanine)
Session Chairs: Pierre Lucas, Univ of Arizona; Yong Gyu Choi, Korea Aerospace University

1:20 PM

(ICG-SI-001-2019) Switching between Crystallization from the Glassy to Crystallization from the undercooled Liquid Phase in the Phase Change Material $Ge_2Sb_2Te_5$ (Invited)

J. Pries[1]; P. Lucas[2]; M. Wuttig*[1]; S. Wei[1]

1. RWTH Aachen University, Germany
2. University of Arizona, Materials Science and Engineering, USA

Controlling crystallization kinetics is key to overcome the temperature-time-dilemma in phase change materials employed for data storage. While the amorphous phase must be preserved for more than 10 years slightly above room temperature to ensure data integrity, it must crystallize in less than 10 ns following a moderate temperature increase near 2/3 T_m to ensure rapid data transfer. Here we provide a calorimetric demonstration that this striking variation in kinetics involves crystallization occurring either from the glassy or the undercooled liquid state. Measurements of crystallization kinetics with heating rates spanning over 6 orders of magnitude

reveal a fourfold decrease in the activation barrier for crystallization upon the glass transition. This enables rapid crystallization and low power consumption above the glass transition temperature T_g. Moreover, highly unusual for glass-forming systems, fast crystallization is observed more than 50 °C below T_g, where the atomic mobility should be vanishingly small. These findings are related to the unique bonding mechanism that prevails in crystalline phase change materials but is not observed in GeSe.

1:50 PM

(ICG-SI-002-2019) Complementarity of experimental and theoretical approaches to solve the short- and intermediate range order in telluride glasses (Invited)

D. Le Coq*[1]; L. Bouëssel du Bourg[1]; H. Balout[1]; E. Bychkov[2]; C. Boussard-Pledel[1]; B. Bureau[1]; L. Le Pollès[1]; E. Furet[1]

1. University of Rennes, ISCR, France
2. Université du Littoral, France

The structure of pure chalcogenide glasses is mainly governed by covalent bonding but once other elements such halide, alkaline or earth-alkaline are added, a competition between ionic and covalent bonding occurs. In the case of tellurium halide (TeX) glasses, a Te-chain structure with terminal halide atoms was firstly supposed, but some high scale facility experiments evidence that their structural network is more complicated. In case of TeX glasses with X=Cl, the complementarity of Neutron and High-Energy X-ray diffractions is very interesting since the neutron coherent scattering lengths and the X-ray scattering factors are significantly different. Moreover, the molecular dynamics simulations performed on some specific compositions are also in good agreement with experimental data. Finally, solid-state NMR experiments and NMR parameters calculations allow validation of the presence of Te highly coordinated with Cl in these glasses. The effect on the structure of the size of the halide atom by replacing Cl by Br will be shown. Other telluride glass families, containing Ag and I exhibit a crossover between ionic and electronic conductivity. Structural considerations will be given by taking into account both structural and electrical data.

2:20 PM

(ICG-SI-003-2019) Diffraction patterns of amorphous materials as a series expansion of neighbor distribution functions

M. Micoulaut*[1]

1. Sorbonne Université, France

An exact analytical expression for the static structure factor S(k) in disordered materials is derived from Fourier transformed neighbor distribution decompositions in real space, and permits to reconstruct the function S(k) in an iterative fashion. The result is successfully compared to experimental data of archetypal glasses or amorphous materials (GeS_2, As_2Se_3, GeTe), and links quantitatively knowledge of structural information on short and intermediate -range order with the motifs found on the diffraction patterns in reciprocal space. The approach furthermore reveals that only a limited number of neighbor shells is sufficient to reasonably describe the structure factor for $k>2$ A^{-1}. In the limit of the high momentum transfer, the oscillation characteristics of the interference function are related with new informations on the short-range order of disordered materials.

2:40 PM

(ICG-SI-004-2019) A Review of Scanning Calorimetry and X-ray Diffraction Studies of Non-Crystalline Phases in Various Glass-Forming Chalcogenide Systems as Evidence for the Temperature and Compositional Dependence of Local Structural and Chemical Order

J. P. de Neufville*[1]

1. Eutectix, LLC, USA

In the early 1970's, Energy Conversion Devices, Inc. (ECD) was exploring the electronic and optical application of sputtered and evaporated multi-component chalcogenide semiconducting glasses. Beginning in the spring of 1970, the DOD, under its then Advanced Research Projects Agency (ARPA), funded three years of fundamental materials science research at ECD in an effort to expand the understanding of these apparently complex materials, both in bulk and thin film form. This talk will review a subset of those studies with a focus on showing how the compositional dependence of the glass transition temperature and the thermally induced reversible and irreversible structural rearrangements as explored over a continuous and wide range of compositions only accessible via the ultra-rapid quenching associated with sputter and evaporative deposition can provide insight regarding the local chemical order and its dependence on temperature and composition.

3:00 PM

(ICG-SI-005-2019) Structural and Thermal Properties of Sm^{3+} Doped Tellurite Glasses

H. R. Vemula*[1]; S. P. Prasad[2]

1. National institute of Technology Raipur, Department of Physics, India
2. National Institute of Technology Warangal, Department of Physics, India

Tellurite glasses being low phonon energy glasses are found to be suitable for several photonic applications due to their higher linear and nonlinear refractive indices, good rare earth ion solubility, large transparency window and low melting temperature. In recent years glasses doped with rare earth ions attracted more attention due to their potential applications in solid state lasers, full color display devices, fiber amplifiers and data storage devices. Among rare earth ions, Sm^{3+} ion has been considered as a promising candidate for the luminescence emission in orange spectral region. This manuscript reports the structural and thermal properties of Sm^{3+} doped heavy metal oxide tellurite glasses in the system of TeO_2-Sb_2O_3-WO_3. A series of glasses were prepared by standard melt quenching method by varying the concentration of Sm^{3+} ions (from 0.2 to 1.5 mol%). The glass samples were investigated by SEM-EDX, FTIR and Raman spectroscopy and DSC. Thermal properties of the glasses such as glass transition temperature and crystallization temperatures were determined using DSC profiles and were discussed in terms of the varying concentration of Sm^{3+} ions. Results from FTIR and Raman spectra reveals that the glasses are built with TeO_3, TeO_{3+1}, TeO_4, WO_4 and WO_6 structural units. The transformation of structural units from TeO_4 to TeO_{3+1} and TeO_3 with varying concentration of Sm^{3+} ions was discussed in detail.

3:40 PM

(ICG-SI-006-2019) More Than One Way to Make a Glass: A Comparative Investigation of Sodium Oxy-thio Phosphate Glasses

A. Joyce*[1]; S. Kmiec[1]; S. W. Martin[1]; D. Bayko[1]; J. M. Lovi[1]

1. Iowa State University, Materials Science and Engineering, USA

Planetary ball milling (PBM) and melt quenching (MQ) are vastly different synthesis techniques, although both are known to produce amorphous materials. Previous studies have shown that the reaction of the (x)Na2S+(1-x)P2S5 system by the two synthesis techniques produce structurally similar, if not identical, glasses. This study investigates further the effect that synthesis technique has on the structure-property relationship of glasses, using NMR, IR, and Raman spectroscopies, as well as DSC to compare their thermal properties. Looking at the Na4P2S7-xOx, $0<x<5$, series, the two techniques create glasses that share some short range order (SRO) structures, but the populations of SRO units and the intermediate-range-order networking differs between the glasses. The disproportionation reaction that occurs between glass forming units as phosphorus pentasulfide is replaced by phosphorus pentoxide occurs at a different rate, and to a different degree, depending on the synthesis technique.

4:00 PM

(ICG-SI-007-2019) Structural Investigation of (x) $Li_6Si_2S_7$ + (1-x) $Li_4P_2S_7$ glases prepared via mechanochemcial synthesis

S. Kmiec*[1]; R. Zhao[1]; M. P. Aguilar[1]; S. W. Martin[1]

1. Iowa State University, USA

Lithium based thio-phosphate glasses and glass-ceramics exhibit extraordinarily high ionic conductivities, and have received a lot of attention as potential electrolyte materials in solid state batteries. However due to the poor chemical and electrochemical stability of sulfide materials efforts have been made to improve these properties through the addition of Si and the Mixed Glass Former Effect (MGFE). The short-range order (SRO) structures of the glasses in the (1-x)$Li_4P_2S_7$ + (x)$Li_6Si_2S_7$, $0 \leq x \leq 1$ system were investigated on samples prepared by planetary ball mill (PBM) technique. The SRO units of the glasses were characterized using Raman, ^{29}Si, and ^{31}P Magic Angle Spinning NMR (MAS NMR) spectroscopies to better understand how the structure is influcenced by the MGFE influences. Additional evidence from Raman and NMR suggests that Li has a greater affinity for P than Si in the mixed glass former glasses.

4:20 PM

(ICG-SI-008-2019) Investigation of all-solid-state Li / Na Ion Batteries based on chalcogenides

A. Castro[1]; L. Calvez*[1]; S. Cozic[3]; V. Labas[2]; M. Kubliha[2]; O. Bosak[2]; D. Le Coq[1]

1. Univ. Rennes, ISCR, UMR 6226, Glass and Ceramic Team, France
2. Slovak University of Technology, Faculty of Materials Science and Technology, Slovakia
3. Le Verre Fluoré, France

The energy storage is very challenging for numerous electric devices of the daily life, such as laptops, mobile phones, etc. For the commercial batteries, some organic electrolytes are conventionally used but they can present a risk of flammability and leakage. To solve safety issues, all solid-state batteries using non-flammable electrolyte with high energy density have to be developed. Glasses are potential candidates for electrolytes in solid-state batteries. The vitreous system GeS_2-Ga_2S_3 can incorporate a large amount of various alkali salt as for example LiX / NaX and allows electrolytes to be synthesized for all-solid-state batteries. Conductivity measurements were performed on pseudo ternary GeS_2-Ga_2S_3-NaI/ LiCl glasses showing that conductivities up to 5.10^{-5} $S.cm^{-1}$ and 9.10^{-5} $S.cm^{-1}$ can be achieved respectively at room temperature. Their poor stability against moisture was improved by adding P_2S_5 was added at a low content. Moreover, in this pseudo-quaternary system, higher conductivities have been implemented since a conductivity close to 10^{-4} $S.cm^{-1}$ with a NaI molar content of 35 mol. % was obtained. Based on these very promising results, Na-ion Batteries (NIBs) have been experimented using specific electrodes.

Session 8: Crystallization of Glasses and Glass-Ceramics I (TC 07)

Room: Terrace (lower level)

Session Chairs: Mark Davis, SCHOTT North America, Inc.; Ralf Müller, Bundesanstalt für Materialforschung und -prüfung (BAM)

1:20 PM

(ICG-SI-009-2019) High Strength Fusion Formable Glass-Ceramics (Invited)

M. Dejneka*[1]; C. Smith[1]; I. Dutta[1]

1. Corning Incorporated, USA

Strong, opaque, dielectric materials are needed for electronic device backs for wireless charging, aesthetics and device protection. While glass ceramics have good strength and toughness, their liquidus viscosity is too low to enable economical forming of these devices by the fusion or slot draw methods. Thus we invented a new class of low crystallinity glass ceramics with 10-20nm crystallites in the Fe_2O_3-TiO_2-MgO system. These materials were formed into transparent glasses and then heat treated to make black opaque glass-ceramics containing magnetite, pseudobrookite, and/or ε-Fe_2O_3. The blackness and opacity of the ε-Fe_2O_3 glass-ceramics increased by more than 10x and peaked at a ceram temperature of 750°C where the Fe^{2+} in the crystallites was maximized, resulting in peak Fe^{2+} - Ti^{4+} charge transfer absorption. The liquidus viscosity was improved to more than 100 kPa*s by optimizing the base glass composition and minimizing the amount of crystallinity thereby enabling fusion formability. These fusion formable glass-ceramics had strengths exceeding the best commercially available glasses after ion exchange. This work provides a new class of low crystallinity fusion formable glass ceramics with high strength.

1:50 PM

(ICG-SI-010-2019) Toughening of CaO-Al_2O_3-SiO_2 glass by precipitation of hexagonal $CaAl_2Si_2O_8$ crystals

K. Maeda*[1]; S. Urata[1]; K. Akatsuka[1]; Y. Takato[1]; K. Iwasaki[2]; T. Nakanishi[2]; A. Yasumori[2]

1. AGC Inc., Japan
2. Tokyo University of Science, Japan

Among inorganic materials, glass is known to be one of the most brittle materials, as it has no grain boundaries which can prevent crack propagation. Recently we found the CaO-Al_2O_3-SiO_2 glass can be toughened by precipitation of hexagonal $CaAl_2Si_2O_8$ crystal. The partially crystallized CaO-Al_2O_3-SiO_2 glass exhibited a unique fracture behavior; i.e., non-elastic behavior was observed when it was broken. The microstructure of the material was characterized as a "house-of-cards" structure composed of thin plate $CaAl_2Si_2O_8$ crystals with 10-20 μm in length. The toughness of the material was attributed to the formation of microcracks, which occurred along with the cleavage plane of hexagonal $CaAl_2Si_2O_8$ crystal or at the interface between crystal cleavage plane and the residual glassy phase. Similar fracture behavior was observed in the house-of-cards type glass-ceramics based on mica crystal, which also has a cleavage characteristic. In this presentation, we show the experimental results, as well as the molecular dynamic simulation results of the material, and discuss the possible toughening mechanism.

2:10 PM

(ICG-SI-011-2019) Advanced Glass-Ceramic Materials for Modern Applications (Invited)

I. Mitra*[1]

1. SCHOTT AG, Material Development, Germany

Glass-Ceramic materials are on the market for decades, but need to increase their performance to meet the expectation for established products as well as to anticipate the requirements of new evolving applications. Examples of industrial research are presented covering different systems of functional glass-ceramic materials designed for products of today's trend markets such as components for home appliances, industrial optics, communications, electronic packaging and energy storage devices. Key features of glass-ceramic materials of the Li_2O-Al_2O_3-SiO_2 –system are the controllable nano-sized crystallization leading to highest level of transparency in combination with unique thermal expansion behavior. These technical properties enable products such as CERAN® cooktop panels or ROBAX® fireplace windows while the design of optical appearance and effects are lasting trends. Recent results of industrial R&D now opened up innovative lighting and coloring solutions as well as new functional performance for modern home demands and ambience. ZERODUR® represents a substrate material currently used e.g. for optics of telescopes as well as for devices in microlithography due to its extremely low expansion and its excellent homogeneity. Latest achievements of R&D reveal tailored thermal expansion behavior to be minimal on a ppb-level throughout various temperature ranges according to demands of modern manufacturing technologies.

2:40 PM

(ICG-SI-012-2019) Machinability of Fluormica Glass-Ceramics of High Mica Volume Fraction

R. Hill*[1]; A. Alzahrani[1]

1. Queen Mary, DPS, United Kingdom

Mica glass-ceramics can be machined without resorting to expensive diamond tooling. The objective of this study is to investigate barium mica glass-ceramics (BMGcs) for use in CAD/CAM dental applications, with specific reference to i) the parameters, which determine the microstructure that govern hardness and machinability. ii) explore the validity of Baik's model for high mica volume fractions. BMGCs were synthesized by the melt-quench route and cast into rods and subsequently heat-treated at 1175 and 1200°C for various times. The microstructure was determined by SEM and the volume fraction and aspect ratio of the crystals were determined. The hardness of the glass-ceramics was measured and a machinability test was used to measure the force during machining. An interlocking 'House of Card's microstructure was successfully obtained upon heat treatment. The formation of the House of Cards microstructure was associated with the volume fraction, aspect ratio and connectivity of crystals. The volume fraction of the crystals was almost identical for all samples. However crystal length and width increased with increasing holding time. Hardness and machinability decreased with the aspect ratio and Effective Crystallinity. The Hardness and Machinability data agreed well with Baik's data and extend the validity of the model to much higher volume fractions.

3:00 PM

(ICG-SI-013-2019) Synthesis of a Novel Zirconia Reinforced glass-ceramics for Dentistry

M. R. Mohamed*[1]; N. Karpukhina[1]; R. Hill[1]

1. Barts and The London School of Medicine and Dentistry, Dental Institute, United Kingdom

This work studies the effect of addition of yttria stabilised zirconia on crystalllisation and mechanical properties of fluormica glass-ceramics in order to develop novel glass-ceramics for dentistry. Methods: Fluormica glasses were produced using quench-melt method and charactrized using Differential Scanning Calorimetry, X-ray Diffraction, Simultaneous Thermal Analysis and Vickers Microhardness tests. The glass–zirconia composites with different amounts of zirconia were ball milled, compacted in a disc and sintered to obtain zirconia reinforced glass-ceramic. The produced composites were characterzied using X-ray diffraction and Scanning electron microscope, Vickers hardness, and Biaxial flexural strength. Results: Crystallographic analysis showed thecharacteristic peaks of flourmica and tetragonal zirconia. SEM photomicrographs reveled interlocking mica crystals with embedded zirconia particles. Both vicker microhardness and biaxial strength values increase with increasing zirconia content. Conclusions:Novel zirconia reinforced glass-ceramics produced and could be a good candidate for the use with CAD/CAM in fabrication of dental restorations.

3:40 PM

(ICG-SI-014-2019) A new insight for nucleation and crystal growth in laser-induced crystallization (Invited)

T. Komatsu*[1]

1. Nagaoka University of Technology, Japan

There has been a great progress in the spatially selected patterning of crystals with high orientation architectures by continuous wave (CW) laser irradiations in oxide glasses. Highly c-axis oriented nonlinear optical crystals with different morphologies such as straight/bending/spiral lines and two-dimensional planar shapes were patterned through the heat-driven type CW laser irradiations. The origin of the c-axis orientation along the laser scanning direction was discussed from the viewpoint of surface energy and interfacial free energy between crystal and surrounding glassy phase. The structural anisotropy in the a-plane and c-plane induces different interfacial free energies, consequently determining the preferential crystal growth orientation. The homo-epitaxial crystal growth in the laser patterning of nonlinear optical β-BaB_2O_4 and $BaAlBO_3F_2$ crystals was demonstrated as a unique feature of the laser-induced crystallization. The importance of glass composition was also emphasized in the laser patterning of orientation designed crystals. The laser patterning of crystals results in a large flexibility for the nucleation and crystal growth in oxide glasses and is regarded as a frontier not only for a more deep understanding of glasses but also for the creation of new glass-crystal hybrid materials.

Session 10: Hybrid Glasses and Metal-Organic Framework Glasses

Room: Statler (mezzanine)
Session Chairs: Thomas Bennett, Cambridge University; Satoshi Horike, Kyoto University

1:20 PM

(ICG-SI-015-2019) Disorder in soft porous crystals (Invited)

F. Coudert*[1]

1. CNRS, France

Recent years have seen a large increase of the research effort focused on framework materials, including the nowadays-ubiquitous metal–organic frameworks, but also dense coordination polymers, covalent organic frameworks, and molecular frameworks. A large number of these frameworks flexible, or stimuli-responsive, and there is growing evidence that large-scale flexibility, the presence of defects and long-range disorder are not the exception in metal-organic frameworks, but the rule. Our group has put together a "toolbox" of theoretical approaches to shed light into these materials' properties, and in particular to understand the presence of disorder in soft porous crystals, and its impact on the materials' properties. By means of molecular simulation at varying scale, we can now probe, rationalize and predict the behavior of disordered framework materials, producing a coherent description of soft porous crystals from the unit cell scale all the way to the behavior of the whole crystal. This is particularly important in understanding the links between flexibility, defects and disorder, all of which arise from the large dimensionality of these complex supramolecular assemblies.

1:50 PM

(ICG-SI-016-2019) Enabling computational design of ZIFs using ReaxFF (Invited)

Y. Yang*[1]; Y. K. Shin[2]; S. Li[3]; T. Bennett[4]; A. C. van Duin[2]; J. C. Mauro[1]

1. Pennsylvania State University, Materials Science and Engineering, USA
2. Pennsylvania State University, Department of Mechanical and Nuclear Engineering, USA
3. China Academy of Engineering Physics, China
4. University of Cambridge, United Kingdom

Classical force fields have been broadly used in studies of metal-organic framework crystals. However, processes involving bonds breaking or forming are prohibited due to the non-reactive nature of the potentials. With emerging trends in the study of ZIFs that include glass formation, defect engineering, and chemical stability, enhanced computational methods are needed for efficient computational screening of ZIF materials. Here, we present simulations of three ZIF compounds using a ReaxFF reactive force field. By simulating the melt-quench process of ZIF-4, ReaxFF can reproduce the atomic structure, density, thermal properties, and pore morphology of the glass formed (a_gZIF-4), showing remarkable agreement with experimental and first-principle molecular dynamics results. The predictive capability of ReaxFF is further exemplified in the melting of ZIF-62, where the balancing of electronic and steric effects of benzimidazolate yields a lower T_m. Based on electron withdrawing effect of $–NO_2$ group, ReaxFF simulations predict that ZIF-77 has

an even lower T_m in terms of Zn-N interaction but its low chemical stability makes it unsuitable as a glass former. Because of its low computational cost and transferability, ReaxFF will enable the computational design of ZIF materials by accounting for properties associated with disorder/defects.

2:10 PM

(ICG-SI-017-2019) Deformation behavior of amorphous zeolitic imidazolate framework: From supersoft material to complex organometallic alloy

P. Adhikari*[1]; N. Li[2]; P. Rulis[1]; W. Ching[1]

1. University of Missouri, Kansas City, Department of Physics and Astronomy, USA
2. Wuhan University of Technology, State Key Laboratory of Silicate Materials for Architectures, China

Zeolitic imadizolate frameworks (ZIFs)—a subset of metal-organic frameworks (MOFs)—have recently attracted immense attention. Many crystalline ZIFs (c-ZIFs) have large-porosity zeolite structures that are ideal for molecular encapsulation. Recently emerging non-crystalline or amorphous ZIFs (a-ZIFs) with similar short-range order are of interest because they can be converted from c-ZIF for large-scale production. Here we present a computational study of the deformation behavior of a unique a-ZIF model by simulating step-wise compression and expansion with strains between -0.389 and +0.376. An insulator-to-metal transition is observed at 51 GPa leading to a multicomponent light amorphous alloy of only 3.68 g/(cm)^3. A high-density amorphous-to-amorphous phase transition is observed due to the sudden formation of N-N bond pairs. Systematic expansion of a-ZIF retains the framework softness until it fractures at high strain. Based on the expansion data, we propose an empirical formula for super-soft materials, which is in line with available experimental data.

2:30 PM

(ICG-SI-018-2019) Robust, transparent amorphous inorganic-organic composite materials (Invited)

C. Calahoo*[1]; L. Wondraczek[1]; L. Longley[2]; T. Bennett[2]

1. University of Jena, Otto Schott Institute for Materials Research, Germany
2. University of Cambridge, Department of Materials Science and Metallurgy, United Kingdom

Due to their high porosity, functionality and modularity, metal organic frameworks (MOFs) continue to be of interest for gas storage, purification and separation, as well catalysis and sensing applications. Amorphous MOFs (aMOFs) are of further fundamental interest due to their distinct glassy structure and observable, complex kinetics. Here, we take advantage of glass' unique ability to simply mix and melt components; thereby, creating wholly new and unconventional, fully amorphous composites of a MOF (ZIF-62: $Zn(C_3H_3N_2)_{1.75}(C_7H_5N_2)_{0.25}$) and the inorganic glass series, $(1 - x)NaPO_3$-$xAlF_3$. We have observed robust bonding between these two vastly different phases: if an inorganic phase with a low glass transition temperature (T_g^{inorg}) or a long heating time were used, transparent, mechanically robust monoliths with distinct 'alluvial-looking' flow patterns were produced; higher T_g^{inorg} or shorter heating time yielded opaque, sintered monoliths. We will investigate further the interphasal reaction through DSC, PDF analysis, VT-XRD, nano-indentation, sonography and elemental mapping. We hope to retain the mechanical and chemical robustness of the inorganic component, while introducing additional chemical versatility via the metal-organic component. Given the wide breadth of available glass compositions, we believe this to be the first of many possible inorganic-organic composite materials.

3:00 PM

(ICG-SI-019-2019) Glassy state of metal organic frameworks for proton conductivity (Invited)

S. Horike*[1]

1. Kyoto University, Institute for Integrated Cell-Material Science, Institute for Advanced Study, Japan

We have been interested in the glassy state of metal organic frameworks (MOFs) which are constructed from metal ions and bridging organic ligands. Glass is usually prepared by melt quench technique, but it has not been feasible for most of MOFs, because they do not show stable liquid state upon heating. In last few years, some MOFs and coordination polymer crystals (CPs) have been found to melt in the temperature range of 160 ~ 600 °C, which enables glass formation. The reports suggest the short range (and sometimes even middle range) order around the metal ions in glass is identical to that in crystal. This encourages to design the glass structure from crystal structure of MOFs. We study proton (H^+) conductivity in MOF/CP glasses. By use of protic ligands such as imidazole, $H_2PO_4^-$ to construct MOF glass, we found high anhydrous H^+ conductivity (10^{-2} S cm^{-2} at 140 °C) which is promising for fuel cell vehicle. We also will discuss solvent-free mechanical milling for MOF crystal to transform glassy state and molecular doping into H^+ conductive glass to regulate the mobility of ions.

3:50 PM

(ICG-SI-020-2019) Impact of Pressure on Glass Transition Behavior of a Metal-Organic Framework Glass

A. Qiao*[1]; M. Stepniewska[1]; H. Tao[2]; L. Calvez[3]; X. Zhang[3]; Y. Yue[1]

1. Aalborg University, Department of Chemistry and Bioscience, Denmark
2. Wuhan University of Technology, State Key Laboratory of Silicate Materials for Architectures, China
3. University of Rennes 1, Laboratory of Glasses and Ceramics, Institute of Chemical Science, France

A newly emerged family of melt-quenched glasses - metal-organic framework (MOF) glasses with network structure, show a number of fascinating physical properties, distinct from those of traditional families of glasses (organic, inorganic and metallic glasses). In this presentation, we report on the influences of pressure on the glass transition temperature (T_g) of ZIF-62 ($Zn(Im)_{1.75}(bIm)_{0.25}$) glass, which was prepared by spark plasma sintering (SPS) method. It is found that the T_g (558K) of ZIF-62 glass produced by SPS method is much lower value than that (595K) prepared by the conventional melt-quenching method. This indicates that the pressure (50 MPa) applied by SPS method to the glass samples densify the glass structure, thereby lower T_g. This behavior is in strong contrast to that of other types of network glasses, since their T_g values remain unchanged under such low pressure. Reheating the as-prepared glass leads to relaxation of the compressed structure to the unconstrained state, and hence, its T_g increase to that of the not pressed ZIF-62 glass. We discuss the structural origin of the decrease of T_g induced by pressure. This work sheds light on the glass transition and relaxation in MOF glasses.

4:10 PM

(ICG-SI-021-2019) Mechanical Response of Melt-Quenched Zeolitic Imidazolate Framework Glass to Sharp Contact Loading

M. Stepniewska*[2]; K. Januchta[2]; C. Zhou[2]; A. Qiao[2]; G. Winther[1]; M. M. Smedskjaer[2]; Y. Yue[2]

1. Technical University of Denmark, Department of Mechanical Engineering, Denmark
2. Aalborg University, Department of Chemistry and Bioscience, Denmark

Discovery of the new family of melt-quenched (MQ) glasses - zeolitic imidazolate framework (ZIF) glasses - has induced a substantial interest in exploring the nature and properties of these materials. Despite much progress in the understanding of ZIF glass formation and structure, their deformation behavior has not been well studied,

especially, their fracture behavior has not yet been reported to the best of our knowledge. In this presentation, we report on the deformation and cracking behavior of MQ-ZIF-62 glasses. By employing both Vicker's microindentation and Berkovich nanoindentation techniques, we analyze the mechanical response of the ZIF glass to indentation at different load scales. Atomic force microscopy (AFM) analysis of indents reveals minimal pile up and shear bands on the indent faces, implying a high degree of local plastic deformation and densification. Despite a fully polymerized structure of ZIF glasses, analogous to that of silica glass, they exhibit indentation cracking patterns similar to those of 'normal' oxide glasses. We interpret this mechanical response of the ZIF glasses in terms of the nature of their chemical bonding and structural features, which are significantly different from those of other families of network glasses.

4:30 PM

(ICG-SI-022-2019) Intrinsically Porous Hybrid Glasses from Melt-Quenched Metal-organic Frameworks

T. Bennett*[1]

1. Cambridge University, United Kingdom

Metal–organic frameworks (MOFs) are a family of chemically diverse materials, consisting of inorganic nodes or ions linked by organic ligands. They have applications in a wide range of fields, covering engineering, physics, chemistry, biology and medicine. Until recently, research has focused almost entirely on crystalline structures, with over 60,000 structures now known. We have recently shown a subset of metal-organic frameworks (MOFs), called zeolitic imidazolate frameworks (ZIFs), to melt, and quenching of the resultant liquids forms a new category of glass.[1] Several structures (e.g. ZIF-4 [$Zn(C_3H_3N_2)_2$]) melt between 400 and 600 °C, and the glasses obtained upon cooling retain the short-range order (i.e. local bonding under 6 Å) present in their crystalline counterparts. Here, we explore the mechanism of melting in crystalline hybrid frameworks. We show that melting proceeds with significant structural retention, due to breakage of only part of the metal coordination sphere. The structure of the liquid phase is characterized, as is the mechanism of vitrification upon cooling. The atomic configuration obtained bears striking similarities to that for $aSiO_2$. We also cover the ability to design the starting crystalline framework, so that upon vitrification, without any post-synthetic treatment, a glass porous to both H_2 and CO_2 is formed. The CO2 adsorption of this porous MOF-glass is ca 10 wt %.

SII: Glass Physics

Session 4: Topology and Rigidity I

Room: Berkley (mezzanine)

Session Chairs: Mathieu Bauchy, University of California, Los Angeles; N M Anoop Krishnan, Indian Institute of Technology Delhi

1:20 PM

(ICG-SII-001-2019) Topological approach to manufacturing stronger glass products (Invited)

A. K. Varshneya*[1]

1. Saxon Glass Technologies, Inc., USA

Glass products break because an applied tensile stress causes a flaw to grow into a crack. The usually observed weakness arises from (a) flaws generated before-the-line (during manufacturing) and after-the-line (handling by customer) and (b) stress-assisted flaw growth due to environment all along. It is argued that both these factors depend upon glass network topology critically through network yielding. Network cavitation during glass forming as a precursor to flaw nucleation and indentation-produced stresses that lead to flaw growth during solid state are hydrostatic and shear yield strength-dependent. Glass products, where chemical composition has been tailored to optimize its network topology, could be much stronger. Understanding of atomic network bonding constraints and degrees of freedom through chemical composition control is imperative. These concepts are presented.

1:50 PM

(ICG-SII-002-2019) Disordered Networks of Rigid Polyhedra – Looking Back (Invited)

P. Gupta*[1]

1. Ohio State University, USA

Following Zachariasen's proposal (1932), attempts to build (by hand or on computer) large scale disordered networks of vertex-sharing rigid tetrahedra remained unsuccessful. The condition for the existence of such networks was first rationalized by Cooper (1978) in two dimensions and by Gupta and Cooper (1989) in three dimensions. In this talk, I will present some historical remarks on this approach (Polyhedral Constraint Theory) and highlight its differences from and similarities with Phillips Bond Constraint Theory (1979) of network glasses.

2:20 PM

(ICG-SII-003-2019) Topological Constraint Model for the Elasticity of Glass-Forming Systems

C. Wilkinson*[1]; J. C. Mauro[1]

1. Pennsylvania State University, USA

The elastic response of glass is one of its most important properties for a wide range of applications in architecture, transportation, information display, and healthcare. Unfortunately, there is currently no model to predict elastic moduli from the underlying network topology of the glass. Here we introduce a topological model to calculate the Young's modulus of glass in terms of the free energy density of rigid constraints in the network. The model shows quantitatively accurate agreement with glasses across a variety of compositional families. More remarkably, the variation of modulus with temperature can also be predicted by accounting for the temperature dependence of the constraints, including the approach to the viscoelastic region near the glass transition.

2:40 PM

(ICG-SII-004-2019) Melt Dynamics and Topological phases of $Ge_xAs_xS_{100-2x}$ glasses

B. Almutairi*[1]; R. Chbeir[1]; S. Chakravarty[1]; P. Boolchand[1]

1. University of Cincinnati, USA

Especially homogenized bulk $Ge_xAs_xS_{100-2x}$ glasses are realized by using FT-Raman profiling of melt/glass column in evacuated quartz tube as starting materials are steadily alloyed. We used Modulated-DSC to establish trends in T_g, enthalpy of relaxation at T_g, and melt fragility index m. Our results show, to display an abrupt square-well like window with the onset near $x = x_r = 9.0(5)\%$ (Rigidity transition), and end near $x = x_s = 16.0(5)\%$ (Stress transition). The range $x_r < x < x_s$ represents the reversibility window (RW) defining the Isostatically-Rigid Phase, with compositions at $x < 9\%$ to be in the Flexible Phase, while those at $x > 17\%$ in the Stressed-Rigid Phase. On the other hand, m(x) shows a Gaussian-like minimum with $m < 20$ in the $9.0\% < x < 17.0\%$ range, and $m > 20$ outside that range, thus defining a fragility window (FW) also in the $9.0\% < x < 17.0\%$ range. The RW coinciding with the FW shows that super-strong melts ($m < 20$) lead to isostatically rigid glasses, while fragile melts ($m > 20$) formed outside the window form either Flexible or Stressed-Rigid glasses.

3:00 PM

(ICG-SII-005-2019) Connecting Glass-forming Fragility to Network Topology: A Universal Dependence

D. Sidebottom*[1]

1. Creighton University, Physics, USA

Glass fragility is a measure of how sharply the viscosity of a supercooled liquid responds to small temperature changes in the glass-forming region near the glass transition point, Tg, and is an important consideration for many manufacturing processes. In network-forming glasses, the fragility is influenced by the degree of covalent polymerization as network topology evolves from that of a 3-dimensional network to one of lower dimensional, chain-like structures interacting through weaker van der Waal forces. While others have made extensive use of constraint-counting approaches in an effort to relate the glass-forming dynamics to the underlying network structure, we show how the fragility of over 150 network forming glasses (both oxide and chalcogenide) can be reduced to a universal dependence on just one topological parameter which characterizes the average network connectivity in a coarse-grained manner. Here we review how the coarse-graining can be applied in equal fashion to alkali-phosphate, -borate, -germanate, and, most recently, -silicate glasses to achieve this remarkable result.

3:40 PM

(ICG-SII-006-2019) Nature and Quantification of Stress in Over-Constrained Glasses

X. Li[1]; M. M. Smedskjaer[2]; J. C. Mauro[3]; G. Sant*[1]; M. Bauchy[1]

1. University of California, Los Angeles, USA
2. Aalborg University, Denmark
3. Pennsylvania State University, USA

Topological constraint theory classifies network glasses into three categories, viz., flexible, isostatic, and stressed–rigid, where stressed-rigid glasses have more topological constraints than atomic degrees of freedom. Such over-constrained glasses are expected to exhibit some internal stress due to the competition among the redundant constraints. However, the nature and magnitude of this internal stress remain poorly characterized. Here, based on molecular dynamics simulations of a stressed-rigid sodium silicate glass, we present a new technique allowing us to directly compute the internal stress present within a glass network. We show that the internal stress comprises two main contributions: (i) a residual entropic stress that depends on the cooling rate and (ii) an intrinsic topological stress resulting from the over-constrained nature of the glass. Overall, these results provide a microscopic picture for the structural instability of over-constrained glasses.

4:00 PM

(ICG-SII-007-2019) Effect of water on topological constraints in silica glass

A. Potter*[1]; C. Wilkinson[2]; S. H. Kim[3]; J. C. Mauro[2]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA
2. Pennsylvania State University, Materials Science and Engineering, USA
3. Pennsylvania State University, Chemical Engineering, USA

A fundamental understanding of how water interacts with glass is valuable for many practical concerns due to the myriad effects of water on glass properties. Topological constraint theory, which has been shown in prior studies to be an excellent model for various thermomechanical properties, is expanded herein to account for strain on the glass network, in this application due to unbonded interstitial species. Literature T_g data have been collected for silicate glasses containing various alkali and water contents and an expanded constraint theory model has been successfully applied to describe the effects of water on the glass transition temperature.

4:20 PM

(ICG-SII-008-2019) Prediction of the Glass Transition Temperatures of Zeolitic Imidazolate Glasses through Topological Constraint Theory

Y. Yang*[1]; J. C. Mauro[1]

1. Pennsylvania State University, Materials Science and Engineering, USA

A topological constraint model is developed to predict the compositional scaling of glass transition temperature (T_g) in a metal-organic framework glass, a_gZIF-62 [$Zn(Im_{2-x}bIm_x)$]. A hierarchy of bond constraints is established using a combination of experimental results and molecular dynamic simulations with ReaxFF. The model can explain the topological origin of T_g as a function of the benzimidazolate concentration with an error of 3.5 K. The model is further extended to account for the effect of 5-methylbenzimidazolate, enabling calculation of a ternary diagram of T_g with a mixture of three organic ligands in an as-yet un-synthesized, hypothetical framework. We show that topological constraint theory is an effective tool for understanding the properties of metal-organic framework glasses.

4:40 PM

(ICG-SII-009-2019) Topology of Glassy Silica: Role of the Synthesis Method

Z. Wang*[1]; T. Du[1]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA

There are many ways to produce glassy silica, such as melt-quenching, sol-gel, irradiation, or vapor deposition. Yet, it remains unclear whether the structure, stability, and properties of glassy silica depend on the history of its synthesis. Here, based on reactive molecular dynamics simulations (ReaxFF), we investigate the network topology and thermodynamics of silica glasses prepared by melt-quenching, sol-gel, irradiation, and vapor deposition. We show that, depending on the synthesis route, silica glasses can exhibit an allowable or forbidden structure, that is, which is accessible or not by melt-quenching. These results pave the way toward the development of new "forbidden" glasses with exotic structure and properties.

Session 5: Artificial Intelligence and Machine Learning in Glass Science I (TC 27)

Room: Hancock (mezzanine)
Session Chair: Jincheng Du, University of North Texas

1:20 PM

(ICG-SII-010-2019) Using Artificial Intelligence to decrypt the glass genome (Invited)

A. Tandia*[1]

1. Corning Incorporated, Modeling & Simulation, USA

Glasses are playing a pivotal role in the accelerated development of today's civilization in many different areas such as information technology, energy, architectural, and pharmaceutical. The standard requirements for glassy products for any given application are significantly increasing, making the design of optimal glass compositions very challenging. To meet the fast paste of new technology delivery for glassy products, the traditional trial and error methods, supplemented by experience, are no longer sufficient. Our use of machine learning and artificial intelligence have helped gain a better understanding of the glass chemistries to enable faster, cheaper, and better research and development of new glass compositions. We have combined artificial neural networks, genetic algorithm and probabilistic methods to build a robust framework to model key glass properties such as liquidus temperature, viscosity, Young's modulus, and thermal expansion very accurately. Existence of such framework had led to the very speedy design of multicomponent glass compositions.

1:50 PM

(ICG-SII-011-2019) Advanced statistical methods applied to glass viscosity and glass temperature prediction

D. Perret*[1]; A. Garcin[1]; F. Bergeret[2]; C. Soual[2]; J. Dussossoy[1]; O. Pinet[1]

1. CEA, DE2D/SEVT/LDMC, France
2. Ippon Innovation, France

In situations where theoretical tools such as density functional theory, topological constraints or molecular dynamics cannot be efficiently applied to calculate glass properties, empirical statistical models are often required. It is typically the case when glass contains high number components. Since the end of the 19th century, it is known that under certain conditions, silicate glass properties can be expressed as a simple linear combination of oxide contents. This "Principle of Additivity" was initially introduced to calculate heat capacity of glass, before being extended during the 20th century to a larger number of properties. In the 1990s, American scientists from PNNL developed a statistical methodology to establish robust property-composition models applicable to nuclear glass formulation. Glass viscosity prediction is highly challenging because of its huge variability on temperature and composition scales. An innovative methodology recently developed by glass formulation scientists at CEA combines statistical techniques of experimental designs, multilinear regression and neural networks. It uses glass formulation data generated at CEA over the past 30 years as well as large amount of data collected from the literature and from commercial database. Predictions appear to be very accurate, compared to those obtained from other statistical models already published in the literature.

2:10 PM

(ICG-SII-012-2019) Engineering new glasses using genetic algorithms

D. R. Cassar*[1]; G. Guimarães dos Santos[1]; G. P. Bessa[1]; R. C. Santana[1]; E. D. Zanotto[1]

1. Vitreous Materials Laboratory, Department of Materials Engineering, Brazil

Finding new glasses with a particular set of properties is an important activity in both technological and scientific projects. Recent advances in modeling glass properties are already helping us in the development of new multicomponent glasses, saving a substantial amount of time and resources when compared with the traditional "cook-and-look" approach. In this work, we show how genetic algorithms, a type of evolutionary machine learning algorithms, can help us navigate the multidimensional space of glass compositions while solving multi-objective optimization problems. We give an example of designing an optical glass that is lightweight and has a specific combination of refractive index and Abbe number. Another example is discovering new glasses that undergo observable volumetric (homogeneous) crystal nucleation without the addition of nucleating agents. A relevant feature of these algorithms is the ability to define constraints. For instance, one may want to avoid a particular chemical element that is not available or is too expensive; another constraint might be to avoid specific composition ranges that are protected by patents and cannot be commercially explored. In the end, it seems fitting that genetic algorithms may aid us in decoding the "glass genome."

2:30 PM

(ICG-SII-013-2019) Machine learning based prediction of Young's modulus for glasses with sparse data

S. Singh[1]; S. Bishnoi[1]; R. Ravinder[1]; H. Kodamana*[2]; N. Krishnan[1]

1. Indian Institute of Technology, Department of Civil Engineering, India
2. Indian Institute of Technology, Department of Chemical Engineering, India

Glasses exhibit highly non-linear composition–property relationships. Several machine learning techniques ranging from linear regression to artificial neural networks (ANN) have been used to predict the properties of glassy systems. However, these methods suffer from the following inadequacies: (i) large dataset is required to train these systems reliably, (ii) slight deviations from the optimum parameters could lead to overfitting resulting in poor performance of the systems. To address these deficiencies, herein, we use Gaussian process regression (GPR) to predict the Young's modulus of silicate glasses–namely, calcium aluminosilicate, sodium borosilicate, sodium germanium silicate, calcium sodium silicate. The glasses are chosen such that the available dataset for these systems are small ranging from just 42 to around 100 data points. In particular, we show that GPR can be used even for small datasets reliably without overfitting. Further, it exhibits increased accuracy in comparison to other methods such as ANN. Finally, we show that the reliability of prediction can be obtained for a GPR from the standard deviation of the underlying distribution–a unique feature which makes the method superior to ANN. Overall, such data-driven approaches can be useful in glass science to understand the governing mechanisms, and to accelerate the design of commercial glasses.

Session 5: Artificial Intelligence and Machine Learning in Glass Science II (TC 27)

Room: Hancock (mezzanine)
Session Chair: Walter Kob, University of Montpellier

3:40 PM

(ICG-SII-014-2019) Machine Learning for Glass Science and Engineering (Invited)

M. Bauchy*[1]

1. University of California, Los Angeles, Civil and Environmental Engineering Department, USA

Unlike crystalline materials, glasses can virtually feature any composition and stoichiometry, which creates limitless opportunities to develop new glass formulations with unusual properties. However, this large compositional space renders traditional Edisonian trial-and-error discovery approaches poorly efficient ("curse of dimensionality"). In addition, the complex, disordered atomic structure of glasses makes it challenging to develop some mechanistic models relating composition to macroscopic properties. In this presentation, I will present some of our recent effort in applying machine learning to glass science and engineering, including (i) optimization methods for the parametrization of novel empirical forcefields, (ii) clustering and classification algorithms to identify previously hidden patterns in glass atomic networks, and (iii) regression methods for the predicting of glass engineering properties. I will focus on highlighting how machine learning, molecular dynamics simulations, and topological modeling can mutually inform and advance each other.

4:10 PM

(ICG-SII-015-2019) Data-Driven Predictive Glass Corrosion Models Under Different Chemical Conditions

A. Li*[1]; Y. Zhang[2]; K. Hughes[1]

1. Corning Incorporated, Characterization Science, USA
2. Corning Incorporated, Modeling and Simulation, USA

Chemical Durability is one of the most important attributes when designing composition and is used in multiple areas in glass industry including glass cleaning, thinning, storage, product evaluation in different applications, and waste treatment. Among the test metrics to evaluate glass chemical durability, a normalized weight loss and surface appearance of corroded surfaces are the two major means. In this presentation, several glass corrosion prediction models were created using Machine Learning for acid, base, water, fluoride acid, and weathering resistance based upon the data accumulated over the past nine years in the Chemical Durability group at Corning. Glass composition effect on the weight loss and surface appearance for each chemistry will be discussed and corrosion calculators used to predict glass chemical durability will be presented, too.

4:30 PM

(ICG-SII-016-2019) Quantitative structure-property relationships (QSPR) analysis of various ZrO_2-containing soda-lime borosilicate glasses

X. Lu*[1]; L. Deng[1]; S. Gin[2]; J. Du[1]

1. University of North Texas, Material Science and Engineering, USA
2. French Alternative Energies and Atomic Energy Commission, France

QSPR analysis is a promising approach to correlate structural features with properties of glass materials that lack long-range order and usually have complex structures. By using carefully chosen descriptors based on structural models generated from molecular dynamics (MD) simulations, correlation with properties and insights on glass behaviors can be obtained. Zirconia can significantly alter glass properties including chemical durability, even in a small amount, and hence plays an important role in both industry and vitrification of nuclear waste. In this study, various ZrO_2-containing soda-lime borosilicate glasses were simulated using classical MD simulations with the recently developed composition-dependent potentials. Short- and medium-range (e.g., coordination numbers, network connectivity, and ring-size distribution) structural features were analyzed. The use of a structural descriptor that combines short-range structural characteristics, from MD simulations, and single-bond strength was found to provide excellent linear correlations with the density and initial dissolution rate of these glasses. The results show that by combining MD simulations and QSPR analysis the compositional effect on the properties of complex multicomponent glasses can be elucidated, suggesting QSPR is a promising approach for future glass research and new composition design.

4:50 PM

(ICG-SII-017-2019) Statistical Mechanical Approach to Predict the Structure Evolution in Borosilicate Glasses

M. Bødker*[1]; S. Sørensen[1]; M. M. Smedskjaer[1]

1. Aalborg University, Denmark

Predicting the compositional evolution of the atomic-scale structure and properties of oxide glasses is important for designing new materials for advanced applications. In borosilicate glasses, addition of network modifiers will simultaneously alter the local structure around silicon and boron atoms in the glass based on the competition among various possibilities for modifier/former interaction. Based on both nuclear magnetic resonance (NMR) spectroscopy and molecular dynamics (MD) data, we here develop a statistical mechanical model to predict the compositional evolution of structure in borosilicate glasses by accounting for the relative enthalpic and entropic contributions to the modifier/former interactions. By using previously established parameters for binary silicate and binary borate glass systems, the number of free parameters can be reduced significantly. We discuss the possibilities for transferring established model parameters from systems with different modifiers, with the long-term goal of predicting structural evolutions in oxide glasses without any free parameters.

Session 7: Mean-Field and Low-Dimensional Theories of Glasses

Room: Clarendon (mezzanine)
Session Chairs: Patrick Charbonneau, Duke University; Lisa Manning, Syracuse University

1:20 PM

(ICG-SII-018-2019) Onset of mechanical failure in disordered solids (Invited)

G. Zhang[1]; S. Ridout[1]; A. J. Liu*[1]

1. University of Pennsylvania, Physics and Astronomy, USA

We have introduced an application of machine learning data mining methods to diagnose flow defects in disordered solids from their local structural environments. We define a machine-learned quantity, "softness," that is highly predictive of rearrangements. Within this framework, the key to understanding the shear-response of disordered solids is to study the interplay of softness with rearrangements: softer particles are more likely to rearrange, but rearrangements change the softness not only of a rearranging particles but of other particles in the system. Nearby particles are directly affected because their local structural environments change, while more distant particles are affected via long-ranged elastic strains. Different systems may have different forms of the interplay between softness and rearrangements, which may help to explain the diversity of means by which disordered solids fail under mechanical load.

1:50 PM

(ICG-SII-019-2019) Dynamics of mean-field-like models of glass-forming fluids (Invited)

G. Szamel*[1]

1. Colorado State University, Department of Chemistry, USA

First, we review a simple theory for the dynamics of model glass-forming fluids, which should be solvable using a mean-field-like approach. The theory is based on transparent physical assumptions, which can be tested in computer simulations. The theory predicts an ergodicity-breaking transition that is identical to the so-called dynamic transition predicted within the replica approach. In the large-dimensional limit the theory reproduces the result of the exact calculation of Maimbourg et al. [PRL 116, 015902 (2016)]. Our approach provides an alternative, physically motivated derivation of this result. Next, we apply a similar approach to describe the motion of a single particle moving among randomly distributed, frozen obstacles. In this case, the theory predicts a localization transition. Again, the transition predicted by our dynamic theory coincides with that predicted by the replica approach. Finally, we discuss the relationship of our theories to the well-known mode-coupling theory of the glass transition.

2:20 PM

(ICG-SII-020-2019) Identifying relaxation processes in glass-forming liquids in two dimensions

H. Shiba*[1]; K. Kim[2]; T. Kawasaki[3]

1. Tohoku University, Institute for Materials Research, Japan
2. Osaka University, Graduate School of Engineering Science, Japan
3. Nagoya University, Department of Physics, Japan

It has been recently shown by molecular simulations (including the one by the present authors) and colloidal experiments that a two-dimensional (2D) glass-forming liquid exhibits long-wavelength fluctuation in a manner similar to a 2D crystal, but yet its structural relaxation is similar to its counterpart in three dimensions if it is evaluated in terms of neighbor switching. The mechanism underlying its mechanical relaxation is still an open question. In this presentation, we report our latest numerical analysis of Kob–Andersen binary Lennard-Jones mixture in two dimensions, simulated up to about one million particles that is sufficient to involve long wavelength fluctuations. We compare various time scales that are differently defined to find out relevant ones that play key roles in determining diffusion and relaxation processes.

2:40 PM

(ICG-SII-021-2019) Many-Body Correlations in Hard Spheres: A Morphometric Approach

C. P. Royall*[1]

1. University of Bristol, HH Wills Physics Laboratory, United Kingdom

Much of the challenge in understanding the glass transition lies in obtaining data at sufficient supercooling that theoretical predictions may be rigourously tested. Despite recent advances, the techniques which deliver such particle-resolved data, computer simulation and colloid experiment are both limited in the degree of supercooling they access. Here we introduce a new method to obtain particle resolved data without such limitations by considering a group

of particles within a mean-field hard sphere liquid. We model the thermodynamics of local structures within the hard sphere liquid at arbitrary volume fractions through the morphometric calculation of n-body correlations. We calculate absolute free energies of local geometric motifs in excellent quantitative agreement with molecular dynamics simulations across the liquid and supercooled liquid regimes. We find a bimodality in the density library of states where five-fold symmetric structures appear lower in free energy than four-fold symmetric structures, and from a single reaction path predict an Arrhenius-like scaling of local relaxation dynamics. The method provides a new route to assess changes in the free energy landscape at volume fractions dynamically inaccessible to conventional techniques.

3:00 PM

(ICG-SII-022-2019) Numerical study of the Gardner transition in hard sphere glasses (Invited)

Y. Jin*[1]

1. Institute of Theoretical Physics, Chinese Academy of Sciences, China

Recent advances in the mean-field theory of glasses predict the existence, deep into the glass phase, of a novel phase transition -- the so-called Gardner transition, which is associated to the emergence of a complex free energy landscape and marginality. We numerically study the Gardner transition in a three-dimensional hard sphere glass model, and reveal intrinsic connections between this transition and some dynamical and mechanical properties of hard sphere glasses in the high-density (or low-temperature) regime. We show that the Gardner transition is associated to the onset of secondary relaxation, the spatial heterogeneity of the vibrational cages of particles, and the breakdown of pure elasticity.

3:50 PM

(ICG-SII-023-2019) Experimental and Numerical Evidence of the Gardner Transition in Glasses (Invited)

E. I. Corwin*[1]; R. C. Dennis[1]; A. Hammond[1]

1. University of Oregon, Physics, USA

Recent mean field results in the study of structural glasses have demonstrated the existence of a phase transition that happens within the glass phase, called the Gardner transition. This transition describes a change in the energy landscape from smooth to fractally rough with a heirarchical structure. We report on the first direct experimental evidence of such a transition in colloidal glasses as well as new simulational results in low dimensional finite size systems. Experimentally, we track the motion of a single particle within a densifying colloidal glass and observe an abrupt transition from caged to logarithmically growing mean squared displacements, a signature of this transition. Numerically, we directly we probe the structure of the energy landscape and find it to be both heirarchical and ultrametric.

4:20 PM

(ICG-SII-024-2019) Single particle dynamics in nearly jammed configurations of hard spheres

R. Díaz*[1]; F. Ricci-Tersenghi[1]; G. Parisi[1]

1. Sapienza University of Rome, Physics, Italy

In this work, we propose to investigate how the local structure of a particle determines its dynamics, at least for short times. By using a sequential Linear Programming algorithm we were able to systematically produce isostatic jammed configurations of hard spheres, for which we verified that many features of the systems, such as the distribution of forces and density of states reproduce the behaviours obtained before. Once in the jamming regime, we shrank the particles' radius by a small amount and then performed extensive molecular dynamics simulations to study the temporal evolution of the system's trajectory. We analysed several a single-particle statistics and found significant correlations with the forces of the contact network obtained precisely at jamming. Our results show that the particles' dynamics have well defined distributions for the different values of packing fraction considered here and that this is a persistent feature during the temporal evolution. By linkning the information from the contact network at jamming with the particles' dynamics near to this point, these results provide evidence that the local structure of a particle strongly determines its mobility.

4:40 PM

(ICG-SII-025-2019) Testing mean-field theory for glasses in three-dimensions

M. Baity Jesi*[1]

1. Columbia University, USA

Recently, a series of mean-field results (which are exact in the limit of infinite spatial dimensions) paved the way for a deeper understanding of the glass transition problem. The thermodynamics of supercooled liquids has been characterized through a Replica approach, revealing a liquid-glass transition, and a non-trivial picture for the glassy phase. This was accompanied by a mean-field solution of the dynamics of glasses, which confirmed the presence of an ergodicity-breaking transition in the supercooled liquid phase. This result was rederived through a mode-coupling approach, that emphasized the connection between high and low space dimensionality, through a relation involving autocorrelation functions of the total force acting on the tagged particle evolving with the so-called irreducible dynamics. By calculating these autocorrelations functions in a three dimensional model of glass, we are able to assess the applicability of the mean field results to low-dimensional systems.

5:00 PM

(ICG-SII-026-2019) Fluctuation Distributions of Energy Minima in Complex Landscapes

H. Boltz*[1]

1. University of Chicago, James Franck Institute, USA

We discuss the properties of the distributions of energies of minima obtained by gradient descent in complex energy landscapes. Specifically, we study the distribution of energies of minima in the spherical p-spin model and the distribution of jamming threshold packing fractions in jammed particle configurations as archetypal manifestations of disorder-induced complexity. We numerically find universal distributions that resemble the Tracy-Widom distributions often found in problems of random correlated variables, and non-trivial finite-size scaling. Deeper insight into this problem is achieved by realizing the importance of a first-passage process in the eigenvalues of the Hessian to the termination of the steepest descent process, which also manifests the link to problems where the Tracy-Widom distribution is established. This first-passage view of steepest descent dynamics is generic and therefore we expect similar phenomenology in many problems.

Session 12: Electromagnetic Properties of Glass

Room: Georgian (mezzanine)
Session Chair: B. Potter, University of Arizona

1:20 PM

(ICG-SII-027-2019) Simulations and theory of a conducting bridge memory material: Copper-alloyed amorphous alumina (Invited)

K. Subedi[1]; K. Prasai[2]; M. Kozicki[3]; D. Drabold*[1]

1. Ohio University, Dept. of Physics and Astronomy, USA
2. Stanford University, Department of Applied Physics, USA
3. Arizona State University, School of Electrical, Computer and Energy Engineering, USA

We report an ab initio modeling study of amorphous alumina alloyed with Cu at various concentrations (0,10,20 and 30%) and study structural, electronic and vibrational properties. Cu atoms cluster in the alumina host, and as Cu is added to the system,

Cu-related levels appear in the wide alumina optical gap, and fill it quite uniformly, ultimately producing metallic conduction. A space-projected form of the Kubo formula is invoked to describe the conduction pathways, and we consider the dependence of conductivity on the Cu connectivity within the host. We study large thermal fluctuations of the optical gap in one of the models (20% Cu), and observe the opening and closing of the gap with time, which has an important impact on the electrical conductivity. We also study ion dynamics of the 20% model, and by computing the classical vibrational normal modes, we determine the localization of vibrational states induced by disorder, and identify species-projected vibrational activity.

1:50 PM

(ICG-SII-028-2019) Origin of Conductive Filaments in Chalcogenide-based Conductive-Bridging Random Access Memory

K. Dixit[1]; M. Sundararajan[1]; D. Drabold[1]; G. Chen*[1]

1. Ohio University, USA

The Conductive-bridging Random Access Memory (CBRAM) is a type of Resistive Random Access Memory that shows threshold switching in resistance under external disturbance. While a great deal of effort has been dedicated to commercializing the CBRAM technology, the mechanisms behind the fast switching of the amorphous chalcogenides remain elusive. It has been speculated that the switching was caused by rapid growth of metallic filaments in the amorphous solid electrolyte. In this talk, I will present our recent work on Ag and Cu doped GeSe2 and GeSe3 thin films (with Ag and Cu up to 80 at.%). The electrical, optical and structural properties of the thin films were studied as a function of the metal ion concentration. In contradictory to the conventional view of "metallic filaments", our findings point to an alternative mechanism for the switching.

2:10 PM

(ICG-SII-029-2019) Chalcogenide-based resistive switches

W. Correr*[1]; S. Messaddeq[1]; Y. Messaddeq[1]; E. Bharucha[1]

1. Université Laval, Canada

The conductive bridge memory (CBM) and other resistive switching devices have been in the spotlight in the past decade since the announcement of the HP's memristor. CBMs can provide an alternative to the traditional transistors in data storage and can also be used in arrays for analog data processing, once their use has been demonstrated in artificial neural networks. Despite of their great promise, problems as reproducibility and reliability as well as their endurance have impeded such devices to be implemented in industrial scale. In this work, we focus on the role of glass composition in the switching speed and stability of CBM devices. A chalcogenide/silver bilayer was deposited between two chemically inert electrodes (gold). We used traditional optical lithography and the lift-off technique to build the devices, while the chalcogenide film was deposited by electron-beam. The control of chalcogenide layer thickness and the ratio between chalcogenide and silver was used to fine tune the SET-RESET voltages.

2:30 PM

(ICG-SII-030-2019) Structural Design Criteria for a Mechanically Stiff Ion Conductor (Invited)

R. Mohammadi[1]; W. Wang[1]; C. Beg[1]; J. Kieffer*[1]

1. University of Michigan, USA

We investigated the adiabatic elastic properties and ionic conductivities of two series of mixed network former glasses, sodium borosilicates and borogermanates using Brillouin light scattering (BLS) and dielectric impedance spectroscopy, respectively. Using data from NMR spectroscopy and BLS as input for a reaction equilibrium-based statistical thermodynamic model we derived a quantitative account of all possible network building units. This model yields statistical measures for the distribution of cation hopping pathways in these glasses. Our analysis reveals strong correlations between elastic and transport properties, which allow us to develop a more detailed formulation of transition state theory describing the modifier cation migration in these materials. We find that the structural deformation during a cation jump is almost entirely controlled by the bulk modulus. Our analysis allows us to assess the spatial extent of this deformation, as well as estimate the relative amounts of configurational and vibrational entropy changes associated with this thermally activated process. Atomistic models of these glasses established using MD simulations based on a reactive force field further substantiate our new kinetic theory, and allow us to derive materials design criteria for materials with high ionic conductivity and elastic moduli, we developed. Funding: NSF-DMR_1610742

3:00 PM

(ICG-SII-031-2019) Decoupling mobility and charge carrier concentration in AgR-AgPO$_3$ glasses (R = Cl, Br, I)

B. Poletto Rodrigues*[1]; H. Ebendorff-Heidepriem[1]; L. Wondraczek[2]

1. Institute of Photonics and Advanced Sensing, Australia
2. Otto Schott Institute of Materials Research, Germany

Halide-containing silver phosphate glasses have been used as model systems for the study of the ionic conductivity of oxide glasses for the past 50 years, mostly due to the massive increase in conductivity observed as the halide concentration is increased, even if the molar ratio of silver is kept constant. Furthermore there is still no consensus if the increased conductivity is due to an enhancement of the number of effective charge carriers (glass as a weak electrolyte) or a higher charge carrier mobility (glass as a strong electrolyte). In this work we investigate the electrical properties of silver-halide-containing silver metaphosphate glasses through Impedance Spectroscopy. We find the glasses to follow the "canonical scaling", which coupled with the diffusional nature of the conductivity allows us to show that the number of effective charge carriers remains constant with increasing halide concentration, and that the conductivity follows the same scaling as the ionic mobility.

SIV: Emerging Applications of Glass

Session 2: Glasses in Healthcare I (TC 04)

Room: Stuart (4th floor)
Session Chairs: Delia Brauer, Friedrich-Schiller-Universität; Qiang Fu, Corning Incorporated

1:20 PM

(ICG-SIV-001-2019) Fifty Years of Bioglass - A Retrospective and A Look Forward (Invited)

D. C. Greenspan*[1]

1. Spinode Consulting, USA

It was 50 years ago, in 1969 that Professor Larry Hench performed the first experiments with the material he invented called 'Bioglass'. The results of that first study demonstrated for the first time, that a synthetic biomaterial could form a bond with living tissue and that it could potentially improve the fixation of orthopedic devices. That result literally changed how the biomaterials world viewed the interactions between materials and living tissue. Of course, that change did not occur overnight. While bioactive glass is perhaps the most common synthetic material used in bone graft materials, it is only within the past 10 to 15 years that it has achieved that status. This talk will review a few of the seminal discoveries made by Professor Hench and the team of scientists working with Bioglass in the early days, and discuss how the field of bioactive glasses has evolved over this span of time. It will touch on how this discovery has impacted the field of medical devices and has led to numerous materials of all classes to be called 'bioactive'. It will also touch on what has been

learned with respect to how cellular behavior is modified when exposed to bioactive glasses. Finally, this talk will explore the future of bioactive glasses and discuss the need for standards development, given that the use of these materials has become commonplace in the world of bone regenerative medicine.

1:50 PM

(ICG-SIV-002-2019) Crystallization Mechanism of the Bioactive Glasses: 45S5, 13-93 and their intermediates

Q. Fu*[1]; A. Whittier[1]; E. Coon[2]

1. Corning Incorporated, USA
2. Clemson University, USA

There has been increasing interest in the use of bioactive glasses for soft and hard tissue regeneration due to their excellent ability in supporting angiogenesis and osteogenesis. Silicate 45S5 glass, discovered by Hench in 1969, remains as the "Gold Standard" in this material family. Particles of 45S5 have been commercialized in several successful products including Perioglass®, Novabone® and NovaMin®. However, the ability to form 45S5 into complex 3D shapes is challenging due to its tendency to crystallization upon sintering. Another silicate 13-93 glass, on the hand, shows better processing characteristics by viscous flow sintering. Our work attempts to provide a comprehensive understanding of the crystallization mechanism and kinetics on four bioactive glass compositions: 45S5, 13-93, and two intermediates (designated as 48S1T and 50S2T). Results from this work reveal that the crystallization of 45S5 is controlled by a bulk nucleation mechanism while two intermediates 48S1T and 50S2T by a surface nucleation mechanism. Furthermore, the major crystalline phase gradually changes from combeite to wollastonite with the composition transitioning from 45S5 to 13-93. Both intermediates 48S1T and 50S2T demonstrate promising attributes for further evaluations.

2:10 PM

(ICG-SIV-003-2019) Sol-Gel Derived Binary, Bioactive, Borate Glasses

W. C. Lepry*[1]; S. Naseri[1]; S. N. Nazhat[1]

1. McGill University, Mining and Materials Engineering, Canada

Borate glasses can repair both hard and soft tissues due to their lower chemical durability which stems from boron's preference for three-fold coordination. Processing these glasses via the sol-gel method further increases their bioactivity due the higher specific surface areas and porosities which translates to faster ion release and thus, conversion. Compared to traditional glasses, borate glasses are unique because they do not exhibit linear property trends with the addition of modifying elements. Rather, various property maxima are observed at different modifier content which is termed the borate anomaly. Despite this knowledge, many bioactive borate glasses are based on silicate compositions which may not be ideal for targeted tissue repair. Here we explore six simplified, sol-gel derived, two-component borate glasses with calcium, ranging from 30 – 80 mol% B_2O_3. Calcium content influenced boron coordination according to nuclear magnetic resonance and the textural properties using nitrogen adsorption. The amount of calcium also dictated conversion to calcite or hydroxyapatite in vitro according to infrared spectroscopy, x-ray diffraction, and scanning electron microscopy. Additionally, inductively coupled plasma optical emission spectrometry showed compositionally dependent ion release rates. We believe these findings will provide a basis for designing sol-gel borate glasses for targeted tissue engineering applications.

2:30 PM

(ICG-SIV-004-2019) Creating Ceria Nanoparticles in Glass

D. E. Day*[2]; K. S. Ranasinghe[1]; R. SIngh[3]

1. Kennesaw State University, Physics, USA
2. Missouri University of Science & Technology, USA
3. Kennesaw State University, Chemistry, USA

Studies have shown that the coexistence of Ce^{4+} and Ce^{3+} oxidation states on cerium oxide nanoparticles provides a number of health benefits, most notably the use of mixed valence nanoceria as antioxidant enzyme mimetics. The goal of the present work was to merge the well-known properties of bioactive glass with the therapeutic potential of cerium oxide nanoparticles to create a stable glass that contained nanoceria particles, with specific Ce^{3+}/Ce^{4+} ratios, that would be released, when the bioactive glass came into contact with body fluids. Borate glasses containing varying amounts of CeO_2 were melted in air at different temperatures for chosen times to achieve different Ce^{3+}/Ce^{4+} ratios. The presence of mixed valence cerium oxide nanoparticles was confirmed by XANES and Transmission Electron Microscopy (TEM).

2:50 PM

(ICG-SIV-005-2019) Bioactive glass nanoparticles and the challenge of ion incorporation

P. Naruphontjirakul[1]; S. L. Greasley[1]; S. Chen[1]; A. E. Porter[1]; J. Jones*[1]

1. Imperial College London, Department of Materials, United Kingdom

Bioglass products can claim to have the property "osteostimulation" because it can provoke cells to produce new bone through release of silica and calcium ions that stimulate bone cells. Glass can deliver ions at a sustained rate because they are released as the glass dissolves. Silicate bioactive glasses originally had traditional modifier cations such as calcium and sodium. Substitution of these with alternative cations, such as strontium or zinc can provide therapeutic treatment of diseases such as osteoporosis or cancer. The glass can be delivered in the form of monodispersed nanoparticles that are internalised by cells. This talk will describe the challenges involved in getting cations into Stöber-like nanoparticles. Incorporation is easier in mesoporous nanoparticles but dissolution can be rapid. Fate of the nanoparticles in the cells was tracked by TEM and human stem cells were found to differentiate down a bone pathway when exposed to strontium containing nanoparticles but did not when exposed to bioactive glass particles that did not contain strontium.

3:30 PM

(ICG-SIV-006-2019) Effects of B_2O_3/SiO_2 substitution on structure, proeprties, and in vitro bioactivity of bioactive glasses (Invited)

J. Du*[1]

1. University of North Texas, Materials Science and Engineering, USA

Boron oxide containing bioactive glasses attract significant attention due to their different dissolution behaviors and properties and potential biomedical applications. In this talk, I will present our recent work on combining atomistic computer simulations and experimental studies to understand B_2O_3/SiO_2 substitution effect on the structure, in vitro bioactivity, and other physical properties such as density and glass transition temperature in 45S5 and 55S4 glasses containing SrO. In vitro bioactivity tests were performed in simulated body fluid, where, needle-like hydroxyapatite was found to form on the surface. The structure changes in these glass series were studied using FTIR, Raman spectroscopy, and classical molecular dynamics simulations with recently developed partial charge potentials of boron oxide to understand their short and medium range structures such as local structure around the glass network-formers, Q_n distribution and network connectivity. Lastly, application of boron oxide containing glasses for bioactive coatings on titanium based alloys for medical implants is reported. The structural information from simulations helps to understand the changes of physical properties and bioactivities of these glasses as well as to design compositions for biomedical applications.

4:00 PM

(ICG-SIV-007-2019) Mixed former borosilicophosphate bioactive glasses for soft tissue repair

B. Gorin*[1]; J. C. Mauro[1]

1. Pennsylvania State University, Materials Science and Engineering, USA

With a growing elderly population and nearly 415 million people worldwide with diabetes, there is a significant fraction of the population whose wounds do not heal well on their own and, therefore, there is a high demand for a material that could accelerate the wound healing process. Bioactive glasses have been previously used in the medical field to help with hard tissue repair, and recently new compositions have been proposed to help regenerate soft tissue. The characteristics of the glass required for soft and hard tissue repair differ significantly. Since mechanical load is not supported by soft tissue, the development of glasses for soft tissue repair can focus more on bioactivity. Thus far, no glass has been optimized for both bioactivity in a soft tissue repair application and processability. The current proposal addresses this problem through the development of a mixed former glass that should preserve the rate of healing as seen in the current state-of-the-art 1393-B3, while improving stability against crystallization during glass synthesis, processing, transportation, and storage.

4:20 PM

(ICG-SIV-008-2019) The effect of B_2O_3 incorporation in bioactive glasses towards in vitro apatite forming ability, thermal stability and antibacterial properties

S. Prasad[4]; A. Jana[1]; P. Diwan[2]; S. Tripathy[3]; K. Annapurna[4]; K. Biswas*[4]

1. CSIR-CGCRI, Bioceramics & Coating Division, India
2. Ram Lal Anand College, Delhi University, India
3. CSIR-Indian Institute of Chemical Biology, Structural Biology and Bioinformatics Division, India
4. CSIR-Central Glass & Ceramic Research Institute, Glass Division, India

Keeping in view the increasing importance of borate ions towards imparting antibacterial properties in bioactive glasses, several borosilicate glass compositions were formulated in the present work. The structural modifications in the glasses were studied by X-ray diffraction (XRD), Fourier transform Infrared (FTIR) and Raman spectroscopy. In vitro studies in simulated body fluid (SBF) showed that the apatite forming ability of the glasses remains unaffected due to the incorporation of B_2O_3. The thermal stability (ΔT) of the glasses as evidenced from differential scanning calorimetry (DSC) thermograms were found to be better than commercially available 45S5 and S53P4 glasses. No toxicity from these glasses was observed in the in vitro cell compatibility studies using MTT assay, while all the borosilicate glasses showed better cell proliferation compared to silicate glasses. Antibacterial activity studies performed against S. aureus bacteria using broth micro-dilution method demonstrated bactericidal action in all the glasses. Thus, newly formulated borosilicate based bioactive glasses exhibited an interesting combination of good thermal stability, apatite forming ability, better cell proliferation as well as antibacterial properties.

4:40 PM

(ICG-SIV-009-2019) Cooling rate effects on the structure of 45S5 bioglass

P. Bhaskar[1]; Y. Maurya[1]; R. Kumar*[1]; R. Ravinder[1]; N. Krishnan[1]

1. Indian Institute of Technology Delhi, Department of Civil Engineering, India

Despite being extensively used to study the structure and properties of glasses, molecular dynamics (MD) simulations suffer from an inherent deficiency of being limited to short time scales. This leads to astronomically high cooling rates for glasses prepared by MD simulations, making it extremely challenging to compare with that of experimental structures obtained from laboratory scale cooling rates. Indeed, it is well-known that the thermal history of glasses plays a major role in determining the final structure, which consequently affects the mechanical and chemical properties of the system. Herein, using MD simulations with cooling rates varying over five orders of magnitude, we study structure of 45S5 bioglass, the most successful bioactive glass. We show that the thermal history primarily affects the medium-range order structure, while the short-range order is largely unaffected over the range of cooling rates simulated. Interestingly, we observe that the Si and P tetrahedra exhibits a preferential separation with decreasing cooling rates, with the P tetrahedra preferring to form isolated Q^0 clusters. This suggests the existence of a Loewenstein-like rule for P atoms which prefer isolated clusters over Si atoms as neighbors while completely avoiding P–O–P bridging bonds.

Session 3: Emerging Technologies I

Room: Beacon Hill (4th floor)

Session Chair: Hongtao Lin, Massachusetts Institute of Technology

1:20 PM

(ICG-SIV-010-2019) Seeing glass in a new light: Chalcogenide-glass-enabled integrated optics and photonics (Invited)

J. Hu*[1]

1. Massachusetts Institute of Technology, USA

Chalcogenide glasses (ChGs), a broad family of inorganic amorphous materials containing sulfur, selenium, and/or tellurium, are rapidly gaining recognition as an essential material for integrated optics and photonics. In this talk, I will discuss the key attributes of ChGs that underlie their widespread use in integrated photonics and review our latest progress in this area. Specifically, I will address four singular properties of ChGs: wide infrared transparency enabling mid-infrared integrated photonics, large optical nonlinearity for all-optical signal processing and broadband spectroscopic interrogation, phase change behavior uniquely poised for reconfigurable metasurfaces and photonic devices, and substrate-agnostic integration capacity that leads to a wide range of functional components on 2-D materials, magneto-optical oxides, and flexible plastics. I will also discuss the pathway towards ChG integration with mainstream integrated photonics platforms to facilitate scalable manufacturing and user adoption.

1:50 PM

(ICG-SIV-011-2019) Waveguides in Glass for On-board Optical Interconnects (Invited)

L. Brusberg*[1]; A. R. Zakharian[1]; C. C. Terwilliger[1]

1. Corning Research & Development Corporation, USA

Future high-speed signal switching in data-centers will rely on integration between photonics and electronics to achieve required performance at lower power consumption and lower cost. Optical circuit board is a promising platform to enable future higher density interconnects, such as in co-packaged switches and backplanes. The integration of passive optical waveguides in glass can provide optical interconnects at key wavelengths of 850 nm and 1310 nm for Datacom applications. We explore a novel waveguide design in glass for connecting fibers and active optical components. The waveguides are fabricated by thermal silver ion-exchange. The target refractive index profile is designed by modeling the ion-exchange process based on the investigation of glass diffusivity, and in conjunction with glass waveguide to optical fiber coupling loss simulations. The designed waveguides have a refractive index profile that minimizes modal mismatch and optical coupling loss to the test fiber – for both multimode and single-mode operation at 850 nm and 1310 nm, respectively. Measurements of the refractive index profile and insertion loss of fabricated waveguides were found to be in good agreement with the simulation results. These novel waveguides are characterized by low propagation loss of less than 0.05 dB/cm at 1310 nm wavelength.

2:20 PM

(ICG-SIV-012-2019) Monolithic on-chip chalcogenide glass waveguide magneto-optical isolator

Q. Du*[1]; C. Wang[2]; Y. Zhang[1]; Y. Zhang[2]; T. Fakhrul[1]; W. Zhang[3]; C. Goncalves[4]; C. Blanco[4]; K. Richardson[4]; L. Deng[2]; C. Ross[1]; L. Bi[2]; J. Hu[1]

1. Massachusetts Institute of Technology, Materials Science and Engineering, USA
2. UESTC, China
3. Ningbo Univeristy, China
4. University of Central Florida, USA

An isolator is a nonreciprocal device that permits optical transmission in only one direction. On-chip optical isolators constitute an essential building block for photonic integrated circuits (PICs) as they prevent harmful feedback due to reflection and stabilize laser operation. In this talk, we present our experimental demonstration of a magneto-optical (MO) isolator monolithically integrated on silicon based on chalcogenide glass waveguides strip loaded on cerium substituted yttrium iron garnet MO films. The unique strip-loading geometry solves a major issue facing prior demonstrations of monolithic isolators: by using a planar MO film, parasitic optical absorption due to secondary phase formation is suppressed. We choose chalcogenide glass as our strip-loading waveguide material given its processing versatility and the wide range of refractive index tuning. The devices claim world record performance in terms of both insertion loss and isolation ratio among monolithic isolators demonstrated thus far.

2:40 PM

(ICG-SIV-013-2019) Synthesis, Structural and Optical Characterizations of Tellurium Oxide Based Glasses for Optical Devices: Study of Ionic Mobility of Alkaline Metal Under Thermal Poling

J. Emery*[1]; M. Dussauze[2]; M. Dutreilh-Colas[1]; P. Thomas[1]; T. Cardinal[3]; E. Fargin[3]

1. IRCER, France
2. Institut desSciences Moléculaires, Gironde, France
3. ICMCB-CNRS, France

Tellurium oxide-based glasses are promising materials for telecommunication devices. They show nonlinear refractive indices 20 to 50 times larger than that of SiO_2 based glasses. The aim of this study is to generate a second harmonic signal with a tellurite glass using thermal poling. As it has been proven that the migration of sodium after thermal poling creates a depletion layer that induces second harmonic generation (SHG) in the glass, we have investigated glasses within the TeO_2 – WO_3 – Na_2O system. Moreover, they present a high thermal stability. Measurements of SHG responses were performed by Maker fringes and μSHG mapping. Raman spectroscopy was used to evidence structural changes after thermal poling. This work will point out the unusual behavior of tellurite glasses under thermal poling and highlight the link between the change of structure and the generation of second harmonic signal.

3:00 PM

(ICG-SIV-014-2019) Ferroelectric domain engineering of lithium niobate single crystal confined in glass

K. J. Veenhuizen*[1]; S. McAnany[2]; R. Vasudevan[3]; D. Nolan[4]; B. Aitken[4]; S. Jesse[3]; S. Kalinin[3]; H. Jain[2]; V. Dierolf[5]

1. Lebanon Valley College, Physics, USA
2. Lehigh University, Materials Science and Engineering, USA
3. Oak Ridge National Lab, Center for Nanophase Materials Sciences, USA
4. Corning Incorporated, USA
5. Lehigh University, Physics, USA

Femtosecond laser irradiation enables the spatially selective growth of lithium niobate ($LiNbO_3$) crystals deep within lithium niobosilicate (LNS) glass, making these crystals potentially useful as active optical interconnects in a 3D integrated optical assembly. It has not been recently demonstrated that the ferroelectric behavior of $LiNbO_3$ is indeed preserved within the confines of glass. This work provides the first report that the ferroelectric domains of $LiNbO_3$ single crystal embedded in glass can be reversed and uniformly oriented using a DC bias. A piezoresponse force microscope is used to apply the DC bias as well as further probe the piezoelectric and ferroelectric behavior of the crystals in glass. In addition to the ability to engineer the domains of the confined crystal, we report on the innate domain structure of the as-grown crystal, where a complex structure of oppositely oriented domains at the nano- and microscale is observed. These observations demonstrate the feasibility of rewritable electro-optic devices in glass.

Session 3: Laser Processing of Optical Devices

Room: Beacon Hill (4th floor)
Session Chair: Tian Gu, Massachusetts Institute of Technology

3:40 PM

(ICG-SIV-015-2019) Single fs laser beam induced periodic nanostructures in glass and their applications (Invited)

J. Qiu*[1]

1. State Key Laboratory of Modern Optical Instrumentation, Zhejiang University, China

Femtosecond laser is an extreme physical condition which can be realized in normal laboratories. It has been widely used for microscopic modifications to materials due to its ultra-short laser pulse and ultrahigh light intensity. When a transparent material e.g. glass is irradiated by a tightly focused femtosecond laser, the photo-induced reaction occurs only near the focused part of the laser beam inside the glass due to the multiphoton processes. In this talk, we will describe our observations of various interesting phenomena in glasses, e.g. single fs laser beam induced periodic nanostructures in glass etc. The mechanisms of polarization dependent nanograting and periodic nanovoid array as well as their promising applications in integrated optics are also discussed.

4:10 PM

(ICG-SIV-016-2019) Polarization dependence of laser-induced lithium niobate single crystal growth in glass

C. L. Eppler*[1]; K. J. Veenhuizen[2]; C. Au-Yeung[1]; S. McAnany[3]; L. Hoxha[1]; H. Jain[3]; V. Dierolf[1]

1. Lehigh University, Physics, USA
2. Lebanon Valley College, Physics, USA
3. Lehigh University, Materials Science & Engineering, USA

Spatially selective femtosecond laser induced crystallization of glass emerges as a promising and versatile method to realized 3D integrated optics components within glass. To this end, previous studies in our group have demonstrated the successful formation of single crystal lithium niobate ($LiNbO_3$) lines within lithium niobosilicate (LNS) glass through spatially selective heating via laser irradiation; the formation of such crystals were shown to be highly dependent upon the parameters of the laser, such as pulse intensity and speed of motion. Moreover, it has been shown that the morphology of the crystals formed depend on the polarization direction of the laser in respect to direction of laser motion. We will present a detailed study that shows the quality, size, and orientation of the crystallization depends on the light polarization during the nucleation and the growth of the crystals. We find that when starting from a common seed crystal, the width of $LiNbO_3$ crystal lines can be manipulated by varying the polarization of the laser relative to the growth direction. Moreover, we find that the width can be manipulated dynamically by varying the polarization during growth. We will discuss how such modulations can affect waveguiding properties, therefore enabling effects such as phase matching and mode coupling.

4:30 PM

(ICG-SIV-017-2019) Laser-Induced Crystallization in YAG-SiO_2 Glasses

B. Knorr*[1]; H. Jain[2]; V. Dierolf[2]

1. Fairleigh Dickinson University, USA
2. Lehigh University, USA

Laser induced fabrication of single crystal architectures is a spatially selective process which has the potential to produce photonic integrated circuits (PICs) in a glass matrix. To date, most laser-induced crystallization has targeted the growth of nonlinear optical crystals due to their many applications and the practicality of observing second harmonic generation in-situ to confirm crystallinity. Far less effort has been made to study the formation of crystals-in-glass which exhibit optical isotropy and therefore may be useful for the creation of polarization-independent waveguides. One such crystal is yttrium aluminum garnet (YAG). YAG possesses a large refractive index difference between the glass and crystal phases which makes it an excellent candidate system for waveguides in PICs. Also, Nd:YAG is a common laser material which has many applications in a diverse range of fields. In this work we present the results of our efforts to nucleate and grow YAG crystals in various Y_2O_3-Al_2O_3-SiO_2 glass compositions via femtosecond laser irradiation. Raman spectroscopy is used to characterize the laser-induced modifications, which show evidence of the formation of both an as-yet undetermined YAG-related crystalline phase and nanocrystalline silicon, depending on the specific irradiation conditions used. The latter is of particular interest due the lack of an obvious mechanism for its occurrence relative to what others have seen.

4:50 PM

(ICG-SIV-018-2019) Direct laser writing of mid-infrared S-bend waveguides in chalcogenide glasses

P. Masselin[1]; D. Le Coq*[2]

1. Université du Littoral-Côte d'Opale, Laboratoire de Physico-Chimie de l'Atmosphère, France
2. Université de Rennes, ISCR - Eq. Verres et Céramiques, France

In this contribution, we report on a low loss mid-infrared waveguides in arsenic- free chalcogenide glasses obtained by a direct laser writing technique. The waveguides consist in a multicore-type and are composed of several channels arranged on a hexagonal lattice. If the channels are placed sufficiently close to each other, an evanescent coupling will exist between the waves propagating in the channels and the mode will cover the whole structure. Each channel is obtained by stacking voxels of refractive index variation induced by femtosecond laser pulse burst in a static position. The distance between the channels can be used to vary the diameter of the waveguide, while the duration of laser burst controls the magnitude of the refractive index contrast between the channels and th glass matrix. For straight waveguide the propagation losses are measured to be ~0.2 dB/cm for a wavelength of 4.5 μm. We present also the results for curved waveguides that consists of two straight parts connected by a S-shaped one. The additionnal losses due to the bending are examined for different radius of the S- shape curvature. If the acceptable loss level is set to be 1 dB, the separation between the two straight arms can be as large as 125 μm for a 3-mm length of the S-curve.

Session 7: Photosensitive Glasses and Glass-ceramics

Room: Whittier (4th floor)
Session Chairs: Nadja Lonnroth, Corning Incorporated; Randall Youngman, Corning Incorporated

1:20 PM

(ICG-SIV-019-2019) Irradiation of densified amorphous silica and alpha quartz: Point defects and structural aspects (Invited)

N. Ollier*[1]; M. Lancry[2]; L. Skuja[3]

1. CEA, France
2. ICMMO, France
3. Institute of Solid State Physics, Latvia

We present first recent results obtained on densified silica glasses irradiated with 2.5 MeV electrons in terms of point defects, density and glass structure relaxation. In particular, the unknown point defect emitting at 550 nm (green emission point defect) is exacerbated by the densification and a lower efficiency to form O_2 molecules under irradiation was found in such densified silica glasses. Moreover, the density of all densified glasses independently of their initial stage evolves towards a unique value of 2.26. The silica glass structure versus density will be discussed (Ollier et al. Sc rep 2018). In a second part of the talk, we will pay attention to alpha-quartz irradiated by 2.5 MeV electron at dose below the amorphization threshold compared to fast neutrons-irradiated alpha-quartz. Oxygen dangling bonds ("nonbridging oxygen hole centers", NBOHCs), peculiar to amorphous state of SiO_2, were detected for the first time in electron-irradiated non-amorphized α-quartz crystal. Their presence may signal the formation of nucleation centers in crystal structure as the first step to radiation-induced amorphization. However, silicon oxygen deficiency centers, SiODC(II) and O_2 molecules, characteristic to irradiated glassy SiO_2, were both detected only in α-quartz after neutron irradiation and not in electron-irradiated ones (Skuja et al. 2019).

1:50 PM

(ICG-SIV-020-2019) Changes in Silicate Glass Induced by an Electron Beam (Invited)

O. Gedeon*[1]; T. Gavenda[1]; K. Jurek[2]; P. Jiricek[2]; J. Zemek[2]

1. University of Chemistry and Technology Prague, Czechia
2. Institute of Physics of the Czech Academy of Sciences, Czechia

Impact of an electron beam on glass triggers a series of scattering processes that transform the original glass into the new solid with modified properties. As the electron beam can be easily focused and its energy can be simply modulated, the induced changes can be properly localised and in principle, fine patterns can be formed on the glass surface. The contribution classifies the scattering processes of the dominant significance and reports experimental findings about surface roughness, chemical composition, density, and structure modifications investigated mostly on model alkali-silicate glass. Experimental conditions predominantly cover energy region 1-50 keV and were set to supress the influence of temperature increase in the irradiated volume. Macroscopic alternations in composition and density are shown to be correlated to structural evolution, mainly with formation of dandling oxygen, increase in small rings, volume relaxation around alkali sites, Si-O-Si bond relaxation, and connectivity of the topogical network; surface roughness and changes induced by low energy electrons are intimately related to surface relaxation.

2:20 PM

(ICG-SIV-021-2019) Synchrotron X-ray Interaction with Fused Silica and Soda-Lime Glasses

Q. Ma*[1]; D. T. Keane[1]

1. Northwestern University, Synchrotron Research Center, USA

Photo-induced changes in glassy materials have been studied rather extensively. In this presentation, we present experimental evidence of the reversibility of radiation-induced structural changes in fused silica and soda-lime glasses. The synchrotron-based monochromatic X-ray

source is used for irradiation experiments and simultaneously used to probe structural changes through scattering and absorption channels. We will also show the radiation effect on the local structures and chemistry around specific elements that are heavier than Potassium. These results should shine some light on the structural mechanism of coloration of glasses under irradiation by high energy photons.

2:40 PM

(ICG-SIV-022-2019) Structure-properties relationship in silver-containing phosphate glasses under nanosecond and femtosecond laser irradiations

T. Guerineau*[1]; C. Strutynski[1]; S. Danto[1]; M. Dussauze[2]; L. Loi[3]; J. Rampnoux[3]; A. Abou Khalil[4]; R. Vallée[4]; L. Canioni[3]; Y. Petit[3]; T. Cardinal[1]

1. CNRS - ICMCB, France
2. ISM, France
3. LOMA, France
4. COPL, Canada

In the two last decades, Direct Laser Writing (DLW) using femtosecond (fs) laser has been carried out to perform glass network photo-structuration leading to multiple applications. In the specific case of silver-containing phosphate glass, DLW by extrinsic photo-structuration leads to the formation of silver clusters, locally giving rise to remarkable optical properties such as photoluminescence, 2nd- and 3rd -harmonic generation, development of silver plasmonic nano-particles and demonstration of a novel type of silver-sustained single-mode waveguides. The control of the fs laser energy deposition and the glass composition has allowed demonstrating two fluorescent sub-micron lines inscription regimes. Various Oxygen/Phosphorus ratio glasses have been investigated by spectroscopy measurements (Raman, photoluminescence, absorption, etc.) to determine both the glass structure and the mechanisms of e^-/h^+ traps and silver cluster formation. The nanosecond (ns) DLW has been studied for the generation of millimetric homogenous photo-induced structures in minutes. The differences in term of DLW structures were compared depending on the laser regimes: fs or ns. Finally, the fiber drawing of selected silver-containing phosphate glasses has been demonstrated, emphasizing the potential of these materials for developing new photosensitive fiber devices.

3:00 PM

(ICG-SIV-023-2019) Femtosecond laser micro-patterning and functionalities in a novel photosensitive silver-contaning oxi-fluoride sodo-phosphate glass

H. Fares*[1]; A. Abou Khalil[2]; Y. Petit[2]; C. Strutynski[2]; S. Danto[2]; V. Jubera[2]; S. J. Ribeiro[1]; M. Nalin[1]; T. Cardinal[2]; T. Castro[1]; R. Laberdesque[2]; L. Canioni[2]

1. Institute of Chemistry - UNESP, Brazil
2. University of Bordeaux, France

Silver-containing glasses are promising candidates for photonic applications, due to the potentiality of spectroscopic properties of silver nanoclusters (NC's) and/or silver metallic nanoparticles. In this framework, silver-doped oxi-fluoride phosphate glasses are candidates with a strong potential. Indeed, combined with femtosecond laser irradiation, silver NC's may be tailored in three-dimensional fluorescent micro-structures, whose spectroscopic properties have been investigated, revealing the creation of silver NC's but also of NP's during laser irradiation in the studied oxi-fluoride glass. Additionaly, the photo-inscription of silver NC's is correlatively accompained by a positive index change, which has led to the demonstration of optical waveguiding behavior. Finally, the management of the reservoir of available silvers for laser inscription is investigated. Unlike previous observations made in standard oxide phosphate glasses, the considered silver-containing oxi-fluoride glass exhbites an intriguing ability to be re-written when subjected to successive overlapping laser irradiations. Upon the optimization of compositions with tailored photo-sensitivity, the re-writable ability of oxi-fluoride glasses paves the way to the design of advanced photonic devices such as photonic optical circuits and 3D high-density optical data storage.

3:40 PM

(ICG-SIV-024-2019) Photosensitive chalcogenide optical coatings: Basic properties and applications (Invited)

A. Bourgade[1]; T. Begou[1]; J. Lumeau*[1]

1. CNRS - Institut Fresnel, France

Very large progress has been made within the fabrication methods and the complexity of optical thin-film filters. However, these filters are generally limited to conventional materials e.g. oxydes materials. In this talk, I will present the development of optical quality photosensitive chalcogenide materials-based layers. I will detail the fabrication (evaporation) and the characterization procedures of these layers. In particular, I will concentrate on the optical properties of these layers including photo-induced phenomena. I will then show how these layers can be included within multilayer structures in order to produce various kinds of optical elements with spatially structured refractive index. Those elements include highly uniform bandpass filters, diffractive optical elements and volume Bragg gratings. Comparison between conventional oxyde based optical elements and those new elements will be provided.

4:10 PM

(ICG-SIV-025-2019) Photothermally-Induced Ge-As-Pb-Se Chalcogenide Glass-Ceramic Films with Infrared Function towards a Gradient Refractive Index Element

M. Kang*[1]; T. Malendevych[1]; G. Yin[2]; I. Murray[4]; J. Hu[2]; M. Richardson[1]; I. Mingareev[3]; K. Richardson[1]

1. University of Central Florida, CREOL, College of Optics & Photonics, USA
2. Massachusetts Institute of Technology, USA
3. Florida Institute of Technology, USA
4. BAE Systems, USA

Infrared (IR) components based on spherical or aspheric lenses have been the norm in IR imaging systems. However, narrow transparency and chromatic aberration lead to an increase in the number, volume, and weight of optical components to compensate the issues, and therefore remain as lingering challenges for broadband and compact demands of IR designs. Meanwhile, IR gradient refractive index (GRIN) materials have been proposed as a solution to the issues and developed to exhibit locally-tailorable index within a single component. We present a scalable approach capable of manufacturing IR GRIN nanocomposites in planar glass-ceramic thin films. We discuss the photo-thermal process to spatially modulate the concentration of sub-wavelength, high-index nanocrystals within chalcogenide thin film glasses, composed of Ge-As-Pb-Se. Specifically, sub-bandgap laser exposure generates a Pb-rich amorphous phase within the glass film, which undergoes crystallization upon post heat treatment, resulting in high-index nanocrystals. Nanocrystal density is modulated by the laser dose, providing a spatially tailorable index change approaching +0.1, while maintaining their IR transparency. We have demonstrated GRIN functionality in films with thicknesses from 1μm to 40 μm, confirming that the photothermally-induced index change is both repeatable and scalable.

4:30 PM

(ICG-SIV-026-2019) Preparation and Luminescence Characteristics of Ce^{3+}-Li^+ Co-doped Magnesium Borate Glass Ceramics for Dosimetry

Y. Kitagawa*[1]; E. G. Yukihara[2]; S. Tanabe[1]

1. Kyoto University, Graduate School of Human and Environmental Studies, Japan
2. Paul Scherrer Institut (PSI), Switzerland

Lanthanide-activated MgB_4O_7 has been studied for thermoluminescence (TL) and optical stimulated luminescence (OSL) dosimetry of ionizing radiation. This is because MgB_4O_7 is an attractive host material for dosimetry due to the two characteristics: its low effective atomic number (Z_{eff} = 8.4), which implies a small photon energy dependence, and its high neutron capture cross-section by

enriching ^{10}B. According to previous reports, Ce^{3+}-Li^{+} co-doped MgB_4O_7 has the potential to show the stronger OSL signal than the well-known dosimetry material Al_2O_3:C. As a way to improve the dosimetric properties of MgB_4O_7:Ce^{3+}-Li^{+}, we propose precipitation of the MgB_4O_7 crystal in the glass matrix. Generally, glass ceramic (GC) materials have advantages such as high formability, low cost, and mass production. In addition, GC materials with high degree of crystallization can be denser than conventional ceramics because of no porosity, and thus may show better luminescent performance. In this study, the Ce^{3+}-doped $25MgO\text{-}72B_2O_3\text{-}3Li_2O$ GCs were obtained by heat-treatment of the glass samples at various temperature, and the luminescent and dosimetric properties of the GCs were investigated and compared.

4:50 PM

(ICG-SIV-027-2019) Longterm stability of defects in laser irradiated glasses doped with polyvalent ions

D. Möncke*[1]

1. Alfred University, USA

Polyvalent ions occur in various oxidation states in glasses, though the variability is less than typically expected for inorganic complexes. Photo-ionisation of polyvalent ions is a well-known phenomenon. Irradiation by X-rays or UV light can form unusual oxidation states, such as Co^{3+}, Ni^{3+}. Interestingly, these for glasses "unstable" oxidation states, can be identified in irradiated samples even 10 to 15 years after the original irradiation, a time in which the glasses where stored in the dark at ambient temperature. The quantity of these photo-ionized ions even increased over time, as positively charged intrinsic hole centre (HC) take up an electron of the remaining divalent species, rather than combining with intrinsic electron centres (EC). Here, we present our recent UV-Vis measurements on a series of transition metal and post-transition metal doped (fluoride-)phosphate glasses which had been irradiated by various lasers in the years of 2001-2007.

SV: Glass Education

Glass Education (TC 23)

Room: Tremont (4th floor)
Session Chairs: Mathieu Hubert, Corning Incorporated; Ana Rodrigues, Federal University of Sao Carlos

1:20 PM

(ICG-SV-001-2019) Education in the field of glass (Invited)

R. Conradt*[1]

1. uniglassAC GmbH, Germany

Providing a comprehensive instruction in glass science and technology is a great challenge. The field comprises a wide number of disciplines and topics, ranging from materials science (the physics and chemistry of glasses with a focus on structure, thermodynamics, atomistic modeling, as well as optics and photonics) towards engineering (thermochemistry; heat, mass, and momentum transfer as well as combustion and reactor technology). The paper summarizes the experience gained during a decade of teaching at the Montpellier Summer School of ICG. A special emphasis is laid on the endeavor to elaborate and highlight the mutual relations among the different sub-disciplines instead of presenting them as quite unrelated individual topics. This applies, in specific, to the relation between science and engineering. Finally, a basic curriculum of indispensible core topics is presentete which should - irrespective of any further specialization - be acquired by any glass student.

1:50 PM

(ICG-SV-002-2019) Group projects in teaching (Invited)

J. M. Parker*[1]

1. University of Sheffield, Materials Science and Engineering, United Kingdom

A central feature of the ICG Summer and Winter Schools in Montpellier and Wuhan is the projects that the participants undertake during the 5 days of the event. This talk will look at the development of suitable topics for the students to tackle and the mechanics of running them, warts and all. Examples, selected from among the best presentations, will be used for illustration throughout the talk. Some of the potential problems in running these in a more formal environment, for example as part of a degree class, will be analysed and in particular the difficulty of assessing individual contributions.

2:20 PM

(ICG-SV-003-2019) Glass Without Walls or Ceilings; Why Artists and Engineers/Scientists Should Not be Separated

A. G. Clare*[1]; S. K. Sundaram[1]; A. Powers[2]; W. LaCourse[1]; S. Blood[2]; D. Möncke[1]; D. Karen[2]

1. New York State College of Ceramics, Alfred University, Kazuo Inamori School of Engineering, USA
2. New York State College of Ceramics, Alfred University, School of Art and Design, USA

Since 2013, we have been offering a yearly course that we call GlassArtEngine/EngineGlassArt, which counts as a Glass elective either in Art and Design (as ART 397) or in Engineering (as CEMS387) as a studio-lab based glass within the New York State College of Ceramics (NYSCC) at Alfred University. Under this course, Artists and Engineers work together on self-initiated projects based on the need of knowledge from both disciplines. Faculty participate as consultants giving advice and assistance from their discipline where needed but the key element is interaction and exchange of knowledge and ideas between the artists and engineers. In most cases, this course has led to the artists applying a more scientific approach to achieving their art and the engineers becoming more adaptable, willing to try things, not assuming that it will not work, both learning to work in open environment as opposed to a rigidly structured engineering curriculum. Moreover, many students have continued to interact across disciplines after the course has finished, which implies that this type of cross-disciplinary interaction is very beneficial and should be expanded. Finally, this course is a part of an ongoing concerted effort to offer an accelerated double major between Engineering and Arts & Design, which will be discussed further in the symposium.

2:40 PM

(ICG-SV-004-2019) Studio-Laboratories for interdisciplinary Glass Art/Engineering Degrees

W. LaCourse*[1]; A. G. Clare[1]; S. K. Sundaram[1]; D. Möncke[1]; A. Powers[2]

1. Alfred University, Inamori School of Engineering, USA
2. Alfred University, School of Art and Design, USA

The NYS College of Ceramics at Alfred University has graduated a number of "Double Degree BS/BFA" students in glass, ceramics and materials science. However, the time required to earn such degrees (often 12-13 semesters) has been prohibitive for most interested students. To increase student access the Glass Art and Glass Engineering Science faculty are developing 5-year "Accelerated Double Degree" (ADD Glass) programs. Other interdisciplinary "single degree" programs are also being considered. To facilitate the condensed program, "Studio-Laboratories" will be implemented. They combine the artist's hands-on approach to hot-working, "forming" and "post-forming" with measurement of the melt, transition range, and glass properties. Where possible, students carry out hands-on experiments with a minimum of

"black box" instrumentation. As an example, thermal expansion measurements using a dial gauge and a simple tube furnace provide results that illustrate the concepts, while additional measurements using a commercial "LVDT" instrument demonstrate the origin of errors and the need for accurate and precise measurements. Similar comparisons can be achieved for viscosity. Melting behavior and fining can be studied in 100 Kg tanks and compared with results from 100 cc lab melts. Several examples will be provided together with a description of the full ADD Glass degree program.

3:00 PM

(ICG-SV-008-2019) Development of a new glass course at Corning Community College

M. Hubert*[1]

1. Corning Incorporated, USA

This past year, scientist at Corning Inc have been working with the Corning Community College (CCC) to develop a new, 2-semester glass course entitled: "Introduction to Glass I & II". This course, approved by the NY State and the college in January 2018 and including lectures, labs, and visits to industrial facilities, is meant as an introduction to glass science and technology for undergraduate students attending CCC. Developed and taught by Corning Inc scientists, the course is intended to give a basic experience in glass for technical degree candidates, for individuals hoping to work at Corning Inc or willing to pursue their career in glass. As we are reaching the end of the first year of teaching, this presentation will narrate the development of the course, its organization, the experience gathered and the lessons learnt during the first year of classes, including feedbacks from the teachers and the students.

3:40 PM

(ICG-SV-006-2019) Partnership with Researchers in Industry for Doctoral Education (PRIDE) - Preparing better educated glass researchers (Invited)

H. Jain*[1]; V. Dierolf[1]; A. Jagota[1]; H. Columba[2]; D. Vaughn[3]

1. Lehigh University, Institute for Functional Materials and Devices, USA
2. Lehigh University, College of Education, USA
3. Corning Incorporated, USA

Much of glass science continues to follow the traditional paradigm of curiosity-driven research: basic research → applied research → development → production → marketplace. A complementary approach is based on use-inspired research, which is driven by critical societal needs directly. While many skills and competencies in both approaches overlap, graduate students may not have the opportunity to fully explore industry-related skillsets and mindsets in a traditional academic setting. We argue that a stronger collaboration between industry and academia can bridge this gap, even prepare stronger faculty candidates. Accordingly, we have developed a new model of graduate education, Partnership with Researchers in Industry for Doctoral Education (PRIDE), which is being tested with support from NSF's Innovation in Graduate Education program via a collaboration between Lehigh University and Corning Incorporated. It represents a student-centered, holistic approach that gives students long-term, hands-on industry experience. Its key features, which will be discussed in detail, include: (a) a pre-program summer experience with a company to identify a research topic; (b) co-advisers from the university and partner company; (c) modular, graduate-level professional development co-taught by faculty and industry researchers; and (d) a one to two semester company residency.

4:10 PM

(ICG-SV-007-2019) The Ceramic and Glass Industry Foundation: Attracting, Inspiring, and Training the Next Generation of Ceramic and Glass Professionals (Invited)

M. J. Fish*[1]

1. The Ceramic and Glass Industry Foundation, USA

Over the past several decades, there has been a clear decline in the number of students being educated in the fundamentals of ceramic and glass science. In the United States, there is very little teaching of Materials Science at the K-12 level and there are only two Universities that offer a BS degree in Ceramic Engineering. It's an industry-wide worry: where will tomorrow's ceramic and glass technicians, engineers, and scientists come from? The Ceramic and Glass Industry Foundation (CGIF) was established by The American Ceramic Society in 2014 with the goal to attract, inspire, and train the next generation of ceramic and glass professionals. Since its inception, the CGIF has launched programs for student outreach, international student exchanges, travel grants, and student leadership development. In addition the CGIF has created university/industry networks, and an online Ceramic and Glass Career Center. The CGIF also provides grants for projects around the world that engage students with learning experiences and events that inspire interest and understanding of ceramic and glass science and engineering. This presentation will review the work of the CGIF over the past five years, highlighting the successful outcomes and challenges we face as we work toward accomplishing our mission.

4:40 PM

(ICG-SV-005-2019) Research on glass with Undergraduates

S. Feller*[1]; M. Affatigato[1]

1. Coe College, Physics, USA

Lessons learned by doing research with undergraduates will be reviewed. Coe College is a liberal arts undergraduate-only college in Cedar Rapids, Iowa. It is home to a thriving physics department where undergraduate research on glass is of central importance. The focus of this talk will be on the mechanisms by which about forty students per year do original research, the majority of whom do it on glass in several allied research groups. Key questions considered include: How to choose suitable research topics? How to secure funding? How to work with the college's administration? How to establish collaborations? How to serve within the glass community? How to balance teaching and research? How to balance life and research? How to grow the research program while sustaining it? This work is supported by the National Science Foundation under grants DMR 1407404 and DMR 1746230

5:00 PM

(ICG-SV-009-2019) First Glass Technician Training Course in South America

A. C. Rodrigues*[1]; M. Akerman[2]

1. Federal University of Sao Carlos, Materials Engineering, Brazil
2. Escola do Vidro, Brazil

In view of the dearth of professional training courses for the glass industry in Brazil, which negatively affects its development, CeRTEV (Center for Research, Technology and Education in Vitreous Materials), an academic association of three public universities, worked in close collaboration with important partners to propose, develop and implement a training course at high school level. In this undertaking, CeRTEV worked in partnership with ABIVIDRO, the Brazilian Technical Association of Glass Industries, and the Paula Souza Center (PSC), an organization of the São Paulo state government that currently manages 214 Technical Schools in 163 municipalities in the state of São Paulo. The Brazilian glass manufacturer Nadir Figueiredo subsequently joined this project,

supporting the renovation of the dedicated laboratory of the PSC. The first "Glass Manufacturing Technician" course started in 2018, with a group of 40 students, who were selected in a public selection procedure from approximately 160 applicants. These first applicants will complete their training course in July 2019, at the end of their third semester. CeRTEV also offers several training sessions for teachers of the Paula Souza Center involved in the course. In this presentation, we will introduce and discuss several aspects of the implementation of such a course.

Poster Session 1

Room: Grand Ballroom A (mezzanine)

6:00 PM

(ICG-P001-2019) Role of Network-forming Ions in Metaphosphate Melts: Results of a Dynamic Light Scattering Study

D. Sidebottom*[1]; D. Vu[1]

1. Creighton University, Physics, USA

Dynamic light scattering conducted on a series of mixed metaphosphate glass melts of the form $[Zn(PO_3)2]_y[NaPO_3]_{1-y}$ and $[Al(PO_3)_3]_y[NaPO_3]_{1-y}$ near the glass transition point measures the temperature dependence of the relaxation time to provide the glass-forming fragility. This glass property is sensitive to the level of covalent bonding in the network and was recently shown to exhibit a universal dependence on coarse-grained network connectivity. Here we examine how the fragility evolves as Na, a modifier atom, is systematically replaced by either Zn or Al, both considered to be network formers in Zachariasen's classification scheme. We demonstrate that both Zn and Al do function as network formers by showing how the systematic decrease in glass fragility with replacement by either Zn or Al only conforms to the universal pattern when these ions are treated as such.

(ICG-UGSP-P002-2019) Study of the structural and optical properties of system CrO_2- TeO_2-V_2O_5

J. J. Bórquez*[1]; O. Soriano-Romero[2]; R. Lozada-Morales[2]; I. García-Amaya[3]; M. Zayas[1]

1. Universidad de Sonora, Investigación en Física, Mexico
2. Benemérita Universidad Autónoma de Puebla, Facultad de Ciencias Físico-Matemático, Mexico
3. Universidad Estatal de Sonora, Geociencias, Mexico

Eight glasses were obtained in the system CrO_2-TeO_2-V_2O_5 varying the composition in each of the reagents TeO_2 and V_2O_5, from 10-80% wt, while the CrO_2 remained constant in 10% wt. The vitrification was in a Coors high alumina crucible at 900°C. The X-ray diffraction patterns show amorphous and crystalline phases, identifying nanocrystals of Cr_2TeO_6 (30.72 nm). The Raman spectra reveal the presence of Te-O-Te vibrational modes which make up the functional groups TeO_3 (773-780 cm^{-1}) and TeO_3+TeO_4 (587-780 cm^{-1}) and identifies V_2O_5 conglomerates in the 840-917 cm^{-1} interval. The value of refractive index increases with the concentration of TeO_2 and varies from 2.1-2.8. The optical absorption shows a wide band centered around 270 nm, which is intensified by increasing the TeO_2 and is associated with absorptions of TeO_2 particles.

(ICG-P003-2019) Competitive formation of metallic glasses and glass-matrix composites in eutectic systems

D. Ma*[1]

1. Oak Ridge National Lab, Neutron Scattering Divison, USA

The competitive growth principle that governs phase selection during solidification has been utilized to investigate the formation of metallic glasses and glass-matrix composites in binary and ternary eutectic systems. The model indicates that full glass formation is due to the suppression of all primary competing crystalline phases and eutectic structures, while glass-matrix composites result from the coexistence of competing crystalline phases and/or eutectic structures with the glass. A new criterion gauging the globally optimum glass-forming ability in eutectic systems is derived, with a corollary that the best glass-forming composition zone can be either symmetric, or asymmetric, about the eutectic composition. Based on the model predictions, we outline a microstructure-based strategy to pinpoint the off-eutectic composition with the optimum glass-forming ability and propose a thermodynamic calculation method to search bulk metallic glass-forming compositions in multicomponent eutectic systems. The practical implementation and significance of the strategies is demonstrated by discovering bulk metallic glasses in Zr–Cu, Zr–Cu–Al and Zr-Cu-Ni-Ti-Al systems. The implications for oxide glass formation in eutectic systems will be also discussed.

(ICG-GSP-P004-2019) Crack initiation in an indented metallic glass with embedded nanoparticle

K. Lee*[1]; Y. Yang[1]; J. C. Mauro[1]

1. Pennsylvania State University, Material Science and Engineering, USA

Nanoindentation was performed on a metallic glass with an embedded glassy nanoparticle using molecular dynamics simulations to investigate the effect of the second phase on shear band formation and crack initiation. It was found that the addition of a nanoparticle having a lower elastic modulus compared to that of matrix centralizes the region of shear strain below the indenter, which facilitates crack initiation. In contrast, the addition of a nanoparticle with a higher elastic modulus has the effect of branching the shear band, which confines the shear bands within the hydrostatic zone and suppresses crack initiation.

(ICG-P005-2019) Structural, optical and thermoluminescence analysis on lithium borate glasses

S. R. de Souza*[1]; D. L. Menezes[1]; J. E. De Souza[1]

1. Federal University of Grande Dourados, Physics, Brazil

Borate glasses have been widely studied due to their physical-chemical characteristics that attributed promising application in technological devices. In this work, glass samples in the $(100\text{-}x)B_2O_3 - xLi_2O$ binary system, to x = 30 to 50 mol%, were prepared by the conventional melting and casting process, with the objective of evaluate the thermoluminescent response of the glasses when exposed to ultraviolet radiation (UV). Analysis were done by applying Arquimedes' principle (density), optical absorption on the ultraviolet-visible region (UV-Vis absorbance), Fourier Transform on the medium-infrared region (FTIR), X-ray diffraction, thermal analysis and thermoluminescence (TL) techniques. The addition of Li_2O as modifier, causes the increase of nonbridging oxygens (NBO's) in the short-range order of the glass structure. Thermoluminescence emissions had shown glow curves with at least two peaks with maximums at temperatures around ~170 and ~250°C. However, a strong influence of triboluminescence was observed due to the friction when grinding the materials, which couldn't be avoided even using N_2 as an inert atmosphere during measurements. Different thermal treatments (TT) were carried out at temperatures varying between 150 to 250 °C in order to minimize the TL spurious effect. Additionally, a static energy discharge process was performed being efficient to reduce the TL spurious signal.

(ICG-P006-2019) Synthesis, structure and physical properties of $1La_2O_3$:$2WO_3$:$1B_2O_3$ glass containing Nb_2O_5

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In the present study our attention was focused on the synthesis of tungstate glasses with nominal composition $50WO_3$-$25La_2O_3$-$25B_2O_3$ (mol%), where Nb_2O_5 is added with the expense of WO_3. Homogenous transparent glasses (80-90% transmittance) containing 10, 15 and 20 mol% Nb_2O_5 were obtained. The thermal parameters

of the synthesized glasses were evaluated by differential thermal analysis. It was found that the glass transition temperature increases with the increase of Nb_2O_5 but the crystallization temperature decreases. Physical parameters of synthesized glasses such as density, molar volume, oxygen molar volume, oxygen packing density and refractive index were measured. It was found that with the addition of niobium into the glass, the density and refractive index increase, while molar volume and oxygen molar volume decrease. Structural model for the glass network was suggested on the base of IR and Raman spectral investigations. It was established that WO_6 and WO_4, NbO_6, BO_3 and BO_4 structural units build up the glass network. Acknowledgments: This work is supported by Bulgarian National Science Fund under project КП-06-H29/7

(ICG-P007-2019) Study of the effect of fluorine and alkaline earth modifiers in the structure and crystallization of oxyfluoroborates glasses

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Interest in the development of glasses and glass ceramics with improved optical properties has been on the rise, given their applications in solar concentrators, waveguides, temperature sensors, among others. One strategy to achieve this goal is the use of active materials such as rare earth elements (REE) doped glasses. When these REE are incorporated into the oxide glass matrix, the interaction between them produces limited emission from the REE. Some time ago, oxide glasses with fluoride nanocrystalline phases were prepared and showed improved optical properties. Despite that, much work has been done on silicate systems, and it is interesting to expand these studies to other matrices such borates glasses. Here, we report the preparation of some alkaline earth oxifluoride glasses to be doped with REE. We used spectroscopy techniques; FTIR, Raman and NMR, to study the structural effect produced by the incorporation of fluoride into the glass structure. Additionally, we studied the compositions where nanocrystalline fluoride phases could be obtained. For this, we used Differential Scanning Calorimetry and High-Resolution Transmission Electron Microscopy. Our results indicate a small variation of N_4 (BO_4 fraction) in the glasses studied, and that the incorporation of BaO encourages glass ceramics with a narrow size distribution of nanocrystals.

(ICG-P008-2019) The composition inhomogeneity and nanocrystalline inclusions in phosphate–silicate glass cores of preforms for optical fibers

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The rare-earth-doped phosphate-silicate glass core of preforms for optical fiber (OF) made by different methods has been studied by using electron microscopy and X-ray microanalysis. The phase separation and the emergence of nanocrystalline inclusions in Yb-doped preforms obtained both by the powder sintering methods (PSM) with the vibrational mixing of the melt and the Yb-containing nanoparticles doping into preforms method (NDM), are characterized. The phase separation consist in formation of Yb-enriched micrometer size spherical inclusions (droplet phase separation). Nanocrystals of $YbPO_4$, SiO_2, and YbP_3O_9 are formed in the preforms obtained by PSM and only $YbPO_4$ nanocrystalls are present in the preforms made by NPM. It is concluded that the $YbPO_4$ are crystallized as a result of the phase separation from the Yb-enriched glass phase. The types of inhomogeneity in spatial distribution of the element in preforms and homogenization of core composition during fiber drawing process has been studied in Ln-doped (Ln = Yb, Sm, Er, Ce) samples obtained by MCVD method. The phenomenon of the droplet phase separation was registered in some cases also for these performs. But both this phenomena within the thin layer and creation of thin ring layer enriched with the rare-earth phosphate allow to construct the dispersion shifted hybrid OF with specially properties.

(ICG-P009-2019) Thermal, structural and crystallization study of Na_2O-P_2O_5-Nb_2O_5 glasses

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Present investigation deals with the study of structure, properties and thermal behaviour of Na_2O-P_2O_5-Nb_2O_5 glasses prepared in the compositional series $40Na_2O$-$(60-x)P_2O_5$-xNb_2O_5 (x=0-40 mol% Nb_2O_5). The modification of starting $40Na_2O$-$60P_2O_5$ glass by Nb_2O_5 revealed changes both in the structure and properties. Glass density steeply increases with increasing Nb_2O_5 content within the range of 2.43-4.16 g cm^{-3} whereas molar volume decreases. Parent sodium ultraphosphate glass was colourless and in air was covered with a thin layer of partially hydrolysed glass. Chemical durability of Nb_2O_5 containing glasses was high. The replacement of P_2O_5 by Nb_2O_5 resulted in a gradual increase of the refraction index as well as in an increase of glass transition temperature and dilatometric softening temperature. DSC measurements showed that glasses crystallize under heating in the temperature range of 330-880°C. The lowest thermal stability was found for the starting $40Na_2O$-$60P_2O_5$ glass and glass containing 40 mol% Nb_2O_5. Raman and NMR spectra showed that the structure of $40Na_2O$-$60P_2O_5$ glass is formed mainly by Q^2 and Q^1 phosphate units interconnected by P–O–P bonds. The replacement of P_2O_5 by Nb_2O_5 leads to the depolymerisation and to the partial transformation of Q^2 units into Q^1 units and finally to the isolated Q^0 units. Nb_2O_5 forms in the glass structure NbO_6 octahedra.

(ICG-P010-2019) Structural Relaxation and Topology of Ionic Fluorophosphate Glasses

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Ionic glasses, whose glass components interact through mostly electrostatic interactions, have different topologies and a broader frequency of relaxation processes than conventional, covalent glass-formers. Here, we present the calorimetric investigation of the structural relaxation of the $(1 - x)NaPO_3$-$xAlF_3$ glass series; to better understand the relaxation processes, the structure is elucidated by ^{31}P, ^{27}Al and ^{19}F MAS NMR. As more AlF_3 is added, some glass regions become increasing constrained due to more Al—F—Al and Al—O—P cross-links, which increases both the E_a^{max} and range of E_a's for the α-relaxation processes. The broad range of E_a's indicates that the glass transition is composed of several different-energy structural processes and that the glass structure is heterogeneous on the length-scale of these processes. We observe that there are phosphate-rich regions which are more like $NaPO_3$ without many bridging bonds to Al, but at the same time, there are $Al(OP)_4F_2$-rich regions that are much more topologically constrained. The ^{31}P NMR shows the average phosphate chains to decrease; commensurate with a decrease in the average cooperatively-rearranging-region (CRR) from DSC analysis. We believe the constrained $Al(OP)_4F_2$ octahedra are behaving similar to pin defects of a harder material in crystals and breaking up the phosphate network into smaller, easily rearranged, phosphate chains.

(ICG-GSP-P011-2019) Revealing the Short-and Medium Range Structures of Sodium Lanthanum Alumino-phosphate Glasses from Molecular Dynamics Simulations

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Rare-earth phosphate glasses are of immense technological importance due to their unparalleled applications in optical lasers and magneto-optical devices. This work sheds light on the short- and medium range structure information of rare-earth phosphate glasses in xLa_2O_3 (100-x) $NaPO_3$: (x=0, 3, 5, 7.5) and alumino-phosphate glasses in xLa_2O_3- yAl_2O_3 - (100-x-y) $NaPO_3$: ($0 \leq x \leq 5$ and $5 \leq y \leq 15$) series using molecular dynamics (MD) simulations. Detailed description of the local environment of lanthanum in the short range was obtained by studying the partial distribution function, bond angle distribution, and coordination number. The local environment of lanthanum was found not be altered due to the presence of Al_2O_3. The coordination numbers of both lanthanum (N_{LaO}) and aluminum (N_{AlO}) transferred to higher values with the increase of La_2O_3 and Al_2O_3 respectively. Distribution of lanthanum ions was studied as a function of glass composition. Network former Q^n distribution and polyhedral connectivity were also analyzed. These results were compared with available experimental data and newly obtained solid state NMR measurements.

(ICG-GSP-P012-2019) Dissolution behavior of Li_2O-ZnO-P_2O_5 glasses in water

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The dissolution behavior of glasses from the Li_2O-ZnO-P_2O_5 (LZP) system was investigated. Heat released as a result of the dissolution and precipitation reactions was measured by a calorimeter. Changes in solution chemistry were monitored using ICP-OES and phosphate anion distributions at different dissolution times were characterized using High Pressure Liquid Chromatography (HPLC). These results will be compared with those predicted from thermodynamic calculations by FactSage. This work was supported by the National Science Foundation (CMMI-1661609).

(ICG-P013-2019) The features of obtaining of bioactive high-silica porous glasses

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The high-silica porous glass (PG) is a promising base material for the production of functional, including composite materials. Due to a unique complex of properties, such as chemical, thermal and biological durability, porous glasses are widely used in various fields of science and technology. A unique set of properties allows the use of PG in biomedicine as carriers for the immobilization of microorganisms and as more effective sorbents than widespread organic and inorganic sorbents, such as silica gels, activated carbon, cellulose acetate, etc. The initial glasses for the synthesis of porous glasses are the basic two-phase sodium borosilicate and sodium alumina borosilicate glasses. Recent works have shown the prospects for the synthesis of composites based on porous glasses with incorporated polyoxometallates in the porous space. It was shown that the formation of silicon polyoxomolybdates occurs due to the interaction of the heteropoly molybdenum anion with the "secondary" silica gel in the porous space. It was shown the biological activity against certain microorganisms for both to porous glasses and to resulted porous composites.

(ICG-P014-2019) Bismuth-doped silica fibers and performs: Microstructure, composition, and nanocrystalline inclusions

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Microstructure, spatial element distributions and nanocrystalline inclusions in Bi-doped silica preforms and fibers made by chemical vapor deposition (CVD) and on the basis of porous glasses (PG) have been studied using electron microscopy and X-ray microanalysis. The attention has been focused on the nano-level homogeneity of core glasses. The CVD cores were composed of $Bi:SiO_2$, $Bi:Al_2O_3$-SiO_2, $Bi:GeO_2$-SiO_2, $Bi:Al_2O_3$-GeO_2-SiO_2, and $Bi:P_2O_5$-Al_2O_3-GeO_2-SiO_2. The nature of nanocrystalline inclusions in these samples depends on Bi concentration and the ratio of the dopant concentrations in the core glass. The following nanocrystalline inclusions were observed: metal Bi, α-SiO_2, α-Bi_2O_3, GeO_2, and $Bi_4(GeO4)_3$. Such inclusions can lead to the background optical loss in fibers. The PG had pores of the average size of 4 nm, while larger pores and channels were up to 40 nm in the surface layer. Transparent colorless consolidated samples with Bi concentration up to 0.8 at. % were prepared by impregnation of PG with aqueous $Bi(NO_3)_3$ or $Bi(NO_3)_3$+$Al(NO_3)_3$ solutions followed by thermal treatment. The samples with the Bi content of <0.25 at.% and the Al content of 0.12–0.18 at.% were chemically homogeneous and had good absorption and luminescence properties. These data point at the prospects of using PG as initial material for Bi-doped fibers.

(ICG-GSP-P015-2019) Non-linear Optical Properties of Rare-earth Aluminosilicate Glasses

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Non-linear rare-earth aluminosilicate glasses were studied, with variations in network modifiers, alkalies (Li, Na, K) and alkaline-earths (Ca, Sr, Mg). Concentrations of selected rare-earth elements, (e.g., La, Ce, Sm, Dy) were systematically varied in a base aluminosillicate glasses and a series of glasses were made and characterized in our laboratory. Density, glass transition temperature, and tendency to crystallization were measured. Ultrashort laser pulses (about 40 femtosecond) were used to irradiate the glass samples and inducing the non-linear optical processes and modifying the glass structure in the process. The irradiated regions were characterized and compared to un-irradiated bulk glasses using differential scanning calorimetry (DSC), x-ray diffraction (XRD), and ultraviolet-visible-near-infrared (UV-Vis-NIR), Raman, and nuclear magnetic resonance (NMR) spectroscopic tools. The non-linear optical properties, specifically the third-order non-linear optical susceptibility properties such as non-linear refractive index and non-linear absorption, were measured. The structural changes are correlated to changes in refractive index, density, and optical band gap. We will present our results and interpretations.

(ICG-UGSP-P016-2019) A multi-spectroscopic study of highly modified sodium silicate glasses

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The typical glass forming region for sodium silicates is below 50 mol% sodium oxide. Through alternative glass making procedures, sodium silicate glass was made at up to 70 mol% soda. In addition to procuring the glass carbon dioxide retention was observed in the highly modified samples. Neutron and x-ray scattering, density, Raman spectroscopy, LECO carbon analysis, and ^{13}C MAS

NMR spectroscopic measurements were undertaken in an effort to understand the physical properties and structural impacts of the carbon dioxide in the glass, including short- and intermediate-range structure. Comparisons were made to samples prepared without carbonates. This work is supported by the National Science Foundation under grants DMR 1407404 and DMR 1746230.

(ICG-GSP-P018-2019) Correlation between Optical Absorption and Local Structure of Ni^{2+} Ion in Aluminosilicate Glasses

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Glass coloration strongly depends on oxidation and coordination states of coloring ions, such as those of transition metal. A precise understanding of the speciation of these ions and their correlation with glass structure will allow to add new functionality to glass. Aluminosilicate glass is well known to show characteristic properties based on its structure. Especially, magnesium aluminosilicate shows strong interaction between Mg^{2+} and AlO polyhedron and it reveal unique properties. However, the method to investigate the structure of modifier cations is limited compared with Si and Al, and its details are not fully understood. Ni ion was picked up as representative ion of divalent modifier cation such as Mg^{2+} ion, because ionic radius of Ni^{2+} is close to that of Mg^{2+}, and Ni ion only presents as divalent ion in glass stably and optical absorption of Ni^{2+} ion are sensitive to ligand field. In this study, $33MO–12Al_2O_3–55SiO_2$ (mol%, MO: modifier oxide) glasses containing 0.2 mol% NiO were prepared and UV-Visible absorption spectra of these glasses were measured. From the comparison with the data of crystalline and solution references containing Ni ion with known local structures, both the coordination number and the ligand field of Ni^{2+} in these glasses is determined. In the presentation, the composition dependence of the local structure of Ni^{2+} ion in glass will be discussed.

(ICG-P019-2019) Effect of addition of lithium phosphate as nucleating agent in lithium disilicate glass ceramic system

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Lithium disilicate glass ceramics have been processed for a long time through a melt route with in-situ formed lithium phosphate nucleating agent. It was decided to explore a powder based route for processing the glass ceramics with externally added lithium phosphate. Also, a powder based route may provide greater flexibility in shape forming lithium disilicate glass ceramics. The present study compares processing of the glass ceramics with in-situ formed lithium phosphate (GC1) and externally added lithium phosphate. Two different ex-situ added Li_3PO_4 based compositions were studied – (i) Overall Li content same as reference composition with Li partitioned between glass and lithium phosphate (GC2) (ii) Overall Li greater with additional Li present as externally added Li_3PO_4 (GC3). Both GC2 and GC3 showed an early crystallization as compared to conventional GC1. Because of same amount of total Li content as GC1, GC2 showed similar crystal phase evolution i.e. lithium disilicate as major crystallization phase, whereas, due to excess Li content GC3 produced lithium metasilicate as major crystalline phase. Details on microstructure, density, phase evolution and hardness will be presented.

(ICG-GSP-P020-2019) Crystallization mechanism and electrical properties of Na_2O-FeO-MnO-SiO_2 glass

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For reasons of cost and safety issues in lithium ion batteries, there is a growing interest in the development of rechargeable sodium ion batteries. Materials development in sodium ion batteries will be interested in being composed of non-rare metal oxides. Silicon is the second most abundant in the crust, and the cathode active material composed of transition metal and sodium silicate is attractive from the viewpoint of resource and price. Na_2MSiO_4(M = Mn, Fe) is one of cathode candidates for sodium ion batteries and it was synthesized by a sol–gel method. Na_2MSiO_4 (M = Mn, Fe) crystal shows a potential around 3.0 V at room temperature, the discharge capacity is 70 mAh / g, and the capacity retention of the 10th cycle is about 80% Has been reported. On the other hand, we reported that optically transparent crystallized glass by heat treatment in the stoichiometric composition of $Na_2Mn_{0.5}Fe_{0.5}SiO_4$. We also clarified the formation of thermodynamically metastable cubic phase in bulk glass matrix. In this study, the preparation and crystallization behavior of Na_2O-FeO-MnO-SiO_2 glass was investigated further and electrical characteristics evaluated.

(ICG-GSP-P021-2019) Laser-induced structural modification in $Na_2FeP_2O_7$ glass-ceramics

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Attempts to add value to the materials surface by heating and melting by laser irradiation are widely performed in metals, plastics and ceramics. Among them, we are promoting morphological control of micro crystals precipitated by laser irradiation to glass in various system. In order to enable heating of glass matrix by laser irradiation, it is necessary to absorb the laser energy into the glass matrix. Therefore, We use continuous wave type near infrared laser (λ = 1080 nm of Yb^{3+}: YVO_4 laser). The energy of the laser effectively absorb by the d-d transition of the Fe^{2+} ion then formation of melt and crystallization occur in shortly. In this study, laser-induced structural modification in $Na_2FeP_2O_7$ (NFP) crystallized, which is promising as an active material for sodium ion batteries, was investigated. When the laser power was 0.22 W, the surface of NFP pellet easily melted. By means of X-ray diffraction vitrification of the surface was confirmed after laser scanning. Further, when the pellet whose surface was vitrified was heat-treated in H_2 / Ar atmosphere at 853 K for 3 hours, the NFP crystal precipitated again.

(ICG-P023-2019) Thermo-mechanical characterization of sealing glass pastes

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Specialized glasses and glass-ceramics are used for electronics, sensors, sealings among many others. For example, doped bismuth-borate-based glasses have gained recent attention due to their outstanding glass-forming ability combined with favorable durability, optical and electrical properties. Bismuth here represents an ideal replacement for lead and allows low-temperature prcoscessing as required for many technological applications. We use oscillatory parallel-plate rheometry measurements on a sealing glass paste to determine the visco-elastic properties with increasing temperature, representing application, glazing and firing processes. With this method, it is possible to observe the glass transition, the viscosity decrease of the sample in the liquid state, followed by devitrification and possibly phase transitions of oxide phases in the solid state. Our measurements provide thermo-mechanical characterization of the entire sealing process and can be used to complement calorimetric investigations. Knowledge on the visco-elastic properties allows reducing processing temperatures and is a useful tool for quality control and sealant development.

(ICG-P024-2019) Introducing a Versatile Chemical Mapping Tool for Your Advanced Glass Ceramics: Tandem Laser Induced Breakdown Spectroscopy and Laser Ablation ICP-MS

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Characterization of the chemical and structural compositions of advanced glass ceramic materials by traditional analytical techniques can be complex and time consuming. We introduce a rapid solid sampling technique that is ideal for non-crystalline or mixed amorphous-crystalline and transparent materials - Tandem LA-ICP-MS/LIBS. This novel approach can provide quantitative elemental analysis from ppm to weight % levels for the full periodic table, including salts, halides, and volatiles. When combined with 3D mapping and PCA data analysis, distribution of any element can be mapped over a variety of spatial scales (100's of nanometers to millimeters). This technique is particularly suitable analytical technique for characterization of traditionally challenging analytical materials, such as chalcogenicides, halide glass-ceramics, and alkali strengthened glasses. We demonstrate that using this powerful approach, direct sampling combined with mapping and PCA can be used to delineate statistically robust information on preferential distribution and affinities of elements within different structural phases (e.g. crystalline vs. glassy), and map variations in the stoichiometric ratios of major elements in high-grade transparent advanced ceramics.

(ICG-P025-2019) High Proton Conductivity Gels at Modest Temperatures

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Proton transport has been studied for a variety of applications in sensors and electrochemical devices. While fast proton conductivity has been measured in oxide ceramics, glasses and hybrid materials, the stability of the proton conductivity is still a problem. In this research, the synthesis of stable organic-inorganic materials with high proton conductivities is being studied in a systematic way, using the sol-gel process. The focus of this study is to synthesize fast-proton conducting gels that exhibit good water retention, high thermal stability and low gas permeability. One way to increase the conductivity is to modify the crosslinking of the gel network. This is accomplished through the substitution of modified precursors for tetra-functional precursors. By combining the characteristics of so-called melting gels with the proton conducting characteristics of hygroscopic oxide particles, such as zirconia and titania phosphosilicates and borosilicates, it is possible to expand the temperature stability. Thermal analysis and conductivity measurements are employed to identify compositions and their range of operation. Ideally, the proton conducting gel is thermally, chemically and mechanically stable for operation in the 200-300°C temperature range.

(ICG-P026-2019) UV Protection with Sol-Gel Coatings

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Over the years, sol-gel coatings have been applied to a variety of substrates, especially soda-lime glass. With coatings in the hundreds of nanometers to a few microns, it has been possible to impart optical effects to the surface of the glass, with a very simple process. Typically, the coatings are applied by dipping the substrate into a solution that is undergoing hydrolysis and condensation polymerization. Gelation occurs when the solution adheres to the substrate, and drying of water and solvents is quick. Since glass is common in situations where sunlight is present, it is important to understand the ability of glass to protect objects from UV effects in sunlight or artificial light. A comparison of coatings containing titania-doped silica, ceria covered by melting gel, and melting gels with gold nanoparticles was made. Two UV light sources were used. The simplest tests involved colored paper that was covered with various coated glass slides. Both the type of coating and the thickness of the coating were noted, and this was correlated with the amount of bleaching that occurred. The practical goal of this project is a recommendation for a coating that does not interfere with the observation of the object, while preventing fading or yellowing.

(ICG-P027-2019) Novel cylindrical glassy-carbon material for energy applications

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Glassy-carbon aerogels can be synthetized via sol-gel in monolith shapes from resorcinol and formaldehyde polymerization in the presence of an acid catalyst by rigorously controlling the precursor solution pH. They are brittle compacts with high surface area (500-800 m^2/g), porosity (40 – 80 %) and low mass densities (0.1-0.6 g/cm^3). We report a new route of the sol-gel process performed in centrifugal field. The carbon aerogel yields improved properties related to density, porosity, mechanical strength and microporous structure. The polycondensation reaction and gelification are performed at different G- force (30-150 g). The pyrolysis and thermal treatment carried at 800 and 1300 °C led to carbon aerogel in cylindrical shapes with high mechanical strength, d up to 0.6-0.7 g/cm^3, specific surface area around of 800m^2/g. The electrochemical properties are dependent on pH and the centrifugation speed. Our results demonstrate the correlation between the primary parameters of the centrifugation process (e.g. G-force) and the physical properties (d, pore structure and specific surface area) of the synthesized aerogel. This allows us to control the gel properties in applications of interest: energy materials, sensors and electrochemical energy conversion. Acknowledgment: PN-III-P1-1.2-PCCDI-2017-0387/2018-2020, PN-III-P1-1.2-PCCDI-2017-0871/47PCCDI/2018, PN-III-P1-1.2-PCCDI2017-0619/42PCCDI/2018, PN 2019 LAPLAS VI.

(ICG-P028-2019) Preparation of closed porous silica film

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Porous SiO_2 anti-reflection film is difficult to be widely used due to its easy adsorption of pollutants in the environment and its weak mechanical strength. In this study, Sodium borosilicate sol with and without pore-forming agent were successively coated on the surface of glass substrate by sol-gel process. Tetraethyl orthosilicate, boric acid and sodium nitrate were used as the main raw materials, and polyethylene glycol was used as the pore-forming agent. After drying and heat treatment at 500 ~ 700 degrees Celsius for 1 ~ 4 h, the film was transformed into a closed porous membrane, which is consist of the dense surface layer and the porous underlying layer with unconnected and closed nano-sized spherical stomata structure. The film thickness ranged from 100 nm to 1600 nm, and the pore sizes ranged from 5 nm to 100 nm. The thickness of the upper and lower film layers can be adjusted by changing the number of coating layers, and the pore size can also be adjusted by the heat treatment process and the molecular weight of the pore-making additive. As a composite structure material that combines the dense membrane and the porous membrane into one, the closed porous silica film not only plays a unique optical and thermal function, but also has good surface smoothness, chemical stability and strength. It could be used as heat insulation film, low refractive index film and other related fields.

(ICG-P029-2019) Synthesis of Mesoporous Silica Glasses Impregnated with Vanadium Oxide to Catalyse the Methanol Oxidation

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We explored mesoporous silica glasses obtained by sol-gel to support vanadium oxide for catalysis. Pure (SiO_2) and phenyl-modified ($Ph_{0.17}SiO_{1.9}$) silica xerogels were synthesized using the ionic liquid 1-butyl-3methyl-imidazolium-tetrafluoroborate as a single soft-templating agent. The xerogels were annealed to remove residual stresses and the ionic liquid extracted in a Soxhlet apparatus with acetonitrile. Vanadium (V^{4+} and V^{5+}) was impregnated in the mesopores as an alcoholic solution of ammonium vanadate and attached on their surface by calcination at 600 °C in air. Characterization by N_2 physisorption analysis, nuclear magnetic resonance spectroscopy (NMR), and transmission electron microscopy (TEM) with energy dispersive x-ray spectroscopy (EDS) showed that the dispersion and the nature of the resulting vanadium species depend strongly on the amount of V loaded. The catalytic potential of the synthesized materials was investigated for the methanol oxidation in a quartz tube fix-bed reactor at ambient pressure. Unconverted reactants and products were analyzed using gas chromatography. The samples containing 9.0 and 4.5 wt% V in the phenyl-modified glass yielded 70% and 37% methanol conversion, respectively, evidencing the catalytic effectiveness of the combined effect of acid sites and porosity in the synthesized materials.

(ICG-P030-2019) Novel nanocomposited phosphate glasses derived by sol-gel route: From photonics to environmental applications

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Novel phosphate nanostrucuture glasses with larger surface area and controlled pore sizes ranging from 2nm to 15 nm, composited with various functional species, have been developed by sol-gel method recently. The incorporation of various photo-active, bio-active, and environ-active species in nanoscale porous structure is currently attracting great attentions as for wide significant applications, including solar cells, laser sources, optical amplifiers, catalyst, biomedical and pollution processing, etc. In this talk, we will report the successful preparations of series of phosphate glasses by a novel sol-gel route: 1) Aluminophosphate, borophosphate, and gallium phosphate glasses were synthesized by sol-gel methods. The structure and structural evolutions of these glasses by investigated and monitored by advanced NMR spectroscopic. 2) Different laser dyes were loaded into mesoporous $AlPO_4$ glasses by a simple dipping process. The interaction of dyes with the glassy $AlPO_4$ network has been probed by ^{27}Al and ^{31}P solid state NMR techniques. 3) Rare earth (e.g. Eu) ions and quantum dots were loaded into nanostructured phosphated glasses by different processing methods. Controllable emissions (e.g. intensity, broad bandwidth, bimodal Luminescence, etc.) were realized, showing the excellent fluorescence tailoring properties.

(ICG-GSP-P031-2019) An Approach towards High Quality Bulk Zeolitic Imidazolate Framework Glasses

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Melt-Quenched Zeolitic Imidazolate Framework (MQ-ZIF) glasses have attracted much attention due to their unique, hybrid structure. Recently several breakthroughs have been reported regarding their unique structure and properties. However, production of bulk, homogenous, bubble-free samples of MQ-ZIF glasses is still challenging, due to facile degradation at their liquid state. In this contribution, we report on the impact of the production method on the quality (including bubble content, homogeneity, optical transparency) of the ZIF glasses by taking ZIF-62 ($ZnIm_{1.75}bIm_{0.25}$) glass as an example. We first produce ZIF-62 ($ZnIm_{1.75}bIm_{0.25}$) glasses with the size of about f10x2 mm by using three different methods (melting under protective gas, hot-pressing-melting in vacuum, and spark plasma sintering). Then we evaluate which method is the most suitable for producing high quality ZIF-62 glass. This glass should be used for property characterizations (particularly for optical properties), up-scale production and functionality studies. Finally, the quality evaluation results show that the spark plasma sintering is a promising technique for fabricating the high quality ZIF glasses in a large scale.

(ICG-GSP-P032-2019) Mechanochemical Synthesis of Mixed Linker Glass Forming Metal-Organic Frameworks

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Metal-organic Frameworks (MOFs) are hybrid materials which consist of metal ion nodes, or clusters, connected by organic linkers. Recently it has been demonstrated that some MOFs have a liquid phase, and can be melt-quenched to form metal-organic hybrid glasses, the first new category of glass since the 1970's. Unfortunately bulk scale production of MOF glasses is limited by the energy intensive production of the crystalline MOF precursors, which relies on large volumes of toxic solvents, high temperatures and long reaction times. A novel metal-organic hybrid glass can be formed from a MOF known as ZIF-62, a mixed organic linker system. Here we present a mechanochemical method to synthesise the glass forming MOF ZIF-62, as well as environmentally friendly solvothermal approaches.

(ICG-GSP-P156-2019) Effects of Ultrashort Laser Pulse Interaction on Glass Structure

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The interaction of ultrafast laser pulses with glasses has proven to affect surface hardness in oxide glasses. Exposing simple aluminosilicates to low-energy laser pulses leads to densification from changes to interatomic bonding environment. Correlating ring-size to densification is used to assign structural changes from laser irradiation. A single family of aluminosilicate glasses with varying modifier content has been prepared and exposed using multiple pulse intensities and repetition rates. Silicon ring structure was characterized post exposure using micro-Raman, aluminum coordination with MAS-NMR and X-ray reflectometry (XRR) to evaluate electronic system density. Mechanical properties characterization of glass surface provides supporting data to density changes and structural modifications from laser exposure. We believe that changes to silicon ring-components are a result of reduced repetition rates providing sufficient thermal energy to cause bonds to break and reform. We will present a case study focused on the evolution of silicon ring structure in aluminosilicate glass after femtosecond pulse irradiation at various intensities and repetition rates.

(ICG-P033-2019) Side-Emitting Fibers: A Flexible Solution for Light Delivery in Turbid Media

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Delivering light into turbid environments which are strongly light-scattering and -absorbing is a challenge encountered in a variety of fields such as interstitial phototherapy in cancer treatment or photoreactors. One approach to this problem is to insert multiple side-emitting fibers (SEF) into the medium. Contrary to normal optical fibers, SEFs work by leaking guided light through

their surface by controlled imperfections. An insertion of SEFs into turbid environments raises the surface-to-volume ratio and thereby the irradiated volume. Due to their principle of operation SEFs represent a light source with unique properties whose emission behavior has angular and positional dependence. It remains unclear, however, which specific qualities a SEF should carry in order to optimally deliver light into such environments. Therefore, in this paper, we compare several different types of SEFs as well as different illumination strategies. We thus aim to derive design routes as to the particular fiber properties and their performance in the irradiation of turbid media. This will answer the question as to how SEF-based illumination strategies can contribute to efficiently deliver light into difficult environments.

(ICG-GSP-P034-2019) Compositional Dependence of Structural, Thermal and Electrochemical Properties of Oxythio-silicophosphate Lithium Glassy Solid-state Electrolytes

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Hazards associated with the utilization of organic liquid electrolyte (OLE) has created a growing concern while the number of lithium rechargeable battery (LRB) applications has been increasing over the last two decades. Glassy solid-state electrolytes (GSSEs) have been considered as a safer alternative credited to its promising thermal stability and physical durability. In addition to this, the elimination of fire and explosion risks provides the chance to adopt high-energy-density metallic lithium as anode material, leading to drastic improvements in overall energy density of LRBs. However, few papers have been reported on lithium oxythio-silicophosphate (LiPSiSO) GSSE, and the compositional dependence on its properties are not clear yet. In this work, LiPSiSO GSSEs were synthesized via melt-quench method. The structural, thermal, and electrochemical properties were characterized using DSC, Raman, IR, NMR, EIS and direct-current cycling methods. Powderized LiPSiSO GSSEs were pressed into thin pellets (~1mm) for electrochemical testing. The experimental results showed the structural, thermal and electrochemical properties of our GSSE are highly composition dependent. This insight allows for the correlation among those properties, and helps optimize the performance of LiPSiSO GSSEs by composition adjustment during synthesis.

(ICG-P035-2019) 13-93 bioactive glass - SiC fiber composites

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Bioactive glass (BG) is soluble and easy to form hydroxyapatite in the body and has a direct chemical bond with the surrounding bone. In this study, we investigated the mechanical properties, porosity and biocompatibility of BG-SiC fiber composites with high toughness and porosity. The 13-93 glass fiber was made using melt spinning with a single nozzle Pt-Rh crucible. The diameter of the glass fibers was controlled by varying the winding speed. The optimal process conditions were derived based on the change in mechanical properties with diameter. In addition, In-vitro tests were carried out using SBF solution to confirm bioactivity. The diameter of the fiber had a quadratic function relation to the winding force and showed a negative linear relationship with the number of rotation. Tensile strength was highest at 852 MPa for glass fibers with an average diameter of 10-15μm. Through the correlation between the diameter and the strength of the fiber, it was confirmed that the winding force of 320 N was the optimal spinning condition. As a result of the in-vitro test, silica-rich layer was from the fiber surface due to dissolution of the Ca at the initial stage of the reaction, and peeling occurred. It was confirmed that a typical calcium phosphate compound was formed as the reaction time elapsed.

(ICG-UGSP-P036-2019) Dissolution behavior and cellular response of glasses in the Na-Sr-Ca-borophosphate system

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The surrounding pH can inhibit or promote healing in various biological applications, such as wound healing, skin grafts, and bone repair. Glasses of the compositional series $16Na_2O$-(24-y)CaO-ySrO-xB_2O_3-(60-x)P_2O_5 (mol%) where x = 0, 10, 20, 30, 40, 50, and 60 and y = 0, 12, 24 were prepared. Dissolution experiments were conducted to determine dissolution rates and solution pH in Simulated Body Fluid (SBF). Dissolution rates initially decreased with addition of B_2O_3, but increased with additional B_2O_3. The solution pH can be varied (6.1-8.3) by composition. The response of human adipose stem cells (ASC) to these new glasses were evaluated to determine the effect of resulting local pH on biological responses via cell vitality and cell migration tests. Cell vitality testing consisted of treating ASC grown in a Complete Culture Medium (CCM) to glass particles for 24 and 72 hours, and cell migration consisted of placing ASC on a permeable barrier with CCM treated with glass particles on the other side for 5 hours. These glasses demonstrated comparable performance to the current industry bioactive glasses, 13-93B3 and 45S5. CCM treated with the x= 0, 40, and 60 compositions achieved the highest cell counts in the series. A borophosphate composition (x=40) attracted the most cells through the barrier, outperforming both 13-93B3 and 45S5 in the cell migration test.

(ICG-P037-2019) Ce-containing bioactive glasses with enzyme-like characteristics

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CeO_2 nanoparticles (CeONPs) have received attention because of their excellent catalytic activities, which are derived from interconversion between Ce^{4+}/Ce^{3+}. CeONPs has been found to have enzymatic mimetic properties (superoxide dismutase-SOD and catalase-CAT). This produce various positive biological effects, such as antioxidant towards almost all noxious intracellular reactive oxygen species (ROS). Among implantology biomaterials, bioactive glasses are widely used for their ability to form chemical bonds with soft/hard tissues, feature known as bioactivity. Since the discovery of the 1st bioactive glass, 45S5 Bioglass®, the research activity has been focused to improve its properties by modifying the original composition. In this context, bioactive glasses with Ce^{4+}/Ce^{3+} (addition of Ce precursor during synthesis) were studied in order to promote the bioactivity with simultaneously enzymatic-like activities. Melting glasses based on 45S5 and mesoporous bioactive glasses with Ce^{4+}/Ce^{3+} present CAT/SOD–like activity. CAT/SOD-like activity increases with the increase of cerium content, but the bioactivity decreases. The presence of Ce promote cell adhesion and proliferation. Moreover, Ce-containing bioactive glasses prevent the oxidative stress caused by ROS. Based on these findings we can conclude that our Ce-containing bioactive glasses can be utilized in the design and development of a new biomaterial class.

(ICG-GSP-P038-2019) Short-range structure of barium tellurite and lead tellurite glasses and its correlation with stress-optic properties

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The atomic parameters of metal ion-oxygen speciation such as bond-lengths/nearest neighbour distances for Ba-O, Pb-O, Te-O and O-O pairs, co-ordination numbers and bond angle distributions for O-Ba-O, O-Pb-O, O-Te-O and O-O-O linkages are determined by neutron diffraction and Reverse Monte Carlo(RMC) simulations on

xBaO-(100-x)TeO_2 and xPbO-(100-x)TeO_2 glasses (x= 10, 15 and 20 mol %). RMC is found to be a powerful technique to determine the atomic partial pair correlation functions and provides accurate coordination and bond-lengths data. Te-O bond-lengths in both the glass series are in the range: 1.97±0.01-1.90±0.01 Å. The tellurite glass network depolymerizes with the addition of modifier metal oxides and the average Te-O coordination decreases from 3.60±0.02 to 3.48±0.02 with increase in BaO concentration, whereas in case of lead tellurite glass series the Te-O co-ordination decreases from 3.55±0.04 to 3.36±0.03 with increase in PbO concentration. Te-O speciation is also determined by Raman spectroscopy and it shows good agreement with the RMC results. The short-range structural parameters of metal- ion coordination (N_c) and bond-lengths (d) are used in the Zwanziger model of stress-induced birefringence to calculate the values of bonding characteristic, B_r and predict the stress-optic response of xBaO-(100-x)TeO_2 and xPbO-(100-x)TeO_2 glasses.

(ICG-P039-2019) A Study of the Kinetics of Apatite Conversion of Bioactive Glasses: 45S5, 13-93 and their Intermediates

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Bioactive glasses have generated enormous interest since the discovery of 45S5 Bioglass® in 1969. These materials have been found to be biocompatible and capable of forming strong bonds with both soft and hard tissues when implanted into the body. The formation of a hydroxyapatite (HA) layer on glass surface enables the excellent bioactivity properties observed in this glass family. Our study investigated the conversion kinetics of four bioactive glass compositions, 45S5, 48S1T, 50S2T, and 13-93, in simulated body fluid (SBF). Our results suggest that the two intermediate compositions (48S1T and 50S2T) are comparable to 45S5 and have better bioactivity performance than 13-93.

(ICG-UGSP-P040-2019) Inhibition of Bacterial Growth by Lithium-Potassium-Borate Glass-Epoxy Composites

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Lithium potassium borate glass has already been proven to inhibit (and even eliminate) bacterial growth. The poor durability of these glasses makes them less than ideal for practical applications. In this work, we present on the development of glass-epoxy composite materials containing lithium-potassium doped borate glasses in varying mass ratios. The effect of these composites on the growth of E. coli, S. aureus, and S. typhimirium is reported, and the durability of the effect (under wet conditions) is also investigated. The structure of the composites was also looked at using SEM and Raman spectroscopy Work supported by Coe College and by the United States National Science Foundation under grant numbers DMR 1407404 and DMR-1746230.

(ICG-P042-2019) New gallium-rich gallo-germate glass optical fibers

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Gallo-germanate oxide glasses offer wide optical transparency, extending from ~280 nm in the UV up to ~5.5 μm in the mid-IR, high glass transition temperature (T_g ~700 °C) and superior mechanical properties and damage threshold. Most of previous work dedicated to these vitreous materials studied multi-component compositions possessing 1:2 $GaO_{3/2}$ to $GeO_{1/2}$ ratio, with gallium oxide behaving like an intermediate. Ga_2O_3 addition enables to reinforce surface hardness, to modulate the refractive index or to improve nonlinear responses. Yet, despite their numerous assets, few studies have been devoted to glasses in which gallium oxide is acting as a network former. Here we present experimental results in the fabrication of glass fibers obtained by the standard preform-to-fiber method in the $GaO_{3/2}$-$GeO_{1/2}$-BaO system stabilized with lanthanides ($LaO_{3/2}$ or $YO_{3/2}$). Glasses with $GaO_{3/2}$ to $GeO_{1/2}$ ratio up to 2:1 were produced and successfully drawn into tens-of-meters-long fiber samples. This is to the best of our knowledge the first report on the production of crystal-free, light guiding fibers from rich Ga_2O_3 compositions. Linear and non-linear properties of the bulk materials are presented here as well as optical fibers characteristics. We believe these results provide insights and practical steps in the shaping ability of new glasses of technological interest into optical fibers.

(ICG-GSP-P043-2019) The study of low temperature deposited durable Ge_xC_{1-x}/DLC protective antireflective films applied on $As_{40}Se_{60}$ chalcogenide glass

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Infrared protective antireflective Ge_xC_{1-x}/DLC film was deposited on $As_{40}Se_{60}$ chalcogenide glass by radio frequency magnetron sputtering method (rf MS) with a concentric germanium and graphite target. The deposition temperature was below 150centigrade. The effect of sputtering power and Ar gas flow rate on the structural, optical, mechanical and environmental durable properties of film was investigated by Raman Spectroscopy, X-ray photoelectron spectroscopy (XPS), Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM), UV-visible spectrophotometer, infrared ellipsometer, Fourier Transformed Spectroscopy, surface profiler, Continuous Stiffness Measurement (CSM) and environmental testing equipment. The results shows that Ge can enhance the H content in films as the sputtering power is low and the structure of amorphous carbon within the Ge_xC_{1-x} film can be assigned as highly hydrogenated graphite-like amorphous carbon (GLCHH) structure, the increasing power can enhance the Ge content and the relative content of aromatic rings and nc-graphtie clusters of sp^2 structure. Ge_xC_{1-x}/DLC films presents well adhesion, antireflective and protective ability on $As_{40}Se_{60}$ chalcogenide glass.

(ICG-P044-2019) High-speed label-free functional photoacoustic imaging based on hollow microcavity

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The prevailing methods for microimaging, such as optical spectrum analysis and tunable laser spectroscopy, are insufficient to distinguish biomolecular dynamic activities which require new imaging technique with high-resolution and high-speed. Photoacoustic imaging (PAI) technique have had profound impact on biomedical research because of its capability to directly sense optical absorption in vivo and to facilitate either label-free of tissue. However, up to date, the challenge of PAI is still how to obtain a volumetric imaging with high resolution, speed, and accuracy. In our previous report, a digitally generated optical frequency comb (DOFC) was demonstrated for spectral measurements with 0.01-pm resolution and 0.7-μs response time, which could facilitate new label-free sensor applications that require both high resolution and fast speed. Recently, we fabricated an array of microbubbles using silica hollow core fiber, which was super-sensitive to US wave. By combining DOFC and the high sensitive microbubble array coupling with only a single mode silica fiber taper, a high speed volumetric image of the measuring object is achieved. This method improves the accuracy and signal-to-noise ratio significantly through a cavity array similar to multipoint positioning. This promising method could noninvasively image the vascular morphology, blood flow dynamic information in biomedical applications.

(ICG-UGSP-P045-2019) Laser-induced crystallization and reduction of copper-doped lithium niobosilicate glass

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Laser irradiation of glass allows for the spatially selective growth of ferroelectric single crystal architectures. These crystalline channels embedded within glass are potentially useful as passive and active optical waveguides for photonic devices. Laser induced crystallization of $LiNbO_3$ within lithium niobosilicate (LNS) glass has already been demonstrated. The next challenge to make functional photonic devices involving $LiNbO_3$ crystalline channels, such as an electro-optic modulator, is the ability to fabricate electrical connections within otherwise insulating matrix. To produce conducting pathways selectively we have investigated the possibility of reduction of copper ions in copper-doped LNS glass using a femtosecond laser. Results are presented for $40Li_2O–32Nb_2O_5–28\ SiO_2$ glass doped with 1 mol% CuO for a variety of processing parameters: laser power, laser scanning speed, and post-laser modification heat treatment temperature.

(ICG-P046-2019) Development of magneto-optical fibers based on heavy oxide glasses

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Glasses containing paramagnetic ions have been used for different purposes, including Faraday isolators and modulators for telecommunication systems and sensors for magnetic field. In this work, we present a systematic study on germanium Oxide-Based Glasses containing high concentrations of Tb^{3+} ions (up to 40 mol%). The glass samples were prepared by the classical melt-quenching method above 1400 °C and then characterized by the following techniques: Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD), Raman Spectroscopy, X-ray absorption techniques (XANES and EXAFS), High-Resolution Transmission Electron Microscopy (HRTEM) and Superconducting Quantum Interference Device (SQUID). The magnetic characterizations confirmed the presence of the paramagnetic effect. The produced glasses showed a thermal stability against crystallization higher than 200 °C, which demonstrates their great potential for optical fiber drawing. Core-cladding preforms were then prepared using rotational casting method. The optical characterizations and the potential application of magneto-optical fibers in medicine will be discussed.

(ICG-GSP-P047-2019) Development of an optical fiber-based sensor for determination of emerging contaminants in wastewater

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The monitoring of emerging contaminants has gained prominence in the last decades, mainly by the population increase and expansion in the pharmaceuticals usage. The source of pharmaceutical compounds in the environment comes from human and veterinary usage and also application for agricultural purposes. The occurrence of pharmaceutical compounds in wastewater is associated with human excreta, inappropriate drug discharges, and inefficient or limited removal in the sewage treatment plants (WWTP). Currently, pharmaceutical compounds determination in wastewater has been carried out through separation techniques such as LC-MS/MS and GC-MS/MS which are high cost, high consumption of sample and solvents, and moreover slow analysis response. In order to monitor the wastewater quality with fast response, lower consumption sample and good chemical stability sensors based on optical fibers have been explored. In this work, a multimode optical fiber sensor have been used using functionalized mesoporous silicates for the detection of carbamazepine and ciprofloxacin in wastewater of selective form. Additionally and using electrochemical impedance spectroscopy for detection of ciprofloxacin showed detection limits of 0.033 mg L^{-1}. These data will be compared with optical fiber technology regarding selectivity and sensitivity.

(ICG-GSP-P048-2019) The interface-coupled dissolution-reprecipitation model of aqueous glass corrosion considering a solution boundary layer and inter-diffusion

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Silicate glasses are frequently used because of their high durability compared to other solids. Therefore, it is the favored matrix material for the immobilization of high-level radioactive waste. Nevertheless, glass is metastable and alters in contact with aqueous solutions, resulting in the formation of a complex surface alteration layer (SAL). In addition to the classical interdiffusion model of glass corrosion there exists an alternative model, based on an interface-coupled dissolution-reprecipitation mechanism (ICDP). Here, we present a refined ICDP model by considering surface charge effects and pH gradients within the solution boundary layer, interdiffusion, and the formation of amorphous silica based on principles of sol-gel chemistry. The focus is on the detailed description of the different chemical reactions, transport processes and their interdependence to identify the rate-limiting reaction steps and feedback effects. We show that the most phenomena observed in experiments and nature can be well explained by the ICDP model. However, a pure ICDP mechanism is not able to explain all phenomena of glass corrosion. When the dissolution and precipitation reactions are slowed down, interdiffusion processes within the pristine glass ahead the ICDP front may start, which is also considered in the refined ICDP model.

(ICG-GSP-P049-2019) Corrosion of 3 – 6 component borosilicate glasses in alkaline pH

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Borosilicate glass has been commonly accepted as medium for immobilization of high-level nuclear waste, and to promote international cooperation the International simple glass (ISG) was chosen as an experimental standard. In this poster, ISG and four derivatives of it which differ in the concentration of key elements (Na, Al, Ca, Zr) were synthesized and their corrosion behavior under TMAH buffer solution with initial pH values of 13 were monitored. The glasses devoid of CaO and ZrO_2 showed congruent dissolution until 120 days at pH 13. The pre- and post-dissolution glass samples have been characterized by a suite of experimental techniques including MAS-NMR, XPS, RBS, ERDA, XRD and Raman spectroscopy. The results will be discussed in the poster.

(ICG-GSP-P050-2019) Long-term Durability of Nuclear Waste Glass Analogues

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The safety case for geological disposal of nuclear waste can be strengthened using geological and archaeological specimens analogous to the internationally-favoured glass wasteform. In this study, partially-welded ('vitrified') rocks that formed the ramparts of a hill-top Scottish fort (Dun Deardail Hillfort) and natural analogues are investigated from a durability perspective. The ~2,000-year-old vitrocrystalline alkali-aluminosilicate hillfort glasses have been prepared (with care taken to avoid disturbing potential alteration products) and characterised. Iridescent surface-coatings and pitting were explored as evidence of potential glass alteration layers and preferential dissolution at micro-heterogeneities respectively; whilst other surface-characterisation techniques were used to gain further insight into long-term glass durability. The role of magnesium in long-term glass durability is also investigated via accelerated dissolution of geological analogues. Basaltic (aluminosilicate) and olivine-type (magnesio/iron-silicate) glasses with a variable magnesium content have been synthesised and prepared according to Materials Characterization Centre (MCC-1) and Product Consistency Test (PCT-B) procedures; with experiments anticipated to last up to 2.5 years. Results are expected to elucidate the importance of magnesium in the generation and potential disintegration of a dissolution rate-limiting alteration layer.

(ICG-P051-2019) DEM&MELT In-Can Melting Technology for the Vitrification of Typical D&D Waste loaded with Cs

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3. ECM Technologies, France
4. Andra, France
5. ANADEC, Japan

The DEM&MELT consortium which gathers Orano, CEA and ECM technologies is currently developing and qualifying a robust, simple and versatile In-Can vitrification process dedicated to D&D and remediation waste. The DEM&MELT In-Can Melting technology is designed for high or intermediate level waste and is compact enough to be implemented in a decommissioned cell or close to the waste to be treated. It is developed to treat liquid and solid waste, to produce a small amount of secondary waste and to minimize investment and operating costs. The in-can vitrification process is also developed with a modular design in order to be adapted regarding to nuclear operators' needs and requirements. This poster presents the in-can vitrification process and its performances for a typical D&D waste highly loaded with Cs. This poster also presents the results of the evaluation of the In-can vitrification process for Fukushima water treatment secondary waste, a project led by Orano, CEA and ANADEC. This R&D project is performed by the funds from Japanese government as The Subsidy Program "Project of Decommissioning and Contaminated Water Management". The vitrification tests results are in particular discussed in terms of process parameters, glass properties and cesium volatility.

(ICG-GSP-P052-2019) Thermodynamic Modeling of Zeolite Precipitation by Ab InitioMolecular Dynamics

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The stage III resumption of corrosion exhibited by select nuclear waste immobilization glasses is usually attributed to the precipitation of zeolite secondary phase. However, the present lack of thermodynamic data for zeolite phases makes it challenging to predict their propensity for nucleation and growth as a function of pH and temperature, which presently limits our ability to confidently predict the long-term dissolution kinetics of nuclear waste immobilization glasses. Here, we present the results of high-throughput ab initio molecular dynamics simulations aiming at accurately computing the thermodynamic properties of a large collection of zeolitic phases. We show that our computed data offer a good agreement with experimental data, when available. This information can be used to predict the domain of pH and temperature for which zeolite precipitation is thermodynamically favored.

(ICG-P053-2019) The formation of a cold-cap from slurry feed: Chemistry and rheology

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The vitrification of radioactive waste is a process, during which is the waste, in a form of slurry, mixed with glass-forming and glass-modifying chemicals and then fed into Joule-heated melter from the top onto a molten glass surface. On the interface between the slurry and glass is created a conversion layer called cold-cap. How is cold-cap formed and how does the freshly fed slurry interact with its surface was not explained, yet. To address the cold-cap formation under 1D laboratory setup, and its chemical composition, we prepared laboratory cold-cap-like samples and analysed them via μ-XRF analysis. The mechanism between the slurry and cold-cap was observed by the addition of a water-soluble tracer into the fresh slurry. The results show that only a negligible amount of the tracer penetrates the cold-cap surface. However, within the cold-cap, water-soluble components, e.g. Na^+, PO^{3-}, which generally contribute to the early molten salt phase, created a concentration gradient near cold-cap hotspots. This could potentially affect the even melting of cold-cap. For this reason, we performed additional analysis via feed expansion tests on model feeds with various alkali contents. These feeds provided information on the foaming, foam onset and maximum temperatures, which could take place in a cold-cap with corresponding composition.

(ICG-P055-2019) Vitrification of Fukushima Water Treatment Wastes: Formulation and Durability Study

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Water processing at the Fukushima Daiichi nuclear power plant generated a significant amount of secondary wastes (spent media, sludges) that will need to be processed before disposal. About 20 representative waste streams were grouped in different families (Ti-rich, Fe-rich…). Glass compositions were formulated to incorporate waste from the various families and were synthesized at crucible scale. The formulation of the glasses aimed to optimize both the efficiency of the processing and the chemical durability, thus providing a proof-of-principle for the vitrification of these wastes. The durability of 15 glasses was evaluated using MCC-1 tests (Static dissolution, 90°C, up to 365 days) and compared to well-characterized HLW glasses. Results and long-term alteration rates from these tests will be presented, discussed, and evaluated with regards to the characterization of the unaltered and altered glass samples. This study includes the results from the works under the subsidy program "Project of Decommissioning and Contaminated Water Management" by METI of JAPAN.

(ICG-GSP-P056-2019) The ultrafast dynamics of $CsPbX_3$ NCs in glass

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All-inorganic $CsPbX_3$ (X=Cl, Br, or I) perovskite nanocrystals (NCs) have promising optoelectronic properties that are attracting widespread attention from researchers. $CsPbX_3$ NCs were incorporated into glasses through the melt-quenching and thermal treatment in order to overcome the weak chemical and thermal stabilities. However, due to the strong interaction of perovskite NCs with the amorphous glass matrix, photoluminescence quantum yield (QY) of perovskite NCs in glasses was low and radiative lifetime was shortened. In this work, $CsPbI_3$ NCs were precipitated in glasses and the ultrafast dynamics of $CsPbI_3$ NCs were investigated using the transient absorption spectra and time-resolved fluorescence spectra. It was found the Stokes shift and photoluminescence lifetime of these $CsPbI_3$ NCs were strongly dependent on the size of $CsPbI_3$ NCs and the composition of the glass, especially the concentration of halide. Results reported here showed that compositional adjustment of the glass was critical to improve the photoluminescence quantum yield of $CsPbI_3$ NCs embedded glasses and promote their applications in optoelectronic devices.

(ICG-P057-2019) Pockels effect and second-harmonic generation in silicate glass-ceramics for photonic application

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Nonlinear optical phenomena that enable us to fabricate the light-wave controlling device is significant for advanced photonic applications, and the devices have been constructed with optical single crystal with large spontaneous polarization. On the other hand, glass has an optical isotropy and good formability due to a random-network structure without transition symmetry: Recently, we have developed a novel glass-ceramics (GCs) consisting of polar fresnoite phases on the basis of perfect surface crystallization (PSC). In this study, we have studied the Pockels effect and second-harmonic generation based on second-order optical nonlinearity, which are essential for optical switching/modulation and wavelength-conversion devices, respectively, in the PSC-GCs, and considered their potential for the practical applications.

(ICG-GSP-P058-2019) Relation of crystallization condition to crystal-orientation and Pockels effect in perfectly-surface-crystallized glass-ceramics

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Evolution of second-order optical nonlinearity in glass material has been vigorously studied in order to construct the light-wave controlling devices. A silicate mineral, fresnoite ($Ba_2TiSi_2O_8$), and its isostructural phases possess an excellent optical nonlinearity, researchers have made an effort to fabricate the glass-ceramics consisting of fresnoite phase toward photonic-device application so far: Our research group have succeeded in developing "perfectry-surface-crystallized glass-ceramics (PSC-GCs)," in which fresnoite-type $Sr_2TiSi_2O_8$ is singly crystallizable, and demonstrated an optical modulation based on Pockels effect. We found that heat-treatment around crystallization-onset temperature (880°C) provides the obtained PSC-GCs a high crystal-orientation compared to the treatment around crystallization-peak temperature (960°C), leading us to expected the enlargement of Pockel constants. Therefore, in this study, we have examined the impact of heat-treatment temperature on the crystal-orientation and Pockels effect in the PSC-GCs, which was fabricated by use of $35SrO–20TiO_2–45SiO_2$ precursor glass.

(ICG-GSP-P059-2019) Thermal and structural properties of MgO-precipitated oxide glass having transparency and high thermal conductivity

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Thermal conductivity of oxide glass is low (~ 1 $Wm^{-1}K^{-1}$) due to its disordered structure. Therefore, we aim to develop new thermal management materials that have both high thermal conductivity and the superiority of oxide glass such as transparency and form controllability by incorporating transparent, high thermal conductivity crystals into oxide glass. In this report, focusing on MgO which has high thermal conductivity (~ 50 $Wm^{-1}K^{-1}$), optical isotropy, and affinity with oxide glass, we aim to produce transparent and high thermal conductivity glass composites by refractive index matching and precipitation of saturated MgO crystals. After MgO reagents corresponding to (A) ~110, (B) ~130 and (C) ~160 mol% were mixed with a mixed reagent having a composition ratio of $28La_2O_3$-$52B_2O_3$-$20SiO_2$ (mol%), samples were prepared by melt quenching method. As a result, it was confirmed that (A) is homogeneous glass and (B) and (C) include non-uniformly dispersed MgO crystals having a diameter of 10 to 30 μm in the glass phase. These samples show high visible transparency, suggesting that light scattering at the interface is suppressed by refractive index matching. The thermal conductivities of (B) and (C) are improved by ~16% and ~54%, respectively, compared with (A). This improvement is attributable to formation of heat conduction paths of the MgO microcrystalline network.

(ICG-P060-2019) Eu^{3+}-Tb^{3+}-Tm^{3+} co-doped oxyfluoride glasses with nanocrystals for wide color gamut UV-LED color converter

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Conventional white LEDs (WLEDs) for LCD-BLU have employed a mixture of green and red phosphors with an organic binder. Due to poor stability of organic binders, they show weak long-term stability. Moreover, it is difficult to realize a high-picture quality LCD because of the broad emission bandwidth of phosphors and resultant limited color gamut. Quantum dots, thus, are being used for efficient color converters with their narrow emission bandwidth. However, they are chemically vulnerable and require high production costs. In previous studies, oxyfluoride glass based on BaF2 showed high quantum yield along with narrow emission bandwidth of red and green colors via doping Eu3+ and Tb3+ ions under UV-LED. However, it lacked blue emission and was hard to achieve a wide color gamut. In this study, in order to provide a robust color conversion material with wide color gamut, a bulk glass phosphor (BGP) has been proposed. So, Tm3+ was adopted as an additional ion to supply blue emission for RGB generation. We varied the contents of Tb3+, Eu3+ and Tm3+ to adjust the blue, green and red emission under 375nm. The fabricated BGPs doped with Eu3+-Tb3+-Tm3+ showed RGB emissions on a single source and their photo-luminescence spectra as well as color gamut were examined. After heat treatment, the effect of nano-crystals within the glass on their optical properties has been also explored.

(ICG-GSP-P061-2019) Precipitation of $CsPbBr_3$ Quantum Dots in Boro-germanate Glass Induced by Femtosecond Laser

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Direct and effective fabrication of luminescent materials based on quantum dots (QDs) is one of the key step to realize the application of QD photonic devices. The present article describes the precipitation of $CsPbBr_3$ QDs in inorganic glass matrix using femtosecond (fs) laser irradiation. Effects of pulse energy, repetition rate, processing speed, and writing direction on the precipitation and optical properties of $CsPbBr_3$ QDs were investigated. Structural

changes induced by fs laser were illustrated using electron probe micro-analyzer and distribution of $CsPbBr_3$ QDs in the fs laser irradiated region was analyzed using the microscopic photoluminescence spectroscopy. This controlled precipitation of $CsPbBr_3$ QDs in glasses make it possible to fabricate luminescent solar concentrator and improve the photoelectric efficiency of solar cells.

(ICG-GSP-P062-2019) Observation of Pockels effect in perfectly surface crystallized glass–ceramics with $BaO–TiO_2–GeO_2$ system

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Recently, we have reported "perfect surface crystallization (PSC)," in which the single-crystal domains grow from glass surfaces, and eventually their growth fronts impinge on each other. The resulting glass-ceramics (PSC-GCs) show a uniform and dense texture of crystalline phase with the large thickness (~0.5 mm). In addition, the PSC-GCs is demonstrated to show Pockels effect (r ~ 2–3 pm/V) due to presence of the polar fresnoite-type $Sr_2TiSi_2O_8$ with high orientation to polar c-axis. In fresnoite family, second-order nonlinearity of $Ba_2TiGe_2O_8$ (d ~ 20 pm/V) is larger than that of $Sr_2TiSi_2O_8$ (d ~ 7 pm/V). Therefore, in this study, we have attempted to fabricate PSC-GCs with $Ba_2TiGe_2O_8$ phase, and to elucidate its Pockels effect.

(ICG-GSP-P063-2019) Silica- and germanate-based glasses doped with rare-earth elements for photonics devices

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Recent photonics devices of daily life frequently rely on materials based on rare-earth doped glasses. Devices, such as fiber lasers or amplified spontaneous emission sources, based on thulium- or holmium-doped silica glass are suitable for operation at wavelengths up to 2.2 μm. Materials hosting rare earths suitable for operation at longer wavelengths are worldwide intensively investigated. For operation in mid-IR region, GeO_2-based glasses doped with thulium and holmium have been proposed. These glasses were synthetized by several ways and their properties such as transmission spectra, refractive index and fluorescence spectra were determined. Special attention was given to the purity of the prepared materials. The obtained characteristics were compared to those achieved with silica-based glasses and suitability of prepared materials for applications in spectral region above 2 μm will be discussed.

(ICG-P064-2019) Spectroscopic analysis of upconversion mechanism in $Nd^{3+}→Yb^{3+}$ codoped boro tellurite niobium glasses for optical device applications

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Conventional melt quenching technique was used to prepare Nd^{3+} doped and Nd^{3+}/Yb^{3+} co-doped TBNAC (TeO_2-B_2O_3-Nb_2O_5-Al_2O_3-CaF_2) glasses. A series of TBNAC glasses were synthesized by co-doping optimized 1.0 mol % of Nd^{3+} ion concentration with different concentrations of Yb^{3+} ions ranging from 0.1 mol % to 2.5 mol %. The prepared samples were characterized through different techniques such as absorption, Photoluminescence (PL) and PL decay etc. Nd^{3+} ions doped TBNAC glasses exhibited near infra-red (NIR) emission under 808 nm excitation in the wavelength region 850-1450 nm. The overlap integral of Nd^{3+} ion emission ($^4F_{3/2}→^4I_{9/2}$) with the Yb^{3+} ion absorption ($^2F_{7/2}→^2F_{5/2}$) in the titled glasses gave an assurance for the efficient resonant $Nd^{3+}→ Yb^{3+}$ energy transfer. The emission spectral data of Nd^{3+}/Yb^{3+} co-doped TBNAC glasses showed the strong dependence of Yb^{3+} ion concentration and the energy transfer mechanism involved in $Nd^{3+}→ Yb^{3+}$ energy transfer have been established. Thus, the strong NIR luminescence through energy transfer in TBNAC glasses has applications in designing solid state NIR lasers and multiple pump channel sources for Yb^{3+} fiber laser systems.

(ICG-P065-2019) The Analysis of Weak Light Performance Varying with Shunt Rsistance of Thin Film Solar Cell on Glass

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This paper mainly focused on the difference of current-voltage performances of thin film solar cell on glass under illumination with normal light and weak light, respectively. By employing the graphic method to solve the transcendental equation, the relationship between open circuit voltage(V_{OC}) and shunt resistance (R_{SH}) of the solar cell was investigated. And the result indicated that for a thin film solar cell module, the variation of V_{OC} between normal light and weak light showed a different behavior with different shunt resistance. When the shunt resistance is too small, the variation of V_{OC} decreased more than that with normal shunt resistance. According to the sharp decrease of V_{OC} under weak light compared to normal light, the solar cell module with defect of shunt resistance could be found, and the problem in product line could also be resolved.

(ICG-GSP-P066-2019) Luminescence-enhanced side-emitting fiber

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Enhancing the luminescence of lanthanide ions with nanometer and sub-nanometer sized metallic structures is a remarkable phenomenon that holds great promise for a broad variety of applications. We report on synthesis and characterization of borosilicate glass fibers with enhanced luminescence obtained by pulling from rod-in-tube preforms. Incorporation of Eu^{3+} and Ag as optical active species into fibers was achieved by a modified rod-in-tube technique. To determine the influence of metallic Ag on the Eu^{3+} fluorescence, sol-gel derived coatings on plate glass were studied separately. In both cases, annealing at 600 °C resulted in the formation of metallic Ag. The obtained coatings and glass fibers were analyzed by UV-VIS and fluorescence spectroscopy, as well as TEM and fluorescence microscopy. Samples doped with Ag up to 5 mol% exhibit strong luminescence enhancement, especially when excited out of resonance with $\lambda < 400$ nm.

(ICG-GSP-P067-2019) Borotungstate glass-ceramics containing high concentration of rare earths with magnetic and-luminescent properties

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Glass-ceramics with high concentration of rare earths (REs), are of great interest in the production of solid state lasers, planar waveguides and, more recently, for magneto-optical properties. The aim of this work was to synthesize borotungstate glasses with high concentration of REs and study the optical, luminescent and thermal properties as well as to prepare glass-ceramics by thermal treatment or by controling the quenching conditions. The materials were prepared in the system (100-x) ($60B_2O_3$-$40WO_3$) -x (RE_2O_3), where (x = 0, 15, 20, 25, 27.5, 30, in mol %) and were later characterized. The REs chosen for this work were Tb, Dy and Ho. The glasses were produced using the melt-quenching methodology. while the thermal, luminescent and optical properties were determined by thermal analysis, Raman and ultraviolet–visible spectroscopy, respectively. The glass-forming region was very limited, with crystallization already occurring in the thermal shock of the glass, indicating that the high concentration of RE induces crystallization in the melting temperature of the glass. The Raman spectroscopy of the amorphous phase showed the stretching vibrations of BO_4 tetrahedra, symmetric and asymmetric stretching vibration of WO_4^{2-}. The crystallized phase shows characteristical peaks of a $REBWO_5$ phase.

(ICG-GSP-P068-2019) The improvement of color gamut of a thick film phosphor-in-glass using Nd^{3+}-doped phosphate glass for white LEDs

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Recently, phosphor-in-glass (PiG) have been used as a color conversion material for white light-emitting diodes (LEDs) due to their high thermal and long-term stability. Since conventional white LEDs are used as a white light source for back light unit (BLU) of the commercial LCD displays, white LEDs with PiG as a color converter can be also used for display application as with their enhanced stability. However, conventional PiGs have limited color gamuts due to wide emission bands of green and red phosphors and they need additional processes after sintering such as polishing and thickness control. Thus, in this study, we fabricated a thick film typed PiG which doesn't require additional processes after sintering and improved its color gamut via doping of Nd^{3+} ion to the glass matrix. Strong absorption of Nd^{3+} at ~580 nm due to $^4I_{9/2} \rightarrow {}^4G_{5/2}+{}^2G_{7/2}$ transition can effectively modify the emission spectrum of green and red phosphors, and thus reduce the emission bandwidth. Thick film typed PiGs with 50 um in thickness via screen printing process were prepared varying phosphor contents of $Lu_3Al5O_{12}:Ce^{3+}$ (green) and $CaAlSiN_3:Eu^{2+}$ (red) and concentration of Nd_2O_3 within the phosphate glass frit. Various LED properties were examined after mounting on top of the blue LED such as color coordinates, color corelated temperature (CCT), color rendering index (CRI) and color gamut.

(ICG-GSP-P069-2019) N-anchoring in rare-earth-doped amorphous semiconductor as a route to broadband down-conversion phosphor

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Developing light-harvesting materials with broadband spectral response has always been at the forefront of photonics and materials science. The variation in dopant and host allows for extension of spectral response, but construction of broadband down-conversion phosphor covering the whole ultra-violet region remains a daunting challenge. Here, we describe a material system in which amorphization and N-doping notably extends the spectral response. We show that the fabricated nitrided amorphous TiO_2 activated with high concentration of Eu^{3+} (~ 15 mol%) can be excited by X-ray and ultraviolet light (200-400 nm) and present intense visible luminescence. We use the hybrid density functional theory to perform structure simulation and clarify that N-anchoring is mediated by coordinately Ti-N bonding between the N lone pairs and the Ti^{IV} center. Our results suggest that simultaneous structure disordering and nitriding in semiconductor, demonstrated here in $TiO_2:Eu^{3+}$, could be extended to other host and dopant systems for applications ranging from spectral modification and X-ray detection.

(ICG-P070-2019) Modification of $CaO-Al_2O_3-P_2O_5$ glass by a metal-microsphere manipulation due to continuous-wave laser irradiation

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Phosphate glass is one of the fascinating materials for various applications because of its transparency, low phonon energy, high solubility of rare-earth ions, proton conductivity, bioactivity, and reversible thermal chromism and bleaching and so on. We have developed the continuous-wave laser-induced metal-microsphere-manipulation (CW-LM3) method for modification of transparent glasses. In this study, we modified the $CaO–Al_2O_3–P_2O_5$ glass by using the CW-LM3 method to induce a visible change in the glass. The glass was prepared by a conventional melt-quenching method, and SUS304 powder was attached on one side of the glass plate. The laser light with the wavelength of 980 nm irradiates to the metal powder, and then a metal microsphere was fabricated inside the glass. Subsequently, the microsphere migrated to the direction of the laser light source by the laser irradiation. After laser stopped, the cylindrical modified zone was observed on the trajectory of the microsphere. From the transmitting optical microscopy, the center part of the modified area was brighter than the outer part. This result indicates that the compositional change may be induced by high temperature and steep temperature gradient of the CW-LM3 method. The changes of composition, morphology, and nanostructures in the trajectory due to CW-LM3 method will be discussed in the presentation.

(ICG-P071-2019) Specialty rare-earth-doped non-silica oxide glasses for compact and coherent light sources

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In recent decades, inorganic rare-earth (RE)-doped glasses have been playing a key role in the development of coherent light sources thanks to their transparency in the visible region, mechanical stiffness and resistance, chemical durability and easy manufacturing into different highly homogenous forms and sizes. The ultra-low propagation loss and outstanding thermo-mechanical properties have made silica glass the material of choice for most fiber-based optical devices and instruments operating in the near-infrared wavelength region. Despite its success, silica glass exhibits several intrinsic drawbacks, the major one being the poor solubility of RE ions. In this scenario, multicomponent phosphate and germanate glasses have demonstrated in last years to be true contenders to silica glass as a fiber material, especially for the realization of compact active devices, due to their ability to withstand a very high RE ions doping level. Phosphate glasses are particularly promising for amplifier/laser operation at 1 and 1.5 μm wavelengths, while germanate glasses are commonly exploited in the 2 μm region for surgery, CO_2 sensing and LIDAR systems. We report on the ongoing activities and the recent results obtained by our research team on the realization of compact lasers and amplifiers using in-house developed RE-doped phosphate and germanate glasses and fibers.

(ICG-GSP-P072-2019) Phase-separation engineering of glass for drastic enhancement of upconversion luminescence

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Optical gain materials are of fundamental importance for various applications, such as lasers, lighting, optical communication, microscopy and spectroscopy. However, the requirements for high luminescence efficiency and excellent thermodynamic stability of materials are always contradictory. As a result, the wide applications of optical materials in high-temperature, high-humidity and high-power laser-irradiated environments are restricted. In this work, a facile approach based on phase-separation engineering is proposed to modulate the thermodynamic stability and enhance the luminescence efficiency of optical materials. It is shown that the thermodynamic stability and luminescence efficiency of the phase-separated fluorosilicate gain glass are both enhanced dramatically when SiO_2 concentration is optimized. The upconversion luminescence efficiency of the designed glass is 150 times higher than that of traditional fluorosilicate glasses and even 7 times higher than that of ZBLAN glass. These intriguing properties of the amorphous glass indicate that phase-separation engineering not only provides a powerful solution to conquer the conventional contradiction between thermodynamic stability and luminescence efficiency but also offers significant opportunities for manufacturing a wide range of optical composites with multiple functions.

(ICG-P073-2019) Re-Interpreting an Ancient Mediterranean Carchesium from Base Glass Composition and Silver-Containing Decoration

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A blue glass carchesium in the Yale University Art Gallery collections, thought to be ~ 1st-century Roman based on form and decorative elements, was studied by a broad array of analytical techniques to provide more complete historical context. XRF, ICP-OES, SEM/EDS, and LA-ICP-MS of the Sr^{87}/Sr^{86} ratio were performed on the base blue glass. SEM/EDS and FIB-TEM were performed on the decorative enamel layer. Among the results obtained were Na_2O/Al_2O_3/CaO concentrations in wt% of 19.47/2.3/7.76, a MnO concentration of 0.56%, Co and Cu ppm concentrations of 841 and 1637, respectively, and a Sr^{87}/Sr^{86} ratio of 0.70924. Additionally, silver nanoparticles were detected in the enamel layer and appear to be the primary source of color, varying by depth in alternating bands of small (~80 nm) and large (~300 nm) spheres. As a whole, results are more consistent with an object of Byzantine origin from the Syro-Palestine region rather than Roman, possibly before the 10th century, and potentially made with recycled glass. This suggests the possibility of an early example of silver-containing glasswork from the Syro-Palestine area. Additional work is planned to perform quantitative EDS measurements of the enamel layer and to locate potentially similar objects in other collections.

(ICG-P074-2019) Characterization of Renaissance glass from Prague Castle

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Nine samples of glass came from vessels which were found in waste pit dated to between the last third of the16th century and the first third of the 17th century. Fragments of less common vessels assumed to be of foreign provenience were purposely selected for the analyses (X-ray fluorescence analysis, micro diffraction analysis, Raman spectroscopy); e.g. a fragment of a chalcedony goblet, a fragment of multi-colored glass, the base of a beaker containing blue filaments, and a fragment of a goblet body painted with enamel. The results of chemical analyses show that the glass belongs to the group of lime-potash glass of Bohemian production, in which the raw materials contained ashes, probably from beech wood. The fragment with the pelican colored decoration contains low-melting lead-quartz enamels. The white color contains mainly cassiterite; the yellow and green colors contain mainly bindheimite. The color intensity and toning is caused by the Sn / Sb ratio and by other components, especially by iron oxides.

(ICG-UGSP-P075-2019) Solarization in Soda-Lime-Silica Glasses Decolorized by Mn and Sb ions

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Early on, MnO_2 - also known as "glass makers soap" - has been known to decolorize naturally green glasses. Glasses melted from plant ash and sand often contain significant levels of iron, the combination of strongly blue colored Fe^{2+} and weakly yellow colored Fe^{3+} ions results in a green appearance. Oxidation of Fe^{2+} to Fe^{3+} ions in combination with traces of purple Mn^{3+} ions, gives a seemingly colorless glass. However, exposure to sunlight or UV radiation can oxide the remaining colorless Mn^{2+} to Mn^{3+} ions and the glass turns purple. This effect was first described by Michael Faraday in 1825. In order to better understand the solarisation effects of archaeological glasses, we prepare soda-lime-silicate glasses without dopants and doped with iron, manganese, or antinomy, as well as with combinations of these ions. For each glass an oxidising and a reducing melt is prepared to shift the various redox equilibria. Polished 1 mm thick sample plates are irradiated by a sun simulator and by X-rays in order to simulate long term exposure. The transmission losses of the samples are evaluated by optical spectroscopy with increasing irradiation doses. Additionally, electron paramagnetic resonance (EPR) is employed for the quantitative and qualitative characterisation of the extrinsic (photo-ionisation) and intrinsic defects (radicals, electron or hole centres that are related to the silicate glass matrix).

(ICG-UGSP-P076-2019) Multilinear Regression Analysis of Alkali Silicate Heritage Glass Degradation

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Signs of alteration are frequently observed on nineteenth century glass heritage objects as a consequence of their sensitivity to moisture. Microscopic evaluation of the glass surface identifies an alkali depleted layer as ingress of atmospheric humidity causes ion-exchange of H_3O^+ for alkali ions and weakens the modified glass, leading to cracking and degradation. Compositional analysis of nineteenth century Claude Laurent potassium silicate glass flutes and soda lime photographic plates by XRF, SEM, and other methods led to identification of a range of damage susceptible compositions. Fifteen model silicate glasses with varying concentrations of CaO, K_2O, and Na_2O within the identified range were prepared. The model glasses were artificially aged at 90°C and 90% relative humidity for seven days and observed in cross-section by SEM to determine the severity of degradation by the thickness of the alteration layer. The layer thicknesses were analyzed using multilinear regression for a four-part matrix (CaO, K_2O, Na_2O, and SiO_2). A linear relationship was found between measured and predicted alteration thickness of model glasses with an R^2 of 0.98. This predictive method could help in evaluation the risk of moisture sensitivity and choosing preservation strategies for an object of known chemical composition.

Tuesday, June 11, 2019

Norbert J. Kreidl Award for Young Scholars

Room: Georgian (mezzanine)
Session Chair: Liping Huang, Rensselaer Polytechnic Institute

12:25 PM

(ICG-PL-006-2019) Surface Stress Relaxation of Silica Glass and the Presence of Composition Fluctuations

E. Aaldenberg*[1]; M. Tomozawa[1]

1. Rensselaer Polytechnic Institute, Materials Engineering, USA

Small amounts of water in the atmosphere have the ability to promote fast relaxation of surface stress as the water diffuses into the glass. This surface stress relaxation has been found to be responsible for the fatigue limit, degradation of the ion-exchanged glass compressive stress profile, and strengthening of thin glass fibers, including silica glass fibers. Until this point, models for surface stress relaxation have assumed the stress to reduce in a surface layer, but the cause of this stress reduction remained a mystery. We propose that water in glass creates composition fluctuations which lead to a reduction in the modulus of the water-rich layer and the presence of delayed elastic relaxation behavior. This presentation will focus on the presence of composition fluctuations between water and glass through three experiments: small angle x-ray scattering, the memory effect, and the formation of bubbles at low temperature.

SI: Glass Structure and Chemistry

Session 1: Definition of Network Formers and Network Modifiers (TC03 & TC26)

Room: Berkley (mezzanine)
Session Chair: Bernard Hehlen, University of Montpellier

8:00 AM

(ICG-SI-023-2019) Structural analyses of complex glassy materials using chemical-bonding approaches (Invited)

S. Elliott*[1]; T. Lee[1]

1. University of Cambridge, Chemistry, United Kingdom

Structural analyses of glasses or amorphous materials are often carried out experimentally using diffraction experiments, from which structural information, such as atomic coordination numbers (CNs), can be gleaned from pair distribution functions (PDFs) obtained by Fourier transformation of the scattering data (structure factor). Conventionally, coordination numbers (e.g. nearest-neighbour CNs) are obtained by integrating over the corresponding peaks in the PDF (e.g. the first peak). However, this approach is incapable of distinguishing different local geometries with the same CN, e.g. tetrahedral or defective-octahedral geometries, both with 4-fold coordination. In addition, this peak-integration approach can include non-bonded atomic-pair correlations in the CN count. In this presentation, we will describe methods for determining the truly-bonded contributions to estimates for the CN using electron-localization function (ELF) and maximally-localized Wannier function (MLWF) approaches, applied to structural models of materials with complex bonding characteristics (e.g. 'phase-change' memory materials, Ge-Sb-Te), generated using density-functional-theory (DFT)-based molecular-dynamics simulations.

8:30 AM

(ICG-SI-024-2019) Oxygen Bridges in Tellurite Glasses

A. Hannon*[1]; E. Barney[2]; D. Holland[3]; S. Feller[4]

1. Rutherford Appleton Laboratory, ISIS Facility, United Kingdom
2. University of Nottingham, Faculty of Engineering, United Kingdom
3. University of Warwick, Physics Department, United Kingdom
4. Coe College, Physics Department, USA

We have recently used neutron diffraction to show that the Te-O coordination number in pure TeO_2 glass has a value of 3.68(4), and that the glass is formed from a mixture of TeO_3 and TeO_4 units. The distribution of Te-O bond lengths in the glass is not like the Te-O distribution for the paratellurite crystal phase, α-TeO_2, which has highly asymmetric Te-O-Te bridges. Instead, the Te-O distribution in the glass is much more similar to that in the γ-TeO_2 phase, which has oxygen bridges that are almost symmetric, as well as asymmetric bridges. Thus the oxygen bridges in tellurite glasses have a much greater variety of degrees of asymmetry than occurs in silicate glasses. Despite this large variation in asymmetry, we use a bond-valence method to show that there is a well-defined locus of possible positions for an oxygen atom between two tellurium atoms. A comparison of the bridges in tellurite and silicate crystal structures shows that there is a much greater variation in Te-Te distances than Si-Si distances, and Te-Ô-Te bond angles are much smaller than Si-Ô-Si bond angles. With reference to the structures of relevant crystals, we have investigated the structural characteristics of Te-O-Te bridges, and we discuss the possible origins and effects of the large variation in bridge asymmetry.

8:50 AM

(ICG-SI-025-2019) Chalcogenide glasses : Composition/structure/conductivity relationships (Invited)

A. Pradel*[1]; A. Piarristeguy[1]

1. Université de Montpellier, Institut Charles Gerhardt, France

Chalcogenide glasses are the homologous of oxide glasses where oxygen is replaced by sulfur or selenide. While the presence of the chalcogen has a strong impact on the structure of the glasses, similar effects such as the mixed former effect and mixed cation effect that both, result in non-linear variations of electrical conductivity upon substitution of an ion by another, can also be observed in this family of glasses. The talk will be focused on thio- and seleno-silicate and germanate glasses. After having described the structure of the network glasses and the role of the modifiers in their depolymerization, two examples of more complex glasses will be given: It will be shown that a phase separation can explain the mixed glass former effect in some glasses of the Li_2S-SiS_2-GeS_2 family while the mixed cation effect observed in Rb_2S-Ag_2S-GeS_2 glasses results, not only from the different cation environments but also by a profound reorganization of the glassy network upon the substitution of Rb^+ cations by Ag^+ ones.

9:20 AM

(ICG-SI-026-2019) Viscosity of TeO_2-based glasses

N. Tagiara*[1]; D. R. Neuville[2]; A. Kyritsis[3]; E. I. Kamitsos[1]

1. National Hellenic Research Foundation, Greece
2. Géomatériaux, CNRS-IPGP, France
3. National Technical University of Athens, Greece

Glasses based on tellurium oxide are of particular interest mainly due to their relatively low melting temperature, high refractive index and high non-linear optical properties. Because of their exceptional properties tellurite glasses are promising materials for a broad range of technological applications. To our knowledge, there are only a few studies on the viscosity of tellurite glass systems. In this work we present results of a study on the viscosity of several binary glasses based on TeO_2 as a function of temperature and added oxide in the systems ZnO-TeO_2 and $R_{2/3}O$-TeO_2 (R=B, Al). All glasses were prepared by melting in Pt crucibles and their structure was characterized by Raman and infrared spectroscopy and correlated to their viscosity-temperature behavior. We acknowledge support of this work by the project "Advanced Materials and Devices" (MIS 5002409) which is implemented under the "Action for the Strategic Development on the Research and Technological Sector", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

10:00 AM

(ICG-SI-027-2019) Insight into chemical bonding in oxide glasses from first principles calculations

S. Ispas*[1]; W. Kob[1]

1. University of Montpellier, Lab. Charles Coulomb, France

The use of a first-principles approach makes possible an in-deep study of the chemical bonds existing in oxide glasses and helps to understand how the disorder and/or the composition do affect them. For a series of binary and ternary aluminosilicate and borosilicate glasses, we have computed their electronic properties, as for example the Bader charges and electron localization function. From the examination of the bonds formed between the individual atoms, we have investigated the relationship between the calculated electronic properties and the atoms local environment and, when possible, compared to those of crystal structures with similar compositions. We have hence obtained more insight into the organization of atoms into well-defined groups in the short range, as well as the reasons that cause some preferential bonding of alkali or alkaline earth atoms.

10:20 AM

(ICG-SI-028-2019) Network modifier cations in single and mixed ion glasses by far-infrared spectroscopy (Invited)

E. I. Kamitsos*[1]

1. National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute (TPCI), Greece

Understanding the complex environment of metal ions in glass is of importance since physical properties such as ionic transport and basicity are related to the nature of metal ion sites and their spatial distribution in the glass structure. In this presentation we review results of far-infrared spectroscopy on metal ion containing oxide glasses, including single and mixed ion borate, silicate and phosphate glasses. Results are discussed in relation to those of molecular dynamics on selected borate glasses and to low-frequency Raman studies on aluminosilicate glasses. We acknowledge support of this work by the project "National Infrastructure in Nanotechnology, Advanced Materials and Micro / Nanoelectronics" (MIS 5002772) which is implemented under the Action "Reinforcement of the Research and Innovation Infrastructure", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

10:50 AM

(ICG-SI-029-2019) Role of titanium in silicate glass network

T. Robine[1]; M. Cicconi[1]; D. R. Neuville*[1]

1. IPGP-CNRS-USPC, Géomatériaux, France

Titanium is a highly interesting element for both earth and material sciences. In earth sciences, Ti is considered a refractory element, which can be found in large quantities in certain parental bodies of the solar system and in some natural glasses such as lunar glasses. This element is also widely interesting in material sciences, since it is generally used as a nucleating agent in glass-ceramics. Furthermore, Ti can be stabilized with different valencies, and coordinations, hence playing several roles in the silicate network, acting either as network former or network modifier. We prepared a series of sodium aluminosilicate glasses with the substitution of Al by Ti. Viscosity measurements near the glass transition temperature, heat capacity and Raman spectra were investigated and we will present these new results about the role of Ti in silicate glasses and melts.

11:10 AM

(ICG-SI-030-2019) The Role of Magnesium and Zinc in Bioactive Glasses (Invited)

D. S. Brauer*[1]; D. A. Avila Salazar[1]; R. Wetzel[1]; X. Lu[2]; L. Chung[3]; R. A. Martin[3]; J. Du[2]

1. Friedrich-Schiller-Universität, Otto-Schott-Institut, Germany
2. University of North Texas, Materials Science and Engineering Department, USA
3. School of Engineering & Applied Science and Aston Institute of Materials Research, Aston University, United Kingdom

Bioactive glasses contain large amounts of modifiers, placing them at the border of glass formation. When replacing CaO with either MgO or ZnO in melt-derived Bioglass 45S5, thermal properties showed similar trends for both series: T_g indicated a mixed cation effect, going through a minimum, while crystallisation tendency decreased and sintering improved with substitution. By contrast, ion release differed markedly for both series, with Mg substitution having a minor effect on ion release but ion release decreasing significantly for Zn-containing glasses. MAS NMR showed the silicate network to consist of Q^2 groups and small amounts of Q^3, while P was present as orthophosphate. ^{29}Si MAS NMR showed no significant change in chemical shift with substitution, but peaks broadened for Zn glasses suggesting a wider distribution of Q species. ^{31}P MAS NMR showed decreasing FWHM with increasing Zn substitution with peaks shifting to more positive ppm, suggesting preferential charge-balancing by sodium. Neutron diffraction and MD simulation showed zinc in nearly perfect four-fold coordination; Mg coordination numbers were slightly higher. Ion release, MD simulation and diffraction results suggest Zn entering the silicate network as a network former. By contrast, NMR results suggest changes in the partitioning of modifier cations between the Si and the P phase with increasing substitution.

11:40 AM

(ICG-SI-031-2019) Superstructural units involving six-coordinated silicon in sodium phosphosilicate glasses studied by advanced NMR methodology

J. Ren*[1]; H. Eckert[2]

1. Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Key Laboratory of Materials for High Power Laser, China
2. Institut für Physikalische Chemie,Westfälische Wilhelms-Universität Münster, Germany

We report such a structural study of sodium phosphosilicate glasses with high phosphate contents, using advanced nuclear magnetic resonance (NMR) methodologies. Quantitative information regarding the medium-range order is obtained from homo and heteronuclear magnetic dipole-dipole couplings measured via ^{31}P and ^{29}Si double quantum NMR as well as ^{31}P/^{29}Si, ^{31}P/^{23}Na, ^{29}Si/^{23}Na double resonance experiments. These glasses contain six-coordinated silicon species ($SiO_{6/2}$ units, which selectively connect to six branching phosphate groups, ($O=PO_{3/2}$). The bond valence gradient of these $Si^{(6)}$-O-$P^{(3)}$ linkages redistributes the anionic charge onto the phosphate non-bridging oxygen species, which attract Na^+ cations. The $Si^{(6)}(P^{(3)})_6Na_2$ superstructural units (stoichiometry $Na_2SiP_6O_{18}$) thus formed represent an exceptionally high degree of medium range order, accounting for high thermal and mechanical stability of these glasses. Assuming that the formation of these units is the main driving force establishing the structure of these glasses, the structural speciation in this system can be predicted from the elemental compositions, in excellent agreement with experimental results.

Session 4: Chalcogenide Glass Structure and Chemistry II

Room: Arlington (mezzanine)
Session Chairs: David Le Coq, University of Rennes; Matthias Wuttig, RWTH Aachen University

8:00 AM

(ICG-SI-032-2019) Correlations between Local Structure and Infrared Transmission Edge of Ge-Sb-S-Se Glass (Invited)

S. Shin[1]; J. Lee[1]; H. Masai[2]; T. Ina[3]; Y. Choi*[1]

1. Korea Aerospace University, Republic of Korea
2. National Institute of Advanced Industrial Science and Technology (AIST), Japan
3. Japan Synchrotron Radiation Research Institute, Japan

Demand on infrared cameras operating in long-wavelength infrared (LWIR) region is rapidly increasing in various civilian applications. Their cost effectiveness is thus becoming more critical. Among LWIR lens materials, chalcogenide glass is quite promising in view of its inherent moldability and property controllability. In addition, minimization of optical aberrations in LWIR range can be realized by combining plural lenses provided that there are lots of compositions available in the LWIR Abbe diagram. Ternary Ge-Sb-Se glass is one of the well-known chalcogenide glasses commercialized already for use as lens material. This ternary glass falls into a low-dispersion category, and therefore a group of high-dispersion glasses need to be developed in an effort to further broaden the LWIR Abbe diagram. Our experimental results on mixed-chalcogen Ge-Sb-S-Se glass confirm that its thermal and mechanical properties are improved with increase of sulfur content, and at the same time refractive index becomes more dispersive. Its local structure verified via EXAFS analysis turns out to support its compositional dependence of infrared transmission edge and refractive index dispersion.

8:30 AM

(ICG-SI-033-2019) Sub-T_g relaxation in network glasses and the role of fragility (Invited)

P. Lucas*[1]; E. A. King[2]; S. Sen[3]; C. Boussard-Pledel[4]; B. Bureau[4]

1. Univ of Arizona, USA
2. Corning Incorporated, USA
3. UC Davis, USA
4. University of Rennes, France

Germanium selenide glasses of compositions corresponding to the opposite ends of the fragility spectrum are annealed at room temperature for up to five years. Both glasses exhibit heat-capacity curves and stretched exponential relaxation which are fully consistent with standard glass relaxation models such as the Tool-Narayanaswamy-Moynihan formalism. A prominent enthalpy relaxation process is observed for both glasses and its structural origin is elucidated by Raman spectroscopy. The structural relaxation in both glasses is manifested in the Raman spectra as a decrease in the ratio of edge to corner-sharing $GeSe_{4/2}$ tetrahedral units. This is consistent with configurational entropy considerations based on the constraint counting principles. It is found that glasses from within the so-called "reversibility window" do not exhibit any unusual relaxation properties other than a relatively low fragility. These results also indicate that the non-reversing enthalpy obtained by modulated differential scanning calorimetry (MDSC) is not a reliable measure of the ability of a glass to relax. Instead, it is suggested that an interpretation of MDSC data in terms of complex heat capacity provides a more complete and reliable assessment of the relaxation properties of a glasses.

9:00 AM

(ICG-SI-034-2019) Athermal chalcogenide glass for infrared optics

M. J. Davis*[1]

1. SCHOTT North America, Inc., R&D, USA

Certain glasses in the As-S-Se ternary system satisfy the challenging combination of optical and physical properties that describe an athermal solid Fabry-Perot etalon. This means that, in the investigated temperature range (roughly 25-35 °C), interference fringes undergo very little movement in resonant wavelength as the temperature changes (i.e. < 5 ppm/K); this same attribute is desired in fiber-based strain sensors. Further, by virtue of their unusual combination of properties, this suite of glasses occupies a unique set of coordinates in the "glass map" approach used by optical designers to fabricate thermally- and chromatically-corrected lens systems.

9:20 AM

(ICG-SI-035-2019) Cryo-EM as a Tool for Structural Characterization of Solution-Processed Chalcogenide Glass

N. Dutta*[1]; C. B. Arnold[1]

1. Princeton University, USA

Solution processing has long been a convenient and inexpensive choice for chalcogenide glasses. It is desirable in part for its flexibility, made possible by a number of readily controllable parameters like solvent chemistry, solution concentration, deposition method, and more. Changes to these parameters lead to structural effects in the deposited material, which in turn affect important properties like optical nonlinearities and losses, but in spite of this, the structure of the glass in solution and its dependence on solution parameters are still poorly understood. We demonstrate that cryo-transmission electron microscopy (cryo-EM) can be used to fill this gap in knowledge. Cryo-EM is a technique from structural biology used to determine 3D structures of hydrated macromolecules. By adapting the method for inorganic materials in non-aqueous solutions, we are able to characterize the structure of arsenic (III) sulfide (As_2S_3) in propylamine and ethylenediamine—two systems with proposed nanoscale solution structures that, until now, had not been experimentally verified. Our results address a long-open question on the structure of As_2S_3 and demonstrate a novel technique for future investigation of solution-processed glasses.

10:00 AM

(ICG-SI-036-2019) Effect of Light on the Packing and Kinetic Stability of Vapor Deposited Amorphous Selenium

A. Zhang*[1]; R. B. Stephens[1]; Z. Fakhraai[1]

1. University of Pennsylvania, Department of Chemistry, USA

Amorphous selenium (a-Se) is a well-known atomic glassformer whose structure depends on preparation methods, post-deposition thermal annealing and above-bandgap (bandgap is around 2 eV) light exposure. Here, white light illumination (1.9 to 2.9 eV) is used to modify the structure of a-Se films which are vapor deposited with a substrate temperature lower than glass transition temperature. Using vapor deposition, glasses with higher density compared to liquid-quenched glasses are formed, with the degree of kinetic stability and increased density depending on the deposition temperature, rate, and illumination. Films deposited under light show a smaller density gain at low temperatures but have higher kinetic stability, suggesting that above-bandgap light illumination during vapor deposition modifies the packing and connectivity of incoming fragments, resulting in higher molecular weight structures with slightly looser but kinetically more stable packings. The deposition rate dependence of stability is also studied. We observed an abrupt change of density gain around 0.6 nm/s under illumination. While lower deposition rates lead to lower densities compared to the deposition without illumination, higher deposition rates produce similar densities. We will discuss how the relation between the photo-excitation and Se deposition rates affect the final structure.

10:20 AM

(ICG-SI-037-2019) $Er3^+$-doped Ga-Ge-Sb-S glass thin films by PVD deposition

G. Louvet*[1]; E. Baudet[3]; S. Normani[2]; F. Starecki[4]; P. Camy[4]; M. Bouška[2]; J. Gutwirth[2]; P. Němec[2]; C. Cardinaud[5]; C. Calers[1]; Y. Ledemi[3]; A. Douaud[3]; S. Messaddeq[3]; L. Bodiou[6]; J. Charrier[6]; J. Adam[1]; Y. Messaddeq[3]; V. Nazabal[1]

1. Institut des Sciences Chimiques de Rennes (ISCR), UMR 6226 CNRS, Université de Rennes, Equipe Verres & Céramiques, France
2. Department of Graphic Arts and Photophysics, Faculty of Chemical Technology, University of Pardubice, Czechia
3. The Center for Optics, Photonics and Lasers (COPL), Laval University, Canada
4. Centre de recherche sur les Ions, les Matériaux et la Photonique (CIMAP), UMR 6252 CEA-CNRS-ENSICAEN, Université de Caen, France
5. Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, France
6. FOTON UMR-CNRS 6082, Université de Rennes 1, ENSSAT, France

In the frame of the major issues related to global warming and pollution, the microsensor based on mid-infrared (MIR) spectroscopy is a useful tool to allow continuous measurement of different bio-chemicals species that disturb our environment. In the aim of developing a MIR source potentially integrated in a microsensor, we fabricated rare earth doped chalcogenide thin films by different phase vapor deposition (PVD) technics. The RF magnetron sputtering, pulsed laser deposition (PLD) and electron beam evaporation were investigated. The selected glass system is Ge-Ga-(Sb)-S with Er^{3+} ions doping. Er^{3+} ions show emissions in NIR and MIR at 1.55 µm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) and at 2.8 µm ($^4I_{11/2} \rightarrow {}^4I_{13/2}$) under excitation at 808 nm. Deposition parameters were optimized for the three PVD techniques based on a comparison to define the higher fluorescence efficiency. Sulphide thin films were characterized by means of transmission, AFM, XPS, SEM, EDS, ellipsometry and Raman spectroscopy to better control the deposition behavior. Acknowledgments : The author would like

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10:40 AM

(ICG-SI-038-2019) Understanding aging in chalcogenide glass thin films using precision resonant cavity refractometry

S. Geiger*[1]; Q. Du[2]; M. Shalaginov[2]; B. Huang[2]; J. Michon[2]; H. Lin[3]; T. Gu[2]; C. Goncalves[4]; K. Richardson[4]; X. Jia[1]; J. Hu[2]

1. University of Delaware, Materials Science and Engineering, USA
2. MIT, Materials Science and Engineering, USA
3. Zhejiang University, College of Information Science & Electronic Engineering, China
4. University of Central Florida, The College of Optics and Photonics, USA

The inherent metastability of glasses below their glass transition temperatures leads to drift in their optical properties over time. Chalcogenide glasses, with their wide transparency windows in the NIR, high nonlinear refractive indices, and amenability to low-temperature processing have a wide range of photonic applications that rely on the stability of their optical properties. Current methods used to detect chalcogenide glass aging have been limited to techniques that track the evolution of their bulk optical properties at low resolution. In this study, resonant cavity refractometry is optimized and employed to study the aging of $Ge_{23}Sb_7S_{70}$ chalcogenide glass. This technique boasts unprecedented sensitivity enabling us to track minute-by-minute changes in refractive index, down to 10^{-6} refractive index unit (RIU). Our study reveals that the changes in refractive index of the glass follow stretch exponential behavior. The Kohlrausch (stretch) exponents fall on different 'magic numbers' according to the Phillips field-free diffusion-to-traps model depending on initial treatment of the glass. The time constants also vary with glass treatment, with values ranging from days to decades.

11:00 AM

(ICG-SI-039-2019) Hydrophobic and transmittance performance of imprinted microstructure on chalcogenide glass surface

B. Xu*[1]; K. Fu[1]; C. Zu[1]; Y. Wang[1]; H. Zhao[1]; Y. Jin[1]

1. China Building Materials Academy, China

Silica mould was applied to imprint microstructure on the surface of As_2Se_3 chalcogenide glass in this paper. Surface microstructures were obtained via controlling heating temperature and loading pressure, without disruption on glass sample profiles. The size of microstructures on silica mould impact the depth and appearance of imprinted microstructures on chalcogenide glass, and then influence the surface contact angle and infrared transmittance. Imprinted by the silica mould with microstructure diameter and period of 5μm, the transmittance of chalcogenide glass samples increase 5% approximately within 10-12μm. Nanoscale irregular particles were obtained on the surface of imprinted microstructures by plasma etching, which can improve the contact angle up to 107°, without damaging the infrared transmittance performance. This study confirmed the practicability of hydrophobic and anti-reflectance microstructure on chalcogenide glass produced by imprinted method.

11:20 AM

(ICG-SI-040-2019) Viscoelastic study of Ge-Sb-Se and Ge(Ga)-Sb-Sn-S glasses around deformation temperature

N. Kitamura*[1]

1. National Institute of Advanced Industrial Science and Technology, Japan

Glass molding is a technique that can produce high performance optical elements with low cost and low energy consumption. Viscosity, elasticity, thermal expiation, thermal conductivity around deformation temperature are important features for a precision molding. In the present study, parallel plate rheometry has been applied to evaluate viscoelastic properties of some Ge-Sb-Se and Ge(Ga)-Sb-Sn-S chalcogenide glasses around their deformation temperatures. Two distinct relaxation process with short and long relaxation times were observed in the shear relaxation modulus for all glasses, while the relaxation modulus in oxide glasses had a simple decay behavior. The structural relaxation obeyed Maxwell model and the activation energies of the two processes estimated from time-temperature superposition principle law were consistent with the dissociation energies of chemical bonds constituting glass network structure. Effect of excess or deficiency of anions and cationic species on the relaxation process will be discussed.

11:40 AM

(ICG-SI-041-2019) Direct Evidence for the Behaviour of Single and Bipolarons in Chalcogenide Glasses

Y. Sharma*[1]; S. Murugavel[1]

1. University of Delhi, Department of Physics, India

We report, for the first time, direct evidence for the characteristic behaviour of single and bipolarons in chalcogenide glasses by using broad band impedance spectroscopy. The measured ac conductivity, σ(f, T) exhibit distinct behaviour from those reported in amorphous semiconductors depending on the temperature and frequency. At low temperatures, the measured total conductivity is exclusively due to the bipolarons (instantaneous hopping of two electron/hole) between two charged defect centres, while at high temperatures we additionally discovered single polaron hopping (hopping of one electron/hole) between a charged and neutral defect centres. Frequency dependent behaviour of single and bipolaronic conduction show distinct relaxation characteristics in the measured frequency window. Remarkably, we observe and quantify the existence of neutral defect centres with large concentrations in tellurium-based chalcogenide glass under dark conditions via electron spin resonance (ESR), which is found to be in agreement with the neutral defect concentration derived from the dc conductivity data. This researh work unequivocally demonstrates the characteristic behaviour of single and bipolarons in $Ge_{20}Te_{80}$ glass and its interdependence on thermal history of the sample. We believe that present findings would provide new way of designing phase change memory material for advanced information storage devices.

Session 8: Crystallization of Glasses and Glass-Ceramics II (TC 07)

Room: Terrace (lower level)
Session Chairs: Mark Davis, SCHOTT North America, Inc.; Ina Mitra, SCHOTT AG

8:00 AM

(ICG-SI-042-2019) Molecular dynamics simulations on fracture toughness of Al_2O_3-SiO_2 glass-ceramics

B. Deng*[1]; J. Luo[1]; J. Harris[1]; C. Smith[1]; M. E. McKenzie[1]

1. Corning Incorporated, USA

Driven by bottom-up microstructure design approaches to enhance glass-ceramic mechanical performance, extensive molecular dynamics simulations on binary aluminosilicate ($50Al_2O_3$-$50SiO_2$) glasses with embedded circular and ellipsoidal nanocrystals have been conducted. Enhancement of fracture toughness K_{IC} is widely observed and correlates with nanocrystal size, aspect ratio, relative position and angle of crystal surface to the crack tip. Crack penetration, deflection and nanocrystal cleavage are activated in different samples, leading to distinct variations in numerically measured K_{IC}. The results provide building blocks for establishing a statistical model to encapsulate the cumulative effect of heterogenous crystalline microstructures on the fracture behaviors in aluminosilicate glass-ceramics.

8:20 AM

(ICG-SI-043-2019) Structural Origins of Ba_2LaF_7 crystals in Phase Separated Aluminosilicate Oxyfluoride Glass: A Molecular Dynamics Simulation Study

X. Xu*[1]; J. Zhao[1]; J. Du[2]; X. Fan[1]; X. Qiao[1]

1. Institute of Inorganic and Nonmetal Materials, Zhejiang University, Department of Materials Science and Enigineering, China
2. Department of Materials Science and Engineering, University of North Texas, USA

Aluminosilicate oxyfluoride glass-ceramics with Ba_2LaF_7 crystals are novel host materials for luminescence applications such as random laser, temperature sensor, WLED, etc. However, in most cases, the preparation of such materials is still a trial-error based approach due to the lack of understanding of detailed glass structure. Recently, molecular dynamics simulations have been proved to be a useful tool to study fluoride phase separation behavior, which is considered as the initial stage for crystallization in oxyfluoride glass. In this study, we simulated a series of Ba^{2+} and La^{3+} fluoride containing aluminosilicate glass by MD simulations. After melting and quenching, fluoride phase separation can be observed from all simulated samples. With LaF_3 substituting BaF_2, the cations enriching in fluoride phase change from Ba^{2+}, to Ba^{2+} and La^{3+}, and finally La^{3+}. These fluoride rich regions are the precursors for BaF_2, Ba_2LaF_7 and LaF_3 crystals' precipitation from the corresponding glass in experiments. This study help us to understand the structural origins of different crystals from separated fluoride phase in aluminosilicate glass, which can help to design optical glass-ceramics more efficiently.

8:40 AM

(ICG-SI-044-2019) Glass structure and nanocrystallization mechanism of BaF_2-ZnO-B_2O_3 glasses

K. Shinozaki*[1]; Y. Ishii[2]; S. Sukenaga[3]; H. Shibata[3]; K. Ohara[4]

1. AIST, Inorganic Functional Materials Research Institute, Japan
2. Osaka University, Graduate school of engineering science, Japan
3. Tohoku University, Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Japan
4. JASRI, Japan

Transparent oxyfluoride glass-ceramics have been received much attention for photonic applications. In this work, oxyfluoride glasses with $(33.3\text{-}x/3)BaF_2–xZnO–(66.7\text{-}x)B_2O_3$ (x=0-50, in mol%) and Er_2O_3-doped compositions were prepared, and glass structure and crystallization behavior were investigated. Radial distribution functions of the glasses which were evaluated using synchrotron X-ray diffraction at a beamline of BL-04B2 in SPring-8, Japan. The short-range order, i.e., B–(O,F) and Ba–(O,F), showed almost same distance, on the other hand, the distance between Ba–Ba was decreased with addition of ZnO despite of the decrease the concentration of Ba ions. In order to investigate the glass structure in detail, molecular dynamic simulation was carried out, and then fluoride segregation was observed in the obtained model with the composition of x=40. We propose that such segregations of fluoride acts as nucleation sites.

9:00 AM

(ICG-SI-045-2019) Challenges in MD Simulation to Develop Nucleation in Glass

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1. Lehigh University, Materials Science and Engineering, USA

Laser-induced crystallization is known as one of the recent achievements in SbS/SbSI glasses. To form a crystal nuclei, a monochromatic light beam of 642 nm (diode laser) is used with 1-4 mW of laser power. Also, the high energy polychromatic X-ray beam (Synchrotron) has been found to crystallize these glasses. Interestingly in the growth process, often the lattice seems to rotate at real time which we called Rotating Lattice Single (RLS) crystal. To get into the insight of these interesting observations, we are trying to develop a theoretical model which would help to understand the mechanism behind this crystallization, such as the change in energy density, the temperature profile of the region (where nucleation/growth takes place), etc. As we know that nucleation in macroscale is hard to observe in Molecular Mechanics (classical), so, we are using Region Heating method (LAMMPS code) to dump certain energy (eV flux) only in a particular section of glass by making the atomic group dynamic. However, the net forces at each timestep are being so high that the system couldn't able to adjust and stabilize the particles in a minimized-energy configuration, eventually lead to a random orientation. Therefore, our intention is to optimize an appropriate set of conditions of energy density, composition which could fit into the best time domain to see any repeating unit of aligned particles.

9:20 AM

(ICG-SI-046-2019) The Role of SnO_2 as Nucleating Agent in BaO-SrO-ZnO-SiO_2 Glasses Studied by Electron and X-ray Microscopy

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2. Otto-Schott-Institut für Materialforschung, Jena University, Germany

BaO-SrO-ZnO-SiO_2 glasses from which a phase with the composition $Ba_{1-x}Sr_xZn_2Si_2O_7$ can be precipitated possess a strong tendency towards surface crystallization. Glass-ceramics based on $Ba_{1-x}Sr_xZn_2Si_2O_7$ show remarkably small or even negative coefficients of thermal expansion. However, the thermal expansion of $Ba_{1-x}Sr_xZn_2Si_2O_7$ is highly anisotropic and hence, for the preparation of such glass ceramics in large dimensions, bulk nucleation is a prerequisite. For this reason, it is necessary to detect appropriate nucleating agents in order to switch the crystallization mechanism from surface to bulk nucleation. This paper describes the role of SnO_2 as nucleating agent in BaO-SrO-ZnO-SiO_2 glasses. A range of different concentrations of SnO_2 was studied using microscopic techniques and thermal analyses regarding their crystallization behavior. SnO_2 provokes volume nucleation, however, with low nucleation rates. The arrangement of the crystals could be visualized in three dimensions by X-ray microscopy. By means of this technique, it is found that the different crystal morphologies apparent in scanning electron micrographs can be ascribed to different crystal orientations in the glass matrix. Moreover, it is indicated that microcracking starts at the center of the crystals.

10:00 AM

(ICG-SI-047-2019) Crystallization shrinkage and crystallization porosity in sintered diopside glass-ceramics (Invited)

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2. Institute of Information and Communication Technologies, Bulgarian Academy of Sciences, Bulgaria

Due to higher density of the forming crystalline phases the crystallization in the supercooled melts leads to shrinkage, accumulations of stresses and/or formation of porosity. These variations are fundamental for the metalworking and the crystallization of polymers. The volume changes, observed at cooling and crystallization of high-viscosity melts, are also important in geology and astronomy. Notwithstanding, the similar density variations accompanying the glass-ceramics manufacture and their effect on the structure and the properties of final materials are still not well elucidated. In the lecture results for the crystallization shrinkage and crystallization porosity in sintered glass-ceramics, synthesized using diopside glasses with surface crystallization and powders with various sizes, are summarized. This data is obtained by parallel isothermal and non-isothermal experiments with optical dilatometer, DTA and hot-stage XRD combined with computed tomography and SEM observations. It is highlighted that the sintering and crystallising shrinkages stop after the formation of crystalline shells with a critical thickness in all particles. After that in the centres of grains

starts the creation of crystallization pores. As a result the crystallization porosity increases with the rise of particle size and attained crystallinity.

10:30 AM

(ICG-SI-048-2019) Nonisothermal crystallization kinetics and stability of leucite and kalsilite from K_2O-Al_2O_3-SiO_2 glasses

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1. Sheffield Hallam University, Materials and Engineering Research Institute, United Kingdom

The crystallization mechanisms and elemental stability of leucite and kalsilite, formed by heat treatment of K_2O-Al_2O_3-SiO_2 glasses, were investigated by X-ray powder diffraction (XRD), X-ray fluorescence (XRF), Raman spectroscopy and differential scanning calorimetry (DSC). Glass samples with compositions along the leucite-kalsilite tie-line were produced by melt processing and were then heat treated at 850, 950, and 1250°C for times ranging from 5 minutes to 1000 hours. Kalsilite is an unstable phase that behaves as an intermediate precursor to leucite. Crystalline materials in which kalsilite is the major phase lose potassium upon prolonged heat treatment (1000 hours at 1250°C), in contrast to those with leucite, for which little or no compositional alteration is detected. The formation of leucite from stoichiometric kalsilite is accompanied by the formation of potassium-doped alumina. The activation energies for leucite and kalsilite crystallization, determined via application of the Kissinger equation to thermal analysis data, were 579 and 548 kJ/mol, respectively. Production of pure leucite can be achieved with more favorable crystallization kinetics when starting with off-stoichiometric compositions.

10:50 AM

(ICG-SI-049-2019) Crystallization kinetics of non-stoichiometric $Na_2O.2CaO.3SiO_2$ – $Na_2O.3CaO.6SiO_2$ glasses

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1. University of Sao Paulo, Department of Materials Engineering, Brazil
2. National Science Center Kharkov, Institute of Physics and Technology, Ukraine
3. Federal University of Sao Carlos, Department of Materials Engineering, Brazil

The crystallization kinetics and glass forming ability are not well known in the important combeite-devitrite ($Na_2O.2CaO.3SiO_2$–$Na_2O.3CaO.6SiO_2$) joint of the classical soda-lime-silica glass-forming system. In this work, we estimated the crystal nucleation and growth rates as a function of temperature for glasses containing 100, 75 and 66.7 mol.% combeite using optical microscopy. With the steady-state nucleation rates and time-lags for combeite, we show that the nucleus/liquid interfacial energy, σ, increases as the glass composition deviates from the stoichiometric $Na_2O.2CaO.3SiO_2$. The increased σ leads to a strong decrease in the maximum nucleation rate and the corresponding temperature with increasing T_g/T_{liq}, i.e., increased reduced glass transition temperature. At the advanced stages of crystallization, the (low-to-high) polymorphic transformation of combeite and the glass transition temperatures measured by DSC were used to track the composition of both crystallized combeite and the residual glass. The results on the crystallization kinetics of these non-stoichiometric glasses are original and relevant, not only for advancing the nucleation theory but also for the microstructural design of new glass-ceramics.

11:10 AM

(ICG-SI-050-2019) Relationship between microstructure and transparency for ion-exchangeable, spinel glass-ceramics

A. Mitchell*[1]

1. Corning Incorporated, Glass Research, USA

Depending on the phase(s) that crystallize, glass-ceramics can provide mechanical advantages over typical commercial glasses that are used in display or cover glass applications. However, these uses require transparent materials and retaining transparency after ceramming remains a significant challenge. High transparency in glass-ceramics is possible if the crystallite size is much smaller than the wavelength of light or if the refractive indices of the residual glass and the crystalline phases are similar. In this study, the effect of microstructure (crystallite size and location) on transparency in the visible range is investigated for ion-exchangeable, spinel glass ceramics. The type and amount of nucleating agent is critical to achieve a consistently nucleated glass-ceramic which, in turn, is necessary for the final material to exhibit >80% axial transmittance at 350 nm.

11:30 AM

(ICG-SI-051-2019) Novel ZnO-Bi_2O_3-B_2O_3 glass-ceramics containing nanocrystals for optical device applications

C. Schwarz*[1]; M. Kang[2]; C. G. Pantano[3]; K. Richardson[2]; C. R. Baleine[4]; S. Kuebler[5]; C. Grabill[5]; J. Rice[3]; Q. Altemose[1]; K. Raichle[1]; B. Schnable[1]; I. Wietecha-Reiman[3]

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2. University of Central Florida, CREOL, The College of Optics and Photonics, USA
3. Pennsylvania State University, Materials Science and Engineering, USA
4. Lockheed Martin, USA
5. University of Central Florida, Chemistry, USA

In this study, three large scale melts and six small test melts of glasses containing stoichiometric ratios of Zn/Bi/B as well as some including As_2O_3 for redox control and $LiNO_3$ as a nucleation species are explored. Transparent optical glass-ceramics consisting of nanocrystals have a potential for use as optical devices such as low-cost UV-MWIR microlenses, waveguides, and photonic crystals. ZnO–Bi_2O_3–B_2O_3 (ZBB) glass ceramics are prepared using the melt quenching technique. Our objective is to maximize homogenous volume crystallization growth in the ZBB systems by thermal treatment while maintaining bulk transmission. Thermal behavior, elemental, transmission, and index of refraction of these melts are characterized and compared to determine their suitability as optical glasses and glass ceramics. ZBB glass ceramics containing BiB_3O_6 and $Bi_2ZnB_2O_7$ nanocrystals are created using heat treatments. Nucleation and heat treatment temperatures as well as heat treatment durations are correlated with induced crystal phase growth. Compositions and heat treatment procedures are developed to encourage volume $Bi_2ZnB_2O_7$ crystallization and reduce unwanted surface crystallization. Direct laser writing (DLW) is used to pattern crystallized subsurface pads and lines to study induced crystal growth with laser dose and post-heat treatment modifications.

Session 8: Crystallization of Glasses and Glass-Ceramics III (TC 07)

Room: Terrace (lower level)
Session Chairs: Matt Dejneka, Corning Incorporated; Ina Mitra, SCHOTT AG

1:20 PM

(ICG-SI-052-2019) Structural properties and non-linear optical effects in Tm^{3+}/Tm^{3+}-Yb^{3+} doped $NaLuF_4$ oxyfluoride glass-ceramics

J. J. Velazquez Garcia*[1]; R. Balda[3]; J. Fernandez[2]; G. Gorni[4]; M. Sedano[4]; A. Durán[4]; M. Pascual[4]

1. FunGlass - Centre for Functional and Surface Functionalized Glass, Alexander Dubček University of Trenčín, Slovakia
2. Donostia International Physics Center (DIPC), Spain
3. Pais Vasco University UPV-EHU, Applied Physic Department I, Spain
4. Institute of Ceramics and Glass (ICV-CSIC), Spain

Rare-earth (RE) doped nanostructured oxyfluoride glass-ceramics (OxGCs) gained an increasing attention in the last decades due to the combination of advantages glass processing and good mechanical, thermal and optical properties. This interest has been reflected in the search of many fluoride crystalline phases with improved

optical applications where the RE ions are effectively incorporated in the nanocrystals (NCs). This is observed especially in the case of $RLnF_4$ (R = K, Na) crystalline phases. In this work, xTm^{3+} and xTm^{3+}-$2Yb^{3+}$ (x = 0.1, 0.5), in mol%, doped transparent OxGCs with $NaLuF_4$ NCs have been analyzed. The crystallization process has been studied using XRD and HRTEM, obtaining NCs ranging 10-50 nm in size. The optical characterization includes the measurement of the up-conversion (UC) as well as the IR emissions. Excited State dynamics have been performed in order to determine the UC mechanisms as a function of dopant concentration.

1:40 PM

(ICG-SI-053-2019) Structure and luminescence of glass-ceramics in the MgO-SrO-SiO_2 system

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2. Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Spain

Aluminates and silicates doped with rare-earth (RE) ions have been studied for many years to obtain a source of persistent luminescence. The most common methods for the synthesis of these phases are solid-state reaction, electrospinning, sol-gel, combustion synthesis, and the molten salt method. The glass-ceramic route has not been very much explored. Aluminates doped with europium and dysprosium have been intensely investigated due to their good luminescent properties, but these materials require very high processing temperatures and exhibit poor chemical properties in the presence of water. The interest for silicates doped with REs resides in the advantageous combination of their high chemical stability, color variety and water resistance. This work reports on the structural and luminescence properties of $Sr_2MgSi_2O_7$: Eu^{3+}/Dy^{3+} based glass-ceramics obtained by sintering and crystallization from glass powders. The starting glass system was MgO-SrO-SiO_2, from which $Sr_2MgSi_2O_7$ was obtained as the only crystalline phase. The crystal structure was characterized by X-ray diffraction and the microstructure studied by cathodoluminescence in a scanning electron microscope. Electron paramagnetic resonance was employed to verify that Eu^{2+} is present in the glass-ceramics. The luminescence properties of different dopant concentrations were compared.

2:00 PM

(ICG-SI-054-2019) Noble Metal Nanoparticles-Embedded Glass towards Light Modulation

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2. Leibniz-IPHT, Germany

We report a novel, universal and simple approach to create noble metal nanoparticles (Au, Ag or Au-Ag NPs) in a large variety of glass hosts, i.e., silicate, germanate, borate and tellurite glasses. Due to their light modulation capability arising from the localized surface plasmon resonance (LSPR), these hybrid optical materials enable applications ranging from colored glasses, dichroic screen to nonlinear devices as well as transparent displays.

2:20 PM

(ICG-SI-055-2019) Ultrastability and color-tunability of $CsPb(Br/I)_3$ nanocrystals in P-Si-Zn glass for white LEDs

X. Liang*[1]

1. Wenzhou University, China

In this work, a series of $CsPbBr_xI_{3-x}$ NCs glasses, showing tunable emission (523 - 693 nm) controlled by different ratios of Br^- and I^-, were successfully prepared by melt-quenching and heat-treatment method. Especially, the X-ray diffraction (XRD) patterns and transmission electronic microscope (TEM) images verified that the $CsPbBr_xI_{3-x}$ NCs were crystallized in the P-Si-Zn glass matrix. The $CsPbBr_xI_{3-x}$ NCs glass exhibited narrow full width at half maximum (FWHM) and a wide color gamut, and showed outstanding stability towards ambient conditions, water and heat. Further, the perovskite-based white light emitting diodes was assembled, demonstrating a white light with a Commission Internationale de I'Eclairage (CIE) color coordinates (0.3299, 0.3322), indicating that the $CsPbBr_xI_{3-x}$ NCs glass could be a promising candidate for solid-state-lighting.

2:40 PM

(ICG-SI-056-2019) Doping manganese into $CsPb(Cl/Br)_3$ QD glasses: Dual-color emission and super thermal stability

W. Xiang*[1]

1. Wenzhou University, China

$CsPbX_3$ perovskite quantum dots (QDs) are still limited in their use due to their extreme instability in the air as they will deteriorate in a few days, and their thermal stability is not optimistic. At the same time, the toxicity of lead is also a major factor restricting its development. As a consequence, we demonstrate the partial replacement of Pb with Mn through conventional melt-quenching and heat-treatment method preparation of Mn-doped $CsPb(Cl/Br)_3$ QD glass. Mn-doped $CsPb(Cl/Br)_3$ QD glass exhibits high luminescent intensity like QDs. It is important that Mn-doped $CsPb(Cl/Br)_3$ QD glass with Dual-Color maintained the same lattice structure like Mn-doped $CsPb(Cl/Br)_3$ QDs, and highly homogeneous spectral characteristics of Mn luminescence. The intensity and position of this Mn-related emission are also tunable by altering the experimental parameters, such as the Pb-to-Mn feed ratio, annealing temperature. Because Mn-doped $CsPb(Cl/Br)_3$ QD glasses have good thermal and air stability, they can be used as a red fluorescent material. We fabricated glass with $Y_3Al_5O_{12}$:Ce^{3+} (YAG:Ce^{3+}) phosphor-in-glass (PiG) realized the chromaticity tuning for YAG:Ce^{3+} phosphor with white light-emitting-diodes (WLED).

3:00 PM

(ICG-SI-057-2019) Structural and electrical properties of the phosphate glasses and glass-ceramics in Na_2O-Nb_2O_5-P_2O_5 system

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2. ENSAM Meknes, University Moulay Ismail, Equipe Matériaux Innovants et Procédés de Fabrication Mécanique, Morocco
3. University Sidi Mohamed Ben Abdellah, Faculty of Sciences Dhar-Mehraz, Physics Department, Morocco

Glasses with compositions50Na_2O-xNb_2O_5-(50-x)P_2O_5(x = 5, 10, 15 20, and 25 mol%) are prepared by the melt quenching method. The work pointed out the effect of replacing P_2O_5 by Nb_2O_5 on the density, molar volume and the structure of these vitreous materials. The structural characteristics of the glasses by Raman spectroscopy are determined and revealed that the glassy-matrix involved many phosphate structural units, mainly metaphosphate and pyrophosphate groups. Their contents depend on the chemical composition. The composition dependence of the density (molar volume) show decrease (increase) by adding Nb_2O_5 to the base sample (x=0). By heat treatments of these glasses we obtain their corresponding glass-ceramics. The identification of the crystalline phases embedded in the glassy network is carried out by X-ray diffraction. The XRD patterns showed the formation of a ferroelectric phase $NaNbO_3$ in samples for which the content of niobium oxide is more than 15mol%. The dielectric constant of the glass-ceramics was measured at the frequency of 10 Hz to 1 MHz under the temperature of 120-650 K. The results indicated that the sample rich in niobium show high dielectric properties.

3:40 PM

(ICG-SI-058-2019) Vanado-tellurite glass-ceramics containing copper oxide: Effect of melting environment on structural-electrical properties

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Previous studies carried out on glasses belonging to the CuO-V_2O_5-TeO_2 system have shown that these glass-ceramics have interesting electrical properties, including high electronic conductivity. A possible explanation to this enhanced properties could be related to the interface between the glass matrix and the grains which forms an extensively ramified system of conducting paths for electrons diffusion. In this context higher number of neighboring V^{4+}/V^{5+} in the interfacial regions possibly leads to smaller average distance between these hopping centers, causing an increase in conductivity. In this study $20CuO$-$48V_2O_5$-$32TeO_2$ glasses were synthesized under different oxidizing conditions: under oxygen, static air, nitrogen atmosphere and with or without elemental Te, and then heat treated to form glass-ceramic materials. All the obtained samples, were characterized by means of FEG-scanning electron microscopy, X-Ray Diffraction and Raman spectroscopy. The electrical properties were measured through impedance spectroscopy and High Resistance Electrometry (at room temperature). Results show changes in the electronic conductivity spanning from 10^{-7} $(\Omega\ cm)^{-1}$ for glass to 10^{-2} $(\Omega\ cm)^{-1}$ for glass-ceramics. Finally, the possible effect of VO_2 microcrystals has also been considered.

4:00 PM

(ICG-SI-059-2019) Inferring the chemical composition of the residual glassy phase of glass-ceramics from ionic conductivity

R. B. Nuernberg[1]; T. S. Bello[1]; V. Fokin[2]; E. D. Zanotto[1]; A. C. Rodrigues*[1]

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2. Vavilov State Optical Institute, Russian Federation

The properties of glass-ceramics are strongly influenced by the crystallized volume fraction, crystal size and shape, as well as the chemical composition of the residual glassy phase (RGP). The analysis of chemical composition of the RGP requires in-situ methods like Energy Dispersive X-Ray Spectroscopy. However, when light elements like lithium are present, this analysis is strongly compromised. On the other hand, Li+ is a mobile ion, which provides ionic conductivity to the glass. We will discuss here the possibility of inferring the chemical composition of the residual glassy phase of a glass-ceramics of the Li2SiO3-CaSiO3 joint. In the chosen composition, only lithium metasilicate (Li2SiO3) crystallizes up to advanced stages of the phase transformation. Thus, as crystallization evolves, the residual glassy phase becomes lithium-depleted, which causes changes in its ionic conductivity. To evaluate the chemical composition of the RGP, a standard curve of ionic conductivity was obtained by preparing standard glasses with known composition and measuring their ionic conductivity. Results show, as expected, that as crystallization evolves, the ionic conductivity of the residual glassy phase decreases, due to the impoverishment in lithium. Limits of the equation applied to estimate the ionic conductivity of heterogeneous media like a glass-ceramic are also discussed.

4:20 PM

(ICG-SI-060-2019) Thermoelectric Properties of Tungsten Phosphate Glass-Ceramics

L. Moore*[1]; B. Aitken[1]

1. Corning Incorporated, Glass Research, USA

Tungsten phosphate glass-ceramics displaying high electrical conductivity have previously been reported. The glass-ceramics are made from glass-forming compositions within the WO_3-TiO_2-P_2O_5 system. They are characterized by an interconnected network of prismatic tungsten monophosphate, $(PO_2)_4(WO_3)_{2m}$, crystals in a matrix of titanium phosphate. Tungsten monophosphate crystals are quasi two-dimensional conductors exhibiting room temperature electrical conductivity in the range of 10^3 to 10^5 S/m, depending on the value of m. The conductivity of the glass-ceramics varies with the phase assemblage and microstructure obtained on ceramming. Tungsten monophosphate (m=7) glass-ceramics have been synthesized which exhibit electrical conductivity on the order of 1000 S/m at room temperature. Furthermore, the electrical conductivity, thermal transport properties, and Seebeck coefficients of these glass-ceramics have been measured as a function of temperature. They are shown to be n-type semiconductors exhibiting electrical conductivity up to 5000 S/m and power factors on the order of 10^{-5} $W/m.K^2$ at 700°C.

SII: Glass Physics

Session 4: Topology and Rigidity II

Room: Berkley (mezzanine)
Session Chairs: David Sidebottom, Creighton University; James Philips, Rutgers University

1:20 PM

(ICG-SII-032-2019) A Personal History of Glass Science at the Molecular Level (Invited)

J. C. Phillips*[1]

1. Rutgers, Physics, USA

Glass technology began thousands of years ago with the discovery of residual shiny clusters of silicates in fire pits. Glass science began with the discovery in monasteries about 1000 years ago that molten glass could be blown into thin sheets for window panes. Glass chemistry began with brilliant Pb silicates for table ware about 350 years ago. Molecular glass technology began with the discovery of strong borosilicates (Germany, late 19the century) and Corning (1915). Molecular glass science began with "continuous random networks" around the time I was born, but it had to wait for a while. I will take up the story around 1979, and bring it forward to Gorilla glass and NAND flash chalcogenide alloy memories. Today the topolgical similarities of glasses and protein networks can be quantified, with the result that what we have learned from glass networks can be transferred to Darwinian evolution at the molecular level of life itself.

1:50 PM

(ICG-SII-033-2019) Linking melt-dynamics with glass-topological phases in network-forming systems (Invited)

P. Boolchand*[1]; R. Chbeir[1]; C. Mohanty[1]; A. Mandal[1]; S. Chakravarty[1]; B. Almutairi[1]; V. Gogi[1]; A. Welton[1]; M. Bauchy[2]; M. Micoulaut[3]

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2. University of California Los Angeles, Civil and Environmental Engineering, USA
3. University Pierre et Marie Curie, France

Melt dynamics are usually described in terms of their fragility index, m, which can either be low (m < 20) identified with strong melts or high (m > 20) associated with fragile melts. On the other hand, glasses exist in one of three possible topological phases. Flexible Phase (FP) glasses occur when the mean coordination number <r> < 2.40 and possess a substantial enthalpy of relaxation at T_g, ΔH_{nr} ~ 1-2 cal/gm range. Isostatically-Rigid Phase (IRP) glasses occur when <r> typically lies in the 2.40-2.50 range and with the ΔH_{nr} term vanishing to ~0 cal/gm. Stressed-Rigid Phase (SRP) glasses occur when <r> > 2.50 and the ΔH_{nr} term again substantially increases. In several families of dry and homogeneous chalcogenides (Ge-S, Ge-Se, Ge-As-Se) and modified oxides, (Na-Borates, Na-Phosphates) examined recently, we observe a general pattern; melts of IRP glasses are invariably super-strong and give rise to glasses possessing a vanishing ΔH_{nr}. In contrast, melts of both SRP and FP are invariably

fragile but give rise to glasses possessing a substantial ΔH_{nr} term that increases with <r> in the former but decreases with <r> in the latter. These findings underscore that melt dynamics uniquely encode glass topological phases.

2:20 PM

(ICG-SII-034-2019) Topology-Informed Machine Learning for the Prediction of Glass Properties

H. Liu*[1]; K. Yang[1]; X. Xu[2]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA
2. University of California, Los Angeles, Mathematics, USA

Data-driven modeling based on machine learning (ML) offers a promising route to develop robust composition-property models in glasses. However, traditional ML shows several limitations: (i) it requires a large amount of consistent data, (ii) it has a poor ability for extrapolation far from the training set, and (iii) it can potentially violate physics laws. To address these limitations, we present a new topology-informed ML framework. We show that the incorporation of a topological description of the glass network greatly enhances the accuracy of the developed models with respect to traditional "blind" ML. Importantly, the network topology acts as reduced-dimensionality parameter, which partially overcome the "curse of dimensionality" that typically affects data-driven modeling. In turn, the decrease in the dimensionality of the model greatly increases its ability to extrapolate predictions far from the training set. Overall, this method offers a promising route toward the development of robust model enabling the discovery of new glasses with improved properties.

2:40 PM

(ICG-SII-035-2019) Evidence of an Intermediate Phase in Calcium–Silicate–Hydrates

Q. Zhou*[1]; M. Bauchy[1]

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By reducing complex atomic networks into mechanical trusses, topological constraint theory (TCT) classifies network glasses as flexible, stressed-rigid, or isostatic if the number of constraints per atom is lower, higher, or equal to the number of atomic degrees of freedom—wherein isostatic glasses are rigid but unstressed. Interestingly, it has been reported for chalcogenide systems that isostatic glasses exist within a window of compositions (the "intermediate phase", IP) rather than at a fixed threshold. Here, based on molecular dynamics simulations, we show that calcium–silicate–hydrates samples exhibit a compositional window that is analogous to the IP observed in chalcogenide glasses. Also, we demonstrate that the compositions belonging to the IP exhibit unusual properties, including maximum fracture toughness, minimum propensity for relaxation, and maximum elastic recovery upon loading. This suggests that the concept of IP might be generic to disordered materials.

3:00 PM

(ICG-SII-036-2019) Statistical Mechanics of Topological Fluctuations in Glass-Forming Liquids

K. A. Kirchner*[1]; S. H. Kim[2]; J. C. Mauro[1]

1. Pennsylvania State University, Materials Science and Engineering, USA
2. Pennsylvania State University, Chemical Engineering, USA

All liquids are topologically disordered materials; however, the degree of disorder can vary as a result of internal fluctuations in structure and topology. These fluctuations depend on both the composition and temperature of the system. Most prior work has considered the mean values of liquid or glass properties, such as the average number of topological degrees of freedom per atom; however, the localized fluctuations in properties also play a key role in governing the macroscopic characteristics of any glass-forming system. Our work proposes a generalized approach for modeling topological fluctuations in glass-forming liquids by linking the statistical mechanics of the disordered structure to topological constraint theory. In doing so we introduce the contributions of localized fluctuations into the calculation of the topological degrees of freedoms in the network. With this approach the full distribution of properties in the disordered network can be calculated as an arbitrary function of composition, temperature, and thermal history (for the nonequilibrium glassy state).

3:40 PM

(ICG-SII-037-2019) Investigation on Simulation of Glasses' Properties Using Topological Constraint Theory and Classical computation

H. Zeng*[1]

1. East China University of Science and Technology, China

An increased need for high performance glass design for display screen, reinforcing fiber and powerful laser devices, have led to renewed interest on fundamental research about simulation. Here we report the investigation on simulation of glasses' properties using topological constraint theory and classical computation, mainly on the topological constraint theory was used to calculate glass transition temperature and hardness of sodium silicophosphate glasses based on the quantitative structural model, and the thermal expansion equation based on the fundamental thermodynamic formula and topological constraint theory. In addition, we tried to simulate elastic moduli, hardness and viscosity simulation of aluminosilicate glasses with molecular dynamics and classcical computaion. Further study is still ongoing.

4:00 PM

(ICG-SII-038-2019) Role of weak constraints on the disorder-induced swelling of silicates

N. Krishnan*[1]; Y. Le Pape[3]; G. Sant[2]; M. Bauchy[2]

1. Indian Institute of Technology Delhi, Civil Engineering, India
2. University of California, Los Angeles, USA
3. Oak Ridge National Lab, USA

Minerals, under exposure to high-energy radiations, undergo significant structural changes. Similarly, when subjected to vitrification, silicate melts solidify to form a disordered glass. Such changes result in the evolution of macroscopic properties and particularly results in a decrease in the density of the material. Despite the fundamental nature of this phenomenon, the origin of such a disorder-induced swelling remains poorly understood. Herein, using realistic molecular dynamics simulations of neutron irradiation, we study the effect of irradiation and vitrification on the structure of eight different minerals. We observe that depending on the structure and topology of the atomic network, disorder-induced swelling varies in different minerals. To explicate this, we use topological constraint theory, which isolates the important features that ultimately affects the macroscopic properties. We show that weak constraints, if present in an atomic network, are broken during the disordering process, namely irradiation or vitrification. A direct correlation is obtained between the number of weak constraints and disorder-induced swelling. Further, we show that the driving force for the swelling is the eigenstress present in the atomic networks. When subjected to disordering, the eigenstress releases by the breakage of weak constraints, leading to an overall increase in the volume of the mineral structure.

4:20 PM

(ICG-SII-039-2019) Ring Size Distribution and Relaxation in Silicate Glasses

X. Li[1]; W. Song[1]; M. M. Smedskjaer[2]; J. C. Mauro[3]; C. G. Hoover[4]; M. Bauchy*[1]

1. University of California, Los Angeles, Civil and Environmental Engineering Department, USA
2. Aalborg University, Denmark
3. Pennsylvania State University, USA
4. Arizona State University, USA

As non-equilibrium materials, glasses continually relax toward the supercooled liquid state. However, the atomic-scale origin and mechanism of glass relaxation remain unclear. Here, based on molecular dynamics simulations of sodium silicate glasses quenched with varying cooling rates, we show that structural relaxation occurs through the transformation of small silicate rings into larger ones. We demonstrate that this mechanism is driven by the fact that small rings (< 6-membered) are topologically overconstrained and experience some internal stress. At the atomic level, such stress manifests itself by a competition between radial and angular constraints, wherein the weaker bond-bending constraints yield to the stronger bond-stretching ones. These results strongly echo von Neumann's "N - 6" rule in grain growth theory and suggest that the stability of both atomic rings and two-dimensional crystal grains is fully topological in nature.

Session 5: First Principles based MD Simulations and Calculations of Glass Properties (TC 27)

Room: Hancock (mezzanine)
Session Chair: Walter Kob, University of Montpellier

8:00 AM

(ICG-SII-040-2019) Understanding the Atomic and Electronic Structures Origin of Defect Luminescence of CdSe Quantum Dots in Glass Matrix

W. Li*[1]; C. Liu[1]; F. Coudert[2]; X. Zhao[1]

1. Wuhan University of Technology, China
2. Chimie Paristech, France

The nature of the interface between CdSe quantum dots(QDs) and glass matrix has been elucidated by a combination of computer simulation and experiments. Molecular dynamics(MD) and ab initio molecular dynamics simulation(AIMD) were used to model the local atomic structure of the interfacial defects. Well-defined density functional theory (DFT) calculations are performed to study the electronic structure of theses interfacial defects and intrinsic defects of CdSe QDs in glass matrix. The calculated electronic structure suggested that the pristine CdSe QDs capped by the structural modifiers or non-bridging oxygen in the amorphous matrix gave rise to the structure reconstruction and paired defect states at the edge of the valence and conduction bands. The results serve as a new paradigm in materials research to explore structural origins of defect emission from QDs and a new strategy to develop glasses containing QDs with high photoluminescence quantum efficiency.

8:20 AM

(ICG-SII-041-2019) Ab initio molecular dynamics study of hydrolysis effects in ion-exchanged alkali aluminosilicate glasses

K. Baral*[1]; A. Li[2]; W. Ching[1]

1. University of Missouri, Kansas City, Department of Physics and Astronomy, USA
2. Corning Incorporated, USA

First-principles calculations have been used to study the structure and properties of hydrated and un-hydrated alkali aluminosilicate glasses for alkali to aluminum ratio R = 1. The Na, (Na+K) and K doped aluminosilicate glasses with composition $(SiO_2)_{0.6}$-$(Al_2O_3)_{0.2}$-$(Na_2O)_{0.2-x}$-$(K_2O)_x$ for x = 0, 0.10 and 0.20 are simulated by density functional theory-based ab initio molecular dynamics (AIMD). The local short- and intermediate-range order in the studied glasses are analyzed in terms of atomic pair, bond length and bond angle and coordination number distributions. The electronic structure, internal bonding, mechanical and optical properties for these glasses are investigated in detail. More importantly, a quantum mechanical parameter, the total bond order density (TBOD) is used to characterize the internal cohesion and strength of the simulated glasses. The dissociated water in aluminosilicate glass ruptures the Si and Al tetrahedral linkage in the network and form hydroxyl groups. The accurate atomistic information of glass-water interaction is critical in understanding the mechanical behavior and long-term chemical durability of the glass product. The hydrolysis mechanism in the three models discussed above is analyzed and its effects on the glass corrosion and durability are discussed and compared with anhydrous models.

8:40 AM

(ICG-SII-042-2019) Structure and optical properties of rare earth ions doped oxyfluoride glasses

H. Inoue*[1]; J. Chung[1]; Y. Nakatsuka[1]

1. The University of Tokyo, Institute of Industrial Science, Japan

Upconversion emission of rare earth ions has been able to be observed even at a low concentration of rare earth ions, when the rare earth ions are added to silicate glasses with fluorides. This indicates that a part of the rare earth ions are coordinated only with fluorine and that the coordination polyhedron is bonded each other. In this study, the structure around rare earth ions in oxy-fluoride glasses, fluorides and silicate, was discussed from its optical properties and structural models. In the structural model of KF-ZnF_2-ErF_3-SiO_2 glasses, the anion coordination number of Si was 4, and 94% was oxygen ion. The anion coordination number of the rare earth ion was 6.1, and 70% was fluorine. The coordination polyhedra centered on rare earth ions by only fluorine not bonded to Si was present. As the concentration of rare earth ions increased in the structural models, the number of the coordinated polyhedra shared with fluorine each other increased. Furthermore, the influences of other components on both aspects of upconversion emission and structural models will be presented.

9:00 AM

(ICG-SII-043-2019) Quantitative prediction of the structure and adsoprtion properties of glassy chalcogenides via First-Principles Molecular Dynamics

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1. IPCMS - CNRS / Université de Strasbourg, France
2. EPFL, Switzerland
3. IEMN / Univ. Lille, France

First-principles molecular dynamics (FPMD) is nowadays fully reliable and mature in terms of structure and electronic properties description for a wide range of different systems. Two case studies will be presented where FPMD is applied to the study of the structure, bonding and thermal properties of a prototypical phase-change material (PCM: $Ge_2Sb_2Te_5$) and the gas adsorption properties of nanoporous glassy chalcogels. First, I will elucidate the network topology of GST and the complex interplay of its local bonding by analyzing its electronic properties by means of maximally localized Wannier functions (MLWF). I will also introduce our recent advances in the exploitation of a FPMD to compute the thermal properties of GST within the approach-to-equilibrium MD method. The second part of this contribution will be devoted to chalcogels. These nanoporous chalcogenides have been demonstrated to be efficient sorbents for environmental remediation from gaseous and water waste media. Producing glassy surface models capable of mimicking realistically the behavior of a chalcogel and its interface is mandatory in order to understand the structure and adsorption properties of such complex materials. Here, I will show how FPMD simulations combined to MLWF formalism can be exploited to gain deep insight into the electronic and dipolar properties of these systems.

Session 5: Development and Evaluation of Empirical Potential for Glass Simulations (TC 27)

Room: Hancock (mezzanine)
Session Chair: Jincheng Du, University of North Texas

9:40 AM

(ICG-SII-044-2019) Molecular Dynamics Simulations and DFT-GIPAW calculations of sodium borosilicate glasses

A. Berselli[1]; M. Fortino[1]; N. Stone-Weiss[3]; L. Deng[2]; A. Goel[3]; J. Du[2]; A. Pedone*[1]

1. University of Modena and Reggio Emilia, Italy
2. University of North Texas, USA
3. Rutgers University, USA

Borates and borosilicates are potential candidates for design and development of glass formulations with important industrial and technological applications. A major challenge that retard the pace of development of borate/borosilicate based glasses using predictive modeling is the lack of reliable computational models to predict the structure–property relationships in these glasses over a wide compositional space. A major hindrance in this pursuit has been the complexity of boron-oxygen bonding due to which it has been difficult to develop adequate B–O interatomic potentials. In this communication, we will report an evaluation the performance of three B–O interatomic potential models recently developed by Bauchy et al., Du et al., and Edèn et al. aiming to reproduce the short–to– medium range structure of sodium borosilicate glasses in the system 25 Na_2O x B_2O_3 (75-x) SiO_2 (x = 0 – 75 mol%).

10:00 AM

(ICG-SII-045-2019) Computer simulation of sodium silicate glasses: The critical role of the interaction potential and simulation protocol

Z. Zhang*[1]; S. Ispas[1]; W. Kob[1]

1. Laboratoire Charles Coulomb (L2C), France

In the present work we examine the reliability of several popular interatomic potentials for molecular dynamics (MD) simulations of silica and sodium silicate systems. The simulated density, structure, and mechanical properties as predicted by the different potentials and simulation protocols are compared to available experimental results. Overall, we find that density and mechanical responses of the simulated glass are significantly more sensitive to the choice of the interaction potential than structural properties. Regarding mechanical tests using MD simulations, we highlight the influence of simulation ensemble and the failing of some potentials in producing a realistic stress-strain behavior of glass under tension. The best performance across the range of properties examined is achieved with the SHIK potential.

10:20 AM

(ICG-SII-046-2019) A Comparative Study of the Effectiveness of Empirical Potentials for Molecular Dynamics Simulations of Borosilicate Glasses

M. I. Tuheen*[1]; L. Deng[1]; J. Du[1]

1. University of North Texas, Department of Materials Science and Engineering, USA

Molecular dynamics (MD) simulation is a vital tool in the field of glass research which can essentially study the structures of glasses and determine the structure-property relationships in the glass materials. However, glasses containing boron oxide (B_2O_3) offer a major challenge to model since the composition and thermal history of theses glasses affect the boron coordination state resulting in a scarcity of well-grounded empirical potential. This work aims to compare several recently developed potentials for MD simulations of sodium borosilicate glasses. A comparison was established in terms of short- and medium range structure features such as total correlation functions, boron N_4 values, bond angle distributions, distribution of Q^n species, and density obtained from the three different potential sets. Comparisons of the calculated mechanical properties and vibrational spectra were also made. These evaluations provide insights on choices of empirical potentials for simulations of borosilicate glasses.

10:40 AM

(ICG-SII-047-2019) Development of a transferable inter-atomic potential for boroaluminosilicate glasses

R. Kumar*[1]; R. Ravinder[1]; N. Krishnan[1]

1. Indian Institute of Technology, India

Boroaluminosilicate glasses are ubiquitously used as a base glass for a variety practical applications ranging from smart phone protective screens to nuclear waste immobilization. Developing a realistic transferable interatomic potential is crucial to study the structure and properties of boroaluminosilicate glasses. The development of such a potential is challenging due to the variable coordination states of boron atom depending on the presence of anions, also known as the boron anomaly. Herein, using a BKS-type pair potential, we develop a transferable potential which can be used to simulate the structure of a wide-range aluminoborosilicate and borosilicate glasses. Glass structures simulated exhibit close match with the experimental structure, both at the short- and medium-range order. The densities of a wide range of glasses exhibit excellent match with experimental values. Further, the coordination states of boron with respect to the anion concentration are well reproduced by the potential. Overall, the inter-atomic potential developed herein will be extremely useful to simulate the structure of a wide range of boroaluminosilicate glasses with applications in nuclear waste immobilization, and bullet-proof glass composites.

11:00 AM

(ICG-SII-048-2019) Machine Learning-Aided Development of Empirical Force-Fields

H. Liu*[1]; Z. Fu[2]; Y. Li[1]; N. Sabri[1]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA
2. University of California, Los Angeles, Computer Science, USA

The development of reliable, yet computationally efficient interatomic forcefields is key to facilitate the modeling of glasses. However, the parametrization of novel forcefields is challenging as the high number of parameters renders traditional optimization methods inefficient or subject to bias. Here, we present a new parametrization method based on machine learning, which combines ab initiomolecular dynamics simulations and Bayesian optimization. By taking the examples of silicate glass and chalcogenide glass, we show that our method yields new interatomic forcefields that offers an unprecedented agreement with ab initiosimulations. This method offers a new route to efficiently parametrize new interatomic forcefields for disordered solids in a non-biased fashion.

Session 5: Simulations of Fracture and Mechanical Behavior of Glasses (TC 27)

Room: Hancock (mezzanine)
Session Chair: Jincheng Du, University of North Texas

1:20 PM

(ICG-SII-049-2019) Mechanisms of Silica Fracture in Aqueous Electrolyte Solutions (Invited)

J. M. Rimsza*[1]; R. Jones[2]; L. Criscenti[1]

1. Sandia National Laboratories, Geochemistry, USA
2. Sandia National Laboratories, Mechanics of Materials, USA

Silica weakening in aqueous conditions is due to interactions between the infiltrating fluid and the fracture tip. Molecular scale simulations provide mechanistic insight into the impact of the fluid on the surface reactions that cause subcritical fracture. Using a suite

of reactive molecular dynamics simulations of silica slit cracks in vacuum, water, and electrolyte (NaCl, NaOH) solutions the impact of the environment on silica fracture are investigated. Any aqueous environment weakens silica and the addition of NaOH forms a basic solution that decreases the fracture toughness, increases surface deprotonation, and lowers dissolution compared with NaCl solutions. Also, the nanoconfined environment of the fracture tip results in unique sodium adsorption complexes and changing fracture mechanisms. The divergent results from the two different electrolyte solutions correspond to experimental phenomena highlighting how anions alter chemical-mechanical fracture in silica. Such information can inform larger scale simulations of silica fracture that can access longer time frames and macroscopic geometries. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

1:50 PM

(ICG-SII-050-2019) Compaction and mixed alkali effect in silicate glass via molecular dynamics

Y. Takato*[1]; S. Urata[1]

1. AGC Inc., Japan

The increasing demand for the macroscopic structural stability of glass substrates during thermal processes requires careful material design to meet quality specifications. Compaction arising from relaxation of the atomic structure of glass is one of the factors that may compromise the stability of glass products. Molecular dynamics is a powerful computational tool and has successfully been applied to examine dynamical properties observed in submicron length scale in detail. However, the typical time scale of the compaction and associated atomic structural relaxation is much longer than that of molecular dynamics simulation. To understand the underlying mechanism of compaction, some accelerated simulation method is necessary for such a long relaxation time. In this talk, we present a methodology for compaction in alkali silicate glass within the molecular dynamics framework, which was inspired by controlled aging/rejuvenation of metallic glass. We also demonstrate the temperature dependent volume compaction and mixed alkali effect observed in our simulations.

2:10 PM

(ICG-SII-051-2019) A mobile device for the evaluation of the current in-situ stress condition in glass

A. Haese*[2]; B. Siebert[2]; M. Glaser[1]; J. Hildebrand[1]; J. Bergmann[1]; B. Schaaf[3]; M. Feldmann[3]

1. Technische Universität Ilmenau, Mechanical Engineering, Germany
2. Ingenieurbüro Siebert, Germany
3. RWTH Aachen University, Germany

Load bearing capacity and resistance against appearing forces becomes increasingly important at the design process of glass constructions. Monitoring the load states during the installation process as well as the utilisation of glass components will be of great value, especially as the stress situation is subjected to significant changes during their life cycle. However, to date, there are no generally accepted standard procedure to evaluate the stress condition of a built-in glass. The intention is to address this gap with the aid of photoelasticity and its synergism with the finite element analysis. The optical procedure of photoelasticity allows to determine a qualitative valuation of the stress behaviour in the glass and especially in the area around connection elements. Considering this feature a functional model for a mobile device will be developed, with which it is possible to measure the qualitative stresses in glass in-situ. Critical stress peaks and transgressions can therefore be pictured. A qualitative statement about the glass stress behaviour can be defined and then be converted into a quantitative statement via a correlation of experimental and numerical simulation results. The screening over a surface area provides an indication of the state of stress for different types of glass under various load scenarios and alterations during the lifecycle can be detected reliably.

2:30 PM

(ICG-SII-052-2019) A continuum constitutive law to describe acoustic attenuation at a molecular scale

H. Luo*[1]; A. Tanguy[1]; A. Gravouil[1]; V. Giordano[3]; W. Schirmacher[2]

1. LGCIE - INSA Lyon, France
2. Universität Mainz, Insitut für Physik, Germany
3. University Lyon1, iLM, France

The interaction between relaxation and elasticity in viscous glass-forming supercooled liquids has been a central issue for the glass researches. Within Maxwell's theory, the relaxation time is defined as $\tau = \eta/G\infty$, where η is shear viscosity and $G\infty$ is the high-frequency shear modulus. Maxwell's theory is appropriate description for the shear modulus, however, the relation between the relaxation and bulk modulus is not always given. In our works, separation between hydrostatic and deviatoric strain-stress has been investigated. A novel continuum constitutive law by combining two most simple viscoelastic model: Maxwell model for the deviatoric part and Kelvin-Voigt model for the hydrostatic part. In this model, two independent relaxation time (τ_a, τ_b) appear which take a bridge form bulk and shear modulus to longitudinal and transverse viscosity. In amorphous material, due to the structural disorder, an apparent amplitude's decay, or progressive scattering, shows when acoustic waves propagates through the samples. This acoustic attenuation is characterized by mean free path. Dynamic analysis of finite element (FE) simulations indicates that, under the Ioffe-Regle limit, acoustic attenuation is in agreement with previous dynamic molecular (DM) simulations for amorphous materials. Our works highlight a continuum constitutive law to describe acoustic attenuation at a molecular scale.

Session 5: Simulations of Crystal Growth and Formability (TC 27)

Room: Hancock (mezzanine)
Session Chair: Walter Kob, University of Montpellier

3:40 PM

(ICG-SII-053-2019) How Structure Controls the Kinetics of Crystal Growth from the Melt (Invited)

G. Sun[1]; P. Harrowell*[1]

1. University of Sydney, Chemistry, Australia

The ability of supercooled liquid to form a glass in lieu of the thermodynamically favored crystal is entirely dependent on the kinetics of crystallization. While slow nucleation kinetics is often the rate determining process, the kinetics of propagation of a crystal interface does also contribute, sometimes crucially as in the case of silica. Of greater fundamental interest, crystal growth provides a substantially more robust and accessible window onto ordering kinetics than that represented by the rare fluctuations associated with nucleation. In this talk we present recent simulation results aimed to understand what controls the rate of crystal growth starting with the fastest of crystal growers - pure metals and some simple molten salts. We show that crystal growth can occur with an activation energy well below that associated with particle diffusion in the liquid. This observation is explained with the introduction of a two new approaches to directly measure the length scale associated with structural transformation of the liquid into the crystal.

4:10 PM

(ICG-SII-054-2019) Factors influencing the glass-formability of bent-core trimers

R. S. Hoy*[1]; A. D. Griffith[1]; E. Salcedo[1]

1. University of South Florida, Physics, USA

We study how the solidification of model bent-core trimers is influenced by their shape and intermonomer interactions. By varying the bond angle θ_0, degree of intermonomer overlap O, and range of attractive interactions r_a, we isolate the factors influencing whether systems will crystallize, glass-form, or jam. Measurements of the jamming density φ_J and thermal solidification temperature T_s indicate a complex interplay of shape and interactions. As expected, trimers composed of tangent (O = 0) monomers crystallize more readily than their overlapping (O > 0) counterparts under thermal cooling. On the other hand, concavity promotes jamming; athermal O = 0 trimers jam at lower packing fractions than their O > 0 counterparts. In O > 0 glass-forming systems, the glass transition temperature $T_g(\theta_0)$ and the inverse jamming density $\varphi_J^{-1}(\theta_0)$ are linearly related for small and large θ_0, but the correlation breaks down at intermediate θ_0, suggesting that the details of intermonomer interactions are the controlling factor in this regime. Frustration of crystallization as θ_0 varies away from optimal values is influenced by factors such as the tendency of systems to form fivefold-symmetric structures in the liquid state. Finally, dimension plays a nontrivial role: for example, straight trimers maximize $\varphi_J(\theta_0)$ in 2D but minimize it in 3D. These results should be useful for molecular-engineering solidification processes.

4:30 PM

(ICG-SII-055-2019) Structural modeling of amorphous silicon via effective inversion of scattering data: A reverse Monte Carlo (RMC) approach

D. K. Limbu*[1]; S. Elliott[2]; P. Biswas[1]

1. The University of Southern Mississippi, Department of Physics and Astronomy, USA
2. University of Cambridge, Department of Chemistry, United Kingdom

We present an efficient reverse Monte Carlo (RMC) simulation of amorphous silicon using experimental pair-correlation data and the geometrical properties of local tetrahedral bonding environment of silicon atoms in the amorphous state. While earlier studies of RMC simulations struggled to produce satisfactory results, the present study shows a significant improvement of the RMC-derived structural models as far as the dangling-bond density, the bond-angle distribution and its width, and the presence of a gap in the density of electronic states are concerned. By using appropriate optimization parameters, we have demonstrated that it is possible to improve significantly the structural quality of existing RMC models of amorphous silicon in the literature without employing any total-energy functional via inversion of experimental diffraction data, assisted by few higher-order correlation functions. A direct comparison of structural, electronic, vibrational and thermodynamic properties of the models with those obtained from the Wooten-Winer-Weaire method and the recent high-quality molecular-dynamics simulations is also presented. The RMC models obtained in this study show a maximum coordination-defect density of up to 4% and a narrow bond-angle distribution, which is characterized by a root-mean-square width of about 11°, as observed in Raman measurements.

4:50 PM

(ICG-SII-056-2019) Glassy structure formation and its nonlocal link to relaxation in glass-forming liquids

H. Tong*[1]; H. Tanaka[1]

1. The University of Tokyo, Department of Fundamental Engineering, Institute of Industrial Science, Japan

Glass transition takes place when a liquid is cooled fast enough to avoid crystallization, during which the viscosity (or structure relaxation time) increases by many orders of magnitude over a narrow temperature window, but without obvious structural change. The possible role of structural ordering in the drastic dynamical slowing down has been intensively discussed over the decades but remains elusive, due to the intrinsic difficulty in the description of the complex liquid structure. Here we tackle this fundamental problem based on a structural order parameter, which captures sterically favored structures with high local packing capability and hence low free energy. We unveil the growth of structural order when approaching the glass transition and establish its direct quantitative relation to relaxation. By comparing the liquid structure with that in the inherent state, we show that the onset of the structural ordering coincides with that of super-Arrhenius dynamics and dynamical heterogeneity. More significantly, we find that such an intimate structure-dynamics correlation is preserved microscopically at a particle level, but in a nonlocal manner. We expect this nonlocal mechanism of structure relaxation, in addition to the glassy structural ordering, to be an essential ingredient for a theoretical description of glass transition as a special type of thermodynamic phase transition.

Session 6: Pharmaceutical and Chemical Durability

Room: Clarendon (mezzanine)
Session Chair: Robert Schaut, Corning

8:00 AM

(ICG-SII-057-2019) Surface related topics in pharmaceutical packaging (Invited)

V. Rupertus*[1]

1. Schott AG, Pharmaceutical Systems, Germany

Drug Container interaction is the most prominent topic for the shelf life of the pharmaceutical products stored in glass containers. Therefore an overview on different corrosion mechanisms as well as influences coming from container manufacturing will be presented. Using a variety of different wet chemical solutions for accelerated corrosive attack onto the inner glass surface (storage time up to 1 year at T=40°C) the collected physical and chemical data will be discussed. Finally a conclusion for the presented effects about the criticality related to pharmaceutical packaging will close this presentation. Glass container of different sizes were filled with various wet chemical solutions (based on e.g. 15% KCl, 10 % Na-Thiosulfate, Phosphate-buffers, Sodium bicarbonate, diluents or just purified water). After definite time /temperature exposure intervals SEM/EDS, optical microscopy as well as Tof-SIMS depth profiles were employed to characterize the near surface region of the respective glass containers. In addition ICP-analysis was used for the quantification of dissolved glass elements also.

8:30 AM

(ICG-SII-058-2019) Mechanisms for surface chemistry alteration in pharmaceutical glasses (Invited)

R. Schaut*[1]

1. Corning Incorporated, S&T, Glass Research, USA

The suitability of a pharmaceutical container to store an aqueous solution is defined by the interactions of the solution with the glass surface. The chemistry of the solution-contacting surface is commonly assumed to be equivalent to the bulk glass from which it was formed, but for some pharmaceutical glasses this is incorrect. Here we will discuss several mechanisms contributing to the altered surface chemistry, illustrate these changes using DSIMS, XPS and NEXAFS, and review their impact upon glass corrosion rates and pharmaceutically-relevant defects. The role of forming method will be highlighted (molded versus tubular) and compared with novel glass compositions that mitigate these mechanisms and prevent delamination-causing heterogeneities.

9:00 AM

(ICG-SII-059-2019) Chemical durability of type I glass vials for parenteral preparations

P. J. Bócoli*[1]; P. R. Mei[2]; S. B. Jaime[1]; G. d. Quijada[1]; P. Kiyataka[1]

1. Institute of Food Technology, Packaging Technology Center, Brazil
2. State University of Campinas, Faculty of Mechanical Engineering, Brazil

Development of new pharmaceutical products with complex formulations and high pH (above 8) requires good packaging performance. In general, Type I glass vials have a historical success related to safety and efficiency to protect pharmaceutical properties and keep the drug efficacy. However, glass delamination, a process involving the interaction and chemical attack of the inner glass surface by the product solution to form thin glass flakes has increased the numbers of recalls in the last years. This study aimed to evaluate the chemical durability of Type I glass vials using the test protocol analysis suggested by USP 41, chapter 1660, using three aggressive screening conditions to accelerate delamination for six 10 mL glass vials types, flint or amber, made by different companies by hot forming of tubular glass, coated or uncoated internally, available for market. The analytical techniques used were visual inspecion, conductivity/pH, ICP-OES and Scanning Electron Microscopy (SEM/EDX). The vials were investigated in an unwahsed and non-depyrogenation state. The results showed that samples were good enough to be used as packaging for injectable products, without presence of glass flakes or internal surface changes. One sample showed inhomogeneity mainly in the heel internal surface after contact with solutions, confirmed by SEM images, but the presence of glass particles could not be observed.

9:20 AM

(ICG-SII-060-2019) Influence of glass composition on the kinetics of glass etching and frosting in concentrated HF solutions

N. Piret*[1]; R. Santoro[1]; L. Dogot[2]; B. Barthelemy[2]; E. Peyroux[2]; J. Proost[1]

1. UCLouvain, Institute of Mechanics, Materials and Civil Engineering, Belgium
2. AGG Glass Europe, AGC Technovation Centre, Belgium

During etching of a multicomponent glass in concentrated hydrofluoric acid (HF) solutions, a crust can gradually appear on the glass surface, resulting from the precipitation of anions released by the glass dissolution, with cations coming from the etching solution or from the glass. To understand the impact of this crust on the overall kinetics of both etching and frosting process, we have studied the dissolution of four types of commercial glass substrates in etching solutions containing various concentrations of HF, by two independent methods: the chemical analysis by ICP-OES of the amount of Si dissolved from the glass as a function of time, and the measurement of the glass weight loss with time. These two methods showed that the glass etching rate decreases with time as a result of crust formation which gradually becomes more protective. Then, increasing the amount of HF in the etching solution increased the etching rate in a non-linear way, and the etching rate increased with the alumina content of the glass. A chemical analysis of the amount of Si present in the crust also revealed that the amount of HF in the etching solution has an impact on the amount of crust deposited on the glass surface. Finally, all these kinetic data were rationalized based on a semi-empirical quantitative model, allowing to extract characteristic dissolution and precipitation constants.

Session 6: Surface Structure and Reactivity

Room: Clarendon (mezzanine)
Session Chair: Stephen Garofalini, Rutgers University

10:00 AM

(ICG-SII-061-2019) Role of the hydrogen bond in water and at the water/glass interface on proton transport

J. Lentz[1]; S. H. Garofalini*[1]

1. Rutgers Univ, USA

Reorientation of the hydrogen bond between water molecules and water/glass interface plays an important role in proton transport. Reorientation affects H-bond chains that can affect the formation, lifetime, and transport of hydronium and hydroxide ions in water. Autoionization of water molecules, forming H_3O^+ and OH^- ions, occurs regularly in water, but the resulting ions are generally fleeting and stabilization of these ions depends upon their migration and separation that is determined by the H-bond reorientation lifetimes and resulting H-bond chains. Simulations of water using an accurate reactive potential that describes this behavior that is consistent with ab-initio calculations in water is used to show the role of the water/glass interface on modifying such behavior. The resulting reactions are also relevant in relation to high proton transport in wet mesoporous silica observed experimentally.

10:20 AM

(ICG-SII-062-2019) IR peak position interpretation in correlation with bond parameters of sodium aluminosilicate glass by MD simulation

H. Liu*[1]; S. Hahn[1]; M. Ren[2]; T. M. Gross[3]; A. C. van Duin[1]; J. Du[2]; S. H. Kim[1]

1. Pennsylvania State University, USA
2. University of North Texas, USA
3. Corning Incorporated, USA

Reflectance infrared (IR) spectra has been measured for a series of sodium aluminosilicate glass. It has been shown that as sodium concentration increases, the dominant peak of asymmetric $\nu_{Si-O-Si}$ shifts to lower wavenumber. The interpretation for shift of peak position has been carried out with assistance of molecular dynamic (MD) simulation. Various MD force fields, like reactive force field (ReaxFF) potential and Teter potential, have been employed in this study. The shift of maximum intensity peak is attributed to changes in distribution of bond parameters, such as bond length and bond angle. Specifically, it has been demonstrated that in MD simulation performed by ReaxFF, the averaged bond length of Si-O and Al-O increase with sodium concentration increasing. The averaged bond angle of Si-O-Si decreases as sodium concentration goes up, while no significant change is observed for bond angle Al-O-Si. The results are compared with simulation performed by Teter's potential. There are some discrepancy between two simulation potentials.

10:40 AM

(ICG-SII-063-2019) Structure and Reactivity of Calcium Alumino-Silicate Glass Surfaces

A. Cormack*[1]; L. Wang[1]; G. Agnello[2]; N. J. Smith[2]; R. Manley[2]

1. Alfred University, USA
2. Corning Incorporated, USA

Calcium alumino-silicate (CAS) glasses form the base composition for the current generation of display glasses, and hence represent an appropriate model system for alkali-free multicomponent glasses. The technological demands of these materials require an understanding of the surface behavior of these glasses. In this presentation, we discuss the application of classical molecular dynamics simulations, using a reactive forcefield, to the development of surface structures of a series of CAS glass, with compositions in the high silica-tectosilicate composition space, with calcia/alumina molar ratios of unity. We will also discuss the dynamic reactivity of water with the surface structure of the 60:20:20 silica:alumina:calcia (by mole) composition. Water molecules interacting with the glass surface create structural moieties, such

as Si-OH or Al-OH, whose stability has been investigated as a function of time. The results suggest that local structural chemistry plays a key role in both the formation and stability of hydroxylated species.

11:00 AM

(ICG-SII-064-2019) Surface structure and corrosion effect in aluminosilicate glass from ab initio molecular dynamics simulation

K. Baral*[1]; W. Ching[1]

1. University of Missouri, Kansas City, Department of Physics and Astronomy, USA

Surface plays an important role to control the physical and chemical properties of glass and its interaction with the environment. Ab initio molecular dynamics (AIMD) simulation is performed to simulate the bulk and surface structural models of aluminosilicate glass $(SiO_2)_{0.6}$-$(Al_2O_3)_{0.4}$. The structural features and defects on the surface are analyzed comparing with the bulk model. The local structural descriptors like coordination number, bond length and bond angle distributions and pair correlation function are systematically studied and compared to the experimental results. The surface is solvated with appropriate number of water molecules. The electronic structure and bonding, mechanical and optical properties in these glasses are evaluated using density functional theory (DFT) method. Accurate information on water-silica interaction is essential to understand the glass properties like mechanical strength and long-term chemical durability of silicate glass. The corrosive effects on the hydrated glass surface by salts like sodium and potassium chloride are discussed.

11:20 AM

(ICG-SII-065-2019) Float Glass Surface: Composition and oxidation state gradient evaluation at the tin side

H. Montigaud*[1]; E. Gouillart[1]; E. Burov[1]; N. Trcera[2]; P. Lagarde[2]; P. Chapon[3]

1. Glass Surface and Interfaces, Joint Unit CNRS/Saint-Gobain, France
2. SOLEIL synchrotron, France
3. Horiba Scientific, France

Commercial float glass exhibits a Sn-rich side as a consequence of the contact with the tin bath during the production process. However the gradients of the composition and the oxidation state also concern other elements such as iron and sulphur. The composition from the topmost glass surface to the bulk can be evaluated by techniques like SIMS, XPS, RBS but the oxidation state of the elements of interest (Sn, Fe, S) is harder to be estimated with similar depth resolution. X ray Absorption Spectroscopy (XAS) is one of the techniques especially used to evaluate the oxidation state with some insights concerning the local coordination environment. Two acquisition modes can be used : the collection of the fluorescence signal (FY for Fluorescence Yield) which integrates up to 5µm and the measurement of the sample drain current (TEY for Total Electron Yield) for which the probed depth is around 100nm. The present work proposes an original combination of XAS with GD-OES technique in order to improve the depth resolution of oxidation state evaluation obtained by the first one. XAS acquisitions in TEY mode were performed at the bottom of craters realized by GD-OES at different depths of the glass surface. The compatibility between the two techniques has been evaluated. First results concerning Fe and Sn on float glass as produced and after thermal post-treatment in air are presented.

11:40 AM

(ICG-SII-066-2019) Synchrotron X-ray Scattering and Absorption Studies of Surface Structure and Surface Chemistry of Glassy Systems

Q. Ma*[1]; D. T. Keane[1]

1. Northwestern University, Synchrotron Research Center, USA

In this presentation, we showcase some of our activities in the use of synchrotron x-ray scattering and absorption techniques to study the surface structures of glassy systems through a number of examples from commercial glasses to amorphous transparent conducting/semiconducting thin films. These modern techniques reveal unprecedented structural details of the surfaces of these disordered systems. These surface structures are integral, yet distinct, parts of the systems' structures, and allow understanding of surface physics and chemistry, from elemental distribution including various valence states of an element, surface instability and its effect on structural relaxation of disordered systems, to likely structural-entropy surface stabilization and its relation to the crystallization of amorphous thin films.

Session 6: Surface Films and Coatings

Room: Clarendon (mezzanine)

Session Chairs: Temel Buyuklimanli, EAG Laboratories; Paula Clark, Tascon USA

1:20 PM

(ICG-SII-067-2019) Analyses of Modified Glass Surfaces and Thin Coatings on Glass (Invited)

T. Buyuklimanli*[1]

1. EAG Laboratories, USA

Secondary Ion Mass Spectrometry (SIMS) is a unique technique often used to investigate the elemental profile of solid materials with depth. SIMS has the sensitivity to detect parts per billion concentrations as well as to quantify atomic percent level matrix compositions. Layers of several nanometers to micrometers thickness can be characterized using proper SIMS analytical protocols. This ability to profile >6 orders of magnitude concentration and thickness (or depth) ranges has made SIMS the routine technique for in-depth chemical characterization for a variety of materials, including inter-diffusion and impurity analyses of 1-2nm layers in low-e glass coatings. Examples of low-e film stack changes with variety of processes will be shown. Beam induced migration of the alkalis, especially Na and Li, in oxide thin films and bulk glass have made it difficult to acquire accurate concentration depth profiles by any surface analytical technique. However, carefully set up SIMS analyses can provide accurate glass composition analyses of modified glass surfaces, even for layers as thin as 10nm. This ability has been successfully applied to analyses of pharmaceutical glass containers for delamination studies, and it can be used as a fast durability check. Examples of glass vial surface composition changes with variety of leaching solutions will be shown.

1:50 PM

(ICG-SII-068-2019) Characterization of Glass Surfaces and Coatings Using Time-of-flight Secondary Ion Mass Spectrometry (Invited)

P. A. Clark*[1]

1. Tascon USA, USA

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has emerged as an important tool for characterizing a wide variety of materials. This paper highlights the application of ToF-SIMS for characterizing glass surfaces, optical coatings, and organic light emitting diode devices. The first part of this presentation will review the fundamental aspects of the SIMS; including, the collision cascade, the characteristics of sputter particles, and typical operational modes. The second part of the presentation will discuss applications of ToF-SIMS to study glass corrosion, to monitor the efficiency of cleaning processes, and to identify the composition and thickness of multilayer structures on glass. Aspects of dual beam depth profiling, 2D and 3D reconstruction, depth resolution, and the localization of species at buried interfaces will also be discussed. For example, ToF-SIMS was used to evaluate the composition of an optical mirror consisting of alternating layers of SiO and HfO/ZrO. This case illustrates that ToF-SIMS is well suited for survey analysis because all elements can be detected in parallel with good sensitivity. Acquisition of and reconstruction from raw data files reveals higher intensities of Mg and Al contamination at the buried interface between the substrate and the multilayer coating.

2:20 PM

(ICG-SII-069-2019) ToF-SIMS depth-profiling of altered glass: Contributions and limits

S. Gin*[1]; M. Collin[1]; P. Jollivet[1]

1. CEA, DE2D, France

Glass and mineral corrosion usually leads to the formation of morphologically and compositionally complex surface layers that can be characterized by various analytical techniques to infer rate control mechanisms. In this study, we investigate the capabilities and limitations of time-of-flight secondary ion mass spectrometry (ToF-SIMS) to better understand chemical processes of glass corrosion. In particular, we focus on the potential impact of the ToF-SIMS ion beam on the distribution of several elements of interest in alteration layers formed on the ISG (International Simple Glass), a six-oxide reference glass altered in a solution enriched in alkalis and spiked with $H_2{}^{18}O$. A thin flake of glass partially altered on both sides is analyzed entirely from one side to the other to determine whether atoms weakly bonded to the solid are displaced by the beams. We highlight the beam effect on cations weakly bonded to the silicate network (Li, Na, K, and B, Ca, Cs to a lesser extent) affecting the profile shape of these elements. No impact is observed on 18O and H, but it is demonstrated that quantification of isotopic ratios is possible only for a limited range of isotopic enrichment.

2:40 PM

(ICG-SII-070-2019) Investigations on the influence of different ZnO thin film deposition parameters on the optical and mechanical properties of glass

G. Oumessad*[1]

1. LMCPA, UPHF, France

Not only one main drawback of glass, limiting its use for some applications, is its brittle fracture behavior, directly depending of surface flaws, but furthermore, in areas like the South of Algeria (Sahara), sand wind is responsible for huge surface degradation of car and window glass. The impacts induced by the sand particles on the surface significantly reduce the breaking strength and in addition the light transmission is reduced by induced light diffusion. In this work we try to counterbalance the sand wind effect by strengthening the glass by the reinforcement of its surface by thermo-chemical method: thin layer deposition by spray pyrolysis. Optimization of parameters such as deposition time and substrate temperature is important for obtaining ZnO layers with optimal properties. Here we present a study about the induced effects of precursor type and concentration on optical and mechanical properties of ZnO thin films. We performed X-ray diffraction measurements and used it as a tool to get an insight on structural characteristics and homogeneity of ZnO layers. Then different techniques were used to evaluate the influence of the spray-pyrolysis parameters on the surface characteristics of the reinforced glasses such as Vickers indentation, solid particle erosion test, 4-point bending test, and spectroscopy.

3:00 PM

(ICG-SII-071-2019) Electrochromic thin Film Materials and Devices

L. Jin*[1]

1. State Key Laboratory of Advanced Technology for Float Glass, China

The energy saving of glass doors and windows is an important problem in building energy saving. Due to the environmental problems caused by greenhouse effect and energy crisis, electrochromic smart windows become more and more important. In this paper, the electrochromic thin film materials and their devices are introduced, including the concept, category, working principle, preparation method, the application of electrochromic smart window, the development status and the existing problems at home and abroad, etc. The research and development of electrochromic thin film materials and devices are also prospected.

Session 6: Mechanical and Stress

Room: Clarendon (mezzanine)
Session Chair: Seong Kim, Pennsylvania State University

3:40 PM

(ICG-SII-072-2019) Lateral deformation and scratch-induced microabrasion of silicate glasses scraped by a conical diamond indenter (Invited)

S. Sawamura*[1]; R. Limbach[2]; S. Wilhelmy[2]; L. Wondraczek[2]

1. AGC, Inc., Japan
2. Friedrich-Schiller-University Jena, Otto-Schott Institute of Materials Research, Germany

We report on the change of deformation modes during scratching a glass surface, and its change dependency on the mechanical properties of the studied glass. The modal transition from fully elastic to elastic-plastic (EP), and further from EP to ductile fracture was observed in a series of soda lime silicate glasses. The mode-shift manifests in the lateral force, which, during in situ observation, increases abruptly as a result of adhesive force inflection. In addition, the capability of strain energy storage affects the transition of EP to ductile fracture. The scratch resistance before and after transition exhibits a distinct trend: it is higher in the regime of ductile fracture because of the contributions of adhesive forces. Moreover, in the ductile regime the scratch hardness is governed by bond energy, what points to parameters of optimization.

4:10 PM

(ICG-SII-073-2019) Modeling Birefringence from Surface Stress Relaxation in Silica Optical Fibers

B. D. Hausmann*[1]; P. Miller[1]; E. Aaldenberg[1]; T. Blanchet[2]; M. Tomozawa[1]

1. Rensselaer Polytechnic Institute, Materials Science & Engineering, USA
2. Rensselaer Polytechnic Institute, Mechanical Engineering, USA

Silica glass fibers are known to exhibit stress-induced birefringence; however, conventional thermal tempering mechanisms are unlikely able to account for the difference found between surface and bulk birefringence in relatively thin fibers. Previous explanations involving non-Newtonian viscous flow and frozen-in strain do not explain the observed surface effect. Relative retardation in silica glass fibers was measured using polarized light microscopy to characterize the residual axial stress and establish the origin of birefringence. It is proposed that fast surface stress relaxation coupled with slower bulk relaxation during fiber drawing can result in surface compressive stress. Radial retardation distributions of four different fibers were found to exhibit a surface compressive stress in agreement with the proposed model, with variations suspected to be caused by differences in manufacturing parameters such as draw temperature, stress, speed, and dopant composition.

Session 8: Optical Properties of Glass I

Room: Statler (mezzanine)
Session Chair: Jianrong Qiu, South China University of Technology

8:00 AM

(ICG-SII-074-2019) Long persistent luminescence and blue photochromism in Eu^{2+}-Dy^{3+} codoped barium silicate glass ceramic phosphor (Invited)

S. Tanabe*[1]

1. Kyoto University, Japan

Eu^{2+}-Dy^{3+} co-doped barium silicate glass was prepared by a melt quenching method and cerammed at various temperatures between 800 and 1250 °C to obtain glass ceramic (GC) phosphors. The crystal phase of $Ba_5Si_8O_{21}$ was primarily precipitated in the GC samples. The GC sample cerammed at 1250 °C (GC1250) exhibited the longest persistent luminescence over 16 h until the luminance becomes 2 mcd/m^2. The color of GC1250 sample was changed from white to blue after UV light illumination, and then bleached efficiently by red light (660 nm) illumination or heat treatment at 200 °C. From

thermoluminescence (TL) glow curve measurements, four different TL glow peaks were observed at 191 K, 278 K, 446 K, and 494 K. On the other hand, after red-illumination following UV-illumination, the TL intensity of the only 446 K-peak was selectively decreased in the TL glow curve. It was shown that the blue photochromism of GC1250 sample is due to an electron trapping defect strongly related with this glow peak.

8:30 AM

(ICG-SII-075-2019) Glass development for high power optical fiber lasers

J. Ballato*[1]; M. Cavillon[1]; P. Dragic[2]; C. Kucera[1]; T. Hawkins[1]; B. Kokuoz[1]

1. Clemson University, USA
2. University of Illinois at Urbana-Champaign, USA

Optical fiber-based lasers are widely used in defense and manufacturing systems. As output powers have increased, a cornucopia of parasitic optical nonlinearities has come into play that limit continued power scaling. These nonlinearities include stimulated Brillouin scattering (SBS), stimulated Raman scattering (SRS), nonlinear refractive index driven wave mixing, and stimulated thermal Rayleigh scattering (STRS)-mediated transverse mode instabilities (TMI) induced both thermo-optically and through the quantum defect. Whereas the majority of the optical fiber community has attacked this problem using every-more complex fiber waveguide designs, this presentation will discuss how glass composition, structure, and properties can provide a simpler and more practical route to mitigating present and future limitations. More specifically, glass compositions and their structure, based on molecular dynamic modeling, will be discussed that greatly reduce, and possibly wholly negate, these parasitic nonlinearities.

8:50 AM

(ICG-SII-076-2019) EPR and XAS study of the RE ions local environment in oxfluoride glass-ceramics

G. Gorni[1]; A. Serrano[2]; G. R. Castro[2]; D. Bravo[3]; R. Balda[4]; J. Fernandez[5]; M. Pascual*[1]; A. Durán[1]

1. Institute of Ceramics and Glass, CSIC, Spain
2. SpLine CRG BM25 beamline at the ESRF - The European Synchrotron, France
3. Universidad Autonoma de Madrid, Dpto. Física de Materiales, Spain
4. Escuela Superior de Ingeniería, UPV-EHU, Dpto. Física Aplicada I, Spain
5. Donostia International Physics Center DIPC, Spain

Oxyfluoride glass-ceramics (GCs) have been extensively studied since the 1990s. The crystallisation of fluoride nanocrystals (NCs) in chemically and mechanically stable aluminosilicate glasses showed interesting optical properties even for small crystal fractions (10-15 wt%). When Rare-Earth (RE) ions are used as dopants, crystal-like features can be reproduced and an increase in the emission and/or energy transfer (ET) processes, with respect to the starting glasses, is observed. A crucial point for these materials is the study of the local surrounding of RE ions and their incorporation in the NCs. In fact, the effective concentration in the NCs can be much higher than the nominal concentration, up to one order of magnitude or even higher. The knowledge of RE ions incorporation in the NCs permits choosing proper doping levels to optimize both linear and nonlinear optical properties. In this work the study of the RE ions local surrounding was performed by Electron Paramagnetic Resonance (EPR) and X-Ray Absorption spectroscopy (XAS). Interesting results showed that most of RE ions are already in a fluorine-rich amorphous environment even in the initial glass. The crystallisation process provokes the RE ions redistribution and incorporation in the fluoride NCs. Moreover, different RE precursors, used as oxides or fluorides, can influence the final optical properties.

9:10 AM

(ICG-SII-077-2019) Chemically purified Dy^{3+}-doped chalcogenide glass fiber and Co^{2+}/Fe^{2+} : ZnSe nanocrystal-glass composite towards mid-infrared laser beyond 4μm

H. Guo*[1]

1. Xi'an Institute of Optics and precision Mechanics, Chinese Academy of Science (CAS), China

A serial Dy^{3+} ions doped $Ga_{0.8}As_{39.2}S_{60}$ chalcogenide glasses were synthesized, and their MIR spectroscopic properties at 2.9 and 4.3μm were investigated. It indicates that this glass shows relatively large laser quality factor $\sigma_{emi}\times\tau_{mea}$ and excellent thermal stability. On this basis, through using the chemically purified methods with chlorine gascombined with the dynamic distillation process, high-purified $Ga_{0.8}As_{39.2}S_{60}$ glasses with low O-H and S-H absorptions were successfully fabricated, which was confirmed by the optimized mid-infrared linear transmittance and improved fluorescent lifetimes of Dy^{3+}: $^6H_{13/2}$, $^6H_{11/2}$ levels. Then the single-mode double-cladding 0.3% Dy^{3+} ions doped $Ga_{0.8}As_{39.2}S_{60}$ glass fiber was firstly fabricated and its MIR spectroscopy under 1.7μm pumping was also investigated. On the other hand, Co^{2+}/Fe^{2+}: ZnSe nanocrystals emitting mid-infrared photoluminescence centered at around 3.0 and 4.3 μm were firstly synthesized via a simple hydrothermal process, and a composite containing the Co^{2+}/Fe^{2+}: ZnSe nanocrystals and $Ga_{0.8}As_{39.2}S_{60}$ chalcogenide glass was fabricated by hot-pressing process. These two different gain materials based on chalcogenide glass should be ideal efficient and low-threshold medium towards mid-infrared fiber laser beyond 4μm.

Session 8: Optical Properties of Glass II

Room: Statler (mezzanine)

Session Chair: Mingying Peng, South China University of Technology

10:00 AM

(ICG-SII-078-2019) Transparent glass ceramics for photonic devices (Invited)

J. Qiu*[1]

1. State Key Laboratory of Modern Optical Instrumentation, Zhejiang University, China

In this talk, we will introduce our research progress on transparent glass-ceramics for photonic devices. We discuss about the mechanisms for enhanced upconversion luminescence observed in rare-earth doped glass ceramics. We conclude that local symmetry of the ligand field around rare earth ions is rather important than widely accepted phonon enegy change after crystallization. We will also introduce some observation of luminescence phenomena in rare earth doped glass ceramics excited by multi-wavelength lasers or broadband light source. The mechanisms and promising applications will be proposed. A new approach for fabrication of various functional glass ceramic fibers with low optical attenuation will be highlighted.

10:30 AM

(ICG-SII-079-2019) Inside the black box: Thermal-induced compositional ion migration in lanthanide-based lasing materials

S. Ye*[1]

1. South China University of Technology, China

The common thermal effect inevitably generated by optical pumping in the high power lanthanide-based lasing devices, would cause short-range random compositional ion migration in the functional materials. The extreme case is a fracture of the materials. This research utilizes the accompanied upconversion (UC) of Er^{3+} with additional reference to its optical temperature feature in the Er^{3+}-lasing device to achieve some alarming effects for ion migration. In-situ recorded lasing behaviours and the accompanied UC spectra

show strong correspondence when there is ion migration revealed by the latter, theoretically bridging via a larger thermal conductivity. This study not only provides a technique to monitor the working condition of the lasing materials with large thermal effect in the black box, but also throws some light on the microstructure variation of the lanthanide-based functional materials in the optoelectric devices upon heat accumulation.

10:50 AM

(ICG-SII-080-2019) "Molten-core" fabrication of bismuthate glass fiber containning metal nanocrystals

Z. Ma*[1]

1. South China University of Technology, China

Optical devices realized on the basis of nonlinear optical fibers, such as optical switchers etc., possess the concomitant advantages of high optical conversion efficiency and fast response. Meanwhile, they have tight structure, and easy to integrate with conventional optical communication networks, thus play a key role in constructing the all-optical communication networks. The bismuthate glass is acknowledged as one of the most promising candidates for fabricating high-performance nonlinear optical fibers, due to its very high nonlinear coefficient, excellent chemical and thermal stability, high mechanical strength and fiber drawing processibility. The doping of metal nanocrystals can dramatically enhance the optical nonlinearity of bismuthate glass fiber, thus shortening the length of fiber in practical applications, and effectively inhibit the signal deformation induced by group velocity dispersion. However, it is challenging to control the crystalization of metal nanoparticles during fiber drawing by the conventional technique. The present work investigated the fabrication of bismuthate glass optical fibers doped with crystallization-controllable metal nanocrystals by a "Molten-core" fabrication method, and the structure, morphology, and optical property of the glass fibers were studied.

11:10 AM

(ICG-SII-081-2019) Development of LaF_3-$LaO_{3/2}$-$NbO_{5/2}$ novel oxyfluoride glasses with high refractive index and low dispersion by a containerless processing

J. Chung*[1]; H. Inoue[1]; Y. Nakatsuka[1]

1. University of Tokyo, Institute of Industrial Science, Japan

Heretofore research about the optical properties of oxyfluoride glasses were mainly for the crown type glasses which have low dispersion and low refractive index. Unlike previous studies, if it is possible to make full use of low dispersion effect of fluorine in glasses which has high refractive index, various new optical glasses which have low wavelength dispersion together with high refractive indices can be obtained. In this study, new lanthanum-niobium oxyfluoride glasses were prepared by containerless processing. The obtained glasses were all colorless and transparent in visible to IR region. The Abbe numbers increased with the content of fluorine while keeping high refractive indices resulting in outstanding compatibility between high refractive index and low dispersion. The effects of the substitution of fluorine for oxygen on the refractive index and wavelength dispersion were discussed on the basis of the Lorenzt-Lorenz equation and Drude-Voigt relation. Electronic polarizability and the resonance wavelength of oscillators were preponderantly analyzed in order to find the effect of fluorine substitutions. This study proposed the materials which should be the great candidates for the use in various optical applications.

Session 8: Optical Properties of Glass III

Room: Statler (mezzanine)
Session Chair: Setsuhisa Tanabe, Kyoto University

1:20 PM

(ICG-SII-082-2019) The effect of melting atmosphere on near infrared photoluminescence in bismuth-doped BaO-Ga_2O_3-GeO_2 glasses

S. Dubuis*[1]; S. Messaddeq[1]; Y. Ledemi[1]; Y. Messaddeq[1]

1. Université Laval, Canada

Bi-doped BGG glasses of composition 40 GeO_2 – 20 Ga_2O_3 – 40 BaO – x Bi_2O_3, with x = 0, 1, 2, 4, 6, and 8 mol% were prepared using melting and quenching method. The influence of the Bi_2O_3 on the thermal, structural, and optical properties were studied. Thermal properties were measured using differential thermal analysis (DSC). The results indicate that the glass transition temperature, T_g, decreases from 699 to 619 °C whereas the thermal stability against devitrification decreases too, with the increase of the Bi2O3 content. The linear refractive index, optical energy bandgap and density was also investigated. The structural evolution of the BGG glass matrix by the incorporation of Bi_2O_3 was studied using Raman spectroscopy. It is shown that bismuth insertion occurs into the germanium tetrahedra by sharing some of its oxygen bonds with pyramidal bismuth units. Moreover, starting at 4 mol % of Bi2O3 pyramidal [BiO3] units gradually reaches saturation and the network becomes less connected, inducing precipitation of bismuth metallic in the glass matrix confirmed by TEM microscopy analysis. Photoluminescence (PL) properties of bismuth doped BGG glasses prepared at different atmospheres were studied. The broad near infrared emission observed may be correlated to the existence of different oxidation states confirmed by XPS measurements.

1:40 PM

(ICG-SII-083-2019) Kinetic behavior of transient photoinduced optical effects in spin-coated and thermally deposited chalcogenide glass thin films

A. Kovalskiy[1]; J. Allen[1]; M. White[1]; J. R. Oelgoetz*[1]; R. Golovchak[1]; O. Shpotyuk[2]; K. Palka[3]; M. Vlcek[3]

1. Austin Peay State University, Department of Physics and Astronomy, USA
2. Institute of Physical Optics, Ukraine
3. University of Pardubice, Center of Materials and Nanotechnologies, Czechia

Thermally deposited chalcogenide glass thin films (ChGTF) are known to be highly photosensitive to the band gap and superbandgap irradiation revealing both metastable and transient photoinduced changes of optical transmittance at the fundamental absorption edge region. Spin-coated thin films of chalcogenide glasses, which are usually obtained through chemical dissolution of bulk glasses in different amine-based solvents with subsequent spin-coating of the liquid onto silica substrate and appropriate one-stage or multi-stage thermal treatment, are relatively stable to the influence of near bandgap irradiation in comparison with their thermally evaporated counterparts. However, it was found that they reveal quite significant transient photoinduced optical effects when irradiated with relatively powerful (~90 mW/cm^2) superbandgap light. The kinetics of transient photodarkening and following relaxation for Ge- and As- based thermally deposited and spin-coated binary thin films is studied and fitted with stretched exponential function. Values of kinetic parameters β and τ are analyzed for different irradiation conditions. Obtained results are discussed in relation to the existing approaches to modeling and mechanisms of kinetic phenomena and structural relaxation in glasses.

2:00 PM

(ICG-SII-084-2019) Ultra-broad photoemission (0.8-1.9 μm) from Bi-doped multi-component glasses via chemical reduction

J. Cao*[1]; M. Peng[1]

1. South China University of Technology, School of Materials Science and Engineering, China

Wideband NIR-emitting materials are of current interest due to their practical utilization in light sources and tunable fiber lasers for optical sensing, imaging and amplification. Though massive research has been devoted to exploring materials activated by rare-earth ions, transition-metals and semiconductor nano-crystals, the pursuit of photonic materials with ultra-wideband emission over an extremely wide wavelength range is still not satisfied, especially for transparent amorphous solids which are suitable for active-fiber applications. Here, we realized such NIR emission in Bismuth doped glasses, which extends its NIR emission to abnormal 0.8-1.9 μm with an incomparable bandwidth of >600 nm, which fully covers the whole NIR region under a single wavelength excitation, i.e., from the transparency windows of biological tissue over the technically-essential low-loss optical communication. This should help improve the optical performance of Bi-doped glasses and contribute to exploring new photonic materials.

2:20 PM

(ICG-SII-085-2019) Pr^{3+} and Tm^{3+} Doped Oxyfluoride Silicate Glasses for Light Emitting Diodes Applications

C. Zhu*[1]; Z. He[1]; L. Niu[1]; Y. Zhou[1]; X. Meng[1]

1. Qilu University of Technology (Shandong Academy of Sciences), China

With the rapid growth of the next-generation lighting devices based on white light emitting diodes (W-LEDs), development of novel luminescent materials is in high demand to meet various purposes. In comparison to phosphors and organic resins, luminescent glasses are of particular interest for W-LED applications owing to their unique merits in ease of fabrication, better thermal stability, and open topological structure to accomodate various light activators. Herein, we present our recent findings about Pr^{3+} and Tm^{3+} doped oxyfluoride silicate glasses that can be used for W-LEDs. These glasses were prepared using the melt-quenching method. The luminescence of Pr^{3+} mainly shows two intensified emission peaks in blue and reddish orange regions corresponding to the transitions $^3P_0 \rightarrow {}^3H_4$ and $^3P_0 \rightarrow {}^3H_6$ ($^1D_2 \rightarrow {}^3H_4$) of Pr^{3+} ions. The relative emission intensity of these two emissions can be tailored by varying the chemical composition of the glass matrix. For certain base glass compositions, the formation of CaF_2 crystals occurred during the melt quenching process, which can modify the luminescence properties of the glasses. In addition, we find that the Tm^{3+} ions play a significant role in modifying the luminescence of Pr^{3+}. Our study shows that the as-developed Pr^{3+} and Tm^{3+}doped oxyfluoride silicate glasses may provide a new platform to design and fabricate novel luminescent materials for W-LEDs.

2:40 PM

(ICG-SII-086-2019) Color manipulation in transparent nanocrystals-in-glass composite via low-temperature combustion processing

Q. Pan*[1]; X. Huang[1]; G. Dong[1]; J. Qiu[2]

1. South China University of Technology, China
2. Zhejiang University, China

Developing transparent luminescent glass with tunable emission colors have been at the forefront of lighting and display technologies. We recently designed and demonstrated a transparent color tunable nanocrystals-in-glass composites (NGC) with highly bright characteristics. Color manipulation is demonstrated by controlling the concentration of three independent nanocrystals with stable red (R), green (G) and blue (B) emission under a single ultraviolet-light excitation. The combination of the three primary RGB colors are employed to produce flexible full-color emission, and white light source can be achieved by mixing two or three different types of luminescent nanocrystals in NGC materials with appropriate ratios. To improve the transparency, we report a low-temperature solution-based combustion method to ensure the homogeneous distribution of the embedding nanocrystals with great integrity. The flexible color manipulation and the facile preparation would thus open a door for exploiting glass materials for light-emitting devices and full-color display sources.

3:00 PM

(ICG-SII-087-2019) Tellurite and germanate glasses for mid-infrared fiber lasers

Y. Ye*[1]; W. Wang[1]; Q. Zhang[1]

1. South China University of Technology, Material Science, China

Mid-infrared fiber lasers lies in the "fingerprint region" of small molecules in the atmosphere, which provides broad application prospects in medical surgery, air pollution monitoring and material processing. Tellurite and germanate glasses have received extensive research due to their moderate maximum phonon energy, high transmittance and high rare earth solubility. Nevertheless, there are existing challenges which hinder their full commercialization. Among them, the high fiber loss in comparison to conventional silica glass is the most pronounced issue. This study mainly focuses on the fabrication of tellurite and germanate glass fibers with low loss. A series of glasses are developed through a thermodynamic calculation of eutectic point between each component pair and verified by experiments. Various techniques of hydroxyl and platinum removal are adopted to reduce the fiber loss, namely preparing under vacuum atmosphere and dehydration pretreatment. Starting from small scale glass-forming verification to preform preparation, different characterization techniques are applied to investigate the properties of the glass materials.

Session 8: Optical Properties of Glass IV

Room: Statler (mezzanine)
Session Chair: John Ballato, Clemson University

3:40 PM

(ICG-SII-088-2019) Organophosphorus doped phosphate hybrid glass for light-emitting electrochemical cell

M. Cai*[1]; L. Calvez[1]; J. Rocherullé[1]; N. Ledos[1]; P. Bouit[1]; M. Hissler[1]; X. Zhang[1]

1. University of Rennes 1, Institut des Sciences Chimiques de Rennes, France

Light-emitting electrochemical cells (LECs) comprising of a single active layer placed in between a transparent anode and an air-stable cathode have been considered as the leading example of the simplest thin-film lighting device. Unlike OLEDs, LEECs also contain an electrolyte material that is as important as the emitting material. Until now, most researches focus on the organic electrolyte, however, very few works focus on inorganic electrolyte for LECs, especially glass. Here, we report an attempt of using phosphate glass as the electrolyte and organophosphorous as an emitter for LEC. Strong photoluminescence was observed from the prepared hybrid glass samples, which indicates the organic molecule was successfully doped into the glass matrix. Besides, SEM images show that the blend morphology is good: no phase separation was found around the micrometer order. The electrical impedance spectroscopy (EIS) suggests the hybrid glass has relatively high conductivity (10^{-7}S/cm at RT). The results provide that the glass host can be used as an electrolyte of a LEC.

4:00 PM

(ICG-SII-089-2019) Colorimetric modeling of poorly crystallized glass-ceramics via the four-flux method: Discrimination between scattering and absorption effects

S. Rio*[1]

1. Institut des Matériaux Jean Rouxel - CNRS, France

Opal glasses could be obtained by melting a mixture of oxides and fluorides raw materials at high temperature (approximately 1500 °C), then after a casting at about 1100 °C, the final item was annealed and eventually subsequently quenched in air. These glass-ceramics consist of a glassy matrix built upon silicon dioxide network containing crystalline fluoride phases (about 10 wt%) such as NaF and CaF_2 that cause the opalescent effect. Indeed, intrinsic parameters of colorless crystalline particles such as refractive index, concentration, size and dispersion strongly control the overall scattering effect. In this study, chromophores were added to the initial composition to color the material by absorption phenomenon. The color rendering of this new series of materials is determined on the basis of the four-flux model by calculating transmitted and reflected, diffuse and specular fluxes to take into account the absorption contribution. From a good correlation between simulations and observations, the color and transparency of these glass-ceramics will be discussed.

4:20 PM

(ICG-SII-090-2019) The theoretical prediction and experiment of glass-forming regions in new photonic glasses

W. Wang*[1]; Y. Xiao[1]; Y. Ye[1]; Q. Zhang[1]

1. South China University of Technology, China

Compared with the traditional silica glass, photonic glasses have the advantages of higher rare-earth-doping concentration, lower phonon energy and higher luminescent efficiency, which are expected to be the core gain medium of laser glass and glass fiber. In this respect, the "thermodynamic calculation method" is applied to predict the glass-forming regions in new photonic glasses (e.g. fluoro-sulfo-phosphate, barium-antimony-germanate and zinc-molybdenum-tellurite), on the basis of which the actual glass-forming regions are further determined by a few experiments. This calculation method is simple, efficient and widely applicable, and can predict glass-forming regions in various oxide and non-oxide glasses. In order to further explore the optical spectral characteristics of these new types of photonic glasses, the rare-earth-doping was carried out with Nd^{3+} ion as an example. The results show that such glasses have high thermal stability, large glass-forming region and excellent spectral characteristics, which can be good candidates for compact and high-power single-frequency fiber laser materials.

Session 9: Fracture (TC 06)

Room: Arlington (mezzanine)

Session Chair: Lothar Wondraczek, University of Jena

1:20 PM

(ICG-SII-091-2019) Fracture properties of SiO_2-B_2O_3-Na_2O Glasses: How the structure influences macroscale fracture properties (Invited)

C. L. Rountree*[1]; W. Feng[1]; D. Bonamy[1]

1. CEA, Iramis, SPEC, France

In 2022, the global market for flat glass is estimated to exceed 100 billion metric tons. Moreover, the glass industry concerns many sectors of our daily lives (buildings, cars, dishes…) along with being integral parts of heat resistant technologies, protection panels (smart phones, plasma screens…), low-carbon energies (protection for solar panels) and satellites in outer space to name a few. Making them less reactive to Stress Corrosion Cracking (SCC), tougher (increasing their fracture toughness), and lighter, while maintaining other properties, is a fundamental issue plaguing glass scientists and researchers. This presentation will take a closer look on how the chemical composition of SiO_2-B_2O_3-Na_2O ternary glass systems alters the physical, mechanical and fracture properties of these systems. These changes lead to mesoscale changes as revealed by a novel parameter coined the depolymerization index. This parameter reveals surprising trends with the stress corrosion cracking behavior in Region I. The presentation will focus on stress corrosion cracking and how it varies with chemical composition and the depolymerization index.

1:50 PM

(ICG-SII-092-2019) Fracture Toughness and Edge Chipping Resistance of an Ancient Roman Glass from Jalame, Israel

G. D. Quinn*[1]; J. Swab[2]

1. National Institute of Standards and Technology, Materials Measurement Sciences Div, USA
2. US Army Research Laboratory, USA

The fracture toughness of a historical soda lime silica glass made in an ancient Roman glass factory was measured by the single-edged precracked beam (SEPB) method in inert conditions. The factory operated in Jalame, Israel until 383 AD. The glass was exposed to the environment for almost sixteen centuries. Results are compared to those for four contemporary soda lime silica float glasses. The fracture toughness of the Jalame glass is slightly less than that of contemporary glass. The resistance to edge chipping was also measured and quantified, and it was comparable to that for contemporary glass.

2:10 PM

(ICG-SII-093-2019) Search for High Poisson's Ratio Oxide Glasses

M. M. Smedskjaer*[1]; S. R. Hansen[1]; K. Januchta[1]; M. B. Ostergaard[1]; M. Bauchy[2]

1. Aalborg University, Department of Chemistry and Bioscience, Denmark
2. University of California, Los Angeles, Department of Civil and Environmental Engineering, USA

Oxide glasses are brittle materials, i.e., they cannot deform plastically on the macroscale without fracture, which seriously limits the scope of their applications. Intrinsic ductility in metallic glasses has been found to increase with Poisson's ratio, which measures the resistance of a material to volume change balanced against the resistance to shape change. An abrupt brittle-to-ductile (BTD) transition has been found to occur around a Poisson's ratio of 0.32, with simulation results suggesting that the BTD transition is universal and should also occur in silica-based oxide glasses. Moreover, high Poisson's ratio has been related with a high tendency to deform through shear flow during sharp contact loading. Yet, very few oxide glasses with such high Poisson's ratio have been reported and the mechanical properties of oxide glasses with Poisson's ratio ≥ 0.30 are poorly understood. In this talk, we report on our search for oxide glasses with Poisson's ratio > 0.32 using both compositional optimization and pressure treatment. We test the proposed relationships of Poisson's ratio with atomic packing density, indentation deformation mechanism, liquid fragility, and fracture energy.

Session 9: Densification and Compression (TC 06)

Room: Arlington (mezzanine)
Session Chair: Lothar Wondraczek, University of Jena

2:50 PM

(ICG-SII-094-2019) Comparison in densification characteristics among various glass compositions: Under hydrostatic pressure and spherical imprint (Invited)

Y. Kato*[1]; G. A. Rosales-Sosa[1]; H. Yamazaki[1]; S. Yoshida[2]; A. Yamada[2]; J. Matsuoka[2]

1. Nippon Electric Glass Co., Ltd., Fundamental Technology Division, Japan
2. The University of Shiga Prefecture, Center for Glass Science and Technology, Japan

Crack initiation behavior is one of the most important factors which have dominating influence to glass strength. In our previous study, crack initiation behavior was found to be much related to "densification", which is plastic deformation with volume contraction when high pressure is applied. Glasses with high densification tendency show less susceptibility to initiation of radial cracks. To understand crack initiations of glass in more details, characteristics of densification of the glasses should be investigated. In this study, multi-anvil cell and spherical indentation experiments are applied for various commercial glasses. The multi-anvil cell experiments gave the relationship between hydrostatic pressure and densification volume. The spherical indentation experiment with Raman spectroscopy gave densification distributions under the imprint. It was found that the distribution depended much on glass composition, which is thought to be due to some shear effect. The results in this study will be a useful data for calculation of stress distribution under indentation imprints to clarify crack initiation behavior of the commercial glasses.

3:40 PM

(ICG-SII-095-2019) Effects of in-situ SEM imaging on the mechanical properties of vitreous silica during micropillar compression

Z. Rouse*[1]; S. Bhowmick[2]; S. Syed Asif[2]; S. P. Baker[1]

1. Cornell University, Materials Science & Engineering, USA
2. Bruker, Nano Surfaces Division, USA

It has been demonstrated that exposure to electron beams typical of TEM imaging can drastically alter the in-situ mechanical behavior of vitreous silica (v-SiO_2), though there is no consensus as to the origin of this effect. It is often assumed, without much evidence, that the much weaker beam conditions of SEM have negligible impact on the mechanical behavior of v-SiO_2. Since these electron beam interactions are fundamentally not well understood and could potentially impact the validity of mechanical experiments on v-SiO_2 with in-situ SEM, a systematic study of the impact of SEM e-beam conditions on the mechanical behavior of v-SiO_2 was conducted. We fabricated v-SiO_2 micropillars and then subjected them to uniaxial compression with, and without in-situ SEM imaging. By systematically varying the e-beam current and voltage during creep tests, we show that e-beam illumination has a significant impact on the mechanical properties of v-SiO_2 even under very low beam currents and voltages. We demonstrate that the influence of the e-beam on the mechanical properties of v-SiO_2 is very short lived after removal of e-beam illumination and that prior exposure to SEM imaging does not appear to permanently alter the mechanical properties of the glass. Two possible causes of e-beam effects, local heating and bond breaking, are compared and discussed.

4:00 PM

(ICG-SII-096-2019) Quantifying the mechanical behavior of vitreous silica through micropillar compression

Z. Rouse*[1]; S. Bhowmick[2]; S. Syed Asif[2]; S. P. Baker[1]

1. Cornell University, Materials Science & Engineering, USA
2. Bruker, Nano Surfaces Division, USA

While it has long been known that extensive plastic deformation is possible in vitreous silica (v-SiO_2) at room temperature, accurately quantifying the plastic flow properties of silicate glasses is challenging. Micropillar compression has occasionally been performed to probe mechanical behavior since this represents, at least in principle, a well-known and relatively homogeneous stress state. However, previous micropillar compression tests of v-SiO_2 were performed on pillars with highly non-uniform cross-sections, which can lead to heterogeneous stress states that impede the determination of accurate mechanical properties. To address this problem, we developed precise methods for the high-throughput fabrication of highly-cylindrical v-SiO_2 micropillars of various diameters and heights. We then compressed these micropillars within an in-situ SEM system. We describe analysis methods that account for common experimental challenges, such as tip/sample alignment and substrate compliance, and enable the accurate determination of stress-strain data from these tests. We then quantify the non-linear elastic response, yield stress, and strain hardening behavior. We show how these results compare to previous studies and discuss the structural origins of the observed mechanical behavior.

4:20 PM

(ICG-SII-097-2019) Correlation between structural and mechanical properties of tellurite glasses as a function of temperature

M. Dutreilh-Colas*[1]; J. de Clermont Gallerande[1]; F. Célarié[3]; Y. Gueguen[3]; D. de Ligny[4]; T. Hayakawa[2]; P. Thomas[1]

1. IRCER, France
2. Nagoya Institute of Technology, Japan
3. Institut de Physiques de Rennes, France
4. Institute of Glass and Ceramics, Germany

Tellurium oxide-based glasses have a lot of interests due to their specific physical and chemical properties such as high refractive index, wide band infrared transmittance and large third order non-linear optical susceptibility. This work will focus on TeO_2-TiO_2-ZnO and TeO_2-TiO_2-Nb_2O_5 ternary glassy systems. Addition of TiO_2, Nb_2O_5 and ZnO is known to improve the stability of tellurite glasses while preserving their high optical properties. In this communication, the structural properties are studied using in situ temperature Raman spectroscopy, and the mechanical properties are studied using Resonance Frequency Data Analysis (RFDA) as a function of temperature. Finally a simultaneous investigation of thermal, structural and elastic properties has been performed by using the ARABICA setup. Thus a new point of view on the correlation between mechanical and structural properties, and especially around Tg, which could be a key point for the optical fiber shaping of these glasses will be proposed.

SIII: Glass Technology and Manufacturing

Session 4: Glass Forming Operations

Room: Cambridge (4th floor)
Session Chair: Mathieu Hubert, Corning Incorporated

1:20 PM

(ICG-SIII-001-2019) Model-based optimization of the glass-flake production process

T. Gerdes*[1]; K. Ischenbek[1]

1. University of Bayreuth, Keylab Glass Technology, Department CME, Germany

For decades, glass flakes have a wide range of applications, e.g. as reinforcements in polymers, as vapor barrier or effect pigments in coatings. The flakes are usually produced directly from the glass melt using a centrifugal process. In this process, a viscous glass filament hits the center of a rotating atomizer. Due to the centrifugal forces, a thin glass lamella is formed which is thrown over the edge of the cup-like atomizer. This thin glass lamella stretches further and cools down. Thus, thin solid glass flakes are produced. Due to the complex fluid dynamic processes, the optimization of the flake properties

took place so far predominantly empirical. Within the scope of this work, a model for predicting the flake geometry depending on the glass properties as well as the process conditions has been developed. For the production of the flakes, a so-called "Mini-Melter" with a glass melting capacity of 100 kg per day and an in-house build "flaker" has been used. Within the paper, the properties of the flakes will be compared with the calculations and the main influencing parameters on the flake production will be discussed.

1:40 PM

(ICG-SIII-002-2019) Application of machine learning algorithms at data collections of a glass container production

D. K. Orzol*[1]; C. Roos[1]

1. IPGR - International Partners in Glass Research e.V., Germany

A modern container glass line produces about 300.000 containers a day by the use of about 100 to 120 t of glass. To increase the productivity, fulfill tighter specifications and higher quality claims, the process understanding has to be increased. Already today, each container is inspected in respect of different criteria and generates consequently data. Information about the forehearth settings as temperature measurements or gas consumptions and machine settings are recorded, too. So far, they are often not correlated or evaluated. Single influences of production parameters on different aspects of the final glass containers are known, but cross-connections are not yet identified deeply. New developments in respect of data storage and data processing provide new chances in the application of the data for an increased process understanding. In this paper, we present the data evaluation with machine learning algorithms of a glass container production line. The production data is collected from the forehearth, the IS machine and the wall thickness inspection machines. Afterwards, the production data is stored and correlated in a central database before a data preparation is done. Different machine learning algorithms as decision trees or neural networks are used to identify process relevant parameters which influence the wall thickness distribution of the individual bottles.

2:00 PM

(ICG-SIII-003-2019) Numerical and Experimental Study of the Glass Blow and Blow Forming Process

A. Biosca*[1]; S. Borrós[1]; V. Pedret[2]; A. García[1]

1. IQS School of Engineering, Spain
2. RAMON CLEMENTE, Spain

The design of the mold cavities and the definition of machine operation times and process temperatures are key issues to develop and mass produce optimal containers. Glass forming to produce perfume bottles with specific thickness distribution profiles is based on trial and error and requires several tests in production line. These tests are expensive and time-consuming, which increases time to market. The use of a numerical model aims to reduce the number of prototypes by performing virtual tests. Temperature profiles on the glass skin in the different stages of the forming process where glass is visible can be measured with an infrared thermal camera. These data is used as input and to verify the numerical results. Numerical simulations of the B&B forming process have been performed using axysimetric glass perfume bottles. The comparison of the cross sectioned produced bottles with the predicted results of the numerical model shows a good agreement for the glass thickness distribution. The numerical model predicts consistent results in the glass thickness distribution. It has the ability to predict the influence of the blank mold cavity in the thickness distributions of perfume bottles. The glass thickness distribution as a function of the forming process conditions and the blank mold cavity has been validated experimentally for different simulation cases.

2:20 PM

(ICG-SIII-004-2019) Innovative Sintering Process for the Densification of Tellurite Glass

D. J. McGill*[1]; J. Benghozi[2]; L. Roumiguier[2]; M. Kang[1]; C. Blanco[1]; M. Dohlen[2]; G. Delaizir[2]; S. Chenu[2]; J. Duclere[2]; K. Richardson[1]; R. M. Gaume[1]

1. University of Central Florida, Optics, USA
2. University of Limoges, Science of Ceramic Processes and Surface Treatments Laboratory, France

Infrared transparent glassy materials often have unique and complex processing requirements but are an important class of materials for such applications as optical windows and lenses. Sintering of a glassy powder (parent glass) to form near-net shape optical elements is an increasingly studied production technique which will likely have many future applications. This talk will focus on the sintering of a $70TeO_2$-$20WO_3$-$10La_2O_3$ (TWL) glass powder using an innovative uniaxial hot press process which uses a sacrificial pressure-transmitting medium. The characteristics of the sintered TWL glass is compared to that of a parent glass produced through a conventional melt/quench technique to ascertain the impact of process-specific property changes on the resulting material. The potential applications of this technique to future production of optical elements will be discussed.

2:40 PM

(ICG-SIII-005-2019) Modeling and simulation of dehydration and sintering of GeO_2 –doped SiO_2 soot

S. Dixit*[1]; H. Harode[1]; C. Saha[1]

1. Sterlite Technologies ltd., Research and Development, India

During the post-deposition of silica soot in a cylindrical blank, it is exposed to a heating furnace for dehydration and consolidation. Dehydration of soot preform is a critical process as contamination from residual OH- during soot deposition may lead to devitrification preceding the sintering process or higher attenuation in the optical fiber. In the present study, the dehydration and sintering behavior of silica soot preform has been modeled and simulated at an industrial scale to analyze the time-temperature profiles of reaction, heat, and mass transfer involved in the dehydroxylation process of silica soot in a helium and chlorine atmosphere. This developed model has been further employed to predict the OH concentration and sintering behavior of silica soot under different time-temperature profiles and flow of He and Cl. The simulation results depict an impact of dehydration time and atmosphere on the concentration of GeO_2 in the consolidated SiO_2 –GeO_2 glass. Moreover, the study predicts the fluorine doping impact on the sintering behavior of silica soot. The presentation will discuss these results in detail.

3:00 PM

(ICG-SIII-006-2019) A computational investigation to understand the impact of helium on the sintering behavior of silica soot

S. Agarwal*[1]; H. Harode[1]

1. Sterlite Technologies Limited, Research and Development, India

The generation of silica soot by outside vapor deposition (OVD) followed by its sintering and consolidation in the presence of helium is a well-known process in the optical fiber industry. Helium is primarily used because of its small atomic size (helps in diffusion), high thermal conductivity (maintains a uniform temperature along the soot preform), chemical inertness towards silica, and to cut-off any OH content from the ambient atmosphere. In general, three timescales are involved during sintering of silica soot, i.e., helium diffusion, heat conduction and radial shrinkage (consolidation) of silica soot. In this study, a numerical analysis has been performed to study the effect of thermal properties of helium on the sintering behavior of silica soot. An emphasis has been made on understanding the impact of helium flow rate on the weight, density and porosity

of the consolidated preform. The penetration of helium gas and its degassing has also been studied during the analysis. The simulated results have been found to be in good agreement with experiment data. A comparison of helium with other gases such as nitrogen and argon on the sintering behavior of silica has been performed using this model. The results will be discussed in the presentation.

3:20 PM

(ICG-SIII-007-2019) Soot growth prediction modeling in the outside vapor deposition process

H. Harode*[1]; S. Agarwal[1]; A. Pandey[1]

1. Sterlite Tech, R&D, India

Optical fibers are drawn out of glass blanks which are formed by depositing silica soot generated by flame hydrolysis on a growing rotating target followed by its subsequent consolidation. The present work includes detailed modeling and simulation of a two burner set-up used in an outside vapor deposition (OVD) process for the manufacturing optical fibers. Our modeling approach accounts for the kinetics and thermodynamics of material deposition on the bait rod in each pass of the growing cylindrical body. The developed model has been used to predict the deposition profiles of SiO2 on the bait rod, for example, soot diameter, radial density, surface temperature, and material efficiency. The simulation results are in good agreement with the experimental data. The various features of the process such as end cone formation, fuel–to–reactant ratio and burner positions have been covered in the study. A complete run time simulation SiO2 soot deposition in OVD has been performed and compared using two different models – (i) Eisner and Rosner [Combust Flame 61 (1985) 153], and (ii) Kang and Grief [Int. J. Heat Mass Transfer 36 (1993) 1007]. The results will be discussed in the presentation.

Session 7: 3D Printing of Glass and Rapid Prototyping

Room: Cambridge (4th floor)
Session Chairs: Laura Cook, Corning Incorporated; Neil Palumbo, Corning Incorporated

8:00 AM

(ICG-SIII-008-2019) Additive Manufacturing of Glass using a Fused Deposition Modeling

Y. Han*[1]; H. Kim[1]; H. Lee[1]; K. Kim[1]; H. Lee[1]

1. Korea Institute of Ceramic Engineering and Technology (KICET), Engineering Ceramic Center, Republic of Korea

In the case of manufacturing ceramic parts by additive manufacturing, there is a high possibility that pores are formed in the sintered end part because powder is generally used as the starting material. The internal pores cause the catastrophic fracture of the ceramic part in the presence of external stress, which has a great influence on the reliability of the ceramic part. Since the glass part is manufactured from melt, the pore existing in the end part is extremely small as compared with the ceramic part made of powder metallurgy. On the other hand, attempts to extrude molten glass and manufacture 3D parts have been made in the past, but due to the limitations of the equipment, they were manufactured only at a resolution of a few millimeters and were used to produce bulky products such as lighting fixtures. In this study, glass 3D objects were fabricated by stacking molten glass from solid filaments using FDM method. First, a glass filament having a diameter of 1.2 mm and a length of 800 mm was developed. Optimum conditions for glass filament were derived by controlling the pull-out speed and the melting furnace temperature. Glass 3D printers made on a lab scale consist of core modules such as small heaters, nozzles, and beds. The shape of the nozzle tip, the feed rate of the filament, the nozzle tip and bed temperature, and the substrate speed were optimized for determining the quality of the 3D objects.

8:20 AM

(ICG-SIII-009-2019) Laser-heated filament-fed printing of glass for optics and photonics

N. Capps[2]; C. Ketterer[1]; J. Hsu[3]; J. Goldstein[4]; R. Landers[1]; D. Bristow[1]; R. Brow*[3]; E. Kinzel[2]

1. Missouri University of Science & Technology, Mechanical Engineering, USA
2. Notre Dame, Aerospace and Mechanical Engineering, USA
3. Missouri University of Science and Technology, Materials Science and Engineering, USA
4. Air Force Research Laboratory, Materials and Manufacturing, USA

Glass is readily formed using conventional processes as well as techniques developed by artisans. However, it is difficult to print using conventional Additive Manufacturing (AM) processes because of the high processing temperature and bubble entrapment during powder consolidation due the high viscosity of the melt. An alternative is to locally heat glass and continuously fuse it to form a printed body. A CO or CO2 laser precisely delivers heat at a focused spot at the interface of filament and the workpiece which is positioned using a CNC stages. The filament is continuously fed into this molten region and a 4th rotation axis maintains a constant orientation between the travel of the workpiece and the feed. This is necessary because although the glass is heated above its working temperature, it is still viscous and the molten region can be deflected by the feed. Studies show that there is minimal diffusion of the glass during the heating and core/cladding structures are maintained. This permits deposition of complex waveguiding structures using optical fiber. Freeform optical structures can also be created by depositing larger shapes and reheating the glass with the laser beam to reflow the surface to be optically smooth. This paper presents on going work to understand the dynamics of the printing process toward applications in 3D structures, freeform optics, and integrated photonics.

8:40 AM

(ICG-SIII-010-2019) Additive manufacturing of chalcogenide glasses

E. Baudet[1]; Y. Ledemi*[1]; P. Larochelle[1]; S. Morency[1]; Y. Messaddeq[1]

1. Centre d'Optique, Photonique et Laser, Canada

Filament fed was used as an additive manufacturing process for the fabrication of three-dimensional printed optical multimaterial fiber preforms based on chalcogenide glasses. Several challenges were overcome in order to produce 3D-printed chalcogenide glass: preparation of chalcogenide glass filament by fiber-drawing, optimization of extrusion temperature, filament feeding or even annealing process of printed glass. As_2S_3 chalcogenide glasses were selected for their low glass transition temperature (T_g = 191°C) and their facility of synthesis by the conventional melting and quenching method. Chalcogenide glass was extruded using a commercial 3D printer at temperature around 120°C above the glass transition temperature. To obtain 3D-printed As_2S_3 chalcogenide glass with appropriate morphology and transparency, chemical and physical properties were studied (glass transition temperature, chemical composition, transmission…) and compared to the bulk material. Results revealed that extrusion of chalcogenide glasses do not affect the glass properties. Thus, in comparison with other methods of elaboration of fiber preforms, additive manufacturing has a potential to print chalcogenide glasses for optical applications. This work is the first step of the fabrication of complex multimaterial preforms based on chalcogenide glass for fiber drawing.

9:00 AM

(ICG-SIII-011-2019) Lithography-based additive manufacturing of optical ceramics and glass (Invited)

S. M. Allan*[1]; M. Schwentenwein[2]

1. Lithoz America, LLC, USA
2. Lithoz GmbH, Austria

Advancements in additive manufacturing (or 3D printing) of ceramic materials enable complex geometries and net or near-net shape products to be fabricated to high accuracy without tooling. This offers the potential to greatly reduce grinding and polishing of optical surfaces, and allows the creation of novel optical geometries. Lithography-based ceramic manufacturing (LCM) uses suspensions of ceramic or glass powders in photopolymer resins to produce green parts. Digital light projection (DLP) is used to cure the resin layer upon layer. The printed parts follow debinding and sintering regimens comparable to other powder processing methods. The as-sintered parts exhibit density and mechanical properties on par with pressed or injection molded powders, with surface roughness typically less than 1 μm Ra. The results of processing silica-based glasses, translucent polycrystalline alumina, and yttrium aluminum garnet will be presented.

9:50 AM

(ICG-SIII-012-2019) 3D Printed Glass Optics with Tailored Composition (Invited)

R. J. Dylla-Spears*[1]

1. Lawrence Livermore National Laboratory, USA

The direct ink writing (DIW) technique for three-dimensional (3D) printing has opened the door to the realization of novel glass optics with both customizable composition and structure, providing unprecedented degrees of freedom in optical design. In this approach, specially formulated silica-containing inks are extruded at room temperature through a nozzle and deposited in the geometry of interest, forming low density green bodies. The green bodies are then converted to full density, optically homogeneous glass by a series of heat treatments. Printed glass optics containing tailored gradients in composition, such as gradient index (GRIN) lenses, have been achieved by DIW by blending separate inks inline at the print nozzle and directly depositing the desired composition profile before forming the glass. Recent progress toward custom-composition 3d-printed glass optics will be discussed, and characterization of 3d-printed GRIN lenses will be provided. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 within the LDRD program 16-SI-003 and 19-ERD-020. LLNL-ABS-765892

10:20 AM

(ICG-SIII-013-2019) Developing 3D-printed optical quality germania–silica glasses from sol-gel feedstocks

K. Sasan*[1]; R. J. Dylla-Spears[1]; S. Kallontzi[3]; J. Destino[2]; N. Dudukovic[1]; M. Johnson[1]; O. Herrera[1]; J. Yoo[1]; L. Andrew[1]; T. Yee[1]; D. Nguyen[1]

1. Lawrence Livermore National Laboratory, USA
2. Creighton University, USA
3. Rutgers University, USA

Direct Ink Write (DIW) 3D printing provides a revolutionary approach to design functionally graded materials, including new glass compositions. Herein, we present a method for fabricating optical quality germania-silica (GeO_2-SiO_2) glasses by DIW 3D printing. Printable GeO_2-SiO_2 inks were prepared from sol-gel colloidal feedstocks, which were optimized to yield viscous, shear-thinning colloidal suspensions with tuned rheology ideal for DIW. After printing, the parts were dried and sintered under optimized thermal conditions to remove all the organic components and densify to fully dense, transparent and crack-free glasses. Chemical and structural evolution of GeO_2-SiO_2 glasses were confirmed by several techniques such as X-Ray Diffraction (XRD), Raman and Nuclear magnetic resonance (NMR) spectroscopies. Additionally, the role of particle morphology and chemistry are discussed as they relate to the benefits and challenges in preparing the transparent glasses by this method. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 within the LDRD program 16-SI-003 and 19-ERD-020. IM #955979

10:40 AM

(ICG-SIII-014-2019) Additive Manufacturing of Porous Translucent/Transparent Glass Scaffolds

A. Dasan*[1]; J. Kraxner[1]; H. Elsayed[2]; D. Galusek[1]; E. Bernardo[2]

1. FUNGLASS, Alexander Dubcek University of Trencin, Slovakia
2. University of Padova, Department of Industrial Engineering, Italy

Additive Manufacturing or 3D printing of transparent glass offers advantages in design versatility, which is difficult to process using conventional methods; however, achieving transparencies is a great challenge when considering the shape retention, cracks or brittleness behavior and porosity formation (due to incomplete densification) after sintering process. In this presentation, we demonstrated manufacturing of highly porous translucent/transparent glass scaffolds from commercial borosilicate/ aluminosilicate glass powders processed by different printing techniques. The optical transmittance and other critical parameters of the sintered objects will be addressed. The glasses so obtained are finding use in many applications such as optical devices including gas sensors.

11:00 AM

(ICG-SIII-015-2019) Development of silica-based slurries for stereolithographic printed glass structures

F. B. Löffler*[1]; E. C. Bucharsky[1]; G. Schell[1]; M. J. Hoffmann[1]

1. Karlsruhe Institute of Technology, IAM-KWT, Germany

Amorphous silica, which has a high transparency and is chemical as well as mechanical stable, is supposed to be a useful material to produce transparent open-pored glass structures, which have the potential to be used for photocatalytic waste water treatment devices. The research topic of this work is the development of silica based slurries for 3D printing technology with which open pored glass structures can be printed. The method, stereolithography, is based on the principle of photo curing, so it is necessary to develop a slurry based on silica nanoparticles and photo curable materials. Therefore, a photosensitive polymer system with a polymerizable monomer, a cross linker and a photoinitiator was investigated and can be cured with a defined wavelength. The challenge which must be overcome is the homogeneous dispersion of nanoparticles in the system. By adjusting the polymer system, a stable slurry with a very high solid loading of amorphous silica up to 43 vol% can be reached. In addition, different viscosity values can influence the printing process, can be obtained by a variation of the solid loading. Employing the developed silica based slurry, it was proved that structures with complex geometries can be printed exhibiting a high shape accuracy. Subsequently, the parameters for debindering and sintering were evaluated in order to obtain transparent materials.

SIV: Emerging Applications of Glass

Session 2: Glasses in Healthcare II (TC 04)

Room: Stuart (4th floor)
Session Chairs: Julian Jones, Imperial College London; David Greenspan, University of Florida

8:00 AM

(ICG-SIV-028-2019) 4D Viscous Flow Sintering of 3D Printed Bioactive Glass Scaffolds (Invited)

A. Nommeots-Nomm*[1]; J. Jones[2]; P. Lee[3]; G. Poologasundarampillai[4]

1. McGill University, Materials, Canada
2. Imperial College, Materials, United Kingdom
3. University College London, Mechanical Engineering, United Kingdom
4. University of Birmingham, Materials, United Kingdom

Bioglass is a leading synthetic bone graft material as it can help regenerate bone, but it is not commercially available in a highly porous 3D form. This is mainly due to the challenges associated with sintering the glass without crystallization occurring, which reduces its bioactivity. The sintering of glasses can be described as the merging and coalescing of particles above the glass transition temperature which results in a reduction in surface area and in turn reduces overall porosity. Traditional sintering theories are based upon uniformly packed, spherical particles and their evolution is understood in 2D. This, however, is unrepresentative of melt derived bioactive glass powders produced in the lab, which are non-spherical and have wide size distributions with non-uniform particle junctions. This work aims to study the sintering process of melt derived 3D printed bioactive glass scaffolds in real time. Here, we have produced 3D bioactive glass scaffolds using the direct ink writing additive manufacturing technique, with pre-designed porosity. The scaffolds were then sintered while simultaneously conducting continuous 3D tomographic imaging at the UK Diamond Light Source. We present novel insight into the sintering process of non-spherical particles from both a local (particle-particle) and global (scaffold) perspective, and show evidence of pore migration and strut coarsening over the sintering cycle.

8:30 AM

(ICG-SIV-029-2019) Synthesis and characterization of phosphate glass based 3D macroporous scaffolds

J. Rocherullé*[1]; R. Lebullenger[1]; L. Bunetel[1]; H. Oudadesse[1]

1. University of Rennes, Chemical Sciences Institute, Glass and Ceramic Group, France

In the past decades, the demand for bioactive glasses and sintered porous scaffolds has steadily increased. However, silicate glasses are challenging to hot form due to their low stability toward crystallization. Phosphate glasses have been found to be good alternatives to silicate as they are also suitable for biomedical purposes. Nevertheless, there are only a few studies regarding phosphate glass 3D scaffolds as compared to silicate, probably because of their limited chemical durability. However, degradation rates can vary from hours to several weeks by only changing the glass composition. The aim of this work was to prepare and characterize 3D macroporous scaffolds from several phosphate glass compositions. Among the conventional techniques available to generate scaffolds, we used comparatively two methods: the polymer foam replication and the use of various foaming agents (CaCO3, MnO2 and C3N4). The parent glasses were characterized in terms of thermal, mechanical properties and also from a chemical durability point of view. In addition, human osteoblast cells Saos-2 and human endothelial cells EAhy926 were used for viability assays. 3D scaffold manufacturing, involving firing and sintering steps, can lead to the crystallization of the glass which can induce a decrease of the bioactivity. As a consequence, we investigated the devitrification behavior of the different glass matrices.

8:50 AM

(ICG-SIV-030-2019) Bioactive glass scaffolds: 3D printed v foam for in vivo bone regeneration

X. Shi[1]; A. Nommeots-Nomm[2]; N. Todd[3]; A. Devlin-Mullin[3]; P. Lee[4]; C. Mitchell[3]; J. Jones*[1]

1. Imperial College London, Department of Materials, United Kingdom
2. McGill University, Canada
3. University of Ulster at Coleraine, United Kingdom
4. University College London, United Kingdom

The architecture of bone scaffolds can regulate bone defect repair by controlling pore dimensions and rate of degradation, thus optimising bone ingrowth. Direct ink writing (or robocasting) is a 3D printing technique that can produce 3D scaffolds with open pore channels and high strength. we describe two types of bioactive scaffolds made using a sinterable glass composition: a 3D printed grid-like scaffold and a gel-cast foam scaffold with architecture similar to that of cancellous bone. Both had modal interconnect pore diameters of ~122 μm. We used a rabbit lateral femoral defect model to evaluate these two types of scaffolds in comparison to a defect only group (after 4 and 10 weeks implantation). 3D X-ray microcomputed tomography, histology and back-scatter electron microscopy (BS-SEM) permitted quantitative evaluation of new bone ingrowth and degradation of the scaffolds. The printed group showed the least osteogenesis at 4 weeks, but by 10 weeks bone ingrowth was equivalent to the control and foam groups. Different rates of dissolution and apatite formation were observed on the two types of scaffolds using SEM imaging of cross-sections ex vivo.

9:10 AM

(ICG-SIV-031-2019) Physical and structural investigation of Silicate-phosphate glasses formed with biosynthesized silica nanoparticles

D. Kaur*[1]; O. Pandey[1]; M. Reddy[2]

1. Thapar Institute of Engineering and Technology, School of Physics and Materials Science, India
2. Thapar Institute of Engineering and Technology, Department of Biotechnology, India

In the present research, bio-synthesisation of silica nanoparticles has been carried out successfully. For this purpose, agriculture waste rice husk has been utilized. Among several types of agriculture waste, rice husk is considered to be cost-effective and easily accessible. In the present investigation, a simple chemical approach has been employed to extract silica nanoparticles. X-Ray Diffraction (XRD) patterns indicated the amorphous nature of silica at lower temperature range. Silica and other mineral contents have been found using energy dispersive spectroscopy (EDS). Morphological and structural studies have been carried out with the use of Field Emission Scanning Electron Microscopy (FE-SEM) and Fourier Transform Infrared Transmission (FTIR) spectroscopy. Further, extracted silica from rice husk has been used for preparation of the glasses. The appearance of broad humps in XRD patterns confirmed the amorphous nature of prepared glasses. The as-synthesized glass samples can be further used for physical and structural studies for drug loading applications.

9:50 AM

(ICG-SIV-032-2019) The corrosion of glass fibres under different conditions in simulated lung fluids

A. Helebrant*[1]; I. Czudkova[1]; A. Hepnerova[1]; H. Hradecka[1]

1. University of Chemistry and Technology, Dept. of Glass and Ceramics, Czechia

The dissolution of three types of glass fibres (E-glass, alkali-resistant fibres AR 1200 and 1250) was studied. It was tested by flow-through tests (37 °C, SLF flow rate 120 ml/day, pH 7.4). Solution composition and fibres changes were studied using AAS, SEM/EDS and weight changes. The E-fibres dissolution was congruent and nearly complete after 135 days. AR fibres dissolution was significantly slower and incongruent. It was caused by back precipitation and forming of Ca/P and silica gel layers. The dissolution kinetics was in agreement

with developed kinetic model. To simplify the testing, the static test of E-glass was performed under static conditions in SLF with and without $CaCl_2$ a $MgCl_2$, using two glass S/V ratios 3.7 and 1.0 cm^{-1}. The tests without and with stirring were carried out. The fibres dissolved incongruently in both solutions. For higher S/V, the solutions were saturated rapidly and back precipitation were observed. There was neither saturation nor the precipitation for lower S/V. No significant effect of stirring was observed. The mass losses for higher S/V were responding with the in-vivo studies (50% after 40 days), i.e. the static test could be used for the first assessment of the fibres biopersistence.

10:10 AM

(ICG-SIV-033-2019) The impact of fluid flow on dissolution kinetics of bioactive glass S53P4

L. Hupa*[1]; A. Stiller[2]; M. Engblom[1]; O. Karlström[1]; M. Lindén[2]

1. Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Finland
2. Ulm University, Institut für Anorganische Chemie II, Germany

Dissolution of bioactive glasses in static solutions is usually described as a series reactions starting with ion exchange of network modifiers, followed by dissolution of network formers, re-bonding of the dissolved network species and precipitation of apatite-like surface layer. However, the human body is a dynamic environment, and there is a need for a better quantitative understanding of the different physico-chemical processes and their interactions on the reactions of bioactive glasses. To explore bioactive glass dissolution under well-controlled flow conditions, we have studied the impact of the flow rate of fresh Tris-buffer solution (pH 7.4) on the dissolution of bioactive glass S53P4 at 40°C in a flow-through reactor. Three different flow rates were tested: 0.04, 0.2 and 0.6 mL/min for the glass particles of the size fraction 300-500 mm up to 24 h. The pH of the solution was measured and the concentration of the ions released from the glasses was analyzed (ICP-OES) at several time points. Finally, the morphology of the particles was studied using SEM-EDXA. The fluid flow rate had a high impact on the dissolution behavior and on the development of the typical silica-rich and hydroxyapatite layers at the glass surface. The results give fundamental information on the dissolution patterns and reaction mechanisms of low silica glasses such as bioactive glasses in dynamic solutions.

10:30 AM

(ICG-SIV-034-2019) Understanding structure-degradation behavior relationships in Na_2O–P_2O_5–B_2O_3–SiO_2 based model bioactive glasses

N. Stone-Weiss*[2]; N. J. Smith[1]; R. Youngman[1]; E. M. Pierce[3]; H. Eckert[4]; A. Goel[2]

1. Corning Incorporated, Science and Technology Division, USA
2. Rutgers University, Materials Science and Engineering, USA
3. Oak Ridge National Lab, Environmental Sciences Division, USA
4. University of Sao Paulo, Sao Carlos Institute of Physics, Brazil

P_2O_5 plays a vital role in enhancing the bioactivity of most commercial bioactive glasses such as 45S5 and 13-93, largely due to its compatibility with mineral phosphate in bone tissue. Likewise, it is an important component in borosilicate-based bioactive glasses. In order to design novel borosilicate-based bioactive glass compositions, it is imperative to understand the influence of P_2O_5 on glass structure-degradation behavior relationships, as previous literature has shown that small P_2O_5 additions to borosilicate glasses significantly affects both structure and properties. In this study, we aim to understand how P_2O_5 additions impact the structure and degradation behavior of glasses designed in the sodium borosilicate system over a wide composition space including perboric (Na/B <1), metaboric (Na/B = 1), and peralkaline (Na/B >1) regimes. Elemental release characteristics and in-depth structural details of the glasses and their surfaces—both before and after degradation in simulated bodily environments—have been investigated using ICP-OES, multinuclear MAS NMR, as well as other spectroscopic techniques. Accordingly, we aim to develop a comprehensive understanding of compositional and structural drivers of glass degradation in the studied system, which we hope will contribute to the development and design of novel borosilicate-based bioactive glass compositions.

10:50 AM

(ICG-SIV-035-2019) An arrangement of in vitro tests of highly and low reactive inorganic biomaterials

D. Rohanová*[1]; D. Horkavcová[1]; R. Marek[1]; A. R. Boccaccini[2]; A. Helebrant[1]

1. University of Chemistry and Technology, Dep of Glass and Ceramics, Czechia
2. University of Erlangen-Nuremberg, Institute of Biomaterials, Germany

The arrangement of in vitro test for the biomaterials is provided according to ISO standard (ISO 23317:2014). Duration of the test is recommended for 28 days and S/V ratio (a sample surface to the volume of the Simulated Body Fluid (SBF)) is set-up to 0.1 cm^{-1}. We tested both highly reactive glass-ceramic scaffolds (derived from Bioglass®) and low reactive β-TCP (β-tricalcium phosphate ceramics) granules in the form for clinical using. The analysis of the SBF eluates (pH measurement, Ca, Si (by AAS) and P (by spectrophotometry)) as well as the materials study (XRD, SEM/EDS, XRF, and BET) helped us to better understand the interactions running during the in vitro test. The crystalline phase (combeite) of the glass-ceramic scaffold (¾ of whole material weight) was nearly completely dissolved within the first day of the test while granules of β-TCP seemed to be intact after several days of exposition in SBF. We found that set-up of in vitro test for both materials has to be rearranged due to a substantially different reactivity of the glass-ceramic scaffold and β-TCP.

11:10 AM

(ICG-SIV-036-2019) Characterization of bioactive glass coating on titanium plate by direct-bonding lamination

Y. Liu*[1]; R. Jeng[2]; N. Matsushita[1]; T. Kishi[1]; T. Yano[1]

1. Tokyo Institute of Technology, Department of Materials Science and Engineering, Japan
2. Tokyo Institute of Technology, Department of Chemistry and Materials Science, Japan

Bioactive glass coating on metal substrate has aroused much attention as it possesses high bioactivity and high mechanical properties in the load bearing conditions. At the present, high temperature and/or complex process like enameling and plasma spray one is required to obtain this kind of composite. However, ultrathin glass film can be used to make this coating metal structure without complex process because it possesses outstanding characteristics like high mechanical flexibility. In this study, glass thin film with the same composition as 45S5 glass was fabricated by the glass blowing method, and commercial titanium plate with high mechanical strength was employed as the substrate. Bonding of the glass film on metal is achieved by simple attaching of the glass thin film with metal surface in wet condition. The bonding energy was found to increase with aging time in air at room temperature and reached about 1000 mJ/m^2 after 9 hours. SEM, FTIR, XPS and so on were used to investigate the bonding mechanism in detail.

11:30 AM

(ICG-SIV-037-2019) Investigating multiple host glasses for $BaCl_2$:Eu^{2+} layered thin films synthesized by pulsed laser deposition for medical imaging

C. W. Bond*[1]; Y. Jin[3]; R. L. Leonard[1]; A. R. Lubinsky[2]; A. Petford-Long[3]; J. A. Johnson[1]

1. University of Tennesee Space Institue, Mechanical, Aerospace, and Biomedical Engineering, USA
2. Stony Brook University, Radiology, USA
3. Northwestern University, Materials Science and Engineering, USA

A thin film storage phosphor plate has been developed containing multiple transparent layers of orthorhombic phase barium chloride nanocrystals doped with europium, separated by nanolayers of a host glass. Samples were produced employing either fluoride

and silica glasses as the separation layer. These transparent films are synthesized by pulsed laser deposition using a composite target. Manipulation of target movement allows for precision control of layer composition. This synthesis method can result in a higher concentration of luminescent centers compared to glass ceramic plates synthesized via the melt-quench method. Heat treatments were necessary to ensure the barium chloride is present in the orthorhombic phase. Layer composition and morphology, including in-depth TEM analysis, will be presented. In addition, the performance characteristics of these films, as storage phosphor plates for computed radiography, will be reported. This research was supported by the Nation Science Foundation under grants DMR 1600783 and DMR 1600837.

Session 2: Glasses in Healthcare III (TC 04)

Room: Stuart (4th floor)
Session Chairs: Leena Hupa, Åbo Akademi University; Amy Nommeots-Nomm, McGill University

1:20 PM

(ICG-SIV-038-2019) Clinical and preclinical experience of bioactive glass S53P4 in the treatment of bone defects and infected bone (Invited)

N. Lindfors*[1]

1. Helsinki University Hospital, Musculoskeletal and Plastic Surgey, Finland

Bioactive glass (BAG) S53P4, is a bone substitute with osteoconductive, osteostimulative, angiogenetic and antibacterial properties. Clinically BAG-S53P4 has been used in benign tumor surgery, head and neck- spine- and neurosurgery and in the treatment of osteomyelitis. Osteomyelitis is an infectious process that leads to bone destruction. Surgical procedures are usually performed in combination with systemic and local antibiotics using a two-stage procedure, in which autograft or synthetic bone is used for filling the bone defect. In a multinational study involving six countries and eleven centers, 116 patients with verified chronic osteomyelitis were treated using antibacterial BAG-S53P4 granules as part of the treatment. The success rate was 90% and the study showed that BAG-S53P4 could be used in a one-stage procedure with excellent results. Bone formation and fracture healing is a highly regulated process involving several factors e.g. the mechanical environment, inflammatory and osteogenic cells, vascular and inflammatory mediators and an osteogenic scaffold. Combining the osteoconductive, osteostimulative, and angiogenetic effects of BAG-S53P4, with elevated expressions of BMP and VEGF induced by PLGA coating, we have developed a sintered BAG-S53P4 scaffold to be used in a single-stage induced membrane technique, with promising preclinical results.

1:50 PM

(ICG-SIV-039-2019) The Investigation on Biological Effects of Sodium-free Fluoride-containing Bioactive Glasses in Vitro and in Vivo

X. Chen*[1]; L. Zhuo[1]

1. Central South University, Xiangya School of Stomatology, China

Bioactive glasses (BGs) are degradable, releasing therapeutic ions and forming apatite-like layer to bond with the living tissues. Fluoride showed great osteogenic and angiogenic effects. Recently, novel sodium-free fluoride-containing BGs (NaFBGs) were found highly bioactive and offered great potential for medical and dental applications. However, there was very limited studies on their biological effects. This work first time investigated the osteogenesis, angiogenesis and wound healing potential of NaFBGs on fibroblasts in vitro using MTT assay, ALP assay, Alizarin Red S staining, Sirius-red staining, qRT-PCR and scratch wound healing assay. Finally, we examined the wound repair potential of NaFBGs in vivo using a mouse skin wound model (6mm in diameter on the upper back of mouse). Results showed that the culture media-containing ions released from the NaFBGs are non-cytotoxic. The NaFBGs facilitated mineralization, collagen formation, osteogenic and angiogenic genes expression and cells migration on fibroblasts, while, 3 mol% fluoride-containing BG has the most significant promoting effects. The in vivo study showed smaller wound areas measured post-wounding in mice exposed to NaFBGs compared with the control (PBS), suggesting that NaFBGs could accelerate wound closure. These findings make NaFBGs attractive for bone regeneration and wound healing therapies.

2:10 PM

(ICG-SIV-040-2019) Metal ion doped borophosphate bioactive glass: in-vitro dissolution and cytotoxicity

A. Mishra*[1]; M. Ojansivu[3]; R. Autio[2]; S. Vanhatupa[1]; S. Miettinen[1]; J. Massera[1]

1. Tampere University, Faculty of Medicine and Health Technology and BioMediTech Institute, Finland
2. Tampere University, Faculty of Social Sciences and BioMediTech Institute, Finland
3. Karolinska Institutet, Department of Medical Biochemistry and Biophysics (MBB), Sweden

Despite the tremendous clinical results obtained using silicate bioactive glasses, some drawbacks have been pointed out: 1) their non-congruent dissolution leads to glass remnants, even 14 years post-surgery and 2) the narrow hot forming domain inhibits particle sintering or fiber drawing without adverse crystallization. Phosphate glasses are considered to be promising substitute for the typical silicate glasses. However, their rapid dissolution often leads to poor cell attachment. Furthermore, cells suffer initially, due to the fast glass dissolution, and only proliferated once the reactive surface layer was firmly bonded to the glass. Thus, new borophosphate glasses were processed to overcome the fast dissolution rate of metaphosphate glasses, while maintaining a wide hot forming domain. These glasses, with general composition xMO + (100-x) ($47.5P_2O_5$ + $2.5B_2O_3$ + $10Na_2O$ + 20CaO + 20SrO) were doped with metal ions having therapeutic interest (MO = CuO, Ag_2O and CeO_2). Apart from a wide hot forming domain, they exhibited promising in-vitro dissolution properties, in TRIS buffer solution and SBF. Human adipose stem cells (hASC) were cultured in media enriched with glass extract (undiluted, 1:10 and 1:100). Cytotoxicity of the glass extracts was assessed with LDH assay to further understand the impact of the doped metallic ions on cell survival.

2:30 PM

(ICG-SIV-041-2019) In vitro activity assessment of novel silicon oxycarbide-based bioactive glasses for bone regeneration

M. Arango-Ospina*[1]; F. Xie[2]; E. Ionescu[2]; I. Gonzalo-Juan[2]; R. Riedel[2]; A. R. Boccaccini[1]

1. University of Erlangen-Nürnberg, Institute of Biomaterials, Germany
2. Technical University Darmstadt, Germany

Since the discovery of 45S5 Bioglass® by Hench et al. the application of bioactive glasses (BGs) for bone repair and reconstruction has been promising. The incorporation of therapeutic ions, such as Sr, Zn, Mg and B, in the composition of BGs is of great interest to improve the intrinsic properties of this material especially due to their stimulating effect on osteogenesis and angiogenesis. Novel BGs based on silicon oxycarbide are being developed as an alternative to melt-derived silicate BGs because they are able to retain their amorphous structure at high temperatures. In this study, we report the bioactivity and cytotoxicity of silicon oxycarbide-based BG doped with Ca and B (SiCaBOC). The glasses were prepared through thermal conversion (pyrolysis) of a polymeric single-source precursor. In vitro bioactivity of the prepared SiCaBOC was assessed in simulated body fluid (SBF) over a period of 2 weeks, confirming the formation of a hydroxycarbonate apatite layer in less than 1 week of immersion by means of scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). Furthermore,

indirect cell studies were performed using mouse embryonic fibroblasts (MEFs). Cell proliferation results indicated the non-toxicity of the samples after 6 days culture with MEFs.

2:50 PM

(ICG-SIV-042-2019) Advanced Investigation on the Effect of Barium Substitution on In-vitro / In-vivo Bioactivity and Biocompatibility of 45S5 Bioglass®

S. P. Singh*[1]; H. Tripathi[1]; S. K. Arepalli[1]; P. Paliwal[1]

1. Indian Institute of Technology - Banaras Hindu University, India

The objective of the work is to enhance the properties of 45S5 Bioglass® without major alteration of the base glass composition. The bioactive glass system SiO_2–Na_2O–CaO–P_2O_5 was substituted with BaO in small quantities at the cost of silica and prepared using melt-quench route at 1400°C in air. The in vitro bioactivity in SBF had shown the formation of HCA layer on the surface of the bioactive glasses as confirmed by SEM and EDS analysis. Moreover, the barium bioactive glass samples had shown superior bioactivity and higher HCA formation with reference to control sample. The in vitro cell culture studies had shown that substitution of barium in the bioactive glass was compatible with human osteosarcoma U2OS cell. It was also observed that the cells were proliferating. The U2OS cells were found to be significantly attached and grown on the blocks of barium contained glasses as compared to control sample. Moreover the barium contained glasses have not caused for the blood hemolysis of RBC and they were also compatible with WBC. Barium contained BG had shown more active bone healing in vivo than base glass as confirmed by X-ray radiography. In view of the above results, the prepared barium contained bioactive glasses are promising for bone substitutes in biomedical applications.

3:30 PM

(ICG-SIV-043-2019) The effect of Al_2O_3:SiO_2 ratio on the properties of aluminosilicate glass for dental cement application

E. E. Meechoowas*[1]

1. Department of Science Service, Division of Engineering Materials, Thailand

The aluminosilicate glasses for dental cement application were prepared by melting technique. The glass batches composed of Al_2O_3, SiO_2, CaF, $CaCO_3$, Na_2PO_4 and $BaCO_3$. The Al_2O_3:SiO_2 ratio was between 0.57 to 0.76. The batches were melted at 1400°C for 3 hour in an electrical furnace and annealed at 450°C. The glasses were pulverized to powder using the zirconium high speed ball mill to control the particle size to match the commercial dental cement powder. The chemical composition, microstructure and particle size distribution of the powders were characterized. The setting time and mechanical properties were tested according to the dental application ISO 9917 adding with fluoride release compare with the commercial dental cement. The result found that the setting time and mechanical properties depended on the Al_2O_3:SiO_2 ratio. The setting time and mechanical properties increased with increasing Al_2O_3 content. The results tested according to ISO 9917 showed the properties similar to the commercial dental cement. In addition, the results of fluoride release after 4 days was similar to the commercials product. The output of the study exhibited the setting time and mechanical properties of the aluminosilicate glasses that suitable for dental application can be controlled.

3:50 PM

(ICG-SIV-044-2019) Flexural strength testing in lithium disilicate glass-ceramics

X. Xu*[1]; A. Goel[1]

1. Rutgers University, MSE, USA

Glass-ceramics in the Li_2O-SiO_2 system are well-known for their application in the field of dentistry. In order to be approved by the US Food & Drug Authority (FDA), a dental ceramic has to meet a particular flexural strength value as suggested by ISO 6872. The ISO 6872 standard has been revised three times since its inception in 1984 with its latest edition published in 2015. In particular, the protocols for the sample preparation and measurement for three-point flexural strength measurement have been significantly revised between the 1995 vs. 2008 version of the standard, for example, chamfering of specimens. Further, the literature reveals that the researchers deviate from the protocols mentioned in the ISO6972 and apply a thin adhesive film or tape on the compressive side of the specimen while measuring the flexural strength. The impact of these modifications on the flexural strength of glass-ceramics has not been well documented or published in the literature. In the present study, we aim to understand the impact of experimental protocols (polishing, chamfering and tape) on the three-point flexural strength of lithium disilicate glass-ceramics. The results will be discussed in the presentation.

4:10 PM

(ICG-SIV-045-2019) Electrical Filed Assisted Ion Exchange for Dental applications

A. Alzahrani*[1]; G. Pintori[2]; V. M. Sglavo[2]

1. Taif University, College of Dentistry, Dental Physical Sciences and Technology Unit, Saudi Arabia
2. University of Trento, Department of Industrial Engineering, Italy

The advantages of ion exchange are many, one of which can be linked to the treatment of dental glass-ceramics margin areas which is believed to be most vulnerable to crack initiation, as well as opening the possibilities of preparing thin full glass-ceramic restorations without the need of invasive tooth preparation. The aims of the study were to compare Electrical Filed-Assisted Ion Exchange with conventional ion exchange method for a newly developed Dental glass-ceramic. Novel multicomponent glass system was synthesized using melt-quench method and then prepared into glass-ceramics specimens via powder sintering route. The mechanical properties of the investigated material were evaluated using the biaxial flexural strength (BFS) test and Weibull modulus (m) analysis. Compacted discs were sintered into test specimens, polished and then tested for BFS according to the dental ceramics ISO 6872:2015. The BFS testes and data analysis were carried on three groups: a) before ion exchange, b) after conventional ion exchange, and c) after Electrical Filed Assisted Ion Exchange. The ion exchange process was carried out in molten potassium nitrite bath and the penetration depth was determinate using energy dispersion x-ray spectroscopy (EDXS). This presentation will further discuss, the effect of Electrical Filed on ion exchange behaviours of the newly developed dental glass-ceramics.

Session 3: Nonlinear Photonics

Room: Beacon Hill (4th floor)
Session Chair: Hongtao Lin, Massachusetts Institute of Technology

8:00 AM

(ICG-SIV-046-2019) Signal processing based on optoacoustic interactions in chalcogenide waveguides (Invited)

M. Merklein*[1]

1. The University of Sydney, Australia

Integrated chalcogenide waveguides are a promising platform for optoacoustic signal processing as these waveguides can have a large refractive index and are at the same time mechanically soft. Hence, both acoustic and optical modes are well guided and can strongly interact. In this talk, we show that the strong interaction between acoustic and optical waves in chalcogenide waveguides enables unique signal processing capabilities for optical, as well as microwave photonic signals, otherwise hard to achieve in a purely optical system. In particular, we will show how coherent acoustic waves can be used to store optical data pulses, alter the phase of a microwave photonic signal or identify unknown radiofrequency signals.

8:30 AM

(ICG-SIV-047-2019) Chip-scale broadband spectroscopic chemical sensing using chalcogenide glass integrated supercontinuum source

Q. Du*[1]; Z. Luo[2]; H. Zhong[3]; Y. Zhang[1]; Y. Huang[2]; T. Du[2]; W. Zhang[4]; T. Gu[1]; J. Hu[1]

1. Massachusetts Institute of Technology, Materials Science and Engineering, USA
2. Xiamen University, China
3. Zhejiang University, China
4. Ningbo University, China

On-chip spectroscopic sensors have attracted increasing attention for portable and field-deployable chemical detection applications. So far, these sensors largely rely on benchtop tunable lasers for spectroscopic interrogation. Large footprint and mechanical fragility of the sources, however, preclude compact sensing system integration. In this talk, we address the challenge through demonstrating, for the first time, a supercontinuum source integrated on-chip spectroscopic sensor, where we leverage nonlinear $Ge_{22}Sb_{18}Se_{60}$ chalcogenide glass waveguides as a unified platform for both broadband supercontinuum generation and chemical detection. A home-built, palm-sized femtosecond laser centering at 1560 nm wavelength was used as the pumping source. Sensing capability of the system was validated through quantifying the optical absorption of chloroform solutions at 1695 nm. This work represents an important step towards realizing a miniaturized spectroscopic sensing system based on photonic chips.

8:50 AM

(ICG-SIV-048-2019) Dispersion engineering of highly nonlinear chalcogenide waveguides for high efficiency four-wave mixing

B. Zhang*[1]; D. Xia[1]; P. Zeng[1]; Z. Yang[1]; J. Song[1]; M. Zhang[1]; Z. Li[1]

1. Key Laboratory of Optoelectronic Materials and Technologies, School of Electrical and Information Technology, China

Kerr effects enable various nonlinear applications including optical signal processing, metrology, multi-wavelength lasers, and spectroscopy. For enabling high efficiency four-wave mixing effects, desirable material properties for all-optical nonlinear chips are a high Kerr nonlinearity and low linear and nonlinear losses. Chalcogenide (ChG) material offers a high linear and nonlinear properties, and low two photon absorption and three photon absorption effects. Furthermore, it has the ability to engineer the material nonlinear property by varying the alloy composition. Recently, based on facility platform for device fabrication and integration at Sun Yat-sen university, we have fabricated a series of highly nonlinear chalcogenide planar waveguides which are well dispersion engineered to have anomalous dispersion in the telecommunication wavelength range(Fig 1). The ChG waveguides with SiO_2 cladding have a low propagation loss of less than 0.2 dB/cm using electron beam lithography followed by plasma dry etching. We have performed a four-wave mixing experiment on these ChG waveguides and observed a high four-wave mixing conversion efficiency.

9:10 AM

(ICG-SIV-049-2019) Efficient BSBS in Chalcogenide Photonic Chip

J. Song*[1]; Y. Wang[2]; B. Zhang[1]; Z. Yang[1]; P. Zeng[1]; D. Xia[1]; Y. Zhu[1]; L. Yi[2]; Z. Li[1]

1. Key Laboratory of Optoelectronic Materials and Technologies, China
2. state Key Lab of Advanced Communication Systems and Networks, China

Stimulated Brillouin scattering(SBS) comes from the interaction between optical mode and acoustic mode within a highly nonlinear materials, which has widely used in integrated optics. Chalcogenide (ChG) glass, which has both large SBS gain coefficient and Kerr nonlinearity, is a potential platform for exploiting SBS at the chip scale. Recently, we have fabricated an As_2S_3 waveguide with a high density SiO_2 cladding using EBL and RIE followed by ICP-CVD deposition based on facility platform for device fabrication and integration at Sun Yat-sen university. Here, a ChG spiral chip is composed of a As_2S_3 core of 21 cm in length and 2x0.8 μm^2 in cross section area and a Silica cladding of 560nm in thickness. The propagation loss is as low as 0.15 dB/cm. We characterize SBS gain in this ChG chip using pump-probe techniques. The high backward SBS (BSBS) gain in the chip has been observed by reducing loss and improving acousto-optic overlap with this small effective mode area. The measured Brillouin shift of 7.43 GHz and a probe gain of 45 dB were obtained at a CW pump power of ~2 W. It makes possible that Brillouin-based application can be implemented and harnessed on integrated and compact devices.

Session 3: Emerging Technologies II

Room: Beacon Hill (4th floor)

Session Chair: Tian Gu, Massachusetts Institute of Technology

10:00 AM

(ICG-SIV-050-2019) Chalcogenide materials with tailored optical function for on-chip integrated photonics (Invited)

K. Richardson*[1]; M. Kang[1]; T. Malendevych[1]; G. Yin[2]; J. Hu[2]; M. Richardson[1]; I. Mingareev[3]; B. Sohn[4]; D. T. Tan[4]; I. Murray[5]

1. University of Central Florida, CREOL, College of Optics & Photonics, USA
2. Massachusetts Institute of Technology, USA
3. Florida Institute of Technology, USA
4. Singapore University of Technology and Design, Singapore
5. BAE Systems, USA

The creation of new optical components with unique function or enhanced performance requires an understanding of composition-dependent properties and application-specific performance limitations, as well as an appreciation of processing protocols when materials are deployed in formats other than as bulk materials. We describe how multi-material interactions seen in integrated photonic structures can significantly influence resulting optical quality (i.e., loss, scattering, coupling) and ultimate in-use environmental stability (driven by non-ambient thermal stability and potential thermal mechanical mismatch); for example, when chalcogenide glass (ChG) or glass ceramic materials are formed into planar films and must co-exist with other materials and components. We discuss applications of ChG materials in planar optical components and challenges realized when processing in thin film form, performance variation in terms of processing protocols, and how compositional modification can accommodate and mitigate adverse material attributes. We also include examples of linear and nonlinear optical properties of films and discuss how deposition strategies influence photo-induced phase change attributes and how as-formed film properties evolve upon irradiation and/or ceramization.

10:30 AM

(ICG-SIV-051-2019) Phase Change Photonics for Emerging Computing (Invited)

H. Bhaskaran*[1]; C. Rios[1]; N. Youngblood[1]; Z. Cheng[1]; N. Farmakidis[1]; J. Tan[1]; X. Li[1]; W. H. Pernice[2]

1. University of Oxford, United Kingdom
2. University of Munster, Germany

In this talk, I shall explore work by my doctoral, postdoctoral and other senior collaborators in the use of phase change materials as active materials in photonics. Silicon has been dominant in the field of integrated circuits as it is a material whose functionality can be tuned by differential doping - lending itself as a leading functional material. The quest for a similar set of functional photonic materials is well underway and phase change naterials are one of the most promising class of such materials, having already been

commercialized in both optical storage disks as well as in electronic phase change memories. I shall talk about our recent work in exploting many of the advantages of such materials as well as overcoming some of the inherent limitations of these materials.

11:00 AM

(ICG-SIV-052-2019) Demonstration of dimensional control and stabilization of second harmonic electro-optical response in chalcogenide glasses

M. Dussauze*[1]; A. Lepicard[1]; V. Rodriguez[1]; K. Richardson[2]; F. Adamietz[1]

1. CNRS / Université de Bordeaux, France
2. University of Central Florida, CREOL, USA

Second-order optical susceptibility, $\chi^{(2)}$, has been induced in thermally poled chalcogenide glasses, doped with varying levels of sodium. Using alkali-doped chalcogenide glasses, the Second Harmonic Generation (SHG) capability is retained for over a year whereas in alkali-free glasses it disappears in days. The enhanced stability is attributed to a stabilization of the space charge through structural re-arrangements. Polarization-resolved SHG shows that the induced electric field has components in three spatial directions, all with varying extents of stability. Using structured electrodes, we demonstrate the ability to control the various electric field components' geometry, location and stability to realize a long-lived, nonlinear grating in an alkali-doped chalcogenide glass.

11:20 AM

(ICG-SIV-053-2019) Large-Scale Electrical Switching for Optical Phase Change Materials Based Nonvolatile Photonics

Y. Zhang*[1]; C. Ríos[1]; S. Deckoff-Jones[1]; H. Lin[2]; J. B. Chou[3]; J. Liang[1]; Z. Fang[1]; F. Yang[1]; H. Wang[4]; M. Shalaginov[1]; C. Roberts[3]; C. Goncalves[5]; V. Liberman[3]; T. Gu[1]; J. Kong[4]; K. Richardson[2]; J. Hu[1]

1. Massachusetts Institute of Technology, Materials Science and Engineering, USA
2. Zhejiang University, College of Information Science & Electronic Engineering, China
3. Massachusetts Institute of Technology, Lincoln Laboratory, USA
4. Massachusetts Institute of Technology, Electrical Engineering & Computer Science, USA
5. University of Central Florida, The College of Optics & Photonics, Department of Materials Science and Engineering, USA

The integration of optical phase change materials (O-PCMs) into photonic devices enables a plethora of photonic devices with a long-sought functionality: nonvolatile reconfiguration. Examples include nonvolatile photonic switches, multilevel memories, reconfigurable metasurfaces and neuromorphic photonics. Most of the existing switching methods, however, are based on optical absorption induced heating, which is very difficult to scale up. Therefore a robust electrical switching method is desired. Though current-driven switching method has been widely used in electronic memory applications, it is only suitable for small-scale switching with O-PCM width around tens of nms, far from enough for most photonic applications. Here we report large-scale electrical switching methods for O-PCMs employing conductive microheaters. We investigate three complementary material choices for the microheaters, namely metals, graphene and doped silicon. Metallic microheaters provide robust switching performances and are used for reconfigurable metasurfaces and filters. For photonic integrated circuit applications, graphene and doped silicon are used for improving optical performances by reducing optical absorptions from the microheaters. This microheater-based large-scale electrical switching method paves the way for scaling up individual O-PCM devices into nonvolatile photonic systems.

11:40 AM

(ICG-SIV-054-2019) Chalcogenide Glass Waveguide-integrated 2D Tellurium for Optoelectronics

S. Deckoff-Jones*[1]; H. Lin[2]; S. Serna[1]; J. Hu[1]

1. MIT, Materials Science and Engineering, USA
2. Zhejiang University, China

Layered van der Waals (2D) materials have demonstrated huge potential for photonic devices with their varied and tunable optical properties. Furthermore, they often possess physical properties that are lacked by traditional integrated photonic platforms, such as silicon. One new promising material is 2D tellurium, which not only has a 0.35eV bandgap in the mid-IR, but also has exceptional nonlinear properties. Chalcogenide glasses are an ideal waveguiding medium for 2D tellurium because of their transparency in the mid-IR and their low thermal budget, allowing them to be processed at low temperatures without damaging the 2D tellurium. Additionally, because 2D tellurium is strongly anisotropic in plane, the chalcogenide glass waveguides can be patterned along the different crystalline axis of the tellurium to maximize device performance. By leveraging chalcogenide glasses as a light guiding medium, 2D tellurium can be used to realize high performance optoelectronic devices for the mid-IR.

Session 4: Glass in Sensor Technology I

Room: Beacon Hill (4th floor)
Session Chair: Younès Messaddeq, Université Laval

1:20 PM

(ICG-SIV-055-2019) Improving the accuracy of optical fiber sensors by better glass and material science (Invited)

J. Albert*[1]; T. Gang[2]; M. Hu[2]

1. Carleton University, Canada
2. Northwest University, Physics, China

Multimode propagation in nominally single mode structures is opening up new opportunities in high resolution sensing and high bandwidth communication systems, but the propagating mode properties of some of these structures have only recently been the object of detailed studies. In the work to be presented, specially designed fiber grating devices allow for the precise measurements of the effective indices of hundreds of cladding modes with varying radial and azimuthal mode numbers, as well as different dominant polarization states. But such measurements reveal that the refractive index profile and modal dispersion of core- and cladding- guided modes need small corrections from accepted values to fit the experimental data. Methods will be described to carry out such corrections from a "canonical" initial measurement of a fiber in controlled conditions and therefore to generate a better starting point to design and fabricate light manipulating devices with high precision in the fiber thus characterized. A secondary outcome from this approach is the ability to measure the optical properties of anisotropic nanoscale dielectric and metallic thin films on fibers.

1:50 PM

(ICG-SIV-056-2019) Backscattered Waveguide Fluorescence Application of Glass

N. Subbaiyan*[1]; J. S. King[1]

1. Corning Incorporated, Corning Technology Center - Silicon Valley, USA

Optical planar waveguides using glass substrates has never been more interesting than now for integrated applications like photonic integrated circuits, on-chip devices, fiber couplers, sensors and bioreactors. Planar waveguiding components attached directly to the glass in tandem configurations are reported rarely in backscattering mode for plain glass. Introduction of nanoporosity on the glass enhances the backscattering of the waveguided light with little or less outcoupling. In this presentation we demonstrate the application of

the nanoporous glass suface using backscattered waveguide. Also we present having a nanoporous glass surface showed enhanced fluorescence compared to plain glass. Based on this fluorescence enhancement concept we built a simple waveguide based sensor in glass using tandem configuration of the components. The demonstrated wave guided oxygen gas sensor showed better performance and had more oxygen quenching sites available at the nanoporous glass surface compared to plain surface due to the increase in surface area. We belive this integration approach could spur new way to build efficient sensor using glass.

2:10 PM

(ICG-SIV-057-2019) Rare earth doped fluoride-phosphate glasses for high power radiation detection

I. Carvalho Pinto[1]; G. Galleani[1]; A. S. de Camargo*[1]

1. Physics Institute of Sao Carlos, University of Sao Paulo, Brazil

Rare-earth ions (RE) doped fluoride-phosphate (FP) glasses are well-established materials for lasers and other photonic device application. They combine the desirable optical properties of fluoride glasses with the better glass forming ability of the phosphates, while the rich energy level structure of RE allows efficient frequency conversion for usage as potential high power radiation detectors. The glasses have low refractive indices, long-term radiation resistance to high-energy radiation and wide intrinsic transmission range from ~160 – 4000 nm. Of special interest is the application of FP glasses for detection and sensing of UV and x-ray radiation. Two series of FP glasses with compositions $90(InF_3\text{-}BaF_2\text{-}SrF_2\text{-}ZnF_2)\text{-}10In(PO_3)_3\text{-}zREF_3$, RE = Ce and Eu and $0 \leq z \leq 1.0$, and of $65(NaPO_3\text{-}Ba(PO_3)_2)\text{-}35(MgF_2\text{-}YF_3)\text{-}zREF_3$, RE = Eu and Dy and $0 \leq z \leq 1.0$, have been studied. Besides the convetional characterization, several absorption energy possibilities were verified in the UV region for Eu^{3+} and Dy^{3+} doped samples. When excited by UV light, the doped glasses present responses at 482, 575 and 664 nm (Dy^{3+}) and 575, 623, 650 and 700 nm (Eu^{3+}). When doped with Ce^{3+}, a broad emission centered at 420 nm is observed. The results show potential application of these glasses studied at LEMAF in IFSC/USP, for the development of high power radiation detectors and sensors.

2:30 PM

(ICG-SIV-058-2019) SERS optical fiber on synthetic optimization, interfacial bonding and electromagnetic field distribution

Y. Long*[1]; H. Li[1]; Z. Du[1]; Z. Liu[2]; Y. Xie[2]

1. Wuhan University of Technology, State Key Laboratory of Silicate Materials for Architectures, China
2. University of California, Department of Materials Science and Engineering, USA

Combination of surface-enhanced Raman scattering (SERS) technique with optical fiber shows high sensitivity and measurement flexibility, especially for in-situ remote detection in confined places. Herein, silver decorated optical fiber is synthesized. A systematic study of reaction solvents, temperature and time on the microstructure and performance is conducted, accompanied by a growth mechanism proposed. The obtained SERS fiber probe shows high sensitivity, good reproducibility and strong interfacial bonding. Moreover, a sensitization process is introduced to enhance the interfacial bonding between optical fiber and silver. Surprisingly, the sensitization process influences the kinetic growth of silver and further improves SERS performance. Further, electromagnetic field (EMF) distribution on SERS fiber facet, which is vital for SERS performance and scientific understanding yet rarely studied, is performed experimentally and theoretically. Based on the results, waveguide propagation modes of optical fiber and localized surface plasmon resonance of SERS materials in combination gives rise to SERS enhancement of SERS fiber probe in a peculiar, concentric EMF decay configuration. This work not only offers a practical way for high performance SERS fiber probe but also details an in-depth understanding of SERS.

2:50 PM

(ICG-SIV-059-2019) Chalcogenide microstructured optical fibers for optical sensing (Invited)

J. Troles*[1]; L. Brilland[2]; M. Meneghetti[1]; R. Troles[2]; C. Boussard-Pledel[1]; B. Bureau[1]; S. Venck[2]; J. Adam[1]

1. University of Rennes 1, France
2. SelenOptics, France

Compared to oxide based glasses, vitreous materials composed of chalcogen elements (S, Se, Te) show large transparency windows in the infrared. Indeed, chalcogenide fibers can be transparent from the visible up to 12-15 μm, depending on their compositions. The IR signatures of most molecules, including biomolecules, are located in this spectral domain, which allows in situ, non-invasive and real-time detection of gaz or organics molecules. In addition, chalcogenide glasses contain large polarisable atoms and external lone electron pairs which induce exceptional non-linear properties. Consequently, the non-linear properties can be 100 or 1000 times as high as the non-linearity of silica. An original way to obtain fibers and single-mode fibers is to design microstructured optical fibers (MOFs). These fibers present unique optical properties thanks to the high degree of freedom in the design of their geometrical structure. In this context, various chalcogenide MOFs operating in the mid-IR range in order to associate the high non-linear properties of these glasses and the original MOF properties. For example, small core fibers have been drawn to enhance the non linearities for generation of supercontinuum sources. On another hand, endlessly single mode fibers and exposed core fibers have been realized for Gaussian beams propagation and mid-IR optical sensors applications respectively.

Session 4: Glass in Sensor Technology II

Room: Beacon Hill (4th floor)
Session Chair: Pierre Lucas, Univ of Arizona

3:40 PM

(ICG-SIV-060-2019) Scalable nano-fabrication of glass-based optical metasurfaces and multimaterial fibers for advanced sensing (Invited)

F. Sorin*[1]

1. EPFL, Switzerland

The dewetting of thin glass films and the thermal drawing of polymer and glass fibers are two seemingly very different processes. They can however both be described for a large part via an interplay between viscosity and surface tension. In this talk, we will first show how we can control the solid-state dewetting of thin, high refractive index optical glass layers to realize a variety of high–quality optical metasurfaces over large-area rigid and soft substrates. We will investigate how the interplay between viscous flow at the nanoscale and surface tension enables to tailor the size and shape of chaclogenide glasses nano-objects and hence control their optical properties. Second, we will present how we can apply similar principles to the process of thermal drawing – the same process used to fabricate optical fibers – to realize multi-material fibers and ribbons with advanced optical and electronic functionalities. We will demonstrate different glass-based 2D nanostructures and fiber architectures for optical, chemical and mechanical sensing.

4:10 PM

(ICG-SIV-061-2019) Mechanical stress-induced luminescence from ZnS:Mn incorporated into glasses

B. So*[1]; Y. Ding[1]; L. Wondraczek[1]

1. University of Jena, Otto Schott Institute of Materials Research, Germany

Mechanoluminescence (ML) is the light emitted under deformation or fracture. It can lead to potential applications in strucutral health monitoring and mechanical sensing. There are many unexploited applications in which the ML material requires embedding in a host

material. Transparent glass provides such a potential host with high elastic modulus, tailorable compressibility and enhanced chemical stability. Here, manganese doped ZnS was prepared by solid-state reaction. The ZnS with zinc-blende and wurtzite structures exhibited photoluminescence at 585 nm from a d-d transition ($^4T_1$-$^6A_1$). Under compression, its mechanoluminescence was obtained at 605 nm. Spectral shift and shape change were observed as compared to the features of photoluminescence. We obtained a mechanoluminescent glass by direct incorporation of manganese-doped ZnS. The doped glass also showed mechanoluminescence under compression.

Session 8: Fundamentals of Nuclear Waste Glass Corrosion I

Room: Whittier (4th floor)
Session Chair: Joseph Ryan, Pacific Northwest National Lab

8:00 AM

(ICG-SIV-062-2019) Atomistic Origin of the Passivation Effect in Hydrated Silicate Glasses

T. Du[1]; H. Li[3]; Q. Zhou[1]; Z. Wang*[1]; G. Sant[1]; J. V. Ryan[2]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA
2. Pacific Northwest National Lab, Energy and Environmental Directorate, USA
3. Harbin Institute of Technology, School of Civil Egnineering, China

When exposed to water, silicate glasses and minerals can form a hydrated gel surface layer concurrent with a decrease in their dissolution kinetics—a phenomenon known as the "passivation effect." However, the atomic-scale origin of such passivation remains debated. Here, based on reactive molecular dynamics simulations, we investigate the hydration of a series of modified borosilicate glasses with varying compositions. We show that, upon the aging of the gel, the passivation effect manifests itself as a drop in hydrogen mobility. Nevertheless, only select glass compositions are found to exhibit some passivation. Based on these results, we demonstrate that the passivation effect cannot be solely explained by the repolymerization of the hydrated gel upon aging. Rather, we establish that the propensity for passivation is intrinsically governed by the reorganization of the medium-range order structure of the gel upon aging and, specifically, the formation of small silicate rings that hinder water mobility. These results will shed light on the understanding of stage II of the dissolution of nuclear waste glass.

8:20 AM

(ICG-SIV-063-2019) Alteration glass layer modeling by molecular dynamics simulations (Invited)

T. Ohkubo*[1]

1. Chiba University, Faculty of Engineering, Japan

The porous structure and mass transport characteristics of alteration layer on the glass surface were investigated by molecular dynamics simulations. Disordered silicate porous media were constructed to mimic the dissolution behavior of an alkali aluminoborosilicate glass, i.e., soluble Na and B were removed from the bulk glass, and then water molecules and Na were introduced into the pores to provide a complex porous structure filled with water. This modeling approach revealed large surface areas of disordered porous media. In addition, a number of isolated water molecules were observed in the pores, despite accessible porous connectivity. As the fraction of mobile water was approximately 1%, the main water dynamics corresponded to vibrational motion in a confined space. This significantly reduced water mobility was due to strong hydrogen-bonding water-surface interactions resulting from the large surface area. This original approach provides a method for predicting the porous structure and water transport characteristics of disordered silicate porous media. We will also discuss compositional dependence of the porous structure and mass transport properties. anions. This function may induce glass-forming for lithium thiophosphate.

8:50 AM

(ICG-SIV-064-2019) Modelling and experimental study of SON68 glass dissolution in KOH solution at pH 13.5 and 30 °C with three SA/V ratios

S. Liu*[1]; K. Ferrand[1]; K. Lemmens[1]

1. SCK-CEN, Chemistry, Belgium

Short-term experiments with SON68 glass dissolution in KOH solution, at 30 °C and pH 13.5 were carried out at three SA/V ratios, 2450, 4900 and 8050 m^{-1}. Models based on silicon diffusion controlled congruent dissolution of glass components were fitted to the measured solution concentrations of major elements, such as B, Mo, Al and Si from the glass. The modelling results agree very well with the experimental results until 25 days, but deviate from the experimental results when extrapolated to results from 154 days, possibly due to Al incorporation into glass surface to form a protective aluminosilicate surface layer. Depending on the assumptions made for Si concentrations in the surface layer and at the interface between the solution and the glass, the fitted Si diffusion coefficients differ by several orders of magnitude. The results show that when applying a model based on Si diffusion for glass dissolution, Si concentration at the interface between the solution and the glass and within the glass are crucial in determining Si diffusion coefficient. Also glass dissolution models based on a single set of time independent parameters are not enough, as passivating properties of the gel or surface layer evolves with time.

9:10 AM

(ICG-SIV-065-2019) Simulation of silicate gel structures found in Nuclear Waste Glasses using reactive Molecular Dynamics force fields

T. S. Mahadevan*[1]; J. Du[1]

1. University of North Texas, Materials Science and Engineering, USA

Nuclear waste glasses interact with water to produce gel structures of amorphous silicates. The structure and reactions in these porous gels determine the corrosion resistance and durability of the glass. Molecular Dynamics(MD) simulation of these gel structures need to use reactive force fields to properly simulate the chemical reactions in these gels. We use one such reactive potential and demonstrate some of the parameter sets that we developed for simulation multicomponent glasses. Experimentally, the silicate gel structures are characterized by studying the pore fraction, and size distribution. In MD simulations, the gel structures can be generated by several methods that correspond to different physical processes in gel formation. In this study, we optimize the processing parameters for generation of gel structures and study the correlation between the final pore structures and these process parameters. Earlier studies had indicated that cylindrical pores with a diameter of less than 2nm play a major role in slowing down the diffusion of water molecules and hence serve to reduce the reaction rate for diffusion controlled processes. Thus, we recreate gel structures that correspond to experimentally generated gels in terms of pore size distribution and we study the diffusivities of water in these structures.

Session 8: Fundamentals of Nuclear Waste Glass Corrosion II

Room: Whittier (4th floor)

Session Chairs: Takahiro Ohkubo, Chiba University; Stephane Gin, CEA

10:00 AM

(ICG-SIV-066-2019) Toward an Understanding of Altered Layer, Growth, and Transformation at the Glass-Fluid Interface (Invited)

E. M. Pierce*[1]

1. Oak Ridge National Lab, Environmental Sciences Division, USA

Silicate glass is a metastable and durable solid that has application to a number of health, energy, and environmental challenges (e.g., tissue engineering, fiber optics, and nuclear waste storage). Although glass is sufficiently resistant to weathering for the service life of most industrial applications, if allowed to react with aqueous fluid over geologic time scales, an altered layer (amorphous hydrated layer and crystalline reaction products) forms on the surface. Recent advances in nanoscale analytical techniques—such as time-of-flight secondary ion mass spectrometry (ToF SIMS) along with isotope exchange experiments, liquid-cell transmission electron microscopy (LCTEM), and scanning TEM electron energy loss spectroscopy (STEM-EELS)—are providing unprecedented insight into the physico-chemical properties that control altered layer formation. In this presentation we will briefly discuss recent advances, highlight the remaining knowledge gaps, and describe new techniques that are being employed to resolve these knowledge gaps.

10:30 AM

(ICG-SIV-067-2019) How glass composition variations impact passivation properties of surface layers formed on borosilicate glasses?

S. Gin*[1]; P. Jollivet[1]; E. Chauvet[2]; Y. De Puydt[2]

1. CEA, DE2D/SEVT/LCLT, France
2. Tescan Analytics, France

It is acknowledged that glass dissolution kinetics are strongly impacted by small compositional variations, but little is known on how these variations affect both the mechanisms of formation and the passivation properties of the surface layers. To address this question, we have studied six simple and two complex borosilicate glasses of interest for the confinement of high-level nuclear wastes. In this presentation, we show and discuss results from long-term static experiments (up to 26 yr), as well as short-term tests conducted in solutions spiked with Si-29 followed by tracing experiment in water spiked with O-18 and solid characterization by ToF-SIMS depth profiling, an isotope sensitive analytical technique. For the first time we establish a strong positive correlation between the residual dissolution rate of the simple glasses and the water content in the gel. By comparing the behavior of the different glasses we inferred the role of elements such as Al, Ca, Zr, and Ce on the dynamics of formation of the gels.

10:50 AM

(ICG-SIV-068-2019) Dissolution Kinetics of Ternary Calcium Aluminosilicate (Ca-Al-Si) Glasses at 75 ºC, pH = 7: Effects of Glass Chemical Composition on Rates

J. P. Icenhower*[1]; H. McMahon[1]; R. Youngman[1]; N. J. Smith[2]

1. Corning Incorporated, Characterization Sciences, USA
2. Corning Incorporated, Fundamental Sciences, USA

Despite decades of experiments, the link between glass structure and dissolution kinetics remains elusive. We present dissolution rate data for a range of glass chemical compositions in the ternary system Ca-Al-Si obtained from experiments conducted at 75 °C, pH = 7. Experiments were carried out using a Single-Pass Flow-Through (SPFT) system over a flow-rate (q) to surface area (S) ratio interval. Rates were quantified from the release of Si from glass into solution. Two sets of glass compositions were tested. In Set 1, Si varied from 40 to 80 mol.%, but the ratio of Ca to Al remained fixed at one. The purpose of testing these glass compositions was to elucidate the controls of silica on network hydrolysis. In Set 2, the Al concentration remained constant (10 mol.%) while the ratio of Ca to Al increased. The objective for testing this series was to understand the effects of non-bridging oxygens (NBO's) on chemical durability in a systematic fashion. Glass structure will be characterized by Nuclear Magnetic Resonance (NMR) methods with the focus on Al coordination. In addition, experimental run products will be examined by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Rate data for the two sets of glass compositions will be discussed in terms of models for network connectivity and percent NBO's.

11:10 AM

(ICG-SIV-069-2019) Structure-durability relationship of UK high level waste glass

A. J. Fisher*[1]; B. Walkley[1]; J. T. Radford[1]; N. C. Hyatt[1]; R. J. Hand[1]; C. L. Corkhill[1]

1. University of Sheffield, Material Science and Engineering, United Kingdom

Insight is given into the dissolution behaviour of two UK vitrified waste-types (MW and ZnCa MW) in geological disposal environments, such as envisioned temperature and groundwater compositions, and in the presence of canister corrosion near-field material. This has comprised of; 1) standard SPFT, PCT-B and MCC-1 investigations and 2) a freshly proposed cyclic vapour-groundwater dissolution methodology. These procedures were conducted on several variants of MW and ZnCa MW, whereby the base glass compositional ratios and waste loading were sequentially modified. Results also highlight the structure-durability relationship of the pristine and altered base glass provided by NMR, Raman, XRD and SEM. This investigation aims to compare both waste-types and generate data relevant to geological disposal performance assessments.

11:30 AM

(ICG-SIV-070-2019) Degradation Tests on Developmental Iron Phosphate Waste Form for Salt Waste

W. Ebert*[1]; B. Riley[2]; S. Frank[3]

1. Argonne National Lab, USA
2. Pacific Northwest National Lab, USA
3. Idaho National Lab, USA

We are evaluating the capacity of iron phosphate materials to immobilize salt waste from electrochemical treatment of nuclear fuel. A two-step process was used in which the salt was first dehalogenated by reaction with ammonium dihydrogen phosphate (ADP) at about 400 C to evolve and capture ammonium chloride, then iron oxide was added to the residual solids and the mixture heated to 1050 C for about 1 hour to produce an iron phosphate waste form. The chemical durabilities of six materials made with different iron oxide:ADP:salt ratios were measured using a modified ASTM C1308 test method to evaluate the process efficacy and effects of the Cl/P and Fe/P ratios on the dehalogenation efficiency and chemical durability based on the releases of chloride and key salt cations Cs, K, and Sr, respectively. Those results showed salt in mixtures with Cl/P ratios less than 1.0 was almost completely dehalogenated during the processing, and products from mixtures with Cl/P ratios between about 0.66 and 0.99 and Fe/P ratios between about 0.45 and 0.90 were all durable. SEM and XRD analyses indicated various alkali iron phosphate phases (e.g., $LiFePO_4$) formed within a glassy matrix in most products, increasing with the Fe/P ratio, but most of the Cs and Sr reported to the iron phosphate glass phase in all products. On-going optimization and comparisons with other waste form materials will be discussed.

11:50 AM

(ICG-SIV-071-2019) Dissolution of network formers from a model nuclear waste glass at the early stage of aqueous corrosion in initially silica-saturated solution

D. Ngo*[1]; H. Liu[1]; H. Kaya[2]; Z. Chen[1]; S. H. Kim[1]

1. Pennsylvania State University, Chemical Engineering, USA
2. Pennsylvania State University, Materials Science and Engineering, USA

Glass corrosion is a serious problem, especially when glass is used as a host matrix for radioactive nuclear waste. Understanding glass corrosion is therefore critically important to prevent it and to design better corrosion resistant glasses. The corrosion of glass in stage II has been studied with the assumption that no dissolution of silicate network would occur in silica saturated solutions. In this study, surface analysis techniques such as low energy ion scattering (LEIS), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) were used to study a model nuclear waste glass that was corroded in silica saturated solutions. The results from LEIS and XPS show an enrichment of zirconium on glass surface while AFM reveals a stochastic dissolution of glass surface. The study shows that silicate network still dissolves even under silica saturated condition and the long-held assumption of no network dissolution in this condition should be revisited.

Session 8: Fundamentals of Nuclear Waste Glass Corrosion III

Room: Whittier (4th floor)

Session Chairs: Eric Pierce, Oak Ridge National Lab; Robert Schaut, Corning Incorporated

1:20 PM

(ICG-SIV-072-2019) Modeling the morphological evolution of glass in aqueous environments

J. V. Ryan*[1]

1. Pacific Northwest National Laboratory, USA

Transport control, whether in the form of ion exchange, diffusion through a passivating layer, or the movement of rate-limiting ions through tortuous pore structures, has been invoked in the modeling of glass corrosion in aqueous environments for decades. Despite this longevity, there has been limited evidence regarding the detailed manner in which these mechanisms impact the conversion of glass. Further, although some existing transport-based models predict the boron solution concentration with reasonable accuracy, they do not predict the formation of alteration layers and often are very poor at predicting the concentrations of other ions in solution. In this talk, we show how the mechanism of morphological evolution and, in particular, the limitations in transport inherent in the model can account for the dynamic structures and solution responses seen in the study of glass corrosion.

1:40 PM

(ICG-SIV-073-2019) Influence of Tris buffer solution chemistry upon dissolution behavior of silicate-based glasses with varied B_2O_3/Al_2O_3 ratio

N. Stone-Weiss*[1]; N. J. Smith[2]; R. Youngman[2]; E. M. Pierce[3]; A. Goel[1]

1. Rutgers University, Materials Science and Engineering, USA
2. Corning Incorporated, Science and Technology Division, USA
3. Oak Ridge National Lab, Environmental Sciences Division, USA

The influence of pH on the dissolution kinetics and congruency of release in borosilicate and aluminosilicate glasses is well reported in literature. In order to maintain a constant pH in solution during the course of experiments, Tris(hydroxymethyl)aminomethane (commonly referred to as Tris)—in combination with HCl or HNO_3—is a widely used buffer system to study glass corrosion in the pH 7-9 range. However, Tris tends to form complexes with boron in some cases, which can considerably impact the dissolution kinetics of borosilicate glasses. Here, we investigate the influence Tris in solution has upon dissolution behavior of silicate glasses with varied B_2O_3/Al_2O_3 ratio—extending from aluminosilicate to borosilicate endmembers in the sodium aluminoborosilicate space. Experiments were performed in pH 7-9 static media, with the intent to understand the impact of (i) Tris-HCl vs. Tris-HNO_3 buffer solutions and (ii) concentration of Tris in solutions, and correspondingly how each affects elemental release and solution complexation behavior. We employed techniques such as ICP-OES and liquid NMR to quantify elemental release and confirm the presence of complexes in solution, with the goal of generating complexation constants and correction factors which may be used to directly quantify the impact that Tris buffer solutions have upon glass dissolution kinetics.

2:00 PM

(ICG-SIV-074-2019) Solution-Mediated Phase Transformations Induced by Varying Leachate Acid-Base Equilibria: Late Stage Nuclear Waste Glass Dissolution

C. M. Jantzen*[1]; W. Ebert[2]

1. Savannah River National Laboratory, USA
2. Argonne National Lab, USA

Accelerated durability tests are performed on nuclear waste glasses in deionized water to facilitate durability modeling over geologic time scales. Alkali and alkaline earth elements ion-exchange (IE) into the leachate and create OH^- (strong bases). Boric, silicic, and meta-aluminic/ferric acids (weak acids) also hydrolize into the leachate. The composition and molecular structure of a glass controls the establishment and distribution of IE and hydrolysis sites and access of water to those sites, which determines the strong base-weak acid ([SB]-[WA]) equilibrium in the leachate during closed batch testing. For glasses high in boron and alumina, but low in alkali, the acid-base equilibrium is neutral, i.e. buffered. For glasses high in alkali, the leachates are enriched in caustic and unbuffered. Excess caustic creates solution-mediated phase transformation of the aluminosilicate-rich gel to zeolite which triggers an undesirable resumption of dissolution at long times. The phase transformation consumes nutrients from the leachate, gel, and glass until the leachate acid-base equilibria returns to neutral. The [SB]-[WA] equilibria determine if the Si/(Si+Al) gel ratio is stoichiometric with the parent glass or not. Modeling is used to understand the processes.

2:20 PM

(ICG-SIV-075-2019) The role of the diffusion for the reaction interface during glass corrosion

C. Lenting*[1]; M. B. Fritzsche[1]; L. Dohmen[2]; T. Geisler[1]

1. University of Bonn, Institute of Geoscience and Meteorology, Germany
2. SCHOTT AG, Germany

In the on-going debate on the fundamental processes governing borosilicate glass corrosion, the role of ion diffusion beyond the reaction front into the pristine glass needs to be addressed. In traditional models, the interdiffusion of hydrous species and readily solvable cations in the glass, generating silanol groups, is accompanied by the solid state reconstruction of the glass network into a silica gel via the polycondensation of the silanol groups. In contrast, in the dissolution-precipitation (ICDP) model, the glass-to-silica transformation does not require interdiffusion processes, but occurs by the congruent dissolution of the glass that is coupled in space and time to the precipitation of the least soluble phase in the interface solution. However, corroded glasses often reveal diffusion gradients across the reaction interface as shown by nano-scale analytical techniques (e.g., ToF-SIMS, NanoSIMS, APT). The question arises whether the (inter) diffusion of hydrous species and cations affects the ICDP reaction itself or is merely a by-product without a rate-controlling effects. To address this question, isotope tracer experiments with a deuterated solution were conducted with a ternary Na borosilicate glass. The formation of surface alteration layers was thereby monitored by real-time in situ Raman spectroscopy to allow APT analysis of the ICDP front at distinct reaction regimes.

2:40 PM

(ICG-SIV-076-2019) Leaching behavior and mechanisms of vitrified forms for low level radioactive solid wastes

M. Kim*[1]; K. Hong[1]; C. Kim[2]; J. Heo[3]

1. Korea Basic Science Institute, Republic of Korea
2. Korea Hydro & Nuclear Power, Central Research Institute, Republic of Korea
3. Pohang University of Science and Technology(POSTECH), Republic of Korea

Leaching behavior and mechanisms of three commercialized glass wasteforms developed to sequester three types of low level solid wastes were investigated: SG glass for resin waste, DG-2 glass for dry active waste, and AG8W1 glass for mixed waste of resin and dry active wastes. After ANS 16.1 leaching experiment, leachability of target nuclides such as Co, Cs, and Sr were all more than 14, which met the requirement of US-Nuclear Regulatory Commission. Holes of diameters 5-10 um remained on the surface of the SG and the AG8W1, and crevices of lengths 10-50 um were observed on the surface of the DG-2 by measuring a SEM. We used glow discharge spectroscopy and time of flight-secondary ion mass spectroscopy to analyze the variations of elemental concentrations of the SG and the DG-2 with depth. For the SG glass, Si and Al are accumulated and Na is depleted up to nearly 1.5 um compared to internal glass. Especially, Ca, Mg and H were highly accumulated inside the hole formed on the surface of the SG. Based on all these data, we suggested each mechanism of the SG and the DG-2 : alkali elements including H would diffuse through hole on the SG glass, on the other hand, most of elements including Si and Al would diffuse through the crevice on the DG-2 glass.

3:00 PM

(ICG-SIV-077-2019) Thermodynamics of Zeolite Precipitation in Stage III Glass Corrosion

B. Zhen[1]; Z. Wang[1]; G. Sant*[1]; J. V. Ryan[2]; M. Bauchy[1]

1. University of California, Los Angeles, USA
2. Pacific Northwest National Lab, USA

Under specific conditions of pH and temperature, nuclear waste immobilization borosilicate glasses may exhibit a sudden acceleration in their corrosion kinetics (stage III) - a behavior that has been associated with the formation of zeolite crystals. However, it remains unclear if the propensity for zeolite precipitation is controlled by its thermodynamics or kinetics. Here, we present a novel Gibbs energy minimization (GEM) framework allowing us to predict the stability fields of zeolitic phases as a function of pH and temperature. Consequences on the modeling of stage III dissolution in nuclear waste immobilization glasses are discussed.

Session 8: Fundamentals of Nuclear Waste Glass Corrosion IV

Room: Whittier (4th floor)
Session Chair: Nicholas Smith, Corning Incorporated

3:40 PM

(ICG-SIV-078-2019) Understanding the Chemical Durability of Glass beyond the Effect of Orthosilicic Acid: The Impact of All Dissolved Glass Components on the Dissolution Rate

J. Neeway*[1]; B. Parruzot[1]; J. V. Crum[1]; J. V. Ryan[1]; M. Asmussen[1]; G. L. Smith[1]; D. J. Swanberg[2]; E. E. Brown[2]; S. Kerisit[1]

1. Pacific Northwest National Lab, USA
2. Washington River Protection Solutions, USA

Before immobilized low-activity waste glass can be disposed at the Hanford site Integrated Disposal Facility (IDF), the U.S. DOE must conduct a performance assessment (PA) that estimates the facility's long-term impacts on the public and the environment. Central to the current IDF PA glass dissolution rate model is a chemical affinity term that relies solely on the orthosilicic acid activity, $a(H_4SiO_4)$. The $a(H_4SiO_4)$ at which the glass reaches a quasi-equilibrium with the solution is denoted as K_g. K_g is commonly determined from a single-pass flow-through (SPFT) test with varying dissolved silica concentration added to the inlet. However, recent SPFT testing on some glasses has shown that many glasses either do not show the expected dependence of the dissolution rate on $a(H_4SiO_4)$ or have K_g values that are inconsistent with the quasi-equilibrium $a(H_4SiO_4)$ determined from static tests. To understand these discrepancies and identify a more defensible approach for determining K_g, the ALTGLASS database was used to evaluate the relationship between glass composition and K_g obtained from static tests, which show a decreasing rate with increasing concentrations in solution, and provide a one-to-one comparison with K_g determined from SPFT tests. We discuss how this information may be used to predict K_g based on glass composition.

4:00 PM

(ICG-SIV-079-2019) Stage III glass alteration: Impact of pH, zeolite, temperature, and solution composition

B. Parruzot*[1]; J. V. Ryan[1]; J. Neeway[1]; J. V. Crum[1]; J. George[1]; J. F. Bonnett[1]; J. Reiser[1]; L. Seymour[1]

1. Pacific Northwest National Lab, Energy and Environment Directorate, USA

Stage III is a delayed acceleration of a glass' alteration rate, generally observed in concomitance with zeolite and/or CSH precipitation. Stage III is potentially the most impactful behavior to long-term performance of nuclear waste glasses. Multiple sets of experiments, most using zeolite addition as a method to trigger Stage III behavior, focused on determining the effects of common experimental parameters on Stage III. These included: temperature (room temperature to 90 °C), pH (9.5 to 11.5 at 90 °C), cation in solution (Li, Na, K), glass type (different high-level waste and low-activity waste glass compositions), and zeolite type (P1, P2, chabazite, analcime). The effects of these parameters on the onset and persistence of a rate acceleration will be evaluated, compared, and discussed using both solution alteration data (i.e., inductively coupled plasma, in-situ Raman) and solids characterization (e.g., powder x-ray diffraction, scanning electron microscopy).

4:20 PM

(ICG-SIV-080-2019) Predicting the Forward Dissolution Rate of Silicate Glasses by Physics-Informed Machine Learning

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1. University of California, Los Angeles, Civil and Environmental Engineering, USA
2. University of California, Los Angeles, Mathematics, USA
3. Indian Institute of Technology, CE, India

Predicting the dissolution kinetics of silicate glasses is critical to ensure the safety of nuclear waste vitrification activities. However, the structural complexity of glasses and our lack of knowledge regarding the rate-limiting mechanism have limited our ability to accurately model the relationship between glass composition and dissolution kinetics, even for stage I. On the other hand, data-driven modeling based on machine learning offers a promising alternative to physics-based model. However, "blind" machine learning has several limitations: (i) it requires a large amount of consistent data, (ii) it has a poor ability for extrapolation far from the training set, and (iii) it can potentially violate physics laws. Here, we present a new physics-informed machine learning framework that addresses these limitations. We show that, even based on a small dataset of data, our method yields a robust prediction of the forward dissolution rate of silicate glasses. Importantly, the incorporation of physical constraints greatly improves the model to extrapolate prediction toward presently unexplored glass compositions. Overall, this study paves the way toward an improved ability to predict the dissolution kinetics of silicate glasses and discover new glasses with enhanced chemical durability.

SVI: Archaeometry

Archaeometry I (TC 17)

Room: Tremont (4th floor)
Session Chair: Stephen Koob, The Corning Museum of Glass

8:00 AM

(ICG-SVI-001-2019) Archaeometry of 17th-century Flint Glass (Invited)

C. Brain*[1]

1. Private Researcher, United Kingdom

The second half of the 17th-century saw major changes in the manufacture of high-quality glass. Thin, fragile and tinted glasses were quickly replaced with thicker, heavier, stronger and (sometimes) colourless glasses that soon became more popular and affordable. However whilst the analysis needs of these newer glasses differ considerably from their earlier counterparts, they have received surprisingly little attention. This paper adresses some of the challenges facing the glass historian who wishes to use scientific analysis on late 17th-C flint (lead) glass. It is framed within the context of work to try to understand London glass-making residues, both from the vicinity of Old Bedlam Glasshouse (excavated by Museum of London Archaeology) and from the mud on the banks of the river Thames. After briefly recapping on the history of fine glassmaking in this period the paper illustrates some of the key-glass history questions involved and the scientific techniques used to try to answer them using these glass-making residues. This leads on to a summary of the archeaometric issues involved and their likely impact. The paper concludes by considering how some of these issues might be resolved in the future.

8:20 AM

(ICG-SVI-002-2019) Variety of the glass compositions produced in Europe until the 16th century

K. Pánová[1]; D. Rohanová*[1]

1. University of Chemistry and Technology, Dep of Glass and Ceramics, Czechia

The technology of glass production in history remains quite a mystery due to a lack of written evidence, which cannot always be considered 100% trustworthy. It is generally believed that the batch recipe and materials used in Central Europe were the same for the whole area of the Western part of Europe. We analyzed quite a large number of archaeological potassium-calcium glasses, which helped us to gain a better understanding of the technology used in the past. Studying the chemical composition and published analyses allowed us to better distinguish between different European production areas. Based on the chemical compositions we calculated the ratios of raw materials in the glass batches that glassmakers used in history. The calculations show differences in the ratios of raw materials and also the use of different wood ash types (beech, spruce or even bracken) in the individual areas of production (for example Bohemia versus Germany). Acknowledgment: This work was supported by a grant from The Czech Science Foundation: GA 19-05677S.

8:40 AM

(ICG-SVI-003-2019) The relationship between faience and glass: The implications of new LA-ICPMS analyses

R. Brown[1]; V. Kemp[1]; N. Schibille[2]; A. Shortland*[1]

1. Cranfield University, Cranfield Forensic Institute, United Kingdom
2. CNRS, France

Faience, a glazed ceramic with a crushed quartz core, is a common find in the Late Bronze Age (LBA) of the ancient Near East. On some sites, especially Amarna and Malkata (mid 14th century BCE, Egypt) faience making and glass working debris have been found in the same workshops. Since faience and glass were made from the same types of raw materials (a silica source, flux and colorants) it has been supposed that their production has much in common, probably sharing the same raw materials and perhaps the same facilities. Analysis of Egyptian faience and glass was carried out by LA-ICPMS and the results revealed that glass and faience had similar colourants and probably shared a plant ash flux and crushed quartz silica source. However, there were subtle, but important and consistent differences in the inferred compositions of raw materials, which hints that the raw materials were not the same for each class of material. This suggests that the materials are perhaps typologically or geographically different in some way, which implies that the workshops for the making of faience and glass were distinct, with different workers and hierarchy. Analysis also shows that faience found (and therefore potentially made) at different sites can be distinguished compositionally, suggesting for the first time the potential of provenancing LBA faience in the same way that contemporary glass has been.

9:00 AM

(ICG-SVI-004-2019) Portable Laser Ablation Micro-Sampling at 213 nm for Mass Spectrometry Analyses of Cultural Heritage Objects

P. Londero*[1]; D. Asael[2]; N. Planavsky[2]; A. Bezur[1]

1. Yale University, Institute for the Preservation of Cultural Heritage, USA
2. Yale University, Department of Geology and Geophysics, USA

Statistical technical studies across museum collections require portable non- and micro-destructive techniques, a challenge for trace element and isotopic measurements by techniques such as ICP-MS and TIMS. One can use portable laser ablation micro-sampling, but current approaches use a 532 nm laser with ~1 ns pulses and are not suitable for glass and some ceramics. We present preliminary work on the development of a portable laser ablation micro-sampling device operating at 213 nm, suitable for various materials including glass and ceramic objects. The prototype can deliver <5 ns pulses at 213 nm at 50 Hz, with fluence up to 15 J/cm^2. Ablated material is captured by applying suction through a PTFE micropore filter; an integrated miniature microscope monitors sample placement and ablation. Preliminary tests show that holes ~150 μm wide and ~100 μm deep can be produced in 30 s with ~40% capture efficiency. Initial ICP-MS measurements on digested filters containing ablated material from NIST 1412 composite glass showed discrepancies in wt% between ablated and directly digested (non-ablated) material of <10% for most elements, <20% for all. While already useful, we believe these results can be significantly improved upon as the project evolves. Future work will focus on refinement of methodology and initial studies of glass objects in the Yale University Art Gallery.

Archaeometry II (TC 17)

Room: Tremont (4th floor)
Session Chair: Andrew Shortland, Cranfield University

10:15 AM

(ICG-SVI-005-2019) A unique recipe for glass beads at Iron Age Sardis (Invited)

P. Degryse*[1]; A. Van Ham-Meert[1]; S. Dillis[1]; K. Eremin[2]; N. Cahill[4]; A. Shortland[3]

1. KU Leuven - Geology, Centre for Archaeological Sciences, Belgium
2. Harvard Art Museums, USA
3. Cranfield University, United Kingdom
4. University of Wisconsin, USA

Recipes used for making the earliest man-made glass changed gradually from melting mixtures of crushed quartz pebbles and halophytic plant ashes in the Late Bronze Age to the use of quartz sands and mineral soda during the Early Iron Age. Not much is known about this transition and the experimental materials which would inevitably have been connected to such technological change. In this paper we present a unique snapshot of developments in glass technology in Anatolia (modern Turkey) during the Middle Iron Age, when glass is still a relatively rare commodity. The present work

focusses on black glass beads decorated with yellow trails from eight and seventh century BCE Sardis. A full elemental analysis of the beads was made, and Sr, Pb and B isotope ratio compositions were determined. This study reveals the use of a combination of a previously unknown source of silica and of mineral soda, giving rise to elevated (granite-like) Sr isotope signatures, as well as high B concentrations. The yellow trails of glass on the beads are made up of lead-tin yellow type II, showing the earliest occurrence of this type of opacifier/colourant so far, predating any other findings by at least four centuries. The production of these glass beads may be local to Sardis, and experimental in nature. It is therefore suggested that Sardis may have played a role in the technological development of the glass craft during the Iron Age.

10:45 AM

(ICG-SVI-006-2019) Archaeometric characterization of Swahili glass beads from the Ibo Island (Northern Mozambique)

J. Pena-Poza[1]; F. Agua[1]; H. Madiquida[2]; J. de Torres[3]; V. Fernandez[4]; M. Villegas[1]; M. Ruiz-Galvez[4]; M. Garcia-Heras*[1]

1. Spanish National Research Council (CSIC), Institute of History, Spain
2. Eduardo Mondlane University, Archaeology and Anthropology, Mozambique
3. British Museum, Department of Africa, Oceania and the Americas, United Kingdom
4. Complutense University, Prehistory, Ancient History and Archaeology, Spain

With the purpose of shedding new light on technology and probable trading provenance of a set of very small glass beads from Swahili occupations of the Ibo Island (12th-13th to 17th-19th century AD) provided by recent archaeological fieldworks (2015-2017), an archaeometric characterization study was undertaken. Selected glass samples (attending mainly their shape and color) of the set composed of more than one hundred beads were characterized by optical microscopy, field emission scanning electron microscopy (FESEM) equipped with an energy dispersive X-ray (EDS) spectrometer, and UV-Vis spectrophotometry. Resulting data indicated two glass systems: Na_2O-CaO-SiO_2 and Na_2O-ZnO-SiO_2. Soda lime silicate glasses are divided into two groups: mineral soda glasses with high alumina content possibly from Southeast Asia, and plant-ash soda glasses with lower alumina content possibly from the Middle East. Soda silicate glasses with ZnO are only represented by a ruby red glass bead, which is supposed to be a modern production. Color of the glasses shows a great variety of chromophores and obtaining procedures highlighting the copper hematinone opaque red glasses in which the red color is due to cuprous oxide micro-crystallization. The results have served to understand Northern Mozambique historical contexts during the Swahili period and its integration in the trade networks of the area.

11:05 AM

(ICG-SVI-007-2019) Illuminating the History of a Medieval Stained-Glass Panel from Canterbury Cathedral

K. Eremin*[1]; G. Rayner[1]; A. Shortland[3]; A. Chang[1]; M. Clerkin Higgins[2]; C. Gray[4]

1. Harvard Art Museums, Straus Center, USA
2. Clerkin Higgins Stained Glass, USA
3. Cranfield University, Cranfield Forensic Institute, United Kingdom
4. University of New Haven, Department of Art and Design, USA

In 1924 the Fogg Museum at Harvard University was gifted a stained-glass panel depicting Thomas Becket, the Archbishop of Canterbury murdered in Canterbury Cathedral in 1170. Installed in the Cathedral around 1205, this is one of only two surviving panels from a larger window, now lost. Conservation enabled in-depth collaborative study to understand the window's manufacture and history. The panel had been releaded destroying original relationships and introducing replacement glass. Complete disassembly for treatment allowed the edges of over 260 glass pieces to be closely examined, confirming the replacements. Charting the new grozing on original pieces ensured accurate line-up during releading. Non-destructive x-ray florescence (XRF) of every piece was followed by sampling selected pieces for quantification by scanning electron microscopy with energy dispersive microanalysis (SEM-EDS) and laser ablation with inductively coupled mass spectrometry (LA-ICPMS). Despite significant surface alteration and contamination, XRF analysis enabled initial groups to be determined. These were refined following quantification and data compared with other studies. Most replacement glass was found to be medieval, likely reused from related stained-glass panels. Specific pieces form tight compositional groups within a given color, suggesting the use of different batches of glass.

11:25 AM

(ICG-SVI-008-2019) Dissolution of medieval potash-lime-glass and its low pH-dependency

L. Sessegolo*[1]; A. Verney-Carron[1]; P. Ausset[1]; S. Triquet[1]; M. Saheb[1]; A. Chabas[1]

1. Laboratoire Interuniversitaire des Systèmes Atmosphériques, France

Many of stained glass windows that currently decorate religious buildings were made during the medieval period. At this time, glasses were composed of high contents of modifier cations, mainly potassium and calcium (between 10 and 25 wt.% for each oxide) and relatively low content of silica, the main glass network former (around 50 wt.%). Hence, these glasses are known as being low durable over time. Stained glass windows were exposed during hundreds of years at the atmosphere. In this discontinuous and variable medium, there are many alteration factors, but one of the most important is the rainwater. The aim of this study is therefore to determine dissolution rate laws controlling the alteration of this type of glass in water-saturated condition. For that, dissolution experiments at several temperatures and pH were set. Dissolution rate was calculated from elemental concentrations in solution measured by Inductively Coupled Plasma – Atomic Emission Spectroscopy. Experimental data were fitted to obtain a dissolution rate law as a function of these two parameters. Results show that, surprisingly, the alteration of these medieval potash-lime-silicate-glasses presents a very weak dependency of the dissolution as a function of the pH of the solution. This specificity has to be considered in the models used to predict alteration rate of stained-lass windows with the aim to better conserve them.

Archaeometry III (TC 17)

Room: Tremont (4th floor)

Session Chair: Jerzy Kunicki-Goldfinger, independent researcher and conservator of glass

1:20 PM

(ICG-SVI-009-2019) Elemental Analysis of Blaschkas Marine Invertebrate Glass Models

E. Bakowska*[1]; B. Rice[1]; B. Murray[1]; A. Clark[1]; D. White[1]

1. Corning RDC, USA

From 1863 to 1890, Leopold and Rudolph Blaschka carefully crafted glass models of marine invertebrates in their studio in Dresden, Germany. Cornell University acquired 570 Blaschka models and the Boston Natural History Society bought 310 in 1885. Even today researchers at Cornell continue to study those models. The Blaschkas models were made to scale and sometimes close to life size, resulting in dimensions from 1 to 27 cm. Nearly all glass used in their creation was colorless. Those models are less known than 3000+ collection of botanical specimens' models made exclusively for the Harvard Botanical Museum. Recently, a collection of Blaschka models was found under a basement stairwell in the University of Wisconsin Madison Chemistry building. Many of the models were in a terrible state of preservation, but some that were intact enough to put on display. Corning Research and Development Corporation supports the effort to re-make and curate the damaged Blaschka works. The approach is to have the original glass compositions analyzed, to create historically accurate replica glasses, and then use them to repair the damaged models. Several analytical techniques: Inductively Coupled

Plasma Optical Emission Spectroscopy (ICP-OES), Flame Atomic Emission (FAE) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) will be used to determine complete elemental compositions, including trace and ultra trace levels.

1:40 PM

(ICG-SVI-010-2019) Modeling Nature: Understanding conservation issues in the Blaschka glass flowers

S. Fulton*[3]; K. Eremin[1]; G. Rayner[1]; A. Van Giffen[4]; A. Shortland[2]

1. Harvard Art Museums, Straus Center, USA
2. Cranfield Forensic Institute, Cranfield Forensic Institute, United Kingdom
3. Harvard University, Harvard Herberia, USA
4. Corning Museum of Glass, Conservation, USA

In 1886, Harvard University commissioned a series of glass plant models from Leopold and Rudolf Blaschka as pedagogical tools for teaching botany. The Ware Collection of Blaschka Glass Models of Plants (The Glass Flowers) ranges from the humblest native field flowers and grasses to detailed models of diseased fruit and insects. The Blaschkas' work evolved over the 50 years they produced the Glass Flowers. Their raw materials shifted from using only readily available commercial glass to combining this with colored glass enamels manufactured by Rudolf. The earliest plant models were roughly fashioned from colorless glass tubing over copper wires, fused at the joins, and cold-painted with mineral pigments. This proved unstable over time, with frequent delamination of paint and glass. Rudolf Blaschka may have recognized a recurrent problem and developed new methods in response. Some of these innovations were more stable initially but later presented their own unique condition issues. Leaf fragments and corrosion products were analyzed to fully understand the conservation issues. Analysis included scanning electron microscopy with energy dispersive microanalysis (SEM-EDX), laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy and x-ray diffraction (XRD).

2:00 PM

(ICG-SVI-011-2019) Light in museums

E. Greiner-Wrona*[1]

1. AGH University of Science and Technology, Faculty of Materials Science and Ceramics Department of Glass Technology and Amorphous Coating, Poland

This research has been focused on testing the influence of light on the deterioration of glass in museum environments. After many experiments it has been concluded that light is a major source caused of glass deterioration in display as well as in storage area. Analysis was carried out on original elements in situ and on glass sensors too. The sensors were applied to different types of glass after corrosion by a variety of media. The following kinds of lighting were used in the experiment: - halogen bulbs - optical fibres - bulbs. For analysis the following methods were used: SEM,EDS, NEOFOT, FTIR, SIMS, Thermovision, Computer Tomography, Confocal Microscopy.

2:20 PM

(ICG-SVI-012-2019) Understanding the browning of medieval stained-glass windows: Impact of bacteria and bacterial exudates on the dissolution of a Mn-bearing glass

V. Valbi*[1]; A. Perez[1]; A. Verney-Carron[2]; C. Fourdrin[1]; Y. Pechaud[1]; C. Loisel[3]; S. Rossano[1]

1. Université Paris Est Marne la Vallée, Laboratoire Géomatériaux et Environnement, France
2. Laboratoire Interuniversitaire des Systèmes Atmosphériques, France
3. Laboratoire de Recherche des Monuments Historiques, France

While the browning of stained-glass windows is a well-known pathology, the mechanisms responsible for this phenomenon are not understood yet. Previous studies revealed enrichment in Mn in the browned areas and some of them have suggested that manganese migration to the surface, oxidation and/or precipitation might be linked to biological activity. In order to improve our understanding of this phenomenon and investigate the direct and indirect implication of microorganisms, weathering experiments of a model glass representative of medieval stained glasses were designed. Dissolution experiments in presence of bacterial exudates (oxalic acid, siderophore DFOB) and/or bacteria (model strains) were conducted in biotic and abiotic reactors in different experimental conditions. The leachates were periodically sampled and the release of elements from the glass was quantified by ICP-OES. The results show that the presence of bacteria and bacterial exudates modifies the dissolution mechanisms and kinetics, increasing dissolution rates and changing dissolution stoichiometry. This highlights that a biological activity could be involved in the solubilisation of Mn in a Mn-bearing glass, which is the first step of the appearance of the browning phenomenon

2:40 PM

(ICG-SVI-013-2019) Microbial Colonization and Interaction with Silicate Glasses: A Review of a Century of Literature

J. L. Weaver*[1]

1. National Institute of Standards and Technology, Material Measurement Lab, USA

Almost every inorganic surface we touch is covered in, connected to, or supporting a glass. Thus, interactions with glass are now routine, be them via cell phones, car windows, or our mid-afternoon cups of coffee. An often not thought of result of these contacts is the contamination and possible colonization of glass surfaces by micro-organisms. If the organisms are not removed in a timely manner then they and glass surfaces can begin a co-association which can last seconds, hours, years, and even millennia. Although most organism/glass interactions are passive, others are known to be damaging. It is these latter interactions which have stimulated research on for the last century. In this presentation an overview of the last 100+ years of research on the microbial alteration of silicate glasses is presented. The review will focus on, but not be constrained to, research conducted in the field of cultural heritage preservation. A brief historical timeline for research on the bio-alteration of glass will be outlined and then followed by a discussion of the two pathways (biophysicochemical and biochemical) by which bio-induced alteration can occur. The second part of this is talk will cover the types of organisms known to grow on silicate glasses. The talk will conclude with a presentation of state-of-the-art bio-alteration analysis methods.

3:00 PM

(ICG-SVI-014-2019) Understanding and predicting the chemical degradation of historic glass in museum collections

G. Verhaar*[1]; N. H. Tennent[2]; S. Koob[3]; J. T. van Elteren[4]; V. S. Šelih[4]

1. Rijksmuseum, Conservation and Science Department, Netherlands
2. University of Texas at Dallas, Edith O'Donnell Institute of Art History, USA
3. Corning Museum of Glass, USA
4. National Institute of Chemistry, Slovenia

A collaborative research project between the University of Texas at Dallas, the Corning Museum of Glass and the Rijksmuseum in Amsterdam was recently initiated. The research focuses on the chemical degradation of historic glass in museum collections, with the aim of developing an early warning system for chemically unstable glass objects which are prone to undesirable changes in appearance. As a result of the slow, progressive chemical breakdown of glass, ions leach from within the glass to the surface. Accordingly, the research involves the quantitative analysis of these ions on the surface of museum glass in order to assess the relative propensity of glass objects to undergo progressive degradation and, ultimately, removal from view as they become unfit for display. In addition, a prime goal of the research is to establish optimal environmental parameters for display and storage. In so doing, it has become clear that the relationship between the changes in the composition of the glass itself, due to ion leaching, and the accumulation of ions on the

glass surface has received inadequate attention from researchers. The presentation will therefore focus on this relationship, using various analytical techniques such as ion chromatography, LA-ICP-MS, SIMS and electron microscopy, in order to increase understanding of the chemical processes atmospheric degradation of museum glass.

Archaeometry IV (TC 17)

Room: Tremont (4th floor)
Session Chair: Stephen Koob, The Corning Museum of Glass

3:40 PM

(ICG-SVI-015-2019) Caring for glass collections with special focus on central European potassium Baroque objects (Invited)

J. J. Kunicki-Goldfinger*[1]

1. independent researcher and conservator of glass, Warsaw, Poland, Poland

Glass collections consist of various objects. They differ from each other not only in their origin and form but also in chemical durability. A proportion of them are chemically unstable. This phenomenon manifests itself, among other, by a characteristic network of small cracks on the surface, frequently called crizzling. This deterioration process is irreversible and can lead to a complete destruction of the object. The only known solution to protect such objects is to keep them under the right storage conditions, which are typically slightly different from the required for the most glasses. One of the largest groups of such objects originates from the late 17th and 18th century and is represented by a technology of potassium glass developed in central Europe. Identification of these glasses constitutes one of the most important challenges for curators and conservators. It is important to know which single objects can be at risk and how to detect them before the visible symptoms of deterioration occur. Based on the examination of hundreds glasses from the Corning Museum of Glass collection as well as from other collections carried out throughout last years, at least a few relatively simple methods can be proposed to achieve it. They include an inspection of the glass surface, an inspection of glass fluorescence under UV and XRF analysis of glass using a portable analyzer.

4:10 PM

(ICG-SVI-016-2019) Mapping Kapadvanj Glass: Holding a Mirror to the Last Surviving Traditional Tank Furnace in India (Invited)

A. K. Kanungo*[1]

1. IIT Gandhinagar, Archaeological Sciences Centre, India

A last surviving workshop at Kapadvanj (Gujarat, India) uniquely continues to operate a combined glass-making & working tank furnace. Here craftsmen still produce the distinctive convex, hot lead coated mirrors. Mirrors produced at Kapadvanj today are still used besides as mirrors in various contexts: as adornments for facades and clothes alike. At Kapadvanj, over the last fifty years economic reversals & competition over raw materials have reduced what were hundreds of workshops to a last one; yet the skill, expertise & networks of materials & exchange that make these glass worlds are still alive. The site presents today an entire landscape of urban glass works, both as still in use & those that are turning to unrecognizable ruins. This paper will present a detailed spatial, material and taphonomic documentation & analysis of this invaluable site that preserves both a unique kind of furnace & the production of an understudied artifact type. The presentation is not just about the workshop, the techniques of mirror production but the site at large in its spatial complexity. This spatial analysis is intended as providing, the documentation of what this mode of combined glass production and working looks like in spatial & archaeological terms. Through these means the paper archaeologically investigate the material distinctiveness & history of the celebrated glass works at Kapadvanj.

4:30 PM

(ICG-SVI-017-2019) Iron Age Swedish Vitrified Hillfort: Analog for Nuclear Waste Glasses

M. Ahmadzadeh*[1]; J. Marcial[1]; J. Clarke[2]; B. Housen[3]; J. McCloy[1]

1. Washington State University, USA
2. University of Sheffield, United Kingdom
3. Western Washington University, USA

In Pre-Viking Iron Age Sweden, ancient materials engineers consolidated fort walls by melting metamorphic amphibolite rock along with locally available granitic gneiss rocks to create a highly durable, partially vitrified structure. Hundreds of these vitrified hillforts have been identified in Europe. At Broborg in Sweden, this practice may have been carried out by placing wood and charcoal in "firing holes" on opposite sides of ~3×1 m "boxes" which are still visible today. This presentation will describe archaeological excavations at Broborg and recent experimental work to replicate the rock melting practices. Optical microscopy, electron microanalysis, and x-ray diffraction of the vitrified rocks reveal complex microstructure and chemistry and evidence of fast cooling. Two separate glasses can be identified suggesting multiple weakly interacting melts during the process, one very mafic and quite fluid and the other felsic and higher viscosity. Owing to the presence of Fe-bearing magnetic phases within the vitrified rocks, archaeomagnetic dating of the hillfort construction has been performed. The mineralogy and melting behavior of some local amphibolite and gneissic granite rocks were also studied to confirm mineralogical and compositional evolution.

SVII: Arun K. Varshneya Festschrift

Arun K. Varshneya Festschrift I

Room: Georgian (mezzanine)
Session Chairs: John Mauro, Pennsylvania State University; Vijay Jain, Savannah River National Lab

8:00 AM

(ICG-SVII-001-2019) The Essence of Science and Glass Science (Invited)

L. D. Pye*[1]

1. Alfred University, NYS College of Ceramcis, USA

Although there are many facets of modern-day science such as discovery, theorization, experimentation, analysis, and conveyance to appropriate international communities for review, the prima facie essence of science is to predict, id est, to predict what is known to be true - what can be observed, measured, verified, validated. This assertion takes on special meaning when considering topics such as climate change due to accumulation of greenhouse gases in the atmosphere, or acceptable corrosion rates of vitrified nuclear waste glasses to be stored over thousands of years. In the field of glass science, there are several theories where validation of predictions have been accepted by the international community. Among these are microstructure development during amorphous phase separation as predicted by spinodal decomposition theory, and electrical/optical properties as predicted by band/ligand field theory. In other situations, such as homogenous nucleation in undercooled liquids, theory falls far short of this requirement. This presentation will review the fundamental tenets of the essence of science and its role in advancing modern day glass science - where it has worked well in this field and where more work needs to be done.

8:20 AM

(ICG-SVII-002-2019) Dr. Arun K. Varshneya: Educator, Mentor, Scholar, Entrepreneur, and Philanthropist (Invited)

J. C. Mauro*[1]

1. Pennsylvania State University, Materials Science & Engineering, USA

In this presentation, I pay tribute to my academic father, Dr. Arun K. Varshneya. I will provide a brief overview of his many accomplishments in the field of glass science and technology and to his generous service to the broader glass community. This presentation will serve as kick-off for the special Varshneya Festschrift at ICG 2019.

8:40 AM

(ICG-SVII-003-2019) Melting Mechanisms in Alkali Meta-Silicates

A. Cormack*[1]

1. Alfred University, USA

Melting has been called the most important phase change in materials science, but a detailed understanding of the atomic-scale mechanisms involved has not yet been developed. This is particularly true for silicates, which form the basis of most commercially important glass-forming systems. Indeed, for silicates, the converse reaction, namely, the devitrification process, including nucleation and growth, is also lacking a detailed mechanistic understanding. However, whilst the timescales associated with nucleation represent a challenge for current atomistic simulation techniques such as molecular dynamics, melting is a process which is amenable to such an approach. In this presentation, we will discuss the differences between lithium and sodium meta-silicates as they are heated through their melting temperatures using molecular dynamics. In particular, it will be suggested that the difference in pre-melting behavior, as evidenced by anomalous specific heat changes with temperature, can be associated with differences in the alkali migration mechanisms.

9:00 AM

(ICG-SVII-004-2019) On my fun and educational 3-decade interaction with the Glass Guru (Invited)

E. Dutra Zanotto*[1]

1. Federal University of Sao Carlos, Materials Engineering, Brazil

My nearly three decades of interaction with the "glass guru" includes scientific subjects such as the "chemical strengthening of (hard to strengthen) borosilicate glass, do cathedral glasses flow?, will glass always crystallize as its eventual fate?." We have also worked together in educational topics as teaching a joint short course on glass back where we both learned it (Sheffield University), business topics such as his solid support to CeRTEV, and personal fun together. As an example of fun, I vividly recall that we had not so brilliant an idea during the banquet of the 21st ICG in Strasbourg, 2007 with a disastrous outcome. More recently we have collaborated in other endeavors. Last year, jointly with Kathleen Richardson, John Mauro, Manoj Choudhary and David Pye, we worked on an educational power point presentation entitled "Glass through the ages" delivered by Manoj at the ICG meeting in Yokohama. Currently, Arun, John Mauro and I are writing up a joint paper for a special issue of JNCS in honor of P. K. Gupta. This presentation highlights our scientific discussions with glimpses of our outside interaction using photos and short videos.

9:20 AM

(ICG-SVII-005-2019) Lessons learned from Dr. Varshneya and my 25 year journey in the architectural flat glass industry (Invited)

P. C. Anderson*[1]

1. Viracon, USA

My talk will review key lessons learned while working with Dr, Varshneya as an under graduate and graduate student in the early 1990's at Alfred University. I will show how these lessons guided me on my 25 year journey in the architectural glass world working in both product development and process engineering. I will be highlighting some major advancements including developing hurricane resistant glass, producing heat treated glass with minimal distortion, and advancement in the performance of low e coatings.

10:00 AM

(ICG-SVII-006-2019) Fifty years of professional interactions with Professor Arun Varshneya (Invited)

M. Tomozawa*[1]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA

Both Arun Varshneya and I started graduate education in USA around the same time. Both of us worked on glasses almost exclusively. In this talk, I would like to look back his works- research, entrepreneurship, and philanthropy.

10:20 AM

(ICG-SVII-007-2019) Parent glasses and glass-ceramics and their relationship in respect of functionality and properties (Invited)

W. Hoeland*[1]; M. Rampf[1]; M. Dittmer[1]; C. Ritzberger[1]

1. Ivoclar Vivadent AG, Liechtenstein

Prof. Dr. A. Varshneya has comprehensively studied and categorized inorganic glasses with regard to their chemical fundamentals, their structure, crystallization, their microstructure and their properties, and he has described their valuable applications and related process technologies. Therefore, the authors take great pleasure in paying homage to the work of Prof. Varshneya with this presentation of two different bioceramics: lithium disilicate glass-ceramic for restorative dental applications on the one hand and bioactive rhenanite glass-ceramic for hard tissue replacements on the other. Both systems start off with transparent parent glasses, and glass-in-glass phase separation is an important nucleation stage of the materials. Furthermore, the two glass-ceramics undergo both controlled nucleation and crystallization. Nevertheless, the mechanisms involved are very different, which affects the chemical composition and the properties of the individual residual glasses. The dental glass-ceramic is a very strong, translucent and durable product. But rhenanite crystals grow in unique ball-shaped aggregates. Furthermore, the glass matrix and the crystals of the end product show bioactivity, which is a salient feature of the material. The two systems are described on the basis of the formation of their microstructures, crystallization processes and properties.

10:40 AM

(ICG-SVII-008-2019) Fundamental and Applied Aspects of Heat Transfer in Fibrous Insulation (Invited)

M. K. Choudhary*[1]

1. Glass Service a.s., MKC Innovations LLC, USA

The first part of the lecture reviews the basic mechanisms of heat transfer involved (namely conduction, free convection, and radiation) and their relative contributions to the effective thermal conductivity of the fibrous insulation assembly. It is shown that the free convection effects may generally be ignored. Statistical bounds for the combined fiber and gaseous thermal conduction are discussed. The procedure for calculating the radiation conductivity through a solution of Maxwell's equations is discussed and results

are presented to illustrate the effect of fiber diameter, density, and temperature on the effective thermal conductivity of the insulation. The model predictions are found to be in good agreement with the measurements. The second part of the lecture describes mathematical modeling of heat transfer in metal building roof and wall assemblies that contain fibreglass as the main insulating material. These assemblies have one or more layers of fibreglass insulation placed between the metal panels and their supporting structures. The model accounts for the three-dimensional heat conduction in insulation layers and conduction/convection in air gaps between the layers. The calculated and the measured overall heat transfer coefficients are compared. The approach described here is used by to develop energy performance standards of metal buildings.

11:00 AM

(ICG-SVII-041-2019) Glass Lasers for Glass Drilling and Cutting (Invited)

S. Jiang*[1]

1. AdValue Photonics Inc, USA

Glass fiber lasers at various wavelength were developed by using rare-earth doped silicate glass fibers. Their applications in glass drilling and cutting will be presented.

11:20 AM

(ICG-SVII-010-2019) Glass archaeometry in the aspect of cultural heritage (Invited)

E. Greiner-Wrona*[1]

1. AGH University of Science and Technology, Faculty of Materials Science and Ceramics Department of Glass Technology and Amorphous Coating, Poland

Glass has been known for centuries as evidence of the development of a civilization, its culture and industrial progress. First of all we have to divide glass, as a production material, between natural glass and that created by man. The subject of this presentation is focused on the discovery the past, and artefacts of previous generations. The ability to test materials has developed very slowly. Instrumental methods and computerization have evolved, and so has awareness of the need for interdisciplinary cooperation among conservators, as well as engineers. This principle of combining sciences to decipher the history of a material on many history on many levels also enabled technologists to be involved in archaeological research, specialists in materials science. It is a field of archaeological research which aims to confirm the authenticity. Such analysis of historic articles also contributes to the knowledge of the culture and way of life of our ancestors. In addition, during a number of scientific conferences, separate thematic sections under the heading of archaeometry has been prepared. Traces of historical multi-century products and glass elements are proof of our ancient technology, its development and cultural life. Due to well-developed archaeometry we are able to choose the most suitable conservation method to protect these glass objects. This activity preserves our cultural heritage for next generation.

11:40 AM

(ICG-SVII-011-2019) How Observational Learning Can Shape One's Life (Invited)

R. Callahan*[1]

1. Global Infrastructure Partners, USA

Calculus, physics, materials science and fluid dynamics are some of the core principles taught in every engineering program. Students are enthralled by the prospect of learning what those lazy "S" symbols are in calculus books and grasping how materials are processed. STEM professors impart wisdom on the students which gives rise to cognitive learning – knowledge, understanding, and application. However, another plane of learning may take place outside the classroom. There are professors who shape students' lives through their behaviors and actions. The students observe, retain, and ultimately reproduce these behaviors and actions. Arun Varshneya was my thesis advisor. He trained me in materials science but more importantly, he taught me, unbeknownst to him, lessons outside of the classroom. Observing Dr. Varshneya, I learned the following: (i) appropriate style when dealing with difficult situations (ii) addressing conflict (iii) capability to frame a problem and develop solutions (iv) ability to self-learn (v) the importance of clear writing. Engineering knowledge earned me my first position, but these "life lessons" observed from Dr. Varshneya helped propel me forward and shape my career. Thirty years removed from college, graduates typically do not recall the names of the teachers who instructed them in calculus or physics, but they do remember the professors, like Dr. Varshneya, who taught them core lessons in life.

Arun K. Varshneya Festschrift II

Room: Georgian (mezzanine)
Session Chairs: John Mauro, Pennsylvania State University; Vijay Jain, Savannah River National Lab

1:20 PM

(ICG-SVII-012-2019) Cousin Arunsky – Memories of shared times (Invited)

P. Gupta*[1]

1. Ohio State University, USA

Arun, who I fondly call Arunsky, is my first maternal cousin. But what makes our relationship special is that, born a few months apart in the same house, we grew up together in a semi-joint family setup, played together as kids, and finished school and college educations together in Agra (India). Our trajectories diverged in 1962 when he went to Sheffield Univ. and I to IIT Bombay. Chance brought us together again in 1966 as graduate students under Prof. Cooper at Case who instilled in us a love for glass science. The rest is history. In this talk, I will share some memories from the earlier times honoring this unique relationship.

1:40 PM

(ICG-SVII-013-2019) Prof. Arun K. Varshneya's contribution to an early stage of atomistic simulation and a bright outlook on computer simulation (Invited)

A. Takada*[1]

1. University College London, United Kingdom

It is well known that Prof. Varshneya is an eminent experimentalist in glass science and technology. To our amazement, he published an excellent paper in an early stage of atomistic simulation in the world. His paper, which was a joint research with Dr. Soules, used Molecular Dynamics simulation and demonstrated the change of boron coordination number in alkali borate and borosilicate glasses. In this talk, some MD papers published by pioneers in the early stage will be first reviewed. Then the present status and an outlook will be discussed.

2:00 PM

(ICG-SVII-014-2019) Towards High-Strength Infrared Optical Fibers (Invited)

P. Lucas*[1]; S. Jiang[2]; G. Coleman[1]; T. Luo[2]; J. Ari[1]

1. Univ of Arizona, USA
2. Advalue Photonics, USA

Chalcogenide glasses exhibit excellent transparency in the mid infrared wavelength range which make them unique candidates for the fabrication of complex optical elements such as optical fibers. However, one of the main shortcomings of chalcogenide glasses compared to their oxide counterpart is their relatively poor mechanical strength. Nevertheless, the rapid development of infrared technology has raised the need for robust infrared fibers suitable for

use in demanding environments. Here we report the development of triple index hybrid fibers composed of a chalcogenide core-clad structure embedded in an oxide external cladding. This hybrid structure combines the benefits of both glass types with optimized infrared transparency through the chalcogenide core structure and improved mechanical strength of the oxide cladding. The fabrication of this composite fiber requires significant materials engineering to match the rheological properties of each glass during the fiber drawing process. Here we take advantage of the covalent network properties of chalcogenide glasses to optimize and tailor their viscoelastic behavior and thermal expansion coefficient. This offers sufficient design parameters to fabricate hybrid fiber glass structures with optimized interfacial properties and optimal mechanical resistance.

2:20 PM

(ICG-SVII-015-2019) Chalcogenide thin film for photovoltaic applications (Invited)

X. Zhang*[1]; M. Cathelinaud[1]; S. Chen[1]; D. Ren[1]; H. Ma[1]; L. Calvez[1]

1. University of Rennes/CNRS, Institute of Chemistry, Lab. Glasses and Ceramics, France

This work is on the preparation and characterization of chalcogenide thin films, prepared by using the technique of magnetron assisted sputtering, for photovoltaic applications. The earth abundant Sb2Se3 has been particularly studied. The critical parameters for obtaining high performance photovoltaic solar cells based on this compound have been found to be the appropriately controlled crystallization of the as-deposited amorphous thin films and the improvement of the electric conductivity of the absorber. Different doping strategies have been used for obtaining p-type and n-type Sb2Se3 semiconductors with adequate conductivity. It has been found that the doping has however negative effect on the quality of the crystalized thin film, especially on the size of the crystallites which has important influence on the performance of the solar cells. The crystallization mechanism of the doped and un-doped thin films has been carefully studied. The preparation and the performance of Sb2Se3 based homojunction thin film solar cells will be presented.

2:40 PM

(ICG-SVII-016-2019) Practice, theory, and more practice: A sampling of work from 2008 to 2015 (Invited)

P. K. Kreski*[1]

1. SCHOTT North America, Inc., USA

A brief reflection on three projects spanning seven years celebrating contributions by Professor Varshneya to the world of glass science. First, the weakening of spandrel glass by vitreous enamel – a demonstration of the various stress drivers and some pitfalls of enamels on glass. Second, a deep dive into the micromechanics of glass chemical strengthening, where molecular dynamics simulations of ion-exchanged glass structures inform our understanding of where the 'missing Pascals' have gone. And finally, a return to industrial glass with a collection of recipes for curvature-controlled chemically strengthened float glass.

3:00 PM

(ICG-SVII-017-2019) ICG 2019 Roast of Festschrift Honoree Professor Arun K. Varshneya (Invited)

P. Varshneya*[1]; K. V. Baker[1]; R. V. Karnani[1]

1. Saxon Glass Technologies, Inc., Administration, USA

Please join Dr. Varshneya's daughters, Pooja, Kajal, and Rupal as the Glass Guru is subjected to light-hearted jokes and satire to honor a him in a unique way. In addition to jokes and insult comedy, brief anecdotal reflections, genuine praise, and tributes may also be entertained. Be forewarned, though, friends, fans, and well-wishers may receive some of the same treatment too during the course of the evening!

3:40 PM

(ICG-SVII-018-2019) New unique-to-the-world capabilities increase the pace and impact of materials innovation at Dow (Invited)

A. N. Sreeram*[1]

1. Massachusetts Institute of Technology, Materials Science & Engineering, USA

New materials and processes developed by Dow Chemical using high-throughput experimentation, computational modeling and state-of-the-art analysis capabilities are improving the daily lives of hundreds of millions of people. Deploying these resources successfully requires partnership with our customers to gain clear market signals and to gain a seat at the design table. The innovation pipeline is keenly focused on real market needs, aligned with strategic growth areas and addresses global sustainability challenges. Dow cutting-edge technologies receive awards for innovation and sustainability, including pre-composite polymers, olefin block copolymers, silicone materials and hybrids, sustainable dyeing of textiles and high resilience polyurethane foams. Better materials are required to meet many of society's challenges. Dow experience demonstrates that harnessing new technologies for use in materials research delivers results, better targeting research and allowing rapid development of new products.

Poster Session 2

Room: Grand Ballroom A (mezzanine)

5:00 PM

(ICG-P151-2019) Simultaneous Evaluation of Viscosity and Crystallization Behavior of Silicate Melt by Electrical Capacitance Measurement

N. Saito*[1]; K. Nakashima[1]

1. Kyushu University, Department of Materials Science and Engineering, Japan

Silicate melts found in the high temperature processes, as steelmaking, glass smelting, waste melting, etc., are basically utilized and generated not in uniform liquid but in solid-liquid dispersion system. The presence of solid phase will affect many of mass transfer properties, which will be controlled by the fraction and size of the solid phase. A novel- and in situ- quantifying method for the crystallinity of super-cooled silicates was proposed by the measurement of their electrical capacitance at high temperature. It is well known that the electrical capacitance of ionic liquids is much higher than that of solids owing to the differences in their respective polarization mechanisms. These differences were exploited as a sensitive indicator of the crystallization. The system comprised a Pt-based alloy crucible and a rod connected to an impedance analyzer. For the calibration of electrodes employed, a theoretical capacitance model based on their dimensions was proposed. Then after, an experimental setup for simultaneous measurements of viscosity and capacitance was developed for silicate melts at high temperature, which can provide wide-range of rheological information of silicate melts and suspensions with decreasing temperature in super-cooled region, associated with in-situ crystallinity measurement by the strategy proposed in the present work.

(ICG-P152-2019) Effect of alkali oxide substitution on the viscosity and structure in CaO-SiO_2-CaF_2-Na_2O-K_2O melts

M. Seo*[1]; I. Sohn[1]

1. Yonsei University, Republic of Korea

This study investigated the effect of alkali oxides on the viscosity and structure of CaO-SiO_2-CaF_2-based melts at high temperatures. The CaO/SiO_2 mass ratio (C/S) was fixed at 0.8 with 10 mass pct. CaF_2 and 20 mass pct. alkali oxides of Na_2O and K_2O. To understand the substitutional effect of Na_2O with K_2O at a total alkali oxide content of 20 mass pct., Na_2O was substituted with K_2O at 5, 10, 15, 20 mass pct. respectively. Viscosity of the samples were measured using the rotating spindle method during cooling from 1773 K. Viscosity of

the melts increased with higher portions of K_2O in the melts. The apparent activation energy indicated an increase from 95.9 to 153.8 kJ/mol with higher K_2O content. This was correlated to the cation radius and the Pauling electronegativity difference, where K^+ was 30.4% larger and 11.8% smaller than Na^+, respectively. Structure of the melts was studied using Raman spectroscopy and the mole fraction of Q^3 increase, while Q^0 and Q^2 decrease with higher K_2O. NBO/Si (nonbridged oxygen per silicon cation) decreased from 1.97 to 1.58 with increasing K_2O indicating greater complexity in the melt structure with K_2O, which induced a higher viscosity.

(ICG-P153-2019) Structural and Thermal Properties of Alkali Tellurite Glasses

M. R. Jesuit*[1]; M. J. Packard[1]; O. L. Alderman[2]; C. J. Benmore[2]; S. Feller[1]

1. Coe College, Physics, USA
2. Argonne National Lab, USA

The structural and thermal properties of lithium, sodium, and potassium tellurite glasses, written as JM_2O-TeO_2 where M is an alkali metal, were studied. J ranged from 0 to 0.25. Raman spectra were measured on all glasses along with the glass transition onset (T_g), crystallization (T_x), and melting (T_m) temperatures. All thermal measurements were performed on a Perkin-Elmer DSC-7. The thermal measurements were compared to the coordination of the tellurium. Coordination values were found by deconvoluting Raman spectra to find the relative amounts of Q_4 and Q_3 units in the glasses. Pure amorphous TeO_2 was made using a newly reported water-quenching method, then thermally tested against time to observe how the glass transition onset and crystallization changed. We measured T_x and T_g every 30 minutes on glassy TeO_2. Since TeO_2 has a strong crystallization tendency, the samples were prepared in a nitrogen glovebox to minimize the effect of water on the recrystallization. In addition, x-ray and neutron scattering results were used to learn more about the atomic structure of these reluctant glass formers. These data were compared to recent NMR results. *This work was supported by NSF through grant numbers DMR 1407404 and DMR 1746230

(ICG-P154-2019) Which "glass constituents" are responsible for the glass formation?

A. Priven*[1]

1. Corning Korea, Republic of Korea

The phenomenon of glass formation can be thought of in terms of species playing different roles in glass structure; however, selection of proper "structural units" remains unclear. Physically, glass formation is determined by the critical cooling rate of a liquid, i.e. the maximum cooling rate at which the liquid of a given composition solidifies without crystallization. Two major factors prevent the liquid from crystallizing: thermodynamics (roughly, temperature above liquidus) and kinetics (roughly, high viscosity). These characteristics, liquidus temperature and viscosity, have considerably different relation to the atomic structure of liquid. Viscosity is mainly governed by the most mobile species (e.g. Na^+, K^+, $BO_{3/2}$), whereas the liquidus temperature primarily depends on the first crystalline phase (e.g. mullite [$Al_6Si_2O_{13}$], albite [$NaAlSi_3O_8$]). So, which units are responsible for glass formation, or none of them? In this presentation, published diagrams of glass formation will be compared with phase diagrams and viscosity diagrams for the same systems. The results of comparison show that on a large scale, the role of thermodynamics dominates, i.e. the answer to the question "is a given liquid glassforming?" roughly follows from the answer to the question "which species crystallizes from it at liquidus temperature?", rather than "how much the structure is [de]polymerized" etc.

(ICG-P022-2019) Influence of the TiO_2 on the glass stability and activation energies of a SrO-CaO-B_2O_3-SiO_2 system

A. A. Cabral*[1]; M. V. Alencar[1]; L. D. Silva[2]

1. Federal Institute of Maranhão, Physics, Brazil
2. Federal University of Sao Carlos, Materials Engineering, Brazil

It has been assumed that the glass stability (GS) may be related to the overall crystallization activation energy, i.e., the most stable composition against the crystallization requires higher energy to be crystallized. In this paper, seven compositions belonging to the $(26\text{-}0.25x)CaO$-$(26\text{-}0.25x)SrO$-$(4\text{–}0.05x)B_2O_3$-$xTiO_2$-$(44\text{–}0.45x)SiO_2$ glass system, with $0 \le x \le 8$ (mol%), were prepared by the conventional melting/quenching procedures. Then, bulk glass samples were heated in a DSC furnace (air, Pt-Rh crucible) up to 1400oC at different rates (f = 2.5 – 40 K/min) in order to register the correspondent onset glass transition, crystallization and melting/liquidus temperatures. The Avrami coefficient (n) was calculated through the Ozawa method, while the activation energies for the overall crystallization (E) were evaluated using the Kissinger, Marseglia and Matusita & Sakka models, respectively. On the other hand, the glass stability (GS) was evaluated by the Hruby (K_H), Weinberg (K_W) and Lu and Liu (K_{LL}) parameters. Depending on the TiO_2 content (mol%), it was detected two different behaviors: (a) $x \le 3$: E remains almost constant and GS increases, (b) $4 \le x \le 8$: E dramatically decreases, as well GS. These results can be attributed to the changing of the short-range order around the B and Si atoms.

(ICG-P077-2019) The Transition from Liquid Silica to Vitreous Silica

S. Cheng*[1]

1. Lawrence Berkeley National Laboratory, Molecular Foundry, USA

After several decades of study, the ordering structure existing in vitreous silica and the nature of the silica glass transition remain controversial. Although the second-order derivatives of Gibbs energy function, such as coefficient of thermal expansion and heat capacity, exhibit a smooth step through the glass transition temperature, the transition temperature is cooling rate dependent, and the process is not deemed a true second-order phase transition. This work discusses the formation and the evolution of the ordering structure in the glass transition process based on the newly proposed nanoflake model for the medium range structure in vitreous silica. The results show that there is a cooling rate independent critical temperature Tc corresponding to the formation of the ordering structure. This indicates that silica glass transition should be recognized as a second-order phase transition. Experimental data supporting the view will be presented.

(ICG-P078-2019) Atomic delocalization and glass transition criterion

D. S. Sanditov[1]; M. I. Ojovan*[2]; M. V. Darmaev[1]

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2. Imperial College London, Department of Materials, United Kingdom

We analyze glass transition in amorphous materials using the concept of delocalized atoms. The delocalization of an atom is a necessary condition for the realization of a viscous flow of a glass-forming melt. The freezing of atomic delocalization process leads to cessation of fluidity and to transition of an amorphous material to the glassy state, when the energy of lattice thermal oscillations attributed to an atom becomes equal to or less of the enthalpy of delocalization of an atom, hence the glass transition condition is formally set as $\Delta H_e=(i/2)kT_g$. (1) The enthalpy is equal to the work needed for the largest displacement of an atom committed against internal p_i and external p pressures $\Delta H_e=(p_i+p)\Delta v_e=\Delta\varepsilon_e+p\Delta v_e$, (2) where $\Delta\varepsilon_e$ is the delocalization energy of an atom, and Δv_e is the elementary fluctuation volume. From (1) and (2) we obtain $\Delta\varepsilon_e=(i/2)kT_g-p\Delta v_e$. (3) It is well known that viscosity-temperature

dependence of glass-forming melts is successfully described by the generalized Jenckel equation. From the derivation of this equation using the model of delocalized atoms we conclude that D in this equation is uniquely related to energy $\Delta\varepsilon_e$: $\Delta\varepsilon_e$=kD. Using (3) and data on D we have found that for some glasses the energy $\Delta\varepsilon_e$ linearly depends on glass transition temperature, which confirms the above given glass transition criterion (1).

(ICG-P079-2019) The diffusion coefficient in supercooled sugar solutions

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Theoretical and experimental results on the temperature dependence of the traslational diffusion coefficient in one component fragile supercooled liquids have been reported in the literature for several decades. In the case of mixtures namely water and different kinds of sugars, the diffusion coefficient depends also on the concentration of the solute. The study of different behaviors in supercooled sugary mixtures represents, nowadays, an extremely important issue for several biological applications such as pharmaceutics, food science and preservation of cellular tissues. We present results on the coupling between the viscosity of these mixtures and the corresponding diffusion coefficient of a given tracer for different temperatures and concentrations.

(ICG-P080-2019) Structural Relaxation in Water-Free Silica Glass During Chemical Vapor Deposition

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Silica glass synthesized by plasma chemical vapor deposition process is called water-free silica glass or type IV silica glass. It exhibits low optical absorption from 200 nm to about 3 μm benefit from its extremely low content of hydroxyl and other impurities. Structural defects and inhomogeneity generate easily during preparation process of water-free silica glass, and can hardly be eliminated by thermal treatment, because of high purity and long structural relaxation time. The present work studied volume and shear relaxation in silica glass during plasma chemical vapor deposition process. Change of structure from center to edge with deposition of new silica and decrease of temperature was studied. Results showed that visco-elastic deformation occurs in silica body due to applied force. Si-O network can be elongated and even be broken. That needs longer time and higher temperature to recover. So the content of oxygen vacancy and fictive temperature are higher at edge of produced silica glass. The forces on silica melt unit caused by substrate rotating, static pressure and viscosity and the temperature dependence were analyzed. Influence of temperature gradient, rotating speed, depositing speed and diameter on fluxion of silica was studied. A model of glass transition interface was deduced, which can help controlling structural relaxation and improving homogeneity of water-free silica glass.

(ICG-UGSP-P081-2019) A Study of Kinetic Fragility Along the $Na_4P_2S_{7-x}O_x$ Glass Series

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Kinetic fragility (m) characterizes the change in the dynamics of a liquid as it is cooled towards its glass transition (T_g). It is a very telling variable that has applications such as determining the temperature dependent viscosity of a glass using the MYEGA model as well as comparing the relative behavior of glasses along a series. Traditionally a calorimetric method has been used to determine this m value, but recently a new DSC method derived from the MYEGA model has been explored and shows promise in finding more accurate m values. Currently this method can take many days to obtain reliable m values for a single sample, however, trends of the TRRD method suggest that T_g and structure can be directly related to m. If this is true, reliable m values could be found much faster as only a few DSC scans and knowledge of the glass's structure would be needed to calculate m. This poster demonstrates the new method's ability to predict m values across the $Na_4P_2S_{7-x}O_x$ series, along with supporting evidence showing the accuracy of this TRRD method as well as evidence that T_g and structure directly affect m.

(ICG-P082-2019) The viscosity in supercooled binary mixtures: Water and sugars

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The study of relaxation properties in supercooled liquids in the glass transition vicinity provides us with important information on their physical behavior. In the case of binary sugar mixtures, we propose a mathematical form to represent the viscosity of aqueous solutions with sucrose and trehalose over a wide range of concentrations and temperatures. Understanding the behavior of the viscosity in these mixtures is very important in different important applications such as food science, including confectionery and freezing, and biological systems which include cryopreservation of several kinds cells.

(ICG-GSP-P083-2019) Calculating viscosity of glass forming liquids near T_g using molecular dynamics simulations

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Viscosity is one of the most important physical properties for glass-forming liquids, which not only governs every stage of glass manufacturing but also is central to decipher the glass transition. However, due to limitations of accessible time scales, viscosity measurement in computer simulations has been very challenging. Here, we presents a new method to calculate the viscosity using molecular dynamics simulations. First, an analytical viscosity model based on Eyring model, involving the potential energy of the liquids sheared at different shear strain rate, is derived. Then the validation of this model is tested on binary Lennard Jones liquids using molecular dynamics simulations, where the linear correlation between viscosity in logarithmic scale and potential energy has been obtained for liquids in the steady state. By extrapolating such linear relationship, viscosities near the glass transition temperature (T_g) can be computed using the two-fitting-parameter model for liquids with a range of fragilities. The above method of measuring viscosity in computer simulations will help provide fundamental understanding on glass transition of supercooled liquids.

(ICG-P084-2019) Fictive Temperature of fused silica

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The fictive temperature of fused silica was measured using Brillouin-, Raman- and ATR-method. The fictive temperatures of four samples were investigated. Three samples of known fictive temperature served as calibration, so that the fictive temperature could be determined for a unknown sample. It turned out that the measured values for the unknown sample differ greatly between the different measuring methods. With the samples with known fictive temperature, heat treating tests were also carried out. It turned out that the fictive temperature decreases, if the oven temperature is lower than the fictive temperature of the sample.

(ICG-P085-2019) Multicomponent Solution Solidification with Arrested Phase Separation Model for Glass Transition

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Due to nonuniform aggregation in liquid state, from thermodynamic standpoint any glass-forming liquid in vicinity of liquid-to-solid phase transition temperature, irrespective of actual chemical composition, shall be described in terms of multicomponent solution whose comprised of same chemical elements components have characteristic atomic arrangement deviating to various extent from thermodynamic ground state with respect to size, shape, density, structure, and stoichiometry. Therefore, glass transition is a process of non-equilibrium solidification of multicomponent solution while attempts of liquid and solid phases of the solution to separate out are mostly arrested due to quenching. Thus, solidification occurs in absence of solid-liquid interface, so the substance in liquid-to-glass transition region is observed behaving like fluid with rapidly growing viscosity that reflects formation of mechanically rigid and stable bound configurations. It is shown that glass transition shall be classified as phase transition in multicomponent solutions and not a standalone phenomenon.

(ICG-P086-2019) Chemical Characterization of Amorphous Er-doped phase-separated nanoparticles in silicates via Secondary Ion Mass Spectrometry (SIMS) Imaging

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The composition of amorphous Er-doped Dielectric Nano-Particles (DNPs) with diameters spanning a range of 2 – 200 nm has previously been investigated using a combination of various correlative analytical techniques including SIMS, Atom Probe Tomography (APT), Transmission Electron Microscopy (TEM) and Electron Probe Micro Analysis (EPMA). In particular, SIMS allowed to qualitatively evaluate the chemical composition of NPs with diameters greater than 100 nm while NPs of sizes 2-10 nm were successfully characterized using APT. Consequentially, the composition of NPs within the 10 nm to 100 nm size range remains unexplored due to the lack of analytical techniques that covers this range. In an attempt to fill the gap, we present results obtained with the ZEISS ORION NanoFab recently equipped with a Secondary Ion Mass Spectrometer- This novel instrument allows for high-resolution (< 0.5 nm) secondary electron (SE) imaging of samples using a focused He^+ beam with in situ correlative SIMS analysis at 15 nm of spatial resolution using a focused Ne^+ beam.

(ICG-P087-2019) Neutron scattering studies of crystallization in metallic glasses

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Upon heating a metallic glass to above its glass transition temperature, crystallization that promotes long range order will take place, often resulting in a high density of nanocrystallites embedded in a glassy matrix. Understanding how these crystallites nucleate and grow will help to control the microstructure and improve physical and mechanical properties for engineering applications. Here we report in situ neutron total scattering studies of crystallization in Zr-based metallic glasses with pair distribution function analysis. We show a whole pattern analysis approach to extract the relative fraction of crystallites to the remaining glassy matrix. The results can be well interpreted by the Johnson–Mehl–Avrami law, indicative of a three-dimensional nucleation and growth process during crystallization from a supercooled liquid. The approach used in this study is expected to be useful in quantifying, and thus understanding, the kinetics of crystallization in a broad range of non-crystalline materials, particularly, oxide glasses for which neutrons are more sensitive to oxygen.

(ICG-P088-2019) Multicomponent diffusion and crystallization in borosilicate glass melt

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Understanding the phenomena that occur during glass melting is of major concern for better monitoring the process and for finding new matrix compositions. Chemical diffusion is particularly interesting to characterize the driving force for physico-chemical properties and it is a powerful tool for describing how atoms move and their kinetic. This poster is dedicated to experiments designed for getting information on chemical diffusion in a simplified borosilicate glass and on its crystallization behavior. The impact of chemical diffusion on crystallization and liquid homogenization is studied for a sodium borosilicate. For this system, qualified as multicomponent, the description of diffusive phenomena requires the calculation of a diffusion matrix that takes into account diffusive couplings between species. These couplings can be written in the form of diffusive mechanisms that are invariant with temperature. The activation energies associated with these exchanges are close to the activation energy of shear viscosity which suggests that viscous flow and chemical diffusion are driven by a single mechanism related to the frequency of Si-O and B-O bond breaking. It is also highlighted that in the supercooled liquid, the principal and the secondary diffusive exchanges play a significant role on the kinetics and direction of cristobalite growth.

(ICG-GSP-P089-2019) Unmasking the Breakdown of the Classical Nucleation Theory

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Using a fitted value of the nucleus/liquid interfacial energy and viscosity data as a proxy for the diffusivity, the Classical Nucleation Theory, CNT, is a good descriptor of the temperature dependence of homogeneous nucleation rates in supercooled liquids. Allegedly, however, it strongly overestimates the nucleation rates below the temperature of maximum nucleation, T_{max}~T_g (glass transition temperature), originating the so-called nucleation breakdown. This apparent inability of the theory is not related to the breakdown of the Stokes-Einstein relation and has been associated by several authors with some assumptions of the CNT related to its thermodynamic and diffusional parameters. Here, we propose a more straightforward yet robust hypothesis that this problem can be due to an experimental artifact, because the CNT is only valid when the system reaches a steady-state regime. However, it is not easily achieved below T_g, because most researchers do not perform nucleation treatments for long enough time intervals. To test this hypothesis we obtained and analyzed extensive crystal number density versus time data at several temperatures, below and above the alleged break, for lithium and barium disilicate glasses. Then, we verified the datasets through the CNT only using data for which the steady-state was indeed reached. With this rigorous procedure, no breakdown is observed, which corroborates our hypothesis.

(ICG-GSP-P090-2019) Shear-induced deformation and the structural change in aluminosilicate glasses at room-temperature condition

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Stress relaxation by deformation such as densification and/or flow is closely related to the toughness of glass material. Hence, knowledge on the structural evolution via deformation can give an important insight for the understanding glass fracture, further, the

development of strong glass product. Shear stress under confining pressure, 1.5 GPa, was applied to 20(MgO or Na_2O)-20Al_2O_3-60SiO_2 glasses (MAS or NAS) by quasi-uniaxial compression using a hydraulic press. The glass was sandwiched with alumina pistons, cut 45 degrees against compression axis to apply simple shear stress. Degree of deformation was evaluated from strain and density measurement. Structural changes have been investigated by Raman and XANES spectroscopies. MAS showed higher shear strain γ= ~3 than that for NAS (γ= ~1) indicating that the threshold stress for shear deformation of MAS is lower than that of NAS. MAS and NAS were densified by shear stress up to 9% and 6%, respectively, suggesting that MAS is more deformable than NAS. Raman spectra of NAS showed a drastic increase of intensity at ~600 cm^{-1} (D2 structure). Whereas, Al K-edge XANES spectrum suggested that 19% of Al in MAS was transformed to high-coordination state such as 5 or 6-fold ones. These different structural modifications imply that the deformation mechanisms of MAS and NAS glasses under shear stress are different from each other.

(ICG-P091-2019) Alkaline earth mixing effect of CaO-Al_2O_3-SiO_2 glass on plasma resistance under fluorocarbon plasma with Ar^+

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Y or Ca-Al_2O_3-SiO_2 glasses have plasma resistance. Because, some of them have high CTE and the melting point and crystallized easily, there is a limit for application. Therefore, we investigated the change of glass stability and plasma resistance with mixing RO(R: Mg, Sr, Ba and Zn) in Ca-Al_2O_3-SiO_2 glass. The compositions of base CAS glasses were selected following as; A: 48CaO-9.1Al_2O_3-42.2 SiO_2, B: 26.2CaO-14 Al_2O_3-59.8SiO_2 (in mol%). In order to identify RO mixing effect, RO substitute the half of CaO in each compositions and they were named RA and RB, respectively. All of RO decreased transition temperature and softening point of A and B glasses. The half sphere temperature($T_{1/2}$) of glass A increased with RO, except of SrO, however glass B showed the inverse behavior. It is related crystallization phenomenon. That is, RO affects the high temperature stability of A and B glasses. RA and RB showed higher plasma resistance than reference materials. Especially, MgO and SrO enhanced the plasma resistance in glass A. So, it is expected that some of RO mixing may improve the stability and maintained plasma resistance of CAS glasses.

(ICG-GSP-P092-2019) Comparison of plasma resistance between coating and bulk of CaO-Al_2O_3-SiO_2 glasses

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In the display and semiconductor manufacturing process, particles, which occur during the dry etching process, cause defects from ceramic parts. Previous studies suggested that plasma resistant glasses, Y_2O_3- or RO-Al_2O_3-SiO_2 (R, Alkaline earth), may be applied the coating for reducing particle of ceramic parts in etching process. CaO-Al_2O_3-SiO_2 glass was selected to coat ceramic part with spray method. We controlled spray conditions, which are spraying distance, time, and substrate temperature, to obtain a uniform coating. Surface roughness, thickness and microstructures were estimated according to glass frit compositions, coating and sintering conditions. Also, the plasma resistance of samples was examined by analyzing etching rate and their surface morphologies after they were exposed to CF_4/O_2/Ar plasma gases. The etching rate of coated samples was faster than bulk glass, by 3~10 times. The surface roughness of the coating specimen is higher than the glass bulk. It thought that the surface roughness increases because high half sphere temperature and crystallization of glass increased the surface roughness of coat. As a result, surface roughness and uniformity affect plasma corrosion resistance when CAS glass systems was applied to coat to ceramics substrate.

(ICG-GSP-P093-2019) The Effect of composition of Plasma Resistance of CaO - Al_2O_3 - SiO_2 glasses under Fluorocarbon Plasma with Ar^+

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This study investigated the plasma resistance of CaO - Al_2O_3 - SiO_2 (CAS) glass depending on composition. The glass compositions were selected by two methods; (1)glass compositions selected by conventional method around eutectic point and (2)known compositions in previous study. Also, the plasma resistance of each glass composition was examined by analyzing their surface microstructure and etching rate when the glasses were exposed to CF_4/O_2/Ar plasma gases. There was no statistical difference in plasma resistance between two compositions groups. The CAS glasses showed 5~10 times superior plasma resistance compared to sintered Al_2O_3 or sapphire, where the etching rate of the Al_2O_3 and CAS glasses is 76.06 and 6.77~18.42 nm/min, respectively. Within the selected glassification range of the CAS-based glass, it was determined that the Al_2O_3 component most significantly affected plasma resistance. Glass compositions using conventional method can be more advantageous for glass fabrication.

(ICG-GSP-P094-2019) Statistical Mechanical Modeling of Lithium Borate Glass Structure and Topology

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Predicting the compositional evolution of the atomic-scale structure of oxide glasses is important for developing quantitative composition-property models. In binary borate glasses, the addition of network modifiers will either increase the connectivity by converting three-fold into four-fold coordinated boron, or decrease the connectivity by creating non-bridging oxygens. Here, based on ^{10}B nuclear magnetic resonance spectroscopy data from literature, we present a statistical description of the compositional evolution of both intermediate range superstructures (e.g., boroxol rings) and short range Q^n species in lithium borate glasses. This is done by accounting for the relative enthalpic and entropic contributions to the bonding preferences. We show that the entire glass structure evolution can be predicted based on experimental structural information for only a few glass compositions in each series. The developed structural model can be combined with a previously established constraint theory model to also predict the glass transition temperature.

(ICG-GSP-P095-2019) Molecular Dynamics Simulation Study of Cooling Rate Effect on Fluoride Phase Separated SiO_2-Al_2O_3-BaF_2 Glass

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Oxyfluoride glass and glass-ceramics are important optical materials owing to their good mechanical properties and low phonon energy. The thermal history during the sample preparation affects phase separation and crystallization behavior, which have influence on luminescent quality. Here, we use molecular dynamics simulations with Teter potentials to study the effects of thermal history, in terms of cooling rate here, on the alkali earth fluoride containing aluminosilicate glass. Short and medium range structure and glass

properties were analyzed. The results indicate that the cooling rate plays a critical role on glass structural features by affecting the fluorine coordination environment, especially the aggregation of alkali earth ions and fluorine. More alkali earth ions can be extracted from oxide phase to coordinate with fluorine under lower cooling rate, and therefore the rearrangement takes place in oxide phase with fewer glass modifiers. Also, the behaviors of different alkali earth ions against the change of the cooling rate vary. This study gives us a clear idea of the thermal history dependence on the structures and properties of phase separated glass materials.

(ICG-P096-2019) Charge carrier mobility of alkali silicate glasses calculated by molecular dynamics

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Although ionic conductivity is an important property of glasses, with technological applications and relation to fundamental glass science, there is no single model in the literature capable of predicting all experimental results. The main difficulty arises from the challenge of separating experimentally the number of effective charge carriers and their mobility. With molecular dynamics (MD), one can observe the ionic conductivity phenomenon on an atomic level, thus being able to solve this mystery. In this report, a method of utilizing MD simulations is proposed for the study of the ionic mobility of Na, Li, and K ions in binary silicate glasses. Values found for glasses with x = 0.1, x = 0.2, and x = 0.3 alkali content are between 10^{-5} and 10^{-4} cm^2 s^{-1} V^{-1} and did not change significantly with composition or temperature. This is in agreement with the interstitial pair and weak-electrolyte models used to explain ionic conductivity in glasses.

(ICG-P097-2019) Effect of Temperature and Pressure on Molar Volume of ZnO Wurtzite Phase Under Extended Pressure and Temperature a Molecular Dynamics Prediction

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The behavior of molar volume of ZnO wurtzite phase is investigated using parallel molecular dynamics and dl_poly_4 software in RAVEN supercomputer of Cardiff University (UK). In this work we study the effect of temperature and pressure on molar volume of ZnO wurtzite type in the range of 300-3000K and 0-200GPa of temperature and pressure respectively. We analyze the relationship between pressure and temperature on molar volume; our data are in agreement with available results, although no more work under the previous conditions of pressure and temperature. Our work is very important in medicine, pharmacy, and geophysics, which need confirmation in future.

(ICG-P098-2019) Force-Enhanced Atomic Refinement of the Atomic Structure of Calcium Aluminosilicate Glasses

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Calcium aluminosilicate (CAS) glasses are archetypical models for alkali-free glasses used in display applications. However, despite their engineering interest, the atomic structure of CAS glasses remains debated (e.g., the existence of 5- and 6-fold coordinated Al, tri-cluster oxygen, free oxygen, etc.). Here, we apply the Force-enhanced Atomic Refinement (FEAR) method to refine the structure of simulated CAS glasses. We show that the FEAR method yields a structure that shows an excellent agreement with neutron diffraction data. Importantly, the FEAR-based glasses exhibit higher thermodynamical stability that glasses simulated by molecular dynamics or reverse Monte Carlo simulations. We discuss some consequence on the structure of CAS glasses.

(ICG-P099-2019) Force-Enhanced Refinement of the Atomic Structure of Silicate Glasses

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Accessing the structure of silicate glasses by atomistic simulations remains challenging. Indeed, traditional molecular dynamics simulations depending on the melt-quench method are limited to very high cooling rate and, hence, tend to overestimate the degree of disorder in glasses. Also, conventional reverse Monte Carlo simulations can yield unrealistic structures since a virtually infinite number of configurations can have the same pair distribution function. Here, to overcome these limitations, we report a new method that combines energy minimization with reverse Monte Carlo. Through studying the example of sodium silicate glasses, we show that this method provides some glass configurations that exhibit higher stability than those produced by melt-quench or reverse Monte Carlo. Also, we discuss how this increased degree of stability manifests itself in the atomic structure (with a focus on the medium-range order). This paves the way toward an increased ability to accurately model the structure of silicate glasses.

(ICG-GSP-P100-2019) Elasticity and ordering probe the structure of solids at different length scales

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Solids are commonly classified as ordered or amorphous on the basis of their structure. The mechanical properties can also be used to distinguish them, as in ordered solids the bulk and the shear modulus are comparable, while in amorphous ones the shear modulus is comparatively smaller. Systems with low structural order may exhibit mechanical properties typical of crystals and the converse[1] making the relation between structural and mechanical response complex. We investigate this relation in solids with a variable degree of disorder and purely repulsive interparticle interaction. We prepare the system by randomly displacing a fraction m of the atoms in a fcc crystal[1], and minimizing its overall energy. We demonstrate that the ordering properties of the system do not vary continuously with m, exhibiting a first-order like transition from an ordered to a disordered configuration as m increases. Near the transition, the system appears ordered on the basis of standard structural order parameters considering symmetricity of the Voronoi neighbors of each particle. However, it appears disordered from the analysis of its mechanical properties. We rationalize this observation introducing a novel order parameter that consider the spatial symmetry of the contacts of each particle. This indicates that structural ordering and mechanical properties usually probe the structure at different length scales.

(ICG-UGSP-P101-2019) On-chip mid-infrared supercontinuum generation based on chalcogenide waveguide

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As a bright broadband mid-infrared (MIR) source, on-chip supercontinuum (SC) generation has attracted increasing attention for bio-chemical detection, medical imaging and photonic integrated system. Various MIR SC demonstrations have been reported using silicon, sapphire, tellurites, fluorides and chalcogenide fiber. Chalcogenide glasses can transmit well into the MIR and have large third-order nonlinearity making chalcogenides ideal candidates for on-chip MIR SC generation. In this paper, we experimentally present the demonstration of a SC source integrated on-chip where we design and fabricate high nonlinear chalcogenide glass waveguides as a platform for broadband SC generation. Combining the superior dispersion engineering and the commercial femtosecond laser, SC spectra spanning 2-10μm with moderate average output power are obtained. Furthermore, simulations are also performed by

solving the generalized nonlinear Schrödinger equation with dispersion terms up to 20th order which agree well with experiment. This work represents an important step towards realizing a miniaturized photonic chips.

(ICG-UGSP-P102-2019) Bright Mid-infrared Supercontinuum Generation in Chalcogenide Photonic Chip

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Complemented by more recent advancements toward on-chip mid-infrared thin-film and waveguide technology, it is anticipated that label free integrated mid-infrared sensing schemes will readily complement existing in situ chem/bio sensor and assay platforms. However, the challenge, up to date, is still how to get bright, stable and coherence supercontinuum source covering the fingerprint absorption spectra of bio-moleculer. Chalcogenide (ChG) glasses can transmit well into the MIR and have large third-order nonlinearity making ChG ideal candidates for on-chip MIR SC generation. On-chip supercontinuum (SC) sources have attracted increasing attention for the possibility of integrating. In this paper, a ChG spiral waveguide with a Ge-Sb-Se core and Ge-Se cladding was designed and fabricated, which had a propagation loss of 0.2 dB/cm. By pumping waveguide with length of 11 cm at 4μm with 125 fs pulses, we achieved a SC covering 2~10 μm broadband SC generation. Furthermore, simulations were also performed which agree well with experiment. The maximum output average power was ~50 mW, which was the highest one produced so far over this range and may provide adequate brightness for high- sensitivity MIR sensing.

(ICG-GSP-P103-2019) Machine-learning-based Molecular Dynamics Simulations of Silica: Soft vs. Hard Forcefields

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Classical molecular dynamics simulations are widely used to facilitate the modeling and design of silicate glasses. To this end, several empirical have been developed—each of them focusing on distinct features of silicate glasses (e.g., structure, mechanical properties, etc.). Available forcefields relying on fixed partial charges can be divided into "soft" and "hard" depending on the partial charge attributed to Si atoms (around 2.0 and 2.4, respectively). Here, we use machine learning to explore the "landscape of silica forcefields," that is, the evolution of the overall forcefield accuracy as a function of the forcefield parameters. Interestingly, we show that soft and hard forcefields correspond to two distinct, competitive local minima in this landscape. By analyzing the structure of the silica glasses predicted by soft and strong forcefields, we show that these two families of potential yield a distinct medium-range order structure. This work provides a theoretical foundation for the rational modeling of ionocovalent glasses.

(ICG-GSP-P104-2019) Application and Simulation of TeO_2–V_2O_5–CuO glass solder for joining of ceramic substrate

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The reliability of direct bonding copper on ceramic substrates remains a challenge and is a difficult technology applied in high-power semiconductor devices. In this paper, a method proposed investigates bonding with the lead-free TeO_2–V_2O_5–CuO oxide glass solder as an intermediate layer between copper and ceramic substrates. Thermal analyses of the prepared glasses were carried out to determine glass transition and crystallization temperatures. The prepared glass showed surface crystallization with no sign of bulk crystallization. Furthermore, a comprehensive three-dimensional numerical multilayer copper/glass solder/ceramic substrate model was developed to optimize the reliability of DBC sealing with lead-free low temperature TeO_2-V_2O_5-CuO glass solder. We studied and compared the changes of the thermal-stress coupled fields of alumina, aluminum nitride and silicon nitride ceramic materials after applying the same boundary conditions and loads. Results showed that redox reactions occurred between the copper plate and the solder took place. A compound $CuTeO_3$ was observed to form between the ceramic and oxide layer. Aluminum nitride substrate performs the most prominent among the three, which produces the maximum strain displacement of 1.54×10^{-5}m at a heat flux of 20,000J/(m^2×s) after 24 operating hours. The computer simulation was carried out in ANSYS 15.0 platform.

(ICG-GSP-P105-2019) A comparative study of melt-formed and fracture surfaces of silicate glasses using large scale computer simulations

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We present the results of multimillion atom molecular dynamics (MD) simulations in which we study the structure and topology of sodium silicate glass surfaces. Surface images up to a length of 50 nm with atomic resolution are obtained. We find that the fracture surface show more pronounced inhomogeneities in both local structure and composition in comparison with the melt-formed surfaces. Surface roughness indicators such as root mean square (RMS) roughness and roughness exponent for characterizing the self-affine nature of surfaces are calculated and compared with experimental data from the literature. It is found that the melt-formed surfaces are generally smoother than the fracture surfaces. Also, the surface roughness tends to increase with increasing Na_2O concentration in the glass. Finally we discuss how the properties of the fracture surfaces depend on the cooling rate for producing the glass, the strain rate for the fracture, and the fracture temperature.

(ICG-P106-2019) Impact of Ion Exchange on Glass Acid Durability

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The effects of ion exchange on glass mechanical durability have been extensively studied over the last several decades. Less is known about the impact of the ion exchange process on the chemical durability of glass. Previous studies have looked at the effects of ion exchange on glass water durability. In an effort to study the effects of ion exchange on glass acid durability, a series of Li/K/Na glasses were prepared where the Li/Na, Na/K and K/Li ratios were varied through the ion exchange process. These glasses were then leached in 5% hydrochloric acid for eight hours at 95°C. The impact of the ion exchange process was explored through glass weight loss as well as ICP analysis of leached alkali into the acid solution.

(ICG-P107-2019) Study on the Properties of Self-trapping AZO Photoelectric Glass by RF Magnetron Sputtering at Room Temperature

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Underlying Al-doped Zinc Oxide (AZO) thin films were deposited by RF closed field-unbalanced magnetron sputtering system at room temperature. The RF sputtering pressure was adjusted from 1.5Pa to 0.1Pa. After that, Scrape a layer of polystyrene pellets on the surface of underlying AZO film. Finally, a 100nm thick top-layer AZO film was sputtered. As the working pressure decreased, the target voltage gradually increased. When the working pressure was 0.2Pa, the contact angle of the underlying AZO film was the lowest, which is 75.71°. Simultaneously, the distribution of PS spheres was approximately regular, and the self-trapping AZO photoelectric glass has the strongest diffraction peak (002). The test found that the lowest resistivity of self-trapping AZO glass was 3.64×10^{-4}Ωcm. Combined with the carrier concentration and carrier mobility test results, it is

found that the decrease in resistivity was mainly due to the increase of carrier concentration. Self-trapping AZO photoelectric glass from 0.2Pa exhibited the highest haze of 20.8%.

(ICG-P108-2019) Advanced System for the Measurement of Glass Dissolution Rate

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Acid etching is broadly used in many areas of glass research. In keeping with Corning's core expertise in glass and ceramics, the ability to reliably measure etch rates is necessary, especially for HF-containing chemistries. This new instrument was built for this purpose and it's complete with automated valving/sequencing/rinsing to expedite measurements, and custom software for data acquisition and live-processing. It enables in-situ etch rate measurement with a fast and reliable manner for any transparent materials. In addition, its ease of operation, ability to control temperature, flow rate, and many other programmable features allows for researchers to quickly study the effects of different etchant chemistries on numerous glass compositions. This discussion will capture the key features of this new technology, some operational details, start-up and reproducible experiments, and finally, current examples of its application.

(ICG-P109-2019) Patterned Glass Strengthening with Chemical Tempering via Bath Technology

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Chemically tempered patterned glass, with low reflection, high transmission as well as low weight and high strength properties, is a promising material to be used in the photovoltaic industry as the cover glass of solar panels with high performance. In this research, 2 mm thick low-iron containing patterned glass has been investigated from structural, optical and mechanical point of view with respect to time and temperature. For this purpose, mass average diffusion coefficients of exchanged ions have been calculated based on the weight difference before and after chemical tempering. In addition, potassium and sodium concentration depth profiles have been measured using energy dispersive X-ray spectroscopy in a scanning electron microscope (SEM-EDS). Strength of the glass samples has been determined through ring on ring test results and Weibull diagrams. Compressive stress value of the chemically tempered patterned glass has been compared with chemically tempered float glass with the same thickness. In addition, resistance against various atmospheric conditions has been evaluated with aging, salt, acid and abrasion tests. To sum up, it is possible to improve the strength of patterned glass up to three times with chemical tempering without any change in optical properties. The authors acknowledge Yildiz Technical University Scientific Research Fund for the financial support under contract No. FYL-2019-3536.

(ICG-P110-2019) The Effect of Weathering on Chemical Strengthened Thin Glasses

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Investigation of glass corrosion against weathering is of vital importance for the determination of its lifetime and reliability for various applications. In this context, corrosion of glass has been studied from many perspectives. However, the effect of weathering on chemically tempered glass has not been extensively studied so far, although it has a potential to be used in many different environmental conditions. In this work, glass samples with 1.1 mm thickness having different compositions were subjected to weathering tests before and after chemical strengthening. The influence of weathering on the optical, structural and mechanical properties of glass samples were studied in a comparative manner with the glass in non-tempered state. It has been observed that weathering negatively affects fracture strength as well as crack formation probability of chemically strengthened glass. In addition it has been found out that this negative effect of weathering can be compensated by the modification of Al_2O_3 content in the glass structure. *The authors acknowledge to the Yildiz Technical University Scientific Research Fund for the financial support under contract No. FYL-2019-3577.*

(ICG-P111-2019) The thickness and degree of dealkalization of surface layers of industrial glasses, thermochemically modified by fluorine- and chlorine-containing gaseous reagents

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Bottles, jars and flasks of colorless glass, bottles of green glass, sheet glass samples, assorted and illuminating glassware made from transparent colorless and milk glasses have been subjects of investigation. Difluorodichloromethane, difluorochloromethane, hydrogen fluoride and chloride have been used for thermochemical treatment of glass. Thermochemical treatment of glass samples was held in laboratory and industrial conditions. The main regimes of thermochemical treatment of glass samples are the following: temperature - between 573 and 873 K, duration - between 1 s and 30 min, quantity of gas reagent introduced into the reacting vessel - between 0.01 and 1.00 mol. The intensity of glass dealkalization by fluorine- and chlorine-containing gaseous reagents was estimated using the extraction rate of alkaline cations. To analyze the chemical composition and structure of surface layers of industrial glasses, the methods of section etching by HF solution and IR spectroscopy have been used, subsequently, the microhardness has been measured. The experiment determined how various regimes of thermochemical treatment with gases influenced on the thickness and degree of dealkalization of surface layers of industrial glasses for various purposes.

(ICG-P112-2019) Blue upconversion emission in Tm^{3+}/Yb^{3+} co-doped $Pb_2P_2O_7$-Nb_2O_5-XF_2 (X = Mg, Ca, Sr, Ba) glass and glass-ceramics

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Alkali earth niobium fluorophosphate glasses present interesting features such as low characteristic temperatures, high thermal stability against crystallization, transparency from UV to NIR and good rare-earth solubility, which makes them promising materials for photonic applications. In this work, a series of niobium fluorophosphate glasses were synthesized by the conventional melt-quenching method according to the composition rule $97.5[65Pb_2P_2O_7\text{-}20Nb_2O_5\text{-}15XF_2]:0.03Tm^{3+}/0.012Yb^{3+}$ where X = Mg, Ca, Sr and Ba in a platinum crucible under air. Optical, physical and structural properties of the new glass and glass-ceramics samples were investigated by differential scanning calorimetry, X-ray diffraction, Raman spectroscopy, absorption from UV to NIR, IR transmittance, transmission electron microscopy, photoluminescence, and Z-Scan. Glass-ceramics containing the different earth-alkaline ions were obtained through heat treatment at temperatures above glass transition temperatures. Fluorescence, excitation spectra, and UC analysis were recorded at 300 K. The preliminary results show a very intense emission at 450 nm by Tm^{3+} when the sensitizer Yb^{3+} was pumped at 980 nm, both for glass and glass-ceramic materials. Preliminary results showed that spectroscopic properties of Tm^{3+}/Yb^{3+} depend significantly on the kind of alkali earth oxide in glass and glass-ceramic hosts.

(ICG-GSP-P113-2019) Calculation of Judd Ofelt parameters:Sm^{3+} ions doped in Zinc magnesium phosphate glasses

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A series of transparent phosphate glass with composition (60-x) P2O5-30ZnO-10MgO-xSm2O3 where x=0.1, 0.3, 0.6 and 1.0 mol% are prepared and studied using photoluminescence (PL) and optical absorption spectroscopy (UV-VIS). Eight absorption bands are recorded and used to calculate the Judd-Ofelt (JO) intensity parameters (Ω2,Ω4,Ω6) for the glasses which follows the following trend; Ω2>Ω4>Ω6. The JO intensity parameters used to evaluate the spontaneous emission properties such as branching ratio, transition probability and radiative lifetime. From PL spectroscopy, four emission peaks are observed at 561, 593, 643 and 699 nm corresponding to the transitions 4G5/2-.6HJ (J=5/2, 7/2, 9/2 and 11/2) respectively.

(ICG-P114-2019) The new red phosphors based on modified fluorozirconate glasses, doped with manganese ions

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At present, the manganese-doped compounds, mainly Mn^{4+}, attract attention as a promising material for the effective red phosphors for LED warm white light sources. The modified with $BaCl_2$, $BaBr_2$ MnO_2-doped fluorozirconate glasses (ZBLAN) were synthesized and their luminescence and EPR spectra were measured. Manganese ions have green luminescence band peaking at 545 nm in the fluorozirconate glass. Modified glasses emitting in the red region were obtained. Complete $BaCl_2$ substitution for BaF_2 in ZBLAN shifts the peak emission wavelength to 610 nm. To obtain data on the oxidation state of manganese ions, we measured EPR spectra of the glasses. The EPR spectrum of the MnO_2-doped ZBLAN glass corresponds to only one paramagnetic species, Mn^{2+}, whereas the EPR spectrum of the modified glasses indicates the presence of two distinct Mn^{4+} species, differing in hyperfine coupling constant. Comparison of the luminescence and EPR spectra of the glasses demonstrates that there are certain correlations between them. The shift of the emission line with the replacement of fluorine by chlorine or bromine can be caused by an increase of the bond covalence or a change of the local environment of the Mn^{4+} ions symmetry. We have synthesized a new phosphor based on manganese-doped fluorozirconate glass. This work was supported by the Russian Science Foundation (Project No.18-13-00407)

(ICG-GSP-P115-2019) Near infrared emission from Nd^{3+}-Cr^{3+} codoped oxyfluoride glass ceramics containing $KZnF_3$ nanocrystals pumped by a solar simulator

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Transparent Nd^{3+}-Cr^{3+} codoped fluorosilicate precursor glass (PG) and glass ceramics (GCs) containing fluoride nanocrystals have been fabricated by the melt-quenching method followed by thermal treatment. Under the excitation of a solar simulator, intense near infrared emission in the range from 1020 to 1140 nm was observed in the PG sample. The luminescence intensity increased 10 times in GCs on account of the strong crystal field and of the low phonon energy environment. The microstructure was measured by transmission electron microscopy (TEM) and X-Ray diffraction (XRD). The mechanisms of the photoluminescence and energy transfer were confirmed via emission spectra and fluorescence decay. The great stability properties of the PG and GC samples, such as resistance to humidity and temperature, were demonstrated by the transmission spectra under different temperature and humidity levels. Due to their excellent optical property and stability, these PG and GC samples are potential gain materials for optical spectra conversion and solar pumped lasers.

(ICG-P116-2019) Determination of trace elements in glass by ICP-AES after co-precipitation technique using DDTC

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It is important to control the amount of trace elements that affect the transmittance of commercial glass. Regarding soda lime glass, alkali ions and alkaline earth ions as main components remain in solution even after acid decomposition. It is difficult to introduce the decomposition solution into an ICP-MS as well as an ICP-AES. We investigated a separation and concentration method of trace elements from these metal ions to analyze trace elements by ICP-AES. The pH of the glass decomposition solution was adjusted to ca.1 with aqueous sodium hydroxide solution, and aluminum nitrate solution was added as a co-precipitation agent. Then, pH of the solution was adjusted to 5.5 with aqueous sodium hydroxide solution to form the precipitation of aluminum hydroxide. After adding sodium diethyldithiocarbamate (DDTC) solution, the pH of the solution was adjusted to 9 and stirred during overnight to co-precipitate trace elements completely. The precipitation was collected by filtration. The precipitate was dissolved with a small amount of hydrochloric acid. The trace elements were determined by ICP-AES. We were able to determine trace elements in the order of 0.1 μg/g. Recoveries of trace elements were over 90%.

(ICG-GSP-P117-2019) Transition Metal Dopant Effects on UV-Fluorescent Glass

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Elements in the lanthanide series of the periodic table exhibit some interesting optical characteristics due to their f-orbital valence shell. Especially when used as dopants in glass, these optical characteristics range from visible light photochromism to ultraviolet induced visible fluorescence. This can be useful for artistic purposes when displaying glass pieces in a variety of illumination protocols. A multitude of rare-earth oxide dopants were examined for their fluorescence. All dopants produced visually colorless samples; but alone or in combination yielded a wide range of emitted colors. UV-Vis absorbance spectroscopy was conducted to determine the excitation wavelengths each element absorbs to induce fluorescence. Additionally, the effectiveness and intensity of emitted light was studied when pigments are added to the system. Lanthanide dopants were combined with common transition metal oxide colorants. The fluorescence emission was then analyzed visually from an aesthetic standpoint; as well as quantitatively through spectral analysis. Qualitatively, each colorant had a different effect on the dampening or strengthening of the rare-earth fluorescence.

(ICG-GSP-P118-2019) Scintillation, Luminescence and Optical Properties of Ce-Doped Borosilicate Glasses

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The investigation of the luminescence of Ce^{3+} is challenging because the 5d-4f transition is strongly influenced by the chemical composition and atomic arrangement of the host, with an increased effort being devoted to the investigation of the photophysics of Ce^{3+} in glasses particularly toward the development of scintillators. In this

work, the structure, ultraviolet (UV) transparency, luminescence, and scintillation of CeO_2-doped (0.1 mol%) borosilicate glasses containing different amounts of Sb_2O_3 and SnO_2 were investigated. Glasses were prepared by melt quenching in air and characterized by several spectroscopy techniques: Raman scattering, optical transmission and absorption, photo- and radioluminescence, and fluorescence lifetime. Raman scattering results presented two major groups of vibrational modes, within 300-900 cm^{-1}, and within 900-1200 cm^{-1}. Luminescence was dominated by a broad band centered at around 360-380 nm, depending on the chemical composition of the glass. Photoluminescence presented a dominant (96-98 %) fast decay time of 35-40 ns and was ascribed to Ce^{3+}. Scintillation output under X-ray excitation was highest for the SnO_2-containg glasses, in agreement with UV transparency results that revealed the cutoff wavelength to be lower for these glasses than for the Sb_2O_3-containing glass. This material is based upon work supported by the NSF Grant No. 1653016.

(ICG-GSP-P119-2019) Influence of B_2O_3 on structural heterogeneity of ternary SiO_2-Al_2O_3-B_2O_3 glasses doped with small amounts of Yb_2O_3

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Ternary (98.4-x) SiO_2 – x B_2O_3 – 1.5 Al_2O_3 glasses, with 1.25 < x < 9.35 mol %, containing small amounts of Yb_2O_3, were prepared by reactive powder sintering. We report on the role of B_2O_3 addition in the aluminoborosilicate glass network as investigated by UV-Vis-, photoluminescence and vibrational spectroscopy. In affecting super-structural heterogeneity, there is clear evidence that B_2O_3 actively participates in the process of Yb^{3+} dissolution in favour of Yb^{2+} formation.

(ICG-P120-2019) Broad band excitation of Tm^{3+} ions doped in tellurite glasses

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In the course of investigation of rare-earth (RE) ions in glasses and of the role of the host glass in the excitation of 4f electrons we studied photoluminescence (PL) spectra of zinc-tellurite and silica glasses doped with Tm^{3+}. Ternary TeO_2-ZnO-TiO_2 glasses were prepared by melt quenching, and silica glass by MCVD method. Both glass systems investigated by transmission, room- and low-temperature PL spectroscopy are characterized by very different band-gap and phonon energies. For PL excitation we use both the wavelength not in resonance with 4f levels of Tm^{3+} ions (514.5 and/or 532 nm) and also the wavelength that selectively excites only a particular 4f states of Tm^{3+} ions (653 nm). Both Tm-doped matrices excited by 653 nm exhibit photoluminescence related to RE ions. In case of excitation by 514.5 and/or 532 nm lines, only zinc-tellurite glasses show luminescence, no PL signal was observed from Tm^{3+} doped silica glass. For tellurite system we report the observation of a broad host-glass-emission band centred at about 850 nm and of a narrow emission band and/or absorption dips, due to 4f-4f transitions in Tm^{3+} ions, superposed on the broad-band PL. We assign the observed narrow dips in the broad-band host-glass PL to the electronic up-transitions in Tm^{3+} dopants. They are evidence for the energy transfer between electronic structure of the host-glass and 4f electrons of Tm^{3+} ions.

(ICG-P121-2019) The TeO_2-WO_3-$PbCl_2$ system – glass formation and properties

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The glass forming region was determined in the $PbCl_2$-TeO_2-WO_3 system. The thermal analysis showed that these glasses are thermally stable for bulk glasses production and that their glass transition temperatures are in the range of 250 – 350 °C, in dependence on glass composition. Bulk glasses were prepared by conventional melt quenching method from high purity starting compounds – TeO_2, WO_3 and $PbCl_2$. The optical properties were investigated in more detail. While the intensity of colour depend on oxidation-reduction conditions during melting, the position of short wavelength absorption edge and therefore of the band gap energy of the prepared glasses depend especially on material of the crucible used for melting. The platinum crucible, unlike the quarz glass or alumina crucibles, shifts the visible edge to the longer wavelengths (towards red colour). The transparency limits of the investigated glasses are 440 – 480 nm in the visible and around 7 μm in the infrared part of the spectrum, respectively. Their refraction index is up to 2.25. The low-temperature photoluminescence spectra show a broad luminescence band of the host glass matrix on which, in case of rare-earth (RE) doped samples, are superposed narrow emission bands from 4f-4f RE transitions. The intensities of RE inner transitions are weakly temperature dependent but the broad luminescence band can be observed only at low temperature.

(ICG-P123-2019) Investigation of luminescence and up-conversion properties of Ho^{3+}, Tm^{3+} and Yb^{3+}-doped tellurite glasses for solid-state lighting applications

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There are some drawbacks of conventional white LEDs such as large refractive index difference between phosphor and resin encapsulating the LED chip and also poor heat resistance of resin. Therefore, studies were focused on the search of new technologies to overcome these problems and improve solid-state lighting efficiency. Tellurite glasses have drawn attention due to their favorable properties such as high chemical and thermal stability, high rare-earth solubility, high refractive index, and low phonon energy. Ho^{3+}, Tm^{3+} and Yb^{3+} ion-doped glasses establish a promising combination for solid-state lighting through up-conversion energy transfer upon suitable excitation. It is known that the intensity of emissions change with the phonon energy and local crystal field of host matrix. In this study, Ho^{3+}, Tm^{3+} and Yb^{3+} ions were doped in a thermally and chemically durable TeO_2-WO_3-Li_2O glass matrix to investigate their luminescence properties. Photoluminescence and UV-Vis absorption measurements were performed and Judd-Ofelt parameters and CIE color coordinates were calculated to evaluate the potential use of these glasses in solid-state lighting applications. The authors acknowledge TUBITAK and Yildiz Technical University Scientific Research Fund for financial support under the projects numbered 117M206 and FYL-2019-3585, respectively.

(ICG-P124-2019) Composition dependence of chemical strengthening property for aluminosilicate glasses

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Effects of glass compositions and ion exchange (I/E) conditions on chemical strengthening were investigated for SiO_2-Al_2O_3-MgO-Na_2O glasses treated in KNO_3 salt. The obtained results suggest that depth of layer (DOL) changes monotonically with Na_2O content at certain MgO value. In addition, DOL followed Arrhenius equation

for change in both temperature and duration time of I/E process. As for compressive stress (CS), it was found that the original glass compositions could be divided into two compositional areas; A) CS generated by I/E increased with Na_2O content and were well correspond to the estimation based on expected gap of molar volumes at glass surface caused by I/E process and Young's modulus, and B) CS decreased with Na_2O content regardless of the increase in estimated CS. For glass compositions in area A, CS were considered to be almost free from the effect of structural relaxation during I/E, while in area B, structural relaxation during I/E extensively took place and CS was controlled by Tg /T(I/E) and duration time of I/E process. From these results effects of Al_2O_3 and MgO on chemical strengthening were considered.

(ICG-GSP-P125-2019) Structure and Properties of Porous Silica Glass in Response to Compression

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Classical molecular dynamics (MD) simulation was used to study the change of the structure and properties of porous silica glass under compression. Porous silica glass samples with different amount of porosity were prepared by removing K_2O from quenched K_2O-SiO_2 glasses. After compressed and released from a given pressure, the porous silica glass exhibits a higher densification rate than the pristine silica glass. Moreover, the densification rate and the resulting density increase with increasing porosity in the initial sample due to the increased flexibility of the network structure. Structural analysis shows that densified silica glass starting from a porous structure has a larger number of five-coordinated Si atoms than that from a pristine sample. These five-coordinated Si atoms act as plasticity carriers and lead to enhanced ductility in porous silica glass after densification.

(ICG-GSP-P126-2019) Deformation and fracture behavior of Na_2O-Al_2O_3-B_2O_3-SiO_2 glasses

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Understanding the link between the chemical composition of oxide glasses and their mechanical properties is the key to designing novel materials for current and emerging applications. Much insight into this correlation can be gathered from studying glasses in the Na_2O-Al_2O_3-B_2O_3-SiO_2 system, as they exhibit widely different structures, packing efficiencies, and a large span of hardness and modulus values. Using Vickers indentation, we here present a study of the deformation mechanism and resistance to cracking in twenty Na_2O-Al_2O_3-B_2O_3-SiO_2 glasses with fixed soda content. The observed compositional trends in mechanical behavior are discussed in light of the structural characteristics of the investigated glasses, as well as their atomic packing density and fracture toughness values. The latter is measured by the single-edge-precracked-beam method. Our results suggest that network topology considerations are crucial in the design of new crack-resistant and tough silicate glass compositions.

(ICG-GSP-P127-2019) Understanding the crack resistance of boron-containing glass under indentation using molecular dynamics simulation

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Several recent experimental studies have shown that glass systems with high boron content exhibit superior crack resistance under sharp contact loading. However, the underlying mechanism is still not fully understood. In this context, we carried out classical molecular dynamics simulations on sodium aluminoborate and sodium aluminosilicate systems to investigate the effect of boron on the response of glass to nanoindentation. A rigid hollow Vickers indenter made of carbon atoms is used to indent the glass sample with a fixed loading rate, during which the indenter interacts with the glass via a repulsive force field. To minimize the boundary condition effects in simulated nanoindentation tests, large samples of several hundred nm in lateral dimensions are used. The indenter angle is varied to study the effect of the indenter, as what has been done in experiments. These simulated nanoindentation tests reveal how the stress/strain field and the glass structure evolve with the deformation underneath the indenter. It was found that large number of boron atoms in the plastic zone change from three to four-fold coordination during the loading process, and most of them revert back to the three-fold state during the unloading process. Our study shows that this "reversible" boron coordination change plays a critical role in increasing the crack resistance of glass.

(ICG-P128-2019) Scratch hardness of rare-earth substituted calcium aluminosilicate glasses

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We report lateral deformation experiments on rare earth substituted glasses from percalcic CaO-Al_2O_3-SiO_2-Tm_2O_3. Using instrumented Berkovich indentation with normal loads below 100 mN, the scratch hardness was obtained from the work of lateral deformation per deformed volume in the elastic-plastic regime. The positive effect of rare-earth substitution on normal hardness, Poisson's ratio and Young's modulus was found to extent also to scratch hardness: in 25CaO-15Al_2O_3-60SiO_2, partial replacement of alumina by Tm_2O_3 leads to an enhancement of the scratch hardness by about 1 GPa per 2 mol% of substitution, reaching the highest values of scratch hardness which have been reported for oxide glasses thus far. The glass series was found to follow the previously reported linear correlation between scratch hardness and bulk modulus. The enhancement of scratch hardness is attributed to enhanced cation packing fraction and super-structural cohesion as a result of rare earth substitution.

(ICG-GSP-P129-2019) Nano-indentation studies on curved glass fiber surfaces using different tip shapes

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Despite the superior intrinsic strength of glasses, commercially available glass products are typically characterized by a relatively low practical strength. This is due to the high defect susceptibility of glasses along with their brittle fracture behavior. However, such surface flaws are not only created by handling. Microscopic defects may already form during the fabrication and processing of glasses. It is therefore not surprising that the highest practical strengths have been reported for carefully prepared optical glass fibers. Yet, a detailed appraisal of the contact damage resistance of glass fibers is challenging because of the surface curvature, which often impedes the application of common mechanical testing protocols, like micro- or nanoindentation. Here, we report on the elasticity, plastic deformation and fracture behavior of silica glass fibers during sharp contact loading. For this purpose, nanoindentation experiments were performed on glass fibers of varying diameters using standard diamond indenters as well as a wedge-shaped tip. By comparing the experimental results with the findings derived from flat specimens, the effect of surface curvature on the indentation response of glasses is shown, and a method for nanoscale strength-studies is deducted.

(ICG-GSP-P130-2019) Strain rate sensitivity of germanium-selenium glasses

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Chalcogenide glasses are widely used in optical applications either as information carrier or as sensors due to their optical transparency in the mid-infrared window (8-15µm), high refractive index and non linearity. Glasses from the GexSe1-x system have been extensively studied over the last decades because some of their physical properties do show an anomalous behaviour (Tg, density, band gap, indentation fracture toughness) at certain specific compositions for instance at x=20% also called the percolation threshold. In this work we studied the indentation behaviour of GexSe(1-x) ($0 \leq x \leq 30$) under constant strain rate conditions. Instrumented Berkovich micro indentation were performed at different strain rates (from 10^{-3} to 10^{-1} s^{-1}) at ambiante temperature, indentation residual imprints were image by atomic force microscopy. Energies at stake during indentation, strain rate sensitivity (computed from Norton's law) as well as indentation imprints shape and volumes are discussed as a function of the litterature and glass structure. Experimental results are in good agreement with a similar study based on pure Se glass. From AFM pictures a transition behaviour is identified near the percolation threshold.

(ICG-P131-2019) Mechanical Properties of Barium Disilicate Glass-Ceramics

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Barium disilicate glass (BaO.2SiO2 = BS2) is one of the few glass-forming systems that nucleate in the sample interior without the need of nucleating agents. This allows a relatively easy control of the desired microstructure in terms of volume fraction crystallized and crystal size. In this study, the variation of biaxial flexural strength, indentation fracture toughness, hardness and elastic modulus of BS2 glass-ceramics were measured as a function of the crystalline volume fraction keeping a constant crystal size. Glass samples were subjected to a dual heat treatment, ranging from 5 to 90 min at 700 °C for nucleation, and followed by crystal growth for 20 min at 785 °C. The resulting crystal diameter was ~10 µm and the crystallized volume fraction ranged from 0 to 100%. The flexural strength increased with the increase of the crystalline fraction. The fracture strength of the fully crystallized sample is 20% greater than that of the BS2 glass. The indentation fracture toughness increased from 0.56 ± 0.02 $MPa.m^{1/2}$ for the glass to 1.02 ± 0.01 $MPa.m^{1/2}$ for the fully crystallized sample. Unexpectedly, the hardness decreased with crystallization, from 7 GPa for the glass to 4.8 GPa for the fully crystallized sample. The elastic modulus remained practically constant with crystallization. All these changes will be fully discussed in terms of the material's microstructure.

(ICG-P132-2019) Internal friction in silica films via picosecond acoustics

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2. Sorbonne Universités, UPMC, Institut des Nanosciences de Paris, France
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Thin films of amorphous SiO_2 are key materials for a variety of applications that range from insulating layers in integrated circuits to overlays for surface acoustic wave devices or supports for metal nanoparticles in sensors. It is, however, empirically known that properties of SiO_2-films may considerably vary with preparation details. Deposited SiO_2 layers are also key materials for some precision experiments in which reduction of thermal noise is of crucial importance, the latter arising in part from internal friction within the material forming the resonator. It is therefore of fundamental interest to investigate the dissipative mechanisms at the origin of acoustic losses in amorphous dielectric layers and in particular to compare them to those of the bulk material, including the prototypical vitreous silica v-SiO_2. We report here, picosecond acoustic measurements of longitudinal sound dispersion and attenuation in an amorphous SiO_2 layer at temperatures from 20 to 300 K over frequencies ranging from about 40 to 200 GHz.

(ICG-GSP-P133-2019) The ternary alkali effect on characteristic temperatures in the aluminophosphate glass system

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Mixed alkali effect, MAE, has attracted attention and is successfully applied mostly in binary glass systems, such as borate, borosilicate, and phosphates. In order to further utilize the advantages of MAE, lithium, sodium and potassium oxides are incorporated in the aluminophosphate to develop low-temperature glass systems. The target glass system is designed as $0.5P_2O_5$-$0.04Al_2O_3$-xLi_2O-yNa_2O-zK_2O, where x+y+z=0.46. The ratios x:y:z are manipulated to figure out the mixed effect on characteristic temperature. It is demonstrated that the developed glasses obey the MAE prediction, that is when x:y:z reaches 1:1:1 the lowest characteristic temperatures, the transition and crystalline temperatures of 284 and 505 °C are found respectively. The characteristic temperature increases whenever the ratios of x:y:z deviates from 1:1:1. From NMR results, the majority of the bonding structure is Q^2 with a minor portion of <30% for Q^1. The lower characteristic temperatures can be explained by the shift of Q^2 band between 1150~1080cm^{-1} through Raman analysis. In the developed glass, K ion possesses weaker field strength than those of Li and Na ions, leading to a decrease of wavenumber in Raman shift when K is increased.

(ICG-P134-2019) Electric field-induced change of structure and thermal conductivity in spin thermal conductivity film

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We aim to fabricate advanced materials possessing electrically controllable thermal conductivity which contribute effective heat dissipation and high stability in the electronic devices. Therefore, we have focused on spin thermal conductivity materials, e.g., La–Ca–Cu–O (LCCO); In the materials, S=1/2 spins of Cu^{2+} which are antiferromagnetically coupled by O^{2-} are heat carrier, so that the materials show high, anisotropic thermal conductivity even at room temperature. We expect that the thermal conductivity can be controlled by electrically/electrochemically induced structure change. In this report, we fabricated spin thermal conductivity films (and multilayers with SiO_2) sandwiched by top and bottom electrodes. For the LCCO films, we investigated structure and thermal properties under application of an electric field by Raman spectroscopy and thermoreflectance method. We discuss structure and conductivity change on the basis of the results and additionally scanning transmittance microscopy and element mapping.

(ICG-GSP-P135-2019) Orientation of spin thermal conductive film of Sr-Cu-O system for active heat control

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We aim to fabricate heat control devices utilizing high thermal conductivity at room temperature, anisotropy, and their active controllability in spin thermal conductive materials. Here, the orientation structures which do not impair the advantages are required. In this report, we attempt to fabricate the highly oriented film and investigate effects of deposition conditions on structures. Samples were fabricated by conventional rf-magnetron sputtering (gas

type: Ar; pressure: 0.5 Pa; deposition rate: 5 nm/min). As a target, orthorhombic $SrCuO_2$ which was synthesized by press bonding after sintering was used. The substrates were silica glass and $SrTiO_3$(001). The samples were annealed in ambient air, and their structures and thermal properties were investigated by X-ray diffraction (XRD), atomic force microscope observation, spectrophotometer, and thermoreflectance method. The XRD pattern of the sample formed on the silica glass substrate before annealing have no peaks, which means that it was amorphous or microcrystalline. The sample annealed at 600°C for 400 s have peaks attributed to the (020), (040), and (080) planes of $Sr_{14}Cu_{24}O_{41}$, which is a spin ladder material. We discuss the influence of deposition conditions on structures and structural change by annealing. In addition, we will report about solid epitaxial growth using $SrTiO_3$ substrate.

(ICG-P136-2019) Compositional dependence of viscoelastic behavior in ternary aluminophospahte glasses around deformation temperature

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Thermal molding of glass is of great interest in the fabrication of optical elements. Viscosity and elasticity of glass around its deformation temperature are important features in the precision molding. Aluminum phosphate based glass is widely used in the molding application with low cost and low energy consumption. In the present study, viscoelastic behavior of ternary alumino-phosphate glasses has been studied by using parallel plate rheometry with dynamic viscoelastometry. The shear relaxation modulus obeyed a single-term Maxwell model. The elastic term in the model was consistent with the average covalent nature calculated from the glass composition, while the viscous term did not correlate with the glass composition. We discuss the mechanism of structural relaxation process around deformation temperature from the view point of bond strength, free volume, and so on together with the result of dynamic viscoelasticity.

(ICG-P155-2019) Comparative Study on Structural and Electrical Properties of TeO_2 and Sb_2O_3-Based Glasses

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Among heavy metal oxide (HMO) glasses, tellurite and antimonate glasses possess favorable properties such as low phonon energy and high dielectric constant. Additionally, they maintain medium optical band gap energy values comparable with conventional semiconductors. Hence these glasses are promising materials for new generation amorphous semiconductors to be used as optoelectronic materials. It is well known that addition of transition metal oxides to HMO glass systems enhances electrical and optical properties owing to their different oxidation states. In this work, glasses in the WO_3-MoO_3-TeO_2 and WO_3-MoO_3-Sb_2O_3 systems were synthesized using conventional melt-quenching method to investigate the effect of different glass formers on structural and electrical properties. XPS and FTIR techniques were performed for structural analysis. Electrical properties were analyzed through temperature dependent DC conductivity measurements and activation energy values were calculated accordingly. Consequently, structural and electrical properties were interpreted to evaluate the suitability of these glasses as large band gap amorphous semiconductors. The authors acknowledge TUBITAK and Yildiz Technical University Scientific Research Fund for their financial support under the projects numbered 117M206 and FYL-2019-3585, respectively.

(ICG-P137-2019) A method of activation of a quartz-containing raw material component of a glass batch with sodium hydroxide

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A result of an activation of a quartz-containing raw material source of glass batch with sodium hydroxide is an intermediate product, called alkaline concentrate (AC), obtained according to a scheme: quartz-(total) + NaOH(total) = AC(mNa2O;nSiO2), where m, n - mass fractions corresponding to the chemical composition of the glass. The phase composition of the AC is represented by amorphous and low-temperature quartz and sodium silicates. However, the chemical composition of the AC, obtained by known methods, does not correspond to the eutectic composition in the Na2O - SiO2 system, which may cause a later onset of the liquid phase than is supposedly possible. According to the proposed activation method, one part of the total amount of the quartz is activated by NaOH satisfying the production of a eutectic mixture, and a residue of the quartz is activated by the remaining NaOH that has the minimum value for the possibility of obtaining AC: quartz(total) = quartz(eutectic) + qurtz(residue); NaOH (total)= NaOH (eutectic) + NaOH (residue); quartz(eutectic)+ NaOH (eutectic) = AC(eutectic); quartz(residue) + NaOH (residue) = AC(residue); AC(total) = AC(eutectic) + AC(residue). The using of activated quartz by the proposed method might reduce further a melting temperature by 50-100 degree and a melting time by 15 - 25% compared with the known activation methods.

(ICG-P138-2019) Raw material non-destructive quality control in a chain of synthetic crystal quartz-concentrate-silica glass

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2. Quartz Technology LLC, Russian Federation

We propose non-destructive quality control of crystalline quartz used for the production of quartz glass intended for CW laser technology by directly measuring its absorption at the wavelength of CW ytterbium laser (λ=1071 nm). This measurement gives an estimate of the maximum absorption in the final product (quartz glass), since additional purification occurs at the stage of concentrate preparation, leading to a decrease in the impurity content. This proposal has been applied in the production of quartz crystals grown by the hydrothermal method at Quartz Technology LLC. The OH-group content in the investigated samples was 80-140 ppm. The content of all other impurities did not exceed 3 ppm. We used the previously developed method of time-resolved photothermal common-pass interferometry. For the calibration of the setup, calculations were made that took into account the stresses arising in crystalline quartz with inhomogeneous heating of the samples by probe radiation. The absorption measurement gave a value of 6×10^{-7} cm^{-1}±30%. Such an accuracy of absolute measurements in crystalline quartz is currently associated with a low accuracy of measurements of its physical parameters presented in the reference and used in calculations in the calibration procedure. The accuracy of relative measurements, determined by the signal-to-noise ratio (100/1), was no worse than ±2%.

(ICG-P139-2019) Analysis of valence states of sulfur by XRF with single-crystal spectrometer

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The release behavior of SO_2 gas in molten glass depends on the valence of sulfur in the raw material. Therefore, not only the content but also the valence state of sulfur in raw materials can be important data for determining the melting conditions of glass manufacturing process. In X-ray fluorescence analysis (XRF), it is known that the peak angle shifts due to the difference in valence states of elements, which is called chemical shift. In many literatures, high

resolution type XRF equipped with double-crystal spectrometer is used for analyzing valence states of elements. The analysis apparatus is special and expensive. Moreover, this analyzing method is a time-consuming because the fluorescent X-ray intensity detected from double-crystal spectrometer is much lower than that of the single-crystal one. In this paper, a newly developed valence analysis method of sulfur by commercial type XRF with single-crystal spectrometer will be introduced. The valence analysis of sulfur in a short time can be achieved by optimizing analytical conditions and sample preparation method. Calibration curve for sulfur valence analysis was prepared using a standard sample by mixing ZnS (sulfur in reduced state), Na_2SO_4 (sulfur in oxidized state) and high purity silica powder at predetermined ratios. Using this calibration curve, the results of analyzing glasses and raw materials will be reported.

(ICG-P140-2019) Fabrication and properties of MgO-Al_2O_3-SiO_2 glass-ceramics by solid-state reaction at low temperature

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The MgO-Al_2O_3-SiO_2(MAS) glass-ceramics were fabricated by solid-state reaction at 1000° C using compositions richer in MgO than the stoichiometric cordierite and B_2O_3 as sintering aids. The microstructure, mechanical and dielectric properties of the MAS glass-ceramics were investigated. Increasing B_2O_3 facilitated densification and enhanced mechanical performances of the MAS glass-ceramics. The glass-ceramics obtained by non-stoichiometric (richer in MgO) has a smaller grain size of α-cordierite than that of α-cordierite in the glass-ceramic obtained by stoichiometric. Non-stoichiometric sample with 25 wt% B_2O_3 exhibits excellent dielectric property ($\varepsilon = 4.50$, $\tan\delta < 0.005$) and its flexural strength, elastic modulus, fracture toughness are 86 MPa, 144 GPa, 1.6 $MPa \bullet m^{1/2}$. The present technique has a promotion effect on the use of solid-state reaction at a low temperature since its sintering temperature is about 400° C lower than that of the traditional solid-state reaction method.

(ICG-P141-2019) The melting process and properties of alkali-free B_2O_3-Al_2O_3-SiO_2 glasses

L. Shi*[1]; X. Cao[1]; Z. Zhong[1]; Q. Gao[1]; N. Han[1]; J. Cui[1]; P. Wang[1]; L. Ma[1]; S. Peng[1]

1. State Key Laboratory of Advanced Technology for Float Glass, China

The melting process and the properties of alkali-free B_2O_3-Al_2O_3-SiO_2 glasses were studied. The R_2O-Al_2O_3-SiO_2 glasses were also studied as a contrast. The physical and chemical reactions in the melting process were investigated by TG-DSC simultaneous thermal analyzer. The viscosity and thermal expansion were measured. The activation energies were calculated by Arenius equation and the main temperatures applied in the float process design were revealed according to the viscosity- temperature curves. Compared with the R_2O-Al_2O_3-SiO_2 glasses, the melting temperature is 1663° C, increasing about 30° C, while the working temperature increases about 127° C. The difficulty of the production increases drastically. The softening and strain point temperatures are improved with 120~156° C. The coefficient of thermal expansion is lower than the R_2O-Al_2O_3-SiO_2 glasses. Both the softening, strain point temperatures and the coefficient of thermal expansion show better thermal property.

(ICG-P142-2019) Clarification analysis and research of cover glass

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1. State Key Laboratory of Advanced Technology for Float Glass, China

Cover glass as a new type glass has rapid development in recent years. Cover glass has excellent thermodynamic properties, especially in hardness, toughness and scratch resistance etc. Cover glass can be used as a preferred protective material for touch screens and handwriting screens of electronic information product. High alumina silicate is a kind of satisfactory material used for cover glass of touch screen. Normally, the content of Al_2O_3 is above ten percent in the cover glass, which means that the viscosity of glass is relatively high in the melting stage, and it was difficult to clarify. In this paper, the effects of oxide clarifiers, sulfide clarifiers and halide clarifiers on the clarification of cover glass were investigated. The variation of Area refraction, mean bubble size and number of bubbles were quantitatively studied in the clarification process, and a clarification scheme suitable for cover glass was obtained. Results indicated that the effect of clarification was better when the content of $NaSO_4$ was 2wt. % at the temperature of 1600° C, the bubbles in the melting glass had been completely drained.

(ICG-P143-2019) The Correlation between Transmittance and Amount of Injected Oxidizing Gas in the Colored Glass

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1. Nippon Electric Glass Co., Ltd., Japan

The optical filter glass for cutting infrared is widely used for the solid state image sensors to correct their spectral sensitivity. The phosphate or fluoro-phosphate glass containing copper has been used for the applications. It is possible to reduce the thickness of the filter glass maintaining the infrared absorption by increasing the copper content though it causes decrease of visible transmittance. It is known that the injection of oxidizing gas into the molten glass prevents the decrease of transmittance, however there are little work on effective injection method. In this study, it was found that there was a correlation between transmittance and amount of oxygen bubbles in molten glass. The result showed that the transmittance depends on not only the amount of injected oxygen but the gas injecting methods. It is suggested that the configuration of melting and injecting system influences the amount of the oxygen bubbles which can react with the copper ion effectively in the molten glass.

(ICG-P144-2019) The Technology of Highly Transparent Glass

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1. Moscow Bauman State Technical University, Fundamental Sciences, Russian Federation
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Organization of production of highly transparent glass allows the content of Ferrum impurities in glass not more than 0,012-0,013 %. To reduce coloring impurities except for the selection of low-ferrous raw materials some changes were made in technology procedure of batch preparation as well as changes in a glass-melting furnace construction. New solutions were provided: -activation of grain surface SiO_2; -the new scheme of materials dosing; -improvement of batch moistening procedure; -inclusion in batch composition activating and cleaning agents. To meet the requirements to glass in terms of high light transparency it is provided during the glass-melting procedure drain of lower layers of glass through the glass-melting furnace bottom. Those layers are enriched with heavy metals Fe, Ti, Cr, which makes quality characteristics of glass, including the decrease of light transparency worse, so the layers are to be eliminated. Comparison of manufacturing methods and critical estimate of light transparency of visible light and solar energy of glasses manufactured by float-method and rolling method showed that different grades of high transparent float glass (e.g. Optiwhite) have less light transparency than ultra-white glass produced by the rolling method. Developed production technology of highly transparent glass is based on new technological solutions, it is more mobile and economically sound.

(ICG-P145-2019) Application of Modern Nuclear Analytical Methods to Trace Elemental Analyses of Glass

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1. National Institute of Standards and Technology, Material Measurement Laboratory, USA

Knowledge of trace elemental concentrations during glass production is important for the successful creation of modern, high-tech glasses. The inclusion of trace impurities at above-threshold values can cause failures of final products. The quantification of such

impurities rely on the use of carefully qualified standards materials. However, several older, but still widely used, glass standards have not been re-evaluated for trace compositions by modern nuclear analytical techniques. Reassessment of trace elemental values by these methods can be beneficial as they are sensitive to a large inventory of elements at trace levels (ppm, ppb). Results from neutron analyses are also complementary to those obtained by mass spectrometry and x-ray fluorescence methods. In this study, the trace elemental analysis of several reference glasses is revisited by Neutron Activation Analysis and Prompt Gamma Activation Analysis. Previously reported trace elemental concentrations will be compared to newly obtained values, and the identity and quantities of yet unidentified trace elements will be presented. Results will be coupled with μ-XRF mapping of the reference glass surfaces to qualitatively assess elemental homogeneity of the glasses. Data obtained from these studies could be used to more accurately measure trace elements in glasses and glass batching materials.

(ICG-P146-2019) Study on Creep Life Prediction Method of Platinum Alloy Materials for Optical Glass Industry

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Platinum alloys are widely used as production equipment in the production of optical glass, so the prediction of creep life of platinum alloys is particularly important. Based on Larsen-Miller formula, considering the relationship between stress and creep life of platinum alloys at different service temperatures, a formula for predicting maximum allowable stress and creep life of platinum alloys at different service temperatures is proposed, and the correctness of the formula is verified by experimental data. In the process of designing and using of optical glass production equipment, according to the short-term creep failure experimental data of platinum alloy material, the creep life of platinum alloy material in long-term use can be predicted by using the modified formula in this paper, or the maximum stress that platinum alloy can bear in the use process can be predicted.

(ICG-P147-2019) Numerical Simulation and Analysis of Forced Bubbling Arrangements of Glass Furnace Melter

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1. State Key Laboratory of Advanced Technology for Float Glass, China

Recently, bubbling technic has been widely applied in glass furnaces, which plays an important role in increasing glass quality and reducing energy consumption, especially for colored glass with low effective thermal conductivity. In order to study the effect of different arrangements of bubblers, a green container glass furnace with coal gas as fuel has been studied by numerical simulation, in which 1~3 rows of bubblers are settled respectively at the bottom of the glass furnace melter. The comparison and analysis of temperature field, velocity field, furnace energy consumption and glass quality of these simulation cases are made to investigate the influence of bubblers in the melter on batch melting and glass furnace performance. According to the simulation results, with the application of multiple rows of bubblers and setting them at the proper place, the average temperature at the bottom of melter and output temperature of glass melt is increased, the quality is increased, and the furnace thermal efficiency is also enhanced, compared with the application of single row of bubblers.

(ICG-GSP-P148-2019) Topological Engineering of Photoluminescence Properties of Bismuth- or Erbium-Doped Phosphosilicate Glass of Arbitrary P_2O_5 to SiO_2 Ratio

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2. Harbin Engineering University, School of Science, China

Glass attracts considerable attention and the glass making methods are always a hot topic. As one of manufacture methods, glasses made by melt-quenching method are seriously constrained by glass forming ability. Here, a new method is reported to manufacture glasses of arbitrary ratio of SiO_2/P_2O_5 which cannot be made by the conventional melt-quenching method. The new method is termed "melt-in-melt" which encapsulates the key step in the glass manufacturing process, i.e. one molten glass is poured into another molten glass with a stirring at high temperatures. Because of near unlimited possibilities in designing new glass compositions, there is a correspondingly great degree of freedom in the topological engineering of the glass structure, which in turn strongly influences the photoluminescence properties of active dopants. As a proof concept, bismuth and erbium are selected as the indicator dopants for emphasizing the real advantages of the new method as an effective means to tailoring the photoluminescence properties of the doped glasses. The microstructure and element distributions of the glasses are comprehensively characterized by high-resolution Scanning Electron Microscope and high-performance X-Ray Fluorescence, respectively. The new glass-making method may extend the possible applications of glass in some important photonic area.

(ICG-P149-2019) Mass Spectral Glass Inclusion Analysis Within Corning Incorporated

R. Salvagin*[1]; A. Morrell[1]; S. Merenbloom[1]; J. Tubbs[1]; R. Burkhalter[1]

1. Corning Incorporated, USA

Inclusions are an unwanted artifact of glass melting and/or forming processes that can have a non-desirable impact upon glass manufacturing. The identification of the atomic and molecular constituents of inclusions is necessary not only for eliminating these potentially costly faults, but also for better understanding of glass formulation, batching, and melting. For support of fundamental research up through manufacturing at Corning Incorporated, the most widely used technique is Gas Inclusion Mass Spectrometry. Because of the diverse types of glass matrices and inclusions, advanced sample preparation techniques are required. Sample preparation is of the utmost importance to avoid the introduction of external gasses. Currently, Gas Inclusion Mass Spectrometry at Corning Incorporated can analyze blisters down to 100 μm in length, and is limited to gasses only.

(ICG-GSP-P150-2019) Hybrid sol-gel inks for stereolitography of aluminum phosphate hybrid composites

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1. UNESP, Instituto de Química, Brazil
2. Université Laval, Canada

Additive manufacturing is a breakthrough technology which allows the production of complex products in terms of geometry and architecture at reduced time, cost and material comsuption. So far, the lack of a viable technnology hindered its application in inorganic glasses and hybrid composites for optical devices, such as fabrication of structured optical fibers and circuits. In this work, we developed photopolymerizable inks with different contents of aluminum and phosphorus from hybrid sol-gel precursors, with potential use in stereolitography additive manufacturing technique. Upon photopolymerization, a transparent hybrid composite is obtained. Inks work curves and volumetric retraction upon polymerization were assesed and its shelf life stability was studied by NMR and rheometry. The resulting hybrid composites had its mechanical, thermal and optical properties characterized. Finally, structural evolution from ink to hybrid composite was studied by NMR.

Wednesday, June 12, 2019

Michael Cable Memorial Lecture

Room: Grand Ballroom A (mezzanine)
Session Chair: William Brookes, ICG

8:10 AM

(ICG-PL-006-2019) You ought to go away and think again!

R. Hulme*[1]

1. Guardian Industries Corp., USA

Glass making is not a complicated affair but the science underlying the processes involved can be extremely complex. Michael Cable has written extensively about the history and development of glass-making and throughput his career he pioneered research into some of the fundamental principles which are currently taken for granted, have been forgotten or are ignored at our peril. This presentation will cover some of the things I learned from one of the most eminent glass technologists and why we should continue to reflect on and acknowledge his contributions to our field of work.

SI: Glass Structure and Chemistry

Session 7: Silicate Glass Structure I

Room: Berkley (mezzanine)
Session Chair: Randall Youngman, Corning Incorporated

9:30 AM

(ICG-SI-061-2019) Five-coordinated silicon in alkali silicate glasses: Pressure, temperature, and compositional effects, and analogies to borates and germanates (Invited)

J. Stebbins*[1]; S. Bista[1]

1. Stanford University, USA

SiO5 groups have long been considered as possible reactive intermediates in bond-swapping reactions in viscous flow and diffusion, as well as a key part of high pressure densification. However, few data exist to constrain such models. We present new results for K-silicate glasses from ambient and high pressures to 3 GPa. SiO5 is readily detectable by Si-29 NMR at concentrations as low as about 0.02 mol %. In high-P samples, SiO5 and SiO6 concentrations are higher than known previously when pressure drop on quench is taken into account. In 1 bar glasses, SiO5 is higher at higher fictive temperatures, and first increases, then decreases, as K2O is added to SiO2. This latter pattern resembles those in alkali borate and germanates, although high coordinate species (BO4 and GeO5/GeO6) are ca. 100x more abundant. A simple thermodynamic model, based on the link between network cation coordination change and non-bridging oxygens and considering non-ideal mixing of the oxygen species, at least qualitatively predicts the shape of the compositional variation of SiO5 in the K-silicates, and is sensible with respect to tendencies for clustering and unmixing; such a model also predicts curves that resemble those for borates and germanates, suggesting an underlying similarity in the energetics of mixing in all three systems.

10:00 AM

(ICG-SI-062-2019) Structural Origin of the Anomalous Density Maximum in Silica and Alkali Silicate Glasses

Y. Shih*[1]; S. Sundararaman[1]; L. Huang[1]

1. Rensselaer Polytechnic Institute, Department of Materials Science and Engineering, USA

In this work, a density increases upon melting cristobalite silica and a shallow density maximum during cooling of silica liquid are observed in classical molecular dynamics (MD) simulation. The density maximum gradually diminishes with the increase of alkali size/content in alkali silicate glass. The structural origin of the anomalous density maximum is revealed by detailed structural analysis in MD simulation. During the cooling process, the liquid silica tends to transform to the crystalline cristobalite, which consists of 6-member rings that give a more open structure and a lower density than the liquid. However, due to the high viscosity of silica liquid, the long-range order in cristobalite cannot form, but 6-member rings still predominate, which cause the silica network to open up and compensate the regular volume shrinkage upon cooling. These two competing factors lead to a density maximum, but to a less extent than that observed in melting cristobalite. With the increase of modifier size/content in the alkali silicate glass, the connection of silica network gradually breaks down; the population of 6-member rings decreases with the increase of smaller or larger rings, therefore the density maximum becomes less obvious and eventually disappears.

10:20 AM

(ICG-SI-063-2019) Structural characterization of titanium bearing nepheline ($NaAlSiO_4$) glass

E. T. Nienhuis*[1]; J. McCloy[1]

1. Washington State University, USA

In this study, the effect of Ti^{4+} on the structure and crystallization behavior of nepheline glass ($NaAlSiO_4$) is investigated as SiO_2 is replaced with TiO_2. Traditionally, Ti is considered to be a nucleating agent in glass-ceramic applications, but by adding large amounts to the glass, Ti may become four coordinated with oxygen in a tetrahedron (or in rare cases become 5- or 6-coordinated) and incorporate into the glass network. Structural analysis includes pair distribution functions obtained from synchrotron x-ray and neutron total scattering paired with atomistic modeling via Empirical Potential Structure Refinement (EPSR). The structure of the glass has also been evaluated via vibrational spectroscopy. Crystallization studies were conducted on slow cooling of the glass from melt. X-ray Diffraction (XRD) and quantitative Rietveld refinement were conducted to determine crystallization behavior as the Ti^{4+} fraction was increased. A comparison between coordination numbers in the glass and in the respective crystalline phases is made based upon the structure and crystallization studies conducted here.

10:40 AM

(ICG-SI-064-2019) High frequency Raman spectra of silicate glasses (Invited)

G. Henderson*[1]; H. W. Nesbitt[2]; G. M. Bancroft[3]

1. University of Toronto, Earth Sciences, Canada
2. University of Western Ontario, Earth Sciences, Canada
3. University of Western Ontario, Chemistry, Canada

The structure of silicate glasses is often probed using Raman spectroscopy. It is very sensitive to the structural changes that may occur in the glass. The 900-1300 cm^{-1} region is particularly sensitive to vibrations associated with Q^n (n= # of bridging oxygens and ranges from 0-4) species. Analysis of bands in this region is often used to quantify Q^n species and their changes with composition, pressure and temperature. This is done by fitting the high frequency envelope with Gaussian bands representative of the different species. Unfortunately, the number of Gaussian bands often exceeds the number of possible Q^n species present and the widths of the peaks can be highly variable and unrealistic. Our recent work has produced a number of interesting findings. These include: the Q^n (n=0-3) bands are predominantly Lorentzian in character; the full width at half maximum (FWHM) is similar for all Q^n (n=0-3) bands at ~35-55 cm^{-1}; the Raman cross-sections for the different Q^{1-3} species are comparable; the Q^3 band (and possibly the other Q^n bands) is asymmetric due to the presence of bridging oxygens associated with alkali cations; the lower frequency Q^4 band rapidly increases in intensity with added alkali. Several mol% free oxygen is present in glasses with >40 mol% Na_2O. I will review our recent findings and their implications for the structure of alkali- and alkaline-earth silicate glasses, and quantification of Q species.

11:10 AM

(ICG-SI-065-2019) Vibrational signatures of the main structural units in silicate glasses: A first principles study

S. Ispas*[1]; D. Kilymis[2]; B. Hehlen[1]

1. University of Montpellier, Lab. Charles Coulomb, France
2. University of Toulouse Paul Sabatier, France

The vibrational properties of a series of binary as well as ternary aluminosilicate and borosilicate glasses have been investigated in the framework of Density Functional Theory. The vibrational density of states as well as the IR spectrum have been calculated for all systems and the vibrational modes have been assigned to specific atoms or structural units. It is shown that the modifier content as well as the content of the second network-former (B or Al) affect several vibrational features as the position and intensity of the R band, the mixing of the rocking and bending atomic motions of the Si-O-X bridges (X=Si, B, Al) or the vibrational modes of the main structural units (SiO_4, AlO_4, BO_3 or BO_4). For some compositions, the Raman spectra have been calculated as well and have been found to agree with experimental ones. Their decomposition indicates the dominant character of the non-bridging oxygen contribution, in particular for the highfrequency band, above 800 cm^{-1}. The decomposition of the high-frequency Raman feature into vibrations of the depolymerized tetrahedra (i.e. Q_n units) has revealed spectral shapes of the partial contributions that cannot be accounted for by simple gaussians as frequently assumed in the treatment of experimental spectra.

11:30 AM

(ICG-SI-066-2019) Oxide glasses SiO_2 – Al_2O_3 – La_2O_3: Structural investigation

N. Pellerin*[1]; B. Diallo[2]; D. De Sousa Meneses[1]

1. Orléans University, Sciences, France
2. CEMHTI CNRS, France

The aluminosilicate glasses containing large amounts of rare-earth cations in the SiO2-Al2O3-Tr2O3 system are behind numerous applications thanks to their remarkable properties (chemical, optic, thermal…). In the ternary system Al_2O_3-SiO_2-La_2O_3, phase separation has been observed in a large range of network polymerization degree. Aluminum contributes to the solubility of lanthanum, in particular the AlO_5 environment thanks to specific molecular arrangements. NMR and IR spectroscopies have been performed to determine the molecular arrangements in the homogeneous glassy network. The silicon environment was semi-quantitatively described according to Q^n(mAl) species from ^{29}Si NMR spectra deconvolution, taking into account chemical constraints such as Aluminum and NBO contents. NMR and IR spectroscopy results have been compared, in particular to quantify the Al-O-Al units. The results prove the unexpected distribution of NBO in aluminosilicate network in presence of cations of large field strength. ^{17}O NMR and neutron diffusion experiments are in progress to better describe the NBO distribution and lanthanum environments.

11:50 AM

(ICG-SI-067-2019) Temperature-dependent Ring Statistics of Silicate Glasses Revealed by In-situ Neutron Total Scattering

Y. Shi*[1]; O. Gulbiten[1]; D. Ma[2]; J. Neuefeind[2]; B. Wheaton[1]

1. Corning Incorporated, Charaterization Science, USA
2. Neutron Scattering Division, Spallation Neutron Source, USA

The coefficient of thermal expansion of a silicate glass, when heated through the glass transition temperature, often exhibits a two to three times increase. While oxide glasses and their respective supercooled liquids possess similar short-range order as shown qualitatively by a few in-situ high temperature total scattering studies, they have different medium-range order, i.e., different ring structure. However, such ring structure change has never been quantitatively analyzed due to the difficulty in extracting the medium range structural information from the scattering data. Here we report the temperature -dependent ring statistics of three representative silicate glasses using in situ neutron total scattering measurements and a recently developed neutron ring statistic analysis method (RingFSDP). All three glasses display a similar trend: the absolute amounts of all sizes of rings decrease as temperature increases, but the smaller rings decrease more rapidly than larger rings. The change of the absolute amount of rings does not necessarily mean rings decompose by heating; instead, it can infer ring shape change as referenced to the average ring shape measured by neutron scattering. Heating induces more disordered ring shapes, especially for small rings which are heavily constrained and lack the same freedom to adjust as large size rings.

Session 8: Crystallization of Glasses and Glass-Ceramics IV (TC 07)

Room: Terrace (lower level)
Session Chairs: Mark Davis, SCHOTT North America, Inc.; Christian Roos, RWTH Aachen University

9:30 AM

(ICG-SI-068-2019) TiO_2(B) and the nucleation mechanism in sTi-doped lithium aluminosilicate glass-ceramics

A. Zandona*[1]; C. Patzig[3]; B. Rüdinger[2]; O. Hochrein[2]; J. Deubener[1]

1. Clausthal University of Technology, Institute of Non-Metallic Materials, Germany
2. Schott AG, Germany
3. Fraunhofer IMWS, Germany

Three Ti-doped lithium aluminosilicate glasses, possessing different Al/Si ratios, were subjected to several heat treatments and investigated by X-ray diffraction (XRD), Raman spectroscopy and transmission electron microscopy (TEM) to elucidate their nucleation mechanism. After phase separation had occurred, TiO_2(B) could invariably be identified as the first crystalline product. This phase has never been described in glass-ceramics up to now, although it has been previously observed and erroneously interpreted as pseudobrookite. Its gradual transformation into anatase could be analyzed during further annealing and correlated with the eventual volume crystallization of the samples in high quartz solid solution and keatite solid solution.

9:50 AM

(ICG-SI-069-2019) Understanding the Role of Phosphorus in the Nucleation of Lithium Aluminosilicate Glasses via Raman Spectroscopy

G. G. Moore*[1]; C. M. Saunders[1]

1. Corning Incorporated, Characterization Sciences, USA

Lithium Aluminosilicate (LAS) and Lithium Disilicate (LS2) glass ceramics are becoming more and more popular for a wide variety of applications. Often, a nucleating agent is employed to increase the rate of crystal formation and provide homogenous nucleation. One important nucleating agent is phosphorous. To better understand the role of Phosphorus in the nucleation of Li_2O-Al_2O_3-SiO_2 glasses, Raman Spectroscopy has been employed to detect and observe the first structural changes which occur due to thermal treatment and to identify crystal phase assemblage. As a result, Raman demonstrated the ability to monitor and track the phosphorous environment with increased thermal treatment, and for those compositions with low Al/Li ratios, Raman was able to detect the presence of orthophosphate ions in the base glass. The environment of these large polyatomic ions, which are a detected at 962 cm^{-1}, can be observed to gain increased order and ultimately form lithium orthophosphate with thermal treatment. This process results in a shift of the band which can be used to determine the temporal stage of the nucleation process.

10:10 AM

(ICG-SI-070-2019) Evolution of glass structure surrounding a growing crystal characterized by spatially resolved X-ray absorption spectroscopy

S. McAnany*[1]; J. Thieme[2]; D. Nolan[3]; B. Aitken[3]; V. Dierolf[4]; H. Jain[1]

1. Lehigh University, Materials Science & Engineering, USA
2. Brookhaven National Laboratory, National Synchrotron Light Source II, USA
3. Corning Incorporated, USA
4. Lehigh University, Department of Physics, USA

Selective heating of glass using a femtosecond laser offers a unique processing technique for creating optically active 3D single-crystal architecture in glass, which can be used to create photonic integrated circuits for optical telecommunication. It has been previously shown that single crystal $LaBGeO_5$ architectures can be formed in glass of the same stoichiometric composition, providing a useful model system for studying the formation of single crystal structures in glass. Using diffraction techniques, such as electron backscattered diffraction and micro X-ray diffraction, the local structure of the crystal has been probed, but the continuously evolving structure of surrounding glass, which affects crystal lattice, remains unknown. Using the Submicron Resolution X-ray Spectroscopy (SRX) beamline at National Synchrotron Light Source II (NSLS-II), X-ray absorption spectroscopy and X-ray fluorescence mapping is performed with a 500 nm X-ray beam size, allowing for local probing of the glass structure and composition. In this work, these techniques were used to characterize ex-situ the glass structure and composition preceding $LaBGeO_5$ crystallization and surrounding the single crystal growth front for $LaBGeO_5$ single crystals grown by femtosecond laser heating of La_2O_3-B_2O_3-$2GeO_2$ glass.

10:30 AM

(ICG-SI-071-2019) Characterization of rotating-lattice-single crystal growth on the surface of Sb_2S_3 chalcogenide glass via in situ observation

C. Au-Yeung*[1]; C. Stan[2]; B. Shaw[1]; H. Jain[1]; V. Dierolf[1]

1. Lehigh University, USA
2. Lawrence Berkeley National Laboratory, USA

Single crystal growth has been successfully achieved via continuous wave laser heating to create crystal architectures in Sb-S-I chalcogenide glasses. In these crystal architectures formed by a solid-solid transformation under steep temperature gradient, a rotating lattice is identified. This rotating lattice is key to increasing the utility of these crystal structures for applications. To understand the process of lattice formation that proceeds via crystal growth, we observed in-situ Sb_2S_3 crystal formation under x-ray irradiation. Here, an x-ray beam is used as the heating source to fabricate single crystals while Laue diffraction patterns are collected simultaneously. We explore the earliest stages of crystallization in this model system wherein glass transforms into single crystal without change in local composition or long range diffusion. One model for crystal lattice rotation is that it is created through the introduction of edge dislocations during the glass to single crystal transformation. These dislocations can be seen in the in-situ x-ray experiments and through direct observation using transmission electron microscopy. Molecular dynamic simulations have been performed to investigate nucleation within these crystal structures. The implications of these results on the rotating lattice and crystal growth in a confined medium will be discussed

10:50 AM

(ICG-SI-072-2019) Determination of the Crystal Growth Kinetic in Glass Ceramics by Measuring the Young's Modulus at Elevated Temperatures

M. Sander*[1]; J. Grundkowski[1]; C. Roos[1]

1. RWTH Aachen University, Institute of Mineral Engineering, Germany

The macroscopic material properties of a glass ceramic are highly influenced by its crystalline microstructure. Therefore, it is essential to have a good knowledge of the nucleation and crystal growth kinetics. Due to the fact that existing methods (e.g. high temperature X-ray diffractometry, double-stage heat treatment) often need powder samples or focus only at a small part of the sample, an in-situ method was developed to determine the kinetics in bulk samples. The idea of this method is that the elastic moduli of a glass ceramic are a superposition of the elastic moduli of the glass matrix and the crystalline phases. Considering that a crystal has higher bulk moduli than its isochemical glass due to the lower atomic space demand, it is possible to determine the crystalline phase fraction in a glass ceramic. In this study the Young's modulus was measured with an impulse excitation method during the second isotherm of a two-step crystallization process. The results revealed an increase of the Young's modulus due to the crystal growth. The crystal growth kinetic was analyzed using the YMAK equation and verified with samples which were prepared in double-stage heat treatments.

11:10 AM

(ICG-SI-073-2019) Tracking Ceramic Evolution of a Commercial Dental Material with Solid-state NMR Spectroscopy

A. Bhattacharya[1]; Y. Qiu[1]; S. Butler[2]; V. K. Michaelis*[1]

1. University of Alberta, Chemistry, Canada
2. University of Western Ontario, Schulich School of Medicine and Dentistry, Canada

The evolution of next-generation dental materials requires a profound understanding of the structure-property-function relationship of these complex bioglass-ceramics. These solids have far-reaching applications that include dental crowns, bridges, and veneers, while their primary function is to ensure effective mastication, their market is rapidly advancing in cosmetic dentistry. Feldspar, a tectosilicate mineral is a popular commerical dental ceramic offering excellent color tailorability. Unfortunately, conventional commercially available dental ceramics have a propensity to fracture or delaminate from the zirconia core. We will discuss recent results on a feldspar-based dental ceramic studying the materials structural transformation from starting material to hardened ceramic through a series of ex-situ temperature treatments using energy dispersive X-ray spectroscopy, X-ray diffraction, and solid-state nuclear magnetic resonance (NMR) spectroscopy. Atomic-level features are revealed using one- and two-dimensional ^{23}Na, ^{27}Al, and ^{29}S NMR spectroscopy that form in the porcelain ceramic and eventually the bioglass as the temperaure reaches 1100 °C.

11:30 AM

(ICG-SI-074-2019) Sintering, Characterization, and Physical properties Evaluation of Ceramics produced from Soda-lime-silica glass and White corn cob ash

B. Oji*[1]

1. Federal Polytechnic Ado-Ekiti, Glass and Ceramics Technology, Nigeria

This research examines the influence of soda-lime-silica glass on the porosity, crystallization behaviour and phase transformation of ceramics produced from white corn cob ash. The soda lime glass (SLG) was crushed and sieved into grain size of 45μm. The corn cob (CCA) was washed and conditioned at a temperature of 700°C for 6hrs in a furnace before been screened. A mixture of 98, 96, 94, and 92% of CCA and 2, 4, 6, 8% of SLG were mixed in a ball mill and formed into pellets using polyvinyl alcohol (PVA) as binder and then sintered at temperatures of 900°C, 1000°C, 1200°C respectively. Microstructure analysis (SEM), XRD, XRF and FTIR analysis were used to determine the porosity, crystallization behaviour, elemantal composition and chemical bond formed in the developed ceramics materials. Archimedes and geometric measurement were also used to determine the bulk density and linear shrinkage of the material. The SEM image shows that as the sintering temperature increases, the porosity of the formed ceramics decreases. The XRD reveals the Crystallization behaviour of the produced samples after firing with a cristobalite dominant phase and small traces of tridymite phase noted in the samples. Fourier transform infrared spectroscope (FTIR) was used to analyze the chemical bond formed in the material.

SII: Glass Physics

Session 1: Glass Transition and Relaxation I

Room: Hancock (mezzanine)
Session Chairs: Gerardo Naumis, Instituto de Física; Matthieu Micoulaut, Sorbonne Université

9:30 AM

(ICG-SII-098-2019) Ab initio molecular dynamics simulation on the molten salt FLiBe (Invited)

W. Ching*[1]; K. Baral[1]

1. University of Missouri-Kansas City, USA

FLiBe is a molten salt with a 2:1 mixture of LiF and BeF_2 used as coolant and solvent in nuclear reactor. It has a melting point of 732 K and a boiling point of 1803 K. We report the results of ab initio molecular dynamics simulation (AIMD) in the temperature range from 0 K to 2000 K using a supercell model of 504 atoms. The temperature-dependent structure, mechanical and optical properties of FLiBe above and below the melting temperate are calculated and compared with the crystalline phase Li_2BeF_4. The results show some anomalous behavior across the melting point but the general trend is a decrease of mechanical strength and a slight decrease in the refractive index as temperature is increased. These results will be discussed in the context of electronic structure and bonding of the molten salt and their possible connection to experimental characterization using spectrophotometry of FLIB. Possible extension of exploring the eutectic composition and other variations will be discussed.

10:00 AM

(ICG-SII-099-2019) Atomic dynamics in oxide glasses studied with coherent X-rays (Invited)

B. Ruffle*[1]

1. Montpellier University, Physics Department, France

While constant progresses are made in the understanding of the relaxation dynamics of glass-forming liquids, a microscopic theory of glasses, which would describe the rich phenomenology of glass physics, is still missing. It partly relates to the difficulty in probing the structural relaxation at the atomic and the mesoscopic scale around the glass transition temperature, either with experiments or simulations. It is indeed surprising that measuring a fundamental quantity such as the intermediate scattering function f(q,t) at that scale in the time window ranging from nanosecond to second is so difficult. Thanks to an increased flux and coherence of X-ray beams at synchrotrons, X-ray photon correlation spectroscopy (XPCS) has become a very powerful technique able to follow the evolution of the slow dynamics at the atomic length scale in glasses. In this talk I will present some results obtained in silicate glasses using this technique.

10:30 AM

(ICG-SII-100-2019) Understanding, predicting, and tuning the fragility of vitrimers

S. Ciarella[1]; L. M. Janssen*[1]

1. Eindhoven University of Technology, Applied Physics, Netherlands

We study the anomalous glass-forming properties of vitrimers, a recently invented polymer class that combines properties of both thermosets and thermoplastics through a unique reversible-bond mechanism. Here we describe the structure, glassy dynamics, and fragility of a coarse-grained vitrimer model using computer simulations and a first-principles dynamical theory. We find that, depending on the density, the material can switch from fragile (super-Arrhenius) to strong (Arrhenius) and even super-strong (sub-Arrhenius) growth of the relaxation time upon supercooling. Remarkably, we are also able to qualitatively reproduce this broad fragility variation using Mode-Coupling Theory (MCT), a microscopic, fit-parameter-free theory which has thus far been successful only at describing fragile behavior. Our first-principles MCT analysis allows us to identify the microstructural cause of the observed fragile-to-superstrong crossover, which we attribute to a change in the dominant structural length scale, shifting from intrachain repulsion to interchain attraction as the density decreases. Overall, this work sheds new light on the structural origins of fragility, and uncovers a previously unknown application domain for a quantitative first-principles theory of glassy dynamics.

10:50 AM

(ICG-SII-101-2019) Extraction of TNM Model Parameters from DSC Data via Multiparametric Optimization in the $As_xSe_{(1-x)}$ Family of Glasses

E. A. King*[1]; R. Erdmann[2]; P. Lucas[2]

1. Corning Incorporated, Glass Research, USA
2. University of Arizona, Materials Science and Engineering, USA

Understanding structural relaxation is of great interest in the glass community, both from a practical standpoint, and for greater understanding of the fundamental glass transition process. Mathematically, the description of structural relaxation remains difficult due to the inability to compensate for both the time and temperature dependence of the viscosity or other material properties being measured. For this reason, the most frequently utilized mathematical description of structural relaxation is given by the phenomenological Tool-Narayanaswamy-Moynihan (TNM) model. To date, the TNM model has been widely studied and has enjoyed some success in describing glass relaxation. However, most studies took place more thirty years ago, at a time when computational resources were scarce and multiparametric optimization presented considerable difficulties. Therefore, past studies generally focused on determination of one of the four individual model parameters. Here, we've created a hybrid computer model, which utilizes the TNM mathematical formalism and multiparametric optimization, to compare experimental DSC data to the TNM model and determine the TNM parameters which best reproduce the experimental data. This hybrid model is then applied to the $As_xSe_{(1-x)}$ family of glasses to determine its applicability within the entire composition family.

11:10 AM

(ICG-SII-102-2019) Relaxation and Nanocrystal Formation in Vanadium Tellurite Glasses (Invited)

Y. Yue*[1]; Y. Zhang[2]

1. Aalborg University, Denmark
2. Qilu University of Technology, China

Recently we discovered that nanocrystals formed in vanadium tellurite (VT) glass anodes for lithium ion batteries upon Li-ion discharging/charging, and thereby the battery cycling stability was greatly enhanced. This kind of nanocrystal formation has a fundamentally different origin compared to the thermally induced crystallization. This discovery motivates us to do detailed studies in order to understand the origin of the ion-insertion induced nanocrystal formation in VT glasses. To do so, we study a series of VT glasses with various V_2O_5/TeO_2 ratios regarding their enthalpy relaxation, structural heterogeneity and nucleation by differential scanning calorimetry and structural analysis. Our DSC results show that the VT systems are poor glass formers with high fragility (m»80-100). We find that high degree of structural and energetic heterogeneities exist in those glasses, and high potential energy domains are the precursors for nanocrystal formation. Through Li-insertion, the higher energy domains tend to be transformed into ordered domains, nanocrystals with lower potential energy, and simultaneously some of inserted Li ions join the lattice structure. Finally, we propose a possible microscopic picture of the disorder-order transition in TV glasses, and describe the compositional conditions under which such transition can occur.

11:40 AM

(ICG-SII-103-2019) Investigations on the glass transition of oxide glasses by high-temperature oscillatory rheometry

C. Giehl*[1]; M. Kleindienst[1]

1. Anton Paar GmbH, Rheometry, Austria

The influence of heating and cooling rate, as well as the time-dependent relaxation behavior are well-known processes related to the glass transition temperature. However, both energetic and physical processes occuring near the glass transition of are still a matter of debate. We here present quantitative data on visco-elasticity of reference glasses (DGG 1) and oxide glasses obtained from high temperature parallel-plate and concentric cylinder oscillatory rheometry. Measurements at different frequencies allow to determine the frequency dependent isothermal glass transition. Furthermore, by means of oscillatory measurements the quantification of relative contributions of viscosity and elasticity provide insightful information on the strong or fragile character of glass melts and have the potential to derive relaxation time spectra from frequency-dependent measurements.

12:00 PM

(ICG-SII-104-2019) Science, and Art of Glass Properties Measurements: Devoted to Lifetime Contribution of Prof. Oleg V. Mazurin

O. Prokhorenko*[1]

1. L.G.P. International, USA

The first generation of scientists of Laboratory of Glass Properties has begun studies of physical properties of glasses, and melts in early 1960's. The key strategy was to develop the most accurate methods for measurements of physical properies. It took one decade to reach the highest possible levels of reliability, and precision that allowed LGP experts to study key properties of glasses within the glass transition range. Later, in 1980's-90's the range of properties has been extended by adding electrical resistivity, absorption spectra within NIR spectral range, density, and others. From very beginning, LGP lead by Professor Oleg V. Mazurin has been focused on the studies having direct practical application. Thus, properties of glasses within the glass transition range were used to develop annealing, and tempering processes including such unique tasks as annealing of huge billets for making massive optical parts (telescope lenses, etc.). At present LGP, which has become a private enterprise in 1993, follows this proven strategy. In order to stay at frontier of glass science, and be competitive supporting glass technology we need to update our knowledge, hardware, and all types of software continuously. Through the modern art in computer science, physico-mathematical modeling, and a number of interdisciplinary approaches we keep high level of our scientific products.

Session 6: Display and Optical

Room: Clarendon (mezzanine)

Session Chairs: Nick Smith, Corning; Nik Podraza, University of Toledo

9:30 AM

(ICG-SII-105-2019) Surfaces of Alkali-free Glass Substrates for Displays (Invited)

N. J. Smith*[1]; G. Agnello[1]; R. Manley[1]; J. Banerjee[1]; C. V. Cushman[2]; M. R. Linford[2]

1. Corning Incorporated, USA
2. Brigham Young University, USA

In many commercial applications, the native surface of glass provides a—if not, the—critical function for performance, and this statement is especially valid for high-performance, alkali-free glasses used as the substrate of choice in the manufacture of modern displays. In addition to substantial engineering of the bulk composition for optimized performance, many other valuable attributes of glass in this application can be traced directly to its surface. In this talk, we provide an overview of multicomponent glasses used in this space, and provide a discussion on several key aspects and properties of its surface that factor into its use in this application. Highlights include surface aspects impacting contamination, charge buildup, and adhesion properties, as well as the application of some newer characterization techniques to gain direct insight into these fascinating materials and the corresponding physical origins of their surface properties.

10:00 AM

(ICG-SII-106-2019) Assessing Device Performance and Probing Material Properties by Spectroscopic Ellipsometry (Invited)

N. Podraza*[1]; M. Junda[1]; K. Ghimire[1]; I. Subedi[1]; D. Adhikari[1]; P. Uprety[1]; B. Subedi[1]

1. University of Toledo, USA

Ellipsometric spectra are sensitive to the complex optical response and thickness of each layer in multiple layer structures and devices, including optically distinct interfacial regions and surface roughness. Within the complex optical response spectra, features may be present related to electronic transitions, phonon modes from lattice structure and chemical bonding, and free carrier absorption depending on the particular material and the spectral range measured. Here we will describe spectroscopic ellipsometry measurements performed for semiconductor, metallic, transparent conducting oxide, and glass materials relevant to solar cell technologies, including those based on crystal silicon wafers, cadmium telluride films, and organic-inorganic halide perovskite thin films. Measurement and data analysis strategies will be discussed for complete solar cell devices as a means of assessing sources of optical and electronic losses, optical Hall effect to deduce electronic transport properties, and combined wide spectral range measurements spanning vacuum ultraviolet to millimeter wavelengths (140 nm to 3 mm).

10:30 AM

(ICG-SII-107-2019) Electrostatic Charging (ESC) of Glass Surfaces: Chemical and Topographical Considerations

G. Agnello*[1]; R. Manley[1]; N. J. Smith[1]; W. Wanda[1]; A. Cormack[2]; L. Wang[2]

1. Corning Incorporated, USA
2. Alfred University, USA

Accumulation, migration and dissipation of charge on glass surfaces have been closely studied for decades, and have recently garnered even greater interest due to the ever-tightening surface requirements characteristic of high-end consumer electronic devices. Somewhat surprisingly, the significant energy and attention that have been devoted to these phenomena have produced very few definitive explanations for the primary physical/chemical mechanisms responsible for these processes. The purpose of this talk is to outline in some detail what we do know about how glasses can acquire charge, how they may dissipate it, and the primary surface attributes (surface chemistry and topography) that impact these behaviors. The combination of data acquired via experiment and simulation to be presented suggest that some commonly circulated and widely held beliefs about the origins of glass ESC demand reconsideration and that effectively preventing it requires a more sophisticated understanding of surface attributes such as chemistry, atomic-scale structure and topography.

10:50 AM

(ICG-SII-108-2019) Influence of glass composition on chemical thinning characteristics of alkali-free aluminosilicate glass

H. Tokunaga*[1]; K. Hayashi[1]

1. AGC Inc., New Product R&D Center, Japan

Recent mobile devices need thinner display panels. Chemical thinning is a significant process to obtain such panels and the process is employed by most of the panel makers. During this process, insoluble residue, which is called sludge, are generated into the etchant and it affects the production yield and surface quality of the glass substrate. In this study, to understand how the glass composition affects the etching properties such as etching rate, sludge volume weight, particle size and composition, various series of SiO_2-Al_2O_3-B_2O_3-RO (R=Mg, Ca, Sr, Ba) glass have been examined. Etching rate was evaluated by measuring weight loss after soaking into HF-based

etchant. Sludge volume was evaluated by complete dissolution of the glass samples into the etchant. Sludge weight was measured after drying. From all experimental data, compositional parameter for etching rate could be calculated by linear regression and etching rate increased in the order of BaO > SrO > CaO > MgO in case of single alkaline-earth containing glasses. Sludge volume increased in the order of SrO > CaO > MgO = BaO. Sludge weight were almost the same regardless of the type of alkaline-earth oxides. The reason of the composition dependence on sludge volume is considered that sludge including CaO, SrO forms hydrates. The mixed alkaline-earth effect on the sludge generation will be also discussed.

11:10 AM

(ICG-SII-109-2019) Optical property and surface texture of anti-glare technology

S. Tomeno*[1]; T. Kakegawa[1]; Y. Akama[1]; M. Isshiki[1]

1. AGC.Inc, Japan

Anti-Glare (AG) cover glass is widely adopted for various displays which are used in bright conditions, especially for in-vehicle, portable devices. AG glass draw attention to reduce glare. AG glass is very old technology but little is known about the relationship between optical property and surface texture. The Sparkle is the biggest disadvantage of AG glass, and we need to suppress and control the sparkle as low as possible. HF chemical etching makes several types of surface structure in silicate glass. Surface roughness parameter (For example, Ra and Rsm and so on) is linked to optical property. The purpose of this work is to investigate the relationship between optical property and surface texture in anti-glare technology in the viewpoint of industry side.

11:30 AM

(ICG-SII-110-2019) Hydrophobic Glasses Enhanced Through Patterned Surface Microstructure

M. Rusch*[1]; C. Hunzeker[1]; C. Wilkinson[2]; M. Affatigato[1]

1. Coe College, Physics, USA
2. Pennsylvania State University, Materials Science and Engineering, USA

We model our project after the lotus leaf. One main function of the lotus leaf's hydrophobicity is the ability to self clean: raindrops falling onto the leaf do not disperse but stay in their shape while running over the surface and picking up any dirt and dust particles. This ability stems from a two fold surface engineering: The leaf surface is covered with an intrinsically hydrophobic material, and the surface shows a microscopic pattern that helps water drops keep up their surface tension. In our project we make use of both of these effects. In a first part of the project we conduct a survey study creating various glasses and testing them for their hydrophobicity. Here we constantly update our pool of glasses using AI simulations and topological constraint theory on our current data to come up with the next generation of hydrophobic glasses. In the second part of the project we create microscopic patterns on our glasses—using lithographic techniques—to enhance their inherent hydrophobicity. While creating such patterns on novel glasses is uncommon and therefore challenging, several steps from resist spinning to preliminary lithography and chlorine etching get us to the wanted product. Work supported by Coe College and by the United States National Science Foundation under grant numbers DMR 1407404, and DMR-1746230.

11:50 AM

(ICG-SII-111-2019) Direct bonding between tellurite glass ultrathin film and substrates at room temperature

T. Kishi*[1]; R. Jeng[1]; N. Matsushita[1]; T. Yano[1]

1. Tokyo Institute of Technology, Japan

Room-temperature (RT) bonding technique is necessary for the integration of multifunctional materials to realize complicated structures such as three-dimensional integration for photonics, optoelectronic, and microfluidic devices. Previously, we demonstrated the direct bonding between tellurite glass ultrathin film and a silicate glass substrate at RT. In this study, the freestanding tellurite glass film was directly bonded on a substrate of various materials (silicate glass, silicon, sapphire, lithium niobate, and the telluride glass) without heating. The bonding strength was ranging from 50 to 400 mJ/m2. The highest strength was on the tellurite glass substrate, and the lowest one was a silicon substrate with a hydrophobic treatment. The bonding strengths with the other substrates had almost the same values of about 200-250 mJ/m2. These results indicate that both the surface functional group and the internal structure of materials are significant for bonding strength. The existence of Te and Nb on the silicate glass substrate after the tellurite glass thin film was peeled off was confirmed on the substrate surface by using time of flight secondary ion mass spectroscopy. This result implies that the bond between Te (or Nb) and the surface element on the initial substrate, which is stronger than the bond in the tellurite glass, can be formed by the direct bonding technique at RT.

12:10 PM

(ICG-SII-112-2019) Thermal dewetting of chalcogenide glasses as a tool for microlenses arrays fabrication

Y. N. Colmenares*[1]; S. Messaddeq[1]; Y. Messaddeq[1]

1. Laval Univeristy, Physics, Canada

The formation of microstructures in high refractive index glasses is object of technological interest in photonic and optoelectronic. Nevertheless, the design of glass surfaces at a microscopic level with optical quality is expensive and time-consuming. Although the dewetting phenomenon is known in metals and polymeric thin films, it is not exclusive for these materials. It has been observed that the chain-like structure and the bond flexibility of some chalcogenide glasses when heated or exposed to light may favour the formation of dewetted regions on the substrate. This presents a technological potential in solid state-patterning for optical applications in the mid-infrared region. In this work, we study the thermal-assisted dewetting process of As-Se thin films in terms of the glass composition, thickness, substrate, temperature and atmosphere of thermal treatment. These parameters are used to control the size and shape of self-assembled structures of glass, allowing to form microspheres that go from a few microns to hundred microns, through a really low-cost process and low temperatures. The chalcogenide films are obtained by electron-beam deposition process and characterized by UV-Vis and Raman spectroscopies, SEM and AFM. We also combine the dewetting phenomenon with some substrate photolithography process to create an alternative approach to produce microlens arrays.

Session 8: Optical Properties of Glass V

Room: Statler (mezzanine)

Session Chairs: Luyun Yang, Huazhong University of Science and Technology; Haitao Guo, Xi'an Institute of Optics and precision Mechanics, Chinese Academy of Science (CAS)

9:30 AM

(ICG-SII-113-2019) Phase Separation and Crystallization Strategies to Construct Multiphase Glass-ceramics to Stabilize Molecular $[Ag_m]^{n+}$ Quantum Clusters (Invited)

X. Qiao*[1]; X. Xu[1]; K. Ren[1]; X. Chen[1]; J. Zhao[1]; J. Du[2]; X. Fan[1]

1. Zhejiang University, School of Materials Science and Engineering, China
2. University of North Texas, Department of Materials Science and Engineering, USA

$[Ag_m]^{n+}$ quantum clusters (QCs), formed by several to tens of Ag^0 atoms and Ag^+ cations, can fluoresce efficiently with m and/or n determined broad UV-Vis-NIR emission band. It demonstrates their promising photonic applications such as bio-labels, spectral converters and solid state lighting. However, it is still a challenge to well stabilize chemically active Ag QCs. In this talk, with a phase

separation strategy, Ag QCs can be formed in borate, phosphate and silicate glasses, respectively. By controlling solubility or introducing competitive cations, we can manipulate the polymerization degree (m) of $[Ag_m]^{n+}$ QCs. By charge compensating to negatively charged $[BO_4]^-$, $[PO_4]^-$ or $[ZnO_4]^{2-}$, we can charge $[Ag_m]^{n+}$ with a fixed n value. With a crystallization strategy, lanthanide cations can also be selectively enriched into the homogenously precipitated fluoride nanocrystals, such as MF_2 or M_2RF_7 (M = Ca; Sr; Ba; R = Y; La; Gd), in a glass host. To a further step, B_2O_3-rich sub-phase, $[PO_4]^-$-rich sub-phase, $[ZnO_4]^{2-}$-rich sub-phase, and fluoride nanocrystalline phase (MF_2 or M_2RF_7) can integrally formed in a multi-phase glass-ceramics. As results, fluorescence of $[Ag_m]^{n+}$ QCs can be tailored and supplemented with glassy sub-phase (Ag) and crystalline sub-phase (lanthanides), respectively.

10:00 AM

(ICG-SII-114-2019) Eu^{2+}-Nd^{3+} co-doped calcium sodium silicate glasses for solar spectrum modification via NUV/Visible to NIR downcoversion

R. F. Muniz*[1]; A. Steimacher[2]; F. Pedrochi[2]; A. N. Medina[1]

1. State University of Maringa, Physics, Brazil
2. Universidade Federal do Maranhão, Programa de Mestrado em Ciência dos Materiais, Brazil

Optical properties of the materials used as active medium in photovoltaics solar cells (PVSC), especially the absorption spectrum and the photoconversion, have a significant influence on the efficiency of these devices. The mismatch between the absorption/photoconversion of the active materials used in the PVSC with the solar radiation spectrum is one of the main reasons this limitation. The absorption of the radiation and conversion in the PVSC is controlled by the bandgap of the semiconductors used in its manufacture. Bandgap of the semiconductor materials is 1127 nm (E^g = 1.1 eV) for crystaline silicon c-Si. To overcome this problem, many materials (glass, ceramics, phosphors) have been co-doped with rare earths for ultraviolet absorption and emission in the bandgap region of the solar cells. Trivalent ytterbium have been recognized as the most efficient rare earth used as acceptors to convert ions from NUV/Vis to NIR emission for improvements of solar cells. However, now the potential of neodymium has been put into evidence. Nd^{3+} has a important NIR emission at 1064 nm matching very well with spectral response of c-Si semiconductor material. In order to investigate the possibility of energy transfer between Eu^{2+} and Nd^{3+}, we have synthetized for the first time several co-doped calcium sodium silicate glasses.

10:20 AM

(ICG-SII-115-2019) Thermally stable fluorotellurite glass with various types of modifiers

M. J. Reben*[1]; B. Burtan- Gwizdala[2]; E. Yousef[3]; J. Cisowski[4]; I. Grelowska[1]

1. Faculty of Materials Science and Ceramics, AGH – University of Science and Technology, Glass Technology and Amorphous Coatings, Poland
2. Cracow University of Technology, Institute of Physics, Poland
3. King Khalid University, Department of Physics, Saudi Arabia
4. Cracow University of Technology, Institute of Physics, Poland

We focus on the research of glasses as mid-infrared optical fiber candidates and investigate the effects of different modifiers on the thermal stability as well as optical and spectroscopic properties of the main composition of $70TeO_2$ – $5M_xO_y$ – $10P_2O_5$ – 10ZnO – $5PbF_2$ in mol%, where M_xO_y = (modifiers) doped with 2400ppm Er_2O_3. The glasses were prepared by the conventional melt quenching method. Thermal characteristics of glasses like the glass transition temperature T_g, the temperature for the crystallization onset T_x, the maximum crystallization temperature T_c, and the thermal stability parameter were determined by DSC method. The ellipsometric data have provided a Sellmeier-type dispersion relations of the refractive index of the investigated glasses. It appears that the quantum efficiency of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition is quite high. The absorption and fluorescence spectra have been analyzed in terms of the standard Judd–Ofelt theory along with the photoluminescence decay of the $^4I_{13/2}$ and $^4S_{3/2}$ levels of the Er^{3+} ion. The absorption and emission spectra of the $^4I_{15/2} \leftrightarrow {}^4I_{13/2}$ infrared transition have been analyzed within the McCumber theory to yield the peak emission cross-section and figure of merit (FOM) for the amplifier gain.

10:40 AM

(ICG-SII-116-2019) Structure and linear/nonlinear optical properties of silver tellurite glasses

T. Hayakawa*[1]; K. Kato[1]; K. Muramatsu[2]; K. Hayashi[2]; J. Duclere[3]; P. Thomas[3]

1. Nagoya Institute of Technology, Department of Life Science and Applied Chemistry, Japan
2. Nagoya Institute of Technology, Department of Physical Science and Engineering, Japan
3. Limoges University, CNRS-IRCER Lab, France

We've developed a new glass system based on silver and tellurite, Ag_2O-TeO_2, which exhibits high refractive index and third-order nonlinear optical susceptibilities, $\chi^{(3)}$. The glasses showed varied colors (yellow to red) dependent on the melting time and type of crucible (Al_2O_3, Pt). A small amount of Al_2O_3 was incorporated into Ag_2O-TeO_2 glass from the crucible and stabilized Ag_2O-TeO_2 amorphous state. The optical bandgap of the Ag_2O-TeO_2 glasses were estimated by using Tauc plot and found to be changed from 2.0 to 2.6 eV., which was related with a value of $\chi^{(3)}$ so that the decreasing optical bandgap energy enhanced $\chi^{(3)}$. The yellow Ag_2O-TeO_2 glass (E_g^{opt} = 2.60 eV) showed 6.15 x 10^{-13} esu of $\chi^{(3)}$, while the red Ag_2O-TeO_2 glass (E_g^{opt} = 2.07eV) did 7.85x10^{-13} esu. The ab-initio calculation with Gaussian pachage elucidated that the decreasing distance between Ag^+ and TeO_3^{2-} unit reduced a LUMO-HOMO energy, which well explains observed red coloration. Moreover, the glass structures have been very recently investigated by using synchrotoron radiation in SPring-8 and Aichi SR centers. The tenttative resutls of X-ray absorption fine structure (XAFS) analysis shows that averaged Ag-O distance is ~2.28 Å in both the glasses, not different so much but more Ag-Ag correlation can be found in the yellow colored glass.

11:00 AM

(ICG-SII-117-2019) Femtosecond laser induced damage on Ge-As-S chalcogenide glasses

M. Zhang*[1]; Z. Yang[2]

1. Sun Yat-sen University, China
2. Jiangsu Normal University, China

The laser irradiation damage on Ge-As-S chalcogenide glasses was studied with 216-fs pulses with repetition rates (RRs) of 1 kHz-1 MHz at 1030 nm. The compositional dependence of the laser damage threshold was systematically investigated, and the damaged mechanisms corresponding to the irradiation pulses with different RRs were discussed. We found that the stoichiometric compositions have the best resistance to the optical damage irrespective of the RR. When the irradiation pulses operate at 1 kHz, the damage is mainly caused by avalanche ionization. In comparison, thermal accumulation becomes prominent as the RR exceeds 10 kHz and becomes a main factor in the damage when the RR is more than 100 kHz. The results could be helpful for composition choices and pumping scheme designs in nonlinear optics.

11:20 AM

(ICG-SII-118-2019) Fabrication Up-conversion $CaSiO_3$ System Bioglasses

J. Yuye*[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

This work demonstrates bulk-type up-conversion biomaterials which could be used as a bone repair material with the ability to monitor bone mineralization. Er^{3+}/Yb^{3+} co-doped $CaSiO_3$-TiO_2 bioglasses (TiO_2 content is 30 mol%) were prepared via containerless

processing technique in an aerodynamic levitation furnace. The up-conversion fluorescence property was influenced by Yb^{3+} doping concentration, heat-treatment and mineralization in simulated body fluid (SBF). Optimum emission intensities were obtained for the sample with 20 mol% of Yb^{3+} doping concentration and heat treatment at 937 °C for 2 h. Hydroxyapatite (HAP) deposition was observed on the surface of the bioglasses after soaking in SBF for 14 days, and the up-conversion fluorescence intensity of the bioglasses decreased with the increase of soaking time. This indicates that Er^{3+}/Yb^{3+} co-doped bioglasses are bioactive, in which the HAP mineralization in bone repair could be monitored by measuring the intensity change of up-conversion fluorescence.

11:40 AM

(ICG-SII-119-2019) Mechanism for broadening and enhancing Nd^{3+} emission in zinc aluminophosphate glass by addition of Bi_2O_3

Y. Wang*[1]; M. Peng[1]

1. South China University of Technology, China

Nd^{3+}-doped phosphate glasses have been attracting much research interest due to their excellent optical properties. However, the narrow NIR emission bandwidth (<30 nm) of these Nd^{3+}-doped phosphate glasses limits their further application. Here, we demonstrate the broadening and enhancing of Nd^{3+} NIR emission in zinc aluminophosphate glass through tuning the glass structure and covalency of Nd-O bond without limiting the radiative properties of Nd^{3+}. The maximum bandwidth of 1.05 mm is broadened to 50 nm, which is comparable to that of Nd^{3+}-doped aluminate glasses. Our results could enrich our understanding about the relationship between local glass structure and luminescence behaviors of active centers, and may be helpful in designing new RE-doped glass systems.

Session 9: Tribology (TC 06)

Room: Arlington (mezzanine)
Session Chair: Lothar Wondraczek, University of Jena

9:30 AM

(ICG-SII-120-2019) Mechanochemistry governs mechanical and tribological properties of silicate glass in humid air (Invited)

S. H. Kim*[1]

1. Pennsylvania State University, Chemical Engineering, USA

Water or acid soaking treatments have been shown to increase the mechanical strength of silicate glasses. In this talk, the effects of sodium-leaching on the mechanical and tribological properties of soda lime silicate glass in dry and humid conditions will be addressed. Upon normal indentation in humid air, the sodium-leached surface appears to be more resistant to crack initiation than the annealed surface. In contrast, when the surface is subject to tangential shear with a smooth counter surface at a load where indentation damage is negligible, the leaching of sodium ions makes the surface more susceptible to wear in high humidity conditions. These apparently-opposite humidity dependences of surface damages occurring in normal indentation and tangential shear conditions cannot be explained with bulk mechanical properties of glass; it requires considering mechanochemical reactions involving water molecules from the ambient air. The difference in humidity dependences of crack initiation upon normal indentation and wear upon tangential shear also suggests that chemical reactions determining surface damage modes are different in these two mechanical test conditions. This talk will discuss chemical reactions occurring at/in the glass surface induced or facilitated by mechanical compression and shear stresses and how they influence or determine mechanical properties of glass surfaces.

10:00 AM

(ICG-SII-121-2019) The role of plastic flow, densification and mechanochemical wear in the glass nanoscratch deformation (Invited)

J. Yu*[1]; J. Fu[1]; H. He[1]

1. Southwest University of Science and Technology, China

The scratch-induced deformation of oxide glass is of great interest in glass science, since scratch resistance is the key parameter that evaluates the mechanical strength of oxide glass. The glass deformation during nanoscratching is a complicated process, where the main factors affecting the scratch-induced deformation can be classified into three independent aspects: plastic damage, densification, and chemistry-enhanced material-removal (mechanochemical wear). The three factors compete with each other during the sustained scratching. Through comparing the deformation volume of glass subject to different conditions, viz. in dry or humid air and before or after annealing, the contributions of the three factors to the total deformation can be quantified and their evolution mechanisms can be clarified for sustained scratching. Analyses indicate that the combined action of plastic damage and densification dominates the glass deformation in fewer-pass scratching, while plastic damage and chemistry-enhanced material-removal together determine the final deformation volume for multi-pass scratching in humid air.

10:30 AM

(ICG-SII-122-2019) Speed dependence of wear of soda lime silica glass

H. He*[1]; S. H. Kim[2]

1. Southwest University of Science and Technology, China
2. Pennsylvania State University, USA

Using a reciprocating ball-on-flat tribometer, the effects of the sliding speed and humidity on the mechanochemical wear of soda lime silica (SLS) glass were studied by rubbing against a pyrex ball. The experimental results show that wear of SLS glass was very sensitive to the humidity and sliding speed. When water molecules are present at the sliding interfaces in humid air, the wear volume of SLS glass decreases with the increase in sliding speed from 0.25 mm/s to 8 mm/s, which is believed to be originated from the suppressed tribochemical reactions involving water molecules at high speed conditions, therein the wear volume of SLS glass decreases to ~6 times. However, when water molecules are absent at the sliding interfaces in dry air, the wear volume of SLS glass increases to ~12.5 times when the sliding speed increases from 0.25 mm/s to 8 mm/s. Further analyses suggest that the wear of SLS glass in dry air is dominated by the adhesive wear and brittle exfoliation, which can be facilitated by the friction-induced temperature rise and surface cracking at high speed conditions. Our results indicate that the sliding speed can either promote or suppress the wear of SLS glass, depending on the presence of water molecules at the sliding interfaces. These results may provide a deep understanding on the effects of water and speed on the material damage of oxide glass materials during its manufacturing and operation processes.

10:50 AM

(ICG-SII-123-2019) Connection between indentation fracture and grinding behavior in various optical materials

T. I. Suratwala*[1]; W. A. Steele[1]; L. L. Wong[1]; P. E. Miller[1]; N. Shen[1]; M. D. Feit[1]; J. A. Menapace[1]; E. Feigenbaum[1]; G. Tham[1]

1. Lawrence Livermore National Laboratory, Optics and Materials Science & Technology, USA

The following study quantitively evaluates the relationship between the workpiece grinding characteristics (including removal rate, roughness, and sub-surface mechanical damage (SSD)) and its fundamental indentation facture behavior (e.g., lateral and radial crack growth)). A large variety of optical materials (glasses, glass-ceramics, & single crystals) have been systematically processed

using fixed or loose abrasive grinding. The removal rate and surface roughness were measured for each grinding process and workpiece material; for some of the samples, the SSD depth was characterized using the taper wedge technique. Separately, the indentation fracture behavior using indentation was measured for each optical workpiece material as function of load. The grinding rate and roughness are shown to scale with the lateral crack depth slope (i.e., the propensity of lateral crack growth during static indentation on a given workpiece material). Using a fracture mechanics based model for volumetric lateral crack removal or lateral crack depth, the grinding rate and the resulting workpiece surface roughness as a function of the lateral crack growth constant of the workpiece, mean abrasive size, applied pressure and velocity can be quantitatively described. This model serves as a useful predictive tool to determine the grinding behavior for different workpiece materials.

11:10 AM

(ICG-SII-124-2019) Effect of colour pigments on wear behaviour of a mica-based glass-ceramic

D. Chaysuwan*[1]; S. Prasertwong[1]; S. Angkulpipat[1]; T. Srichumpong[1]; R. Sola[3]; C. Thanachayanont[2]; K. Suputtamongkol[4]; P. Veronesi[3]; G. Heness[1]; C. Leonelli[3]

1. Faculty of Engineering, Kasetsart University, Department of Materials Engineering, Thailand
2. National Metal and Materials Technology Center, Thailand Science Park, Thailand
3. Faculty of Engineering, University of Modena and Reggio Emilia, Department of Engineering "Enzo Ferrari", Italy
4. Faculty of Dentistry, Mahidol University, Department of Prosthodontics, Thailand

Glass-ceramics are the biomaterials of choice for dental materials. However, a possible problem with their use is wear between them and natural teeth during mastication. For aesthetic reasons, pigments, CeO_2 and Fe_2O_3, were added. This work investigates whether such additions would affect hardness and wear properties. Specimens were prepared based on a mica-based glass-ceramic (GC) with additions of 1.0 wt% CeO_2 (GC_Ce1), 0.1 wt% Fe_2O_3 (GC_Fe0.1), and 1.0 wt% CeO_2 and 0.1 wt% Fe_2O_3 (GC_Ce1.0Fe0.1). Nanoindentation hardness and tribology tests were performed. The hardness test was determined at a load of 200 mN with a Berkovich indenter and wear was evaluated using a pin-on-disk tribometer with 10 N load for 1,000 cycles. Hardness results for GC, GC_Ce1, GC_Fe0.1 and GC_Ce1Fe0.1 of 3.2, 3.3, 3.6 and 3.6 GPa, respectively, were obtained. From the tribology test, the friction coefficient of GC_Ce1 gave the lowest value of 0.7 and the GC_Ce1Fe0.1 provided a maximum value of 0.85. In addition, the GC_Fe0.1 presented the lowest wear rate of 0.0155 mm^3/Nm. There appears to be no trend between hardness, stiffness and wear behavior for the materials tested. However, phase development and in particular the effect of CeO_2 seems to play an important role. X-ray diffraction and scanning electron microscopy are used to relate the phase and microstructural development to the observed mechanical properties.

Session 9: Strength (TC 06)

Room: Arlington (mezzanine)
Session Chair: Liping Huang, Rensselaer Polytechnic Institute

11:30 AM

(ICG-SII-125-2019) Effect of surface modification with chlorine on the tensile strength of optical fiber glass

A. Srivastava*[1]; H. Harode[1]; C. K. Saha[1]

1. Sterlite Tech, R&D, India

The principal ingredient of an optical fiber is quartz glass. Its thermal history influences the properties of glass at room temperature. The quality of the optical fiber decreases if impure foreign substances are attached to its preform surface. If residual strain inside a preform is significant, it cracks with a small impact during drawing or transporting. Furthermore, damages and unevenness in the surface of an optical fiber base material break the fiber during drawing. The present work signifies that chlorine pre-treatment enhances mechanical properties of the optical fiber glass. SEM techniques confirmed chlorine diffusion profiles in silica glass cladding. FTIR results portray that chlorine gas chemically modifies the structure of silica clad and reduces its softening temperature causing the crack healing easier during fiber draw process. Metallic impurities on the preform surface likely formed volatile metal chlorides. The surface of preform becomes dry, preventing any further particle accumulation. The Weibull analysis of long length tensile strength demarcates a substantial shift in its knee. The slower sub-critical crack growth rate in air implies a more significant strength thereby reducing draw and proof testing breaks.

11:50 AM

(ICG-SII-126-2019) Microwave Heat-treated Crystallization and Microstructural Aspects of ZrO_2 Containing K–Mg-Al–Si–O–F Glass-ceramics

M. Garai*[1]

1. Indian Institute of Technology, Materials Science Centre, India

In understanding the microwave heat-treated crystallization of boroaluminosilicate system (Si-O-Si/B/Al), the varying ZrO2 (2, 5 and 10 wt.%) doped K2O–MgO–Al2O3–SiO2–B2O3–F glasses were synthesized by melt-quenching at 1550°C (for 2 h). Over controlled-crystallization at 700°C followed by 780°C in microwave-furnace, the amorphous -glasses were converted into opaque glass-ceramics; and that temperature is adequate to evolve predominant crystalline phase (XRD) fluorophlogopite-mica, KMg3(AlSi3O10)F2. With increasing ZrO2, higher nucleation is ascertained with respect to increasing average crystal-width; and such microstructure (FESEM) exhibited enhanced machinability. Scratch tests (40N) using glass-ceramics indicate that the rod shaped mica-crystals with higher-width offers the scratching induced crack propagation. Materials deformation, 2 wt.% ZrO2 content> 5 wt.% ZrO2> 10 wt.% ZrO2 through scratch propagation is inversely proportional to strength of matrix. Glass-ceramic with 2 wt.% ZrO2 possess Vickers-microhardness 5.68 GPa and increased to 6.17 and 6.64 GPa when contains 5 and 10 wt.% ZrO2, respectively.

SIII: Glass Technology and Manufacturing

Session 3: Refractory/Glass Interactions

Room: Stuart (4th floor)
Session Chairs: Hong Li, Nippon Electric Glass; Irene Peterson, Corning Incorporated; Kathryn Goetschius, Guardian Glass

9:30 AM

(ICG-SIII-016-2019) Application of diffusion model to the glass melt and refractories interaction at high temperature (Invited)

E. Burov*[1]; M. Ficheux[1]; L. Cormier[2]; E. Gouillart[1]

1. Joint Unit Saint-Gobain/CNRS, Surface, Glass and Interface, France
2. Sorbonne University, IMPMC, France

Zirconium oxide is widely used as a component in several ceramic and refractory materials in order to increase their resistance to high temperatures and to limit their corrosion in glass furnaces. Exchange of matter between the amorphous glass and the crystallized refractories is inevitable during the life of a furnace. This dissolution phenomenon of zircon or refractory directly depends on zirconium mobility from the crystal towards the glass. During several year in order to describe the mobility of each element in glass bath and be more flexible concerning the compositional field we develop a multicomponent diffusion approach to the chemical diffusion. This approach takes in account interaction between elements inside linear model and determines diffusion matrix that describes mobility of an element in the form of exchange reactions and their occurrence coefficients obtained from the eigenvectors and

eigenvalues of the diffusion matrix. In this study, the exchange reactions for the NCAS glass contained 5wt% Zr have been defined and then extrapolated to the interaction glass melt and refractories. In this presentation, the advantage and the limits of this approach will be discussed. Additionally, a structural study of zirconium environment is coupled with the mobility determination.

10:00 AM

(ICG-SIII-017-2019) Fusion Cast Refractories: Roles of Containment - Cover Glass to Waste Glass (Invited)

K. R. Selkregg*[1]

1. Monofrax LLC, Technical, USA

Monofrax has been in the business of providing fusion cast refractories to the glass industry for 70 years. The glass industry manufacturers of plate glass, glass bottles, and smart device cover glasses require glass clarity with no defects. The purpose of quality fusion cast refractories in contact with this glass is to contain the molten glass at high temperatures without introducing defects. Refractory linings in glass furnaces are a critical component of glass-based applications, including encapsulation of nuclear waste through vitrification. Monofrax has more than 30 years of experience in providing melter lining for vitrification of intermediate- and high-level waste both in the US and Asia. This paper compares experiences with corrosion behaviors at the glass/refractory contact of AZS fused cast refractories in typical sodalime glass with that observed in Monofrax fused cast chrome in a nuclear waste borosilicate glass type. In addition, this paper expands on previous corrosion studies by observing corrosion effects in iron phosphate glasses.

10:30 AM

(ICG-SIII-018-2019) Knots and cords originating from the AZS refractory corrosion (Invited)

P. Simurka*[1]; P. Vrabel[2]; V. Vargova[2]

1. Slovak Glass Society, Slovakia
2. Rona a.s., Slovakia

A fused cast Alumina Zirconia Silicate (AZS) is commonly used as a type of refractory material in glass industry because of its remarkable resistance to corrosion by glass melt and glass melting environment. Despite many advantages of this material, the presence of the glassy phase in AZS refractory is realized to be a problem from the viewpoint of applications. While there can be many sources of cord defects, refractory contamination in the glass is frequently cited as a leading source. Objective of this paper is to show the relationship between the composition of defects presented at tableware glass products and a glass phase of the AZS refractory material. Database of 69 chemical compositions of defects, mainly cords, was creating by collecting the final products containing glass defects during regular tableware glass production in a period of 48 months. The concentration profiles of oxides presented in AZS refractory glass phase on refractory samples taken from the same furnace after two consecutive campaigns were determined by SEM and EDX analysis. The same analysis has been performed on the samples after laboratory static corrosion test. The identification of potential source of knots and cords was realized by the comparison of the chemical composition of defects with the results of the AZS refractory corrosion study.

11:00 AM

(ICG-SIII-019-2019) A practical approach to study and prevent refractory corrosion in glass melting furnaces (Invited)

S. Lessmann[1]; A. Faber[1]; O. Verheijen*[1]

1. CelSian Glass and Solar, Netherlands

Furnace lifetime and glass quality control are major factors in maintaining a reliable and cost efficient glass melting process. Corrosion of the crown and superstructure can decrease the lifetime of a furnace drastically and repairs of the refractories can be costly. Furthermore, the reaction products formed during the corrosion process can have an influence on the final glass product quality. The objective of this presentation is to highlight the methods and tools that are available to study and minimize the corrosion rates of (crown) refractories in glass melting furnaces. CelSian uses industrial furnace inspections, thermodynamic simulation tools and laboratory testing equipment to find solutions to prevent rapid refractory degradation and increase the furnace life time. Both refractory corrosion modelling and practical examples from the industry will be discussed during the presentation.

11:30 AM

(ICG-SIII-020-2019) New Zircon Silicate Refractory Solutions for high quality Glass

M. Gaubil*[1]

1. SEFPRO, Marketing, France

Sintered Zircon Silicate Refractory Material are used for glass contact application in different high quality glass composition such as borosilicate or reinforcement glasses. For Alkalii glass, blistering reaction have been reported and described in between glass and Zircon refractory product for different level of temperature that can affect glass production. Some treatments have been developed to cope with this transient blistering problems; Nevertheless SEFPRO developed a new zircon silicate refractory solution that dramatically improve blistering behavior in alkali glasses. We will discuss these new material glass contact properties with borosilicate and sodalime glasses. On top of blistering results, we will analyses corrosion resistance and glass defect ability. Finally, we will come to different applications in end part glass furnace such as spout, expendables or mandrels for high quality glass article manufacturing

11:50 AM

(ICG-SIII-021-2019) Scale dependence on microstructure observations and properties

J. Fourcade*[1]; D. Cetin[2]; T. Hara[3]; D. Bolore[2]; J. Chalard[5]; D. Lechevalier[4]

1. Saint-Gobain, USA
2. Saint-Gobain Research North America, SEFPRO, USA
3. National Institute for Materials Science (NIMS), Research Center for Structural Materials, Japan
4. Saint-Gobain Japan, NIMS - LINK/UMI3629, Japan
5. Saint-Gobain Research Provence, France

Microstructure observations of ceramics and refractories have always been a key component of the material characterization process. Observations are used to assess at the quality of sintering, to identify the position of impurities, to understand the mode of failure and to analyze the reactivity with some elements from atmosphere or slags. From the observation of the initial microstructure to the autopsy of a used product it is essential to have the right tools and the right methods to prepare the samples and to perform the analysis. Metallographic observations, scanning electron observations, electron backscattered diffraction, X-ray computed tomography, etc. are all very useful characterization tools that allow macro and microscale observations in 2 or 3 dimensions. This work will present the characterization of dense isopressed zircon with various techniques and how observations at various scale can help understand some of the material properties. Comparison of results obtained with different techniques will highlight the difficulty of having an accurate representation of microstructures with simple 2D observation techniques and why 3D reconstruction techniques are becoming so important.

12:10 PM

(ICG-SIII-022-2019) Residual quartz importance in crown silica bricks

S. Cappuzzo[1]; S. Ceola*[1]; S. Sanchetti[1]

1. Stazione Sperimentale del Vetro, Italy

Silica bricks are the main constituents of glass furnace crown due to the high resistance at high temperature and their low weight with respect to AZS. But if calling them "Silica bricks" reveals their composition, little is often known about its mineralogical

constituents. Thanks to the experience built on several tested bricks, in this paper SSV goes in all the aspects and details to put attention to, from Bulk Density, Apparent Porosity (BD/AP) and Cold Crushing Strength (CCS), to high temperature tests as Refractoriness Under Load (RUL), with a special focus on the mineralogical characterization via XRD diffraction. As silica undergoes mineralogical transformations, the changes in volume can lead to catastrophic failing of the crown. SSV has finely tuned an experimental diffraction method to test how much residual quartz is present, thus preventing further expansion while in use. This expansion behavior can also be measured by means of 2 thermophysical tests: Refractoriness Under Load (RUL) and a specially crafted Creep test. Thanks to these procedures, the expansion that takes place due to the transformation of the residual quartz content not only at the rising of temperature, but also due to its dwelling at high temperatures, can be correctly evaluated before making strategic decisions in the furnace construction.

Session 6: Glass Recycling and Sustainability

Room: White Hill (4th floor)

Session Chairs: Stefano Ceola, Stazione Sperimentale del Vetro; Sezhian Annamalai, PPG Industries

9:30 AM

(ICG-SIII-023-2019) Sustainability in Glass Manufacturing-Understanding the Role of Glass Recycling (Invited)

S. Bhaduri*[1]

1. Owens Illinois, Inc., USA

Among all of the packaging materials, glass is proven to be one of the most sustainable material that provides tremendous environmental benefit. Glass can be recycled infinitely without losing its physical and chemical properties. The inertness of glass also adds an extra advantage in safeguarding people's health when used as a packaging material. In this presentation, we will discuss the recent sustainability effort at glass manufacturing operation. Notably, the focus of this presentation will be glass recycling and how it plays a significant role in the sustainability effort. In general, by using a high percentage of recycled glass (cullet), the environmental footprint of manufacturing operation can be significantly reduced. In spite of the health-related and other benefits, glass recycling has been facing a paramount of challenges because it is seen as a negatively-sorted recycled material. To overcome this challenge, an enterprise-level initiative in specific targeted regions must be in place as each region of the globe has its problems. However, it is a journey, and it will take a cross-disciplinary team that involves local government and county officials, brand owners, manufacturers, and consumers to understand specific gaps and opportunities. It also needs to be done by a case-by-case basis, as each region has its challenges and opportunities.

10:00 AM

(ICG-SIII-024-2019) Glass recycling in float lines (Invited)

J. G. Cid-Aguilar*[1]

1. Vitro Architectural Glass, R&D/Glass Composition, Mexico

Without doubts recycling cullet represents advantages in float glass manufacturing industry: Cullet is one of the raw materials available to glassmaker, the main benefits are: Reduce fabrication cost, allow a higher production rate, decrease the melting energy requirements, minimize carry over levels, and decrease carbon dioxide emissions (CO_2). The main challenge has been the quality of external or foreign cullet: there are different sources such as subsidiaries, processors (Non-customers) and replacement window/building demolition. External cullet must meet technical specification for regular raw material such as contamination issues: It should be clean of refractory, stones, metals, silicon carbide etc. On the other hand, it is important to sort the glass by color and to analyze base glass composition. Nowadays, for improving recycling external cullet quality, it has been installed different systems: Color sorting processor (CSP), it includes stones and ceramics sensors, Remco GlassMax grinders and windshield processor and has created a recycling culture chain. In recent years have been possible to use up to 80% recycling glass for a tint float process. In fact, sometimes this process might get unpleasant due to possible issues that may happen such as shut downs. Today, there are procedures for processing cullet and it is maximizing its consume from the sources available.

10:30 AM

(ICG-SIII-025-2019) What about mixed cullet? (Invited)

E. Alejandro*[1]

1. Vidrala, Glass Technology, Spain

One of the main concerns in container glass industry nowadays is furnace efficiency, as energy consumption has become one of the biggest costs; together with the increasingly demanding emission limit compliance requirements, it has led to recycled glass or cullet becoming the most important ingredient in glass production. Providing obvious melting benefits, recycled glass has on the other hand specific characteristics that can become a serious drawback when trying to maximize its usage in a glass batch, like, for example, infusible and organic contaminations. Another important feature is its color mixture, as this determines the amount of colorizing, oxidizing and reducing compounds in the batch, thus guaranteeing the glass quality stability. In sensitive reduced amber-type glass production, using mixed cullet can be a forbidden practice in some regions and color sorting is mandatory; in other regions, color sorted cullet is not possible to obtain at sustainable prices, and mixed cullet is the only type available. In this situation, it is necessary to find a procedure in order to maximize it and take advantage of its benefits without affecting glass quality. In this paper, the industrial experience in using mixed cullet in reduced glasses is described. A specific procedure has been defined that describes which are the best practices and boundary conditions, in order to minimize the risks and affection to glass quality.

11:00 AM

(ICG-SIII-026-2019) Cast building components out of waste glass

T. Bristogianni*[1]; F. Oikonomopoulou[2]; F. A. Veer[2]; R. Nijsse[1]

1. TU Delft, Materials, Mechanics, Management & Design (3Md), Netherlands
2. TU Delft, Architectural Engineering +Technology, Netherlands

This research explores the potential and limitations of casting structural glass components from discarded glass. Aim is to achieve reliable building elements of consistent physical and mechanical properties while simultaneously tackling the problems of accumulated glass waste, scarcity of raw material resources, and high energy consumption. Therefore, various different commercial glass recipes are recycled into 50mm cubic glass components at lower forming temperatures (10^3-10^4 dPas viscosity), and are experimentally assessed. Focus is given in the presence of various contaminants in the cullet (coatings, stone/ceramic content) and their effect on the glass matrix. Moreover, the combination of different glass recipes is investigated in relation to the casting parameters. Resulting inhomogeneities in the mesostructure of the cubes are documented with high-resolution photographs, and by employing an imaging real-time polarimeter and a computer tomography scanner. Thereafter, splitting tensile strength tests are conducted and the fracture patterns are analysed and compared to the previously documented flaws. The inhomogeneities at the fractured surfaces are further assessed using X-ray-fluorescence, X-ray diffraction and scanning electron microscope techniques. The results provide strength data and indicate the risks that need to be taken into account during the casting and quality control of the proposed building components.

11:20 AM

(ICG-SIII-027-2019) In-Situ purification of waste glass during the re-melting process

T. Gerdes*[1]; K. Ischenbek[1]

1. University of Bayreuth, Keylab Glass Technology, Department CME, Germany

In Germany, the recycling rate for glass container is now around 88%, in Belgium, even at 95%. Despite sophisticated separation technology of waste glass cullets impurities from special glasses, which often contain unwanted components can not completely be avoided. In combination with the high recycling rates, it leads to a significant enrichment of heavy metals and dissipation of valuable metals in container glass. It is an increasing challenge for the glass industry to stay below the REACH limit of 250 ppm for undesired elements, especially Pb. Within the contribution, two different methods for the removal and separation of heavy or precious metals from container glass will be presented. The first one is based on melt extraction, by using Silicon or Tin melts during re-melting of waste glass. The second method is based on selective chlorination to volatilize undesired elements. It will be shown that over 90% of e.g. Lead can be removed by metal extraction as well as by formation and evaporation of $PbCl_2$ during glass melting without an additional process step. The impurities can be collected in the exhausted gas filter of the melting furnace or drained as a metal alloy from the bottom of the glass smelter. Beside the lab-scale results for removal of Pb, Cr, Ba and Fe, the concept for scale up the new "up-cycling" technology for container glass will be discussed.

SIV: Emerging Applications of Glass

Session 8: Anion Solubility in Nuclear Waste Glasses

Room: Whittier (4th floor)

Session Chairs: Kai Xu, Wuhan University of Technology; Albert Kruger, US Department of Energy

9:30 AM

(ICG-SIV-081-2019) Partitioning of rare-earth cations in multiphase glass-ceramics (Invited)

J. McCloy*[1]

1. Washington State University, School of Mechanical and Materials Engineering, USA

A glass-ceramic waste form has been designed for a mixed transition metal and lanthanide metal waste stream from the aqueous reprocessing of used nuclear fuel. Parametric studies are being conducted to assess melt compositional effects on crystal phase composition and distribution. Summarized in this talk is one set of studies investigating the partitioning of rare earth (RE) cations in three series of aluminoborosilicate glass-ceramics containing oxides of alkali (Na), alkaline earth (Ca), rare earth (single rare earths taken from Sc, Y, or La through Lu), and transition metal (Zr and Mo). Eight-oxide glasses were formulated in three series: 1) peralkaline formulations (defined as Na_2O_{excess}=Na_2O-Al_2O_3-ZrO_2>0) with ~5 mol% RE_2O_3; 2) metaluminous formulations (Na_2O_{excess}~0) with 10 mol% RE_2O_3 and 10 mol% B_2O_3; and 3) peraluminous formulations (Na_2O_{excess}<0) with 10 mol% RE_2O_3 and 15 mol% B_2O_3. Crystal phases produced on slow cooling always include two transition metal phases, ZrO_2-type and a molybdate phase. Peralkaline systems include a silicate phase (oxyapatite or keiviite, depending on RE cation size), while the peraluminous high boron & RE systems include silicate plus borate or borosilicate crystalline phases, depending on the RE size. All phases were found by electron microprobe to contain some RE cations. The crystalline phase distribution is discussed in terms of RE cation size and coordination number.

10:00 AM

(ICG-SIV-082-2019) An insight into the origins of higher molybdenum solubility in alkali aluminoborosilicate glasses as a function of rare-earth oxides

H. Kamat*[1]; A. Tyryshkin[2]; F. Munoz[3]; B. P. Gorman[4]; A. Goel[1]

1. Rutgers - The State University of New Jersey, Department of Materials Science and Engineering, USA
2. Rutgers - The State University of New Jersey, Department of Marine and Coastal Sciences, USA
3. Institute of Ceramics and Glass, CSIC, Spain
4. Colorado School of Mines, Department of Metallurgical and Materials Engineering, USA

Molybdenum (Mo) is present in HLW and exhibits very low solubility in aluminoborosilicate based nuclear waste glassy matrix. The MoO_3 solubility in alkali aluminoborosilicate glasses has been shown to significantly increase with the addition of rare-earth oxides. However, the mechanism of the increase in MoO_3 solubility is still debatable. We had recently proposed a mechanism explaining the higher solubility limit of MoO_3 in rare-earth-containing alkali aluminoborosilicate glasses [J. Phys. Chem. B 2018, 122, 1714-1729]. Accordingly, Nd_2O_3 phase separates the homogeneous aluminoborosilicate glass into borate-rich and aluminosilicate-rich region; Nd^{3+} then preferentially enters the borate-rich region forming an Nd-borate structure and the excess Nd^{3+} clusters in the aluminosilicate-rich region; Mo then enters this glass as $[MoO_4]^{2-}$ and is incorporated into borate-rich region forming a Nd-Mo-B-O glassy region which increases the MoO_3 solubility. Our present study is focused on validating this hypothesis. Thus, we have synthesized a series of glasses with systematic compositional variation in the system Na_2O – CaO – B_2O_3 – Nd_2O_3(La_2O_3) – Al_2O_3 – SiO_2 and investigated them using a suite of characterization techniques including MAS-NMR and EPR spectroscopies along with atom probe tomography (APT). The results will be discussed in the presentation.

10:20 AM

(ICG-SIV-083-2019) Properties of MoO_3-rich iron phosphate waste forms

C. Kim*[1]; R. Brow[2]; J. Hsu[2]; J. Bai[2]; J. Szabo[1]; A. Zervos[1]

1. MO-SCI Corporation, USA
2. Missouri University of Science and Technology, Department of Materials Science and Engineering, USA

Properties of an iron phosphate waste form that contains up to 40 wt% of the high MoO_3 Collins-CLT waste simulant are discussed. The waste form partially crystallizes on cooling, and the chemical stability of the resulting material depends on the nature of those crystals and the properties of the residual glass. Crystals of (Rare Earth)PO_4, ZrP_2O_7, and $Fe_2P_2O_7$ form and these phases affect the composition of the residual glass matrix. The chemical stability of as-cast and CCC-treated waste form samples was evaluated using the product consistency test (PCT). The increased dissolution rate of the CCC-treated sample is attributed to a more reactive residual glassy phase, one that recedes faster in water than does the residual glass in the as-cast sample. The Raman and high-pressure liquid chromatography (HPLC) analyses show that the residual glass in the CCC-treated sample consists of longer P-anions, associated with a lower O/P ratio, and such glasses are generally more reactive. The residual glass in the CCC-treated sample also has a lower Fe/P ratio, due to the precipitation of $Fe(II)_2P_2O_7$ crystals, and greater Cs- and Mo-contents, and these compositional factors also contribute to the faster dissolution rate of the CCC-treated waste form. The precipitation of $Fe(II)_2P_2O_7$, which strongly relates to the increased dissolution rate of the CCC-treated waste form, can be avoided by controlling the waste form melt conditions.

10:40 AM

(ICG-SIV-084-2019) Sulfur Solubility in Low Activity Waste Glass and its Correlation to Melter Tolerance

C. H. Skidmore*[3]; J. Vienna[3]; T. Jin[3]; D. Kim[3]; B. Stanfill[3]; K. M. Fox[1]; A. A. Kruger[2]

1. Savannah River National Lab, USA
2. Office of River Protection, USA
3. Pacific Northwest National Lab, USA

Hanford low activity waste (LAW) glasses with high sulfur concentrations are subject to salt segregation in the melter. Segregated salts hinder melter operation by corroding melter components and shortening the life of the melter. To predict the point at which salt accumulates on the melt surface, the development of sulfate solubility models are needed. Using a sulfur saturation method, crucible scale melts for 13 LAW glasses with varying sulfur solubilities were conducted. The salt and glass compositions were reported and the change in component partitioning after the saturation process was examined to understand changes in glass composition. Both Cr_2O_3 and Cl experience significant losses post saturation, with ~28% of Cr_2O_3 partitioning into the salt phase and Cl primarily volatilizing out of the melt (~23% partitioned to salt and ~40% lost as offgas). Due to the consistency in compositional changes between glasses these patterns can be accounted for during model development. Measured sulfur solubilities were also compared to reported melter tolerance data. Crucible sulfur solubility ranged from 0.947 to 2.137 wt% SO_3. The correlation between the crucible solubility and melter tolerance was high (=0.94), with the data showing a constant offset of -0.328 ± 0.021 wt% SO_3. These results suggest that crucible scale sulfate solubility data can be used to predict SO_3 tolerance in the melter feed.

11:00 AM

(ICG-SIV-085-2019) Compositional dependence of sulfur solubility in alkali aluminoborosilicate glasses

X. Xu*[1]; A. Goel[1]

1. Rutgers University, MSE, USA

Sulfur is an integral component of the Hanford LAW which is destined to be immobilized in borosilicate glass matrix. The presence of sulfur in LAW is problematic for its vitrification because of its low solubility in the borosilicate melts. Due to this reason, once the sulfur concentration in the glass melts increases its solubility limit, it leads to the formation of immiscible sulfate layer on the surface, which is undesirable. Thus, optimizing sulfur loading in borosilicate is of great importance. Our study focuses on understanding the compositional dependency of sulfate solubility in alkali aluminoborosilicate glasses designed over a broad compositional space with distinct structural features. Accordingly, sodium aluminoborosilicate with varying Na/Al and B/Si ratio have been synthesized and investigated for their sulfur (sulfate) solubility. Chemical and structural properties have been investigated by XRD, DSC and ICP-OES, and Raman spectroscopy. An attempt has been made to understand the compositional and structural dependence of sulfur solubility in model nuclear waste glasses.

11:20 AM

(ICG-SIV-086-2019) Impact of Glass Structure on Sulfur Solubility in Borosilicate Glasses

R. Saini*[1]; H. Eckert[2]; A. Goel[1]

1. Rutgers University, Materials Science and Engineering, USA
2. University of São Paulo, São Carlos Institute of Physics, Brazil

The Hanford LAW will be vitrified into borosilicate glasses. Sulfur being an integral component of LAW is a problematic species during vitrification due to its low solubility in borosilicate glass melts. Accordingly, empirical constraints have been proposed by the US DOE to limit sulfur loading in the LAW glasses, thus significantly reducing the total waste loading in the waste form. Therefore, in order to design advanced glass formulations with enhanced waste loadings, it is imperative to understand the underlying compositional and structural drivers controlling the sulfate solubility in borosilicate glasses and melts. In this pursuit, the compositional and structural dependence of sulfate solubility in sodium borosilicate glasses has been investigated over a broad compositional space. A total of three series of glasses in the SiO_2-B_2O_3-Na_2O ternary system with different relative ratios, R = $[Na_2O]/[B_2O_3]$ and K = $[SiO_2]/[B_2O_3]$ have been synthesized by melt quench method. The structure of the sulfur–free baseline glasses has been investigated by Raman and ^{11}B MAS-NMR spectroscopy. Sulfur has been incorporated in the baseline glasses as sulfate using Na_2SO_4 as a precursor, while maintaining a constant Na_2O content (as per baseline glass). The sulfur solubility in glasses has been followed by ICP-OES along with XRD, SEM, DSC-TGA and Raman spectroscopy. The results will be discussed in the presentation.

11:40 AM

(ICG-SIV-087-2019) Effects of V_2O_5 Additions on Anionic Solubilities in Borosilicate Radioactive Waste Glasses

S. Vaishnav*[1]; K. R. Muhammed[1]; P. A. Bingham[1]

1. Sheffield Hallam University, Materials & Engineering Research Institute, United Kingdom

For vitrification of U.S. liquid high-level wastes (HLW) and low-activity wastes (LAW) containing high concentrations of Cl^- and SO_4^{2-} ions, the poor solubility of these anions (< 1wt%) in the borosilicate waste glasses, can limit waste loading and subsequently increase wasteform volumes. This can present logistical and economic consequences. Various studies have been conducted to improve the anionic capacities of radioactive waste glasses, or find alternative host glasses for such wastes. Introduction of V_2O_5 into HLW and LAW glasses is inspired by parallel crystallographic and chemical properties of phosphate and vanadate ions, and prior research indicating the positive effects of V_2O_5 additions on anionic solubilities of borosilicate glasses. To achieve high anionic capacities without compromising the chemical durability of the waste glass, a series of $SO_4^{2-}$and Cl^- doped simple glasses was developed with pro-rata addition of V_2O_5. The final glass compositions and anionic capacities were analysed using XRF and ICP, and structural and thermal effects by Raman spectroscopy and DTA. The glasses were subsequently heat treated and analysed using XRD, which provided useful insight into understanding the bonding around vanadium ions within the glass, and supporting the addition of V_2O_5 as a key enabler to enhance anionic solubilities in HLW glasses.

12:00 PM

(ICG-SIV-088-2019) Influence of vanadium oxide doping on the structure, properties and dissolution behaviors of ISG nuclear waste glasses

X. Lu*[1]; S. Gin[2]; J. V. Ryan[3]; J. Vienna[3]; J. Du[1]

1. University of North Texas, Material Science and Engineering, USA
2. CEA, France
3. Pacific Northwest National Lab, USA

Transition metal oxides are commonly present in nuclear waste and they can alter the structure, physical properties, and dissolution behavior of the glasses used to immobilize these wastes. V_2O_5 has been proven to improve sulfur solubility in borosilicate glasses, which is essential for immobilization of sulfate containing wastes. In this study, we systematically investigated V_2O_5 addition (up to 8.0 mol%) in ISG (International Simple Glass, a model nuclear waste glass system) on the physical properties (e.g., density, glass transition temperature and refractive index) and dissolution behavior. Additionally, mechanical properties as a function of composition and temperature were also investigated. We found that introducing V_2O_5 decreases the glass transition temperature and hardness while increases the refractive index and crack initiation force. V_2O_5 can be a potential candidate of glass components for engineering and insuring a long-term mechanical stability of glass materials. Effect of

V_2O_5 on the initial dissolution rates at pH 10 and pH 2 were studied as well, where the incorporation of V in glass significantly decreases the glass initial durability.

Session 9: Quantum Dots in Glasses

Room: Tremont (4th floor)
Session Chairs: Jong Heo, Pohang University of Science and Technology(POSTECH); Woon Jin Chung, Kongju National University

9:30 AM

(ICG-SIV-089-2019) Inorganic Perovskite Nanocrystals Embedded Glasses and Their Applications (Invited)

C. Liu*[1]; Y. Ye[1]; X. Zhao[1]; J. Han[1]

1. Wuhan University of Technology, State Key Laboratory of Silicate Materials for Architectures (SMART), China

Semiconductor nanocrystals embedded glasses have particular properties arising from the so called quantum confinement effects induced by semiconductor nanocrystals with radius smaller than the exciton Bohr radius. Embedding these semiconductor nanocerystals into glasses can greatly improve their thermal, chemical and phsical stabilities, and thus, promote their wide applications, due to the dense and inert nature of the glasses. However, glass matrix also makes it difficult to manipulate the properties of semicondcutor nanocrystals embedded such as photoluminescence quantum efficiency and spatial distribution, which hiners the practical applications. In this talk, recent progress on inorganic cesium lead halide nanocrystals embedded glasses will be discussed. These perovskite nanocrystals embedded glasses show several striking properties. Photoluminescence efficiency as high as ~80% and external quantum efficiency of green LEDs as high as ~28% are achieved for $CsPbBr_3$ nanocrystals embedded glasses. Using ion-exchange and laser irradiation, controlled spatial precipitation of perovskite nanocrsytals was achieved. These features make perovskite nanocrystals embedded glasses proming for spectral conversion and light emitting devices.

10:00 AM

(ICG-SIV-090-2019) Dual band emission of Cd-S-Se quantum dot embedded glasses as a color converter for white LED with a wide color gamut

K. Han*[2]; J. Heo[1]; W. Chung[2]

1. Pohang Univ. of Sci. and Tech., Dept. of Materials Sci. and Eng., Republic of Korea
2. Kongju National Univ., Div. of Advanced Materials Eng., Republic of Korea

The quantum dots (QDs) have been studied as a next-generation optical material as they can tune their absorption and emission wavelength via their size control with high quantum efficiency even up to 100%. Recently, commercial display using QDs as a color converter has been produced enabling wide color gamut. However, commercially available QDs are chemically synthesized and thus have low chemical, thermal and long-term stability. QDs can be also formed within inorganic glass materials and we have successfully demonstrated a white LED using a Cd-S-Se quantum dot embedded glass (QDEG) which showed a good thermal, long-term stability, and high color conversion efficiency. However, QDEGs showed poor color gamut owing to a single and wide emission bandwidth. In this study, in order to improve the color gamut of white LEDs using QDEGs, we varied fabricating condition of Cd-S-Se QDEGs and examined its color gamut. In order to further improve the color gamut, the green and red QDEGs were synthesized, sliced and then thermally bonded to each other during the heat treatment producing a QDEG with dual-band emission. Optical properties were examined to confirm the QD formation after heat-treatment. After mounting on top of the blue LED, various properties such as color coordination, color rendering index, color conversion efficiency, and color-gamut of QDEGs were examined.

10:20 AM

(ICG-SIV-091-2019) Temperature-dependent photoluminescence and energy transfer of PbS quantum dot-doped glasses

X. Huang[1]; Q. Pan[1]; J. Qiu[2]; G. Dong*[1]

1. South China University of Technology, State Key Laboratory of Luminescent Materials and Devices, and Guangdong Provincial Key Laboratory of Fiber Laser Materials and Applied Techniques, China
2. Zhejiang University, State Key Laboratory of Modern Optical Instrumentation, College of Optical Science and Engineering, China

PbS quantum dot (QD) doped glass has been drawing great attention for its size-tunable photoluminescence (PL), which can be used as tunable gain material at near-infrared (NIR) region. Herein, the PbS QD-doped glass was obtained by the melt-quenching method followed by heat treatment. Temperature-dependent PL spectra and decay time revealed the strong relationship between temperature and bandgap of PbS QDs. And it can be seen that the emission bands of PbS QD-doped glass originated from intrinsic 1S-1S exciton state and trap state. Furthermore, a model was proposed to explain the reason for the increase of the decay time with temperature decreasing. Meanwhile, energy transfer from smaller QDs with higher energy to bigger QDs with lower energy was observed in PbS QD-doped glass. A model established through density functional theory (DFT) revealed the energy transfer mechanism between QDs with different sizes.

10:40 AM

(ICG-SIV-092-2019) External Field-induced Crystallization of Quantum Dots in Glass

X. Huang*[1]; Q. Pan[1]; J. Qiu[2]; G. Dong[1]

1. South China University of Technology, China
2. Zhejiang University, China

Quantum dots (QDs)-based devices exhibit unique performance in optoelectronic and photonic fields owing to their tunable bandgap. Herein, QDs (such as PbS QDs and so on) can be space-selected crystallized in glass by external fields (such as thermal, light and electric field, etc.). Intense tunable emission can be obtained from the field-induced regions, which exhibits high signal-to-noise ratio. Such a glass with space-selected QDs provides a promising material for 3D optical storage and QDs-based photonic devices, etc.

11:00 AM

(ICG-SIV-093-2019) Composition and Morphology of CdSe/$Cd_{1-x}Zn_xSe$ Graded Shell QDs in Silicate Glasses Fabricated by Continuous Wave Laser Irradiation

H. Lee*[1]; W. Park[1]; J. Heo[1]

1. Pohang University of Science and Technology(POSTECH), Material Science & Engineering, Republic of Korea

Cadmium chalocogenide quantum dots (QDs) have been considered promising materials for display, bio-imaging and photo-catalysts because of high quantum efficiencies in the visible range. However, their large surface-to-volume ratios generate dangling bonds and many defect sites on the surface. These defects can result in undesired radiative and non-radiative recombination. Therefore, core/shell structures were introduced to prevent these unwanted process by confining the electrons and holes in the core region. There have been remarkable progresses on fabrication of QDs in a solution process, however, it has been difficult to apply into the glass system due to QDs-host interaction. In this work, we precipitated CdSe/$Cd_{1-x}Zn_xSe$ QDs in silicate glasses using continuous wave laser. Defect emission at λ=620 nm was quenched significantly. $Cd_{1-x}Zn_xSe$ nano-rod structures appeared because of the enhanced diffusion of ions at the areas under illumination. This anisotropic growth of QDs can provide a polarized emission with significant advantages over spherical types. To investigate the compositions and morphologies of CdSe/$Cd_{1-x}Zn_xSe$ graded structures, Raman scattering and transmission electron microscopy were used. In addition, the gradual incorporation of Zn into CdSe QDs was analyzed by atom probe tomography and extended x-ray absorption fine structure.

11:20 AM

(ICG-SIV-094-2019) Tunable luminescent properties of lead selenide quantum dots embedded in glasses

J. Wang*[1]; J. Han[1]; X. Zhou[1]

1. Wuhan University of Technology, State Key Lab of Silicate Materials for Architectures, China

Glasses doped with quantum dots (QDs) have been intensively investigated in the past few years, due to the tunable absorption and photoluminescence in a wide wavelength range induced by the quantum confinement effects. Even though QDs with high photoluminescence efficiency and various structures have been successfully synthesized through chemical methods, incorporation of these QDs into solid matrices with good thermal, mechanical and chemical properties such as glasses can expand their potential applications in optoelectronics. In this work, we formed lead selenide QDs in glasses to achieve tunable absorption and photoluminescence through the controlling of thermal treatment, modification of glass compositions and even incorporation impurities into PbSe QDs. From near- to mid-infrared photoluminescence at 1.0 ~2.6 μm was obtained from PbSe QDs in the silicate, germanosilicate glasses and lithium aluminosilicate glass-ceramics. Sr^{2+}-doped PbSe QDs was also fabricated in silicate glass and excited by the laser with various wavelength and intensity. We found that the Sr^{2+}-doped PbSe QDs have much better photodarkening resistance than that of pure PbSe QDs, indicating the passivation effect on the surface defects by Sr^{2+}-doping.

11:40 AM

(ICG-SIV-095-2019) Nanostructured zirconia in borosilicate glass: Phase formation and photoluminescent property

Y. Nobuta[1]; Y. Takahashi*[1]; N. Terakado[1]; N. Onoue[2]; T. Shinozaki[2]; T. Fujiwara[1]

1. Tohoku University, Department of Applied Physics, Japan
2. Sendai Medical Center, Japan

Crystallization is a promising way to introduce defects into the crystallized nanophase so that it is potential to activate the functionality in the nanocrystallized glass-ceramics: Since defect-activated zirconia (ZrO_2) shows an excellent afterglow property, it is of particular interest to apply the ZrO_2 to the optical/biological imaging probe. In this study, we prepared the ZrO_2-includng borosilicate glass, in which ZrO_2 is singly crystallizable, and examined the crystallization behavior. dendritic ZrO_2 with a few hundred nanometer-scale were nanostructured in the studied glass-ceramics, and the pronounced photoluminescence (PL) was also observed. In addition, the impurity effect of TiO_2 and Al_2O_3 on the nanostructure and PL in the ZrO_2-nanostructured glass-ceramics was considered.

12:00 PM

(ICG-SIV-096-2019) Depth profiling of nickel nanocrystal populations in borosilicate glasses

L. Briese*[1]; S. Selle[2]; C. Patzig[2]; J. Deubener[1]; T. Höche[2]

1. Intstitue for Non-Metallic Materials, Clausthal University of Technology, Department of Glass and Glass Technology, Germany
2. Center for Applied Microstructure Diagnostics CAM, Fraunhofer Institute IMWS, Nanomaterials and Nanoanalytics, Germany

Nickel nanocrystals show promising magnetic and optical properties like superparamagnetism or surface plasmon resonancy. Therefore, they offer a wide range of new applications as magnetic resonance contrast media or data storage media. Borosilicate glasses are well suited matrices for these kind of applications, as they do not significantly influence the magnetic behavior of the crystals, as well as protect the metal from being oxidized. Nickel nanocrystals in a surface layer up to 57 μm depth were precipitated in the parent glasses by a H_2 gas-flow treatment. XRD, TEM and XRM were used to determine depth-dependent crystal populations from which information on the kinetics were derived. The role of the glass composition on hydrogen permeability, nickel diffusivity and effectiveness of the redox reaction on basis of the tarnishing model are discussed.

Session 10: Advances in Photonic Glasses (TC 20)

Room: Beacon Hill (4th floor)
Session Chairs: Shibin Jiang, AdValue Photonics Inc; Giancarlo Righini, Enrico Fermi Center

9:30 AM

(ICG-SIV-097-2019) Fabrication of low loss chalcogenide microstructured optical fibers for Mid-IR QCL pigtailing (Invited)

J. Troles*[3]; M. Meneghetti[3]; C. Caillaud[1]; L. Brilland[1]; S. Venck[1]; J. Adam[3]; M. Duris[2]; D. Deubel[2]; L. Bodiou[3]; J. Charrier[3]; M. Carras[4]; M. Brun[4]

1. SelenOptics, France
2. Kerdry, France
3. Univ Rennes, France
4. Mirsense, France

The mid-infrared molecular fingerprint region has gained great interest in the last decade thanks to development of on-chip semiconductor lasers. For integrated-optic devices and optical sensors based on interferometric techniques, versatile and easy handling devices can be required. In this context, a low-loss single-mode chalcogenide microstructured optical fiber (MOF) which presents an antireflection coating has been elaborated in order to be connected to a Distributed Feedback Quantum Quantum Cascade Laser (DFB-QCL). In addition, another original design of a chalcogenide MOF has been also realized in order to obtained high birefringence properties that can permit to maintain the polarization of the QCL at the output of the fiber. Finally, the fiber properties have been evaluated using a DFB-QCL emitting at 7.4 μm and the polarization maintaining at the output of the chalcogenide fiber has been demonstrated. The combination between a DFB-QCL with such non-conventional fiber has led to the development of single-mode fibered Mid IR lasers.

10:00 AM

(ICG-SIV-098-2019) Mid-infrared supercontinuum generation from 2 to 14 μm in various arsenic- and antimony-free chalcogenide glass fibers (Invited)

F. Smektala*[1]; A. Lemière[1]; A. Maldonado[1]; F. Désévédavy[1]; B. Kibler[1]; J. Jules[1]; P. Mathey[1]; G. Gadret[1]; P. Béjot[1]; F. Billard[1]; O. Faucher[1]

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We demonstrate the fabrication of arsenic- and antimony-free chalcogenide glasses compatible with glass fiber processing and drawing of optical fibers with low residual losses. Optical fibers with different index profiles are presented and characterized. We have drawn single glass material microstructured fibers with a suspended core as well as standard step-index fibers with varying core diameters. We demonstrate the management of group-velocity dispersion properties as a function of the fibers opto-geometric profile. All normal dispersion profiles or profiles with one or two zero dispersion wavelengths can be designed. Supercontinuum generation experiments are then carried out in the femtosecond regime, thanks to a non-collinear optical parametric amplifier (NOPA) followed by a difference frequency generation (DFG) module, which generate 65 fs pulses with wavelengths tunable from 3.5 to 11μm. Our results illustrate the potential of these new fibers for nonlinear optics in the mid-IR. More particularly, a supercontinuum spectrum spanning from 2 to 12 μm is obtained in a 13 μm diameter core microstructured fiber pumped around 5.5 μm in its anomalous dispersion regime. When pumping around 7 μm a 40-mm-long segment of a 10-μm-core step-index fiber made of a glass pair in the Ge-Se-Te glass system a supercontinuum spectrum spanning from 2 to 14 μm is obtained.

10:30 AM

(ICG-SIV-099-2019) Gradient Refractive INdex (GRIN) of Chalcogenide Glasses for Infrared Application

E. Lavanant*[1]; L. Calvez[1]; M. Roze[2]; T. Hingant[2]; R. Proux[2]; Y. Guimond[2]; X. Zhang[1]

1. University of Rennes 1, Institut des Sciences Chimiques de Rennes, France
2. Umicore IR Glass, France

Gradient Refractive INdex (GRIN) lenses are optics whose refractive index varies spatially. One advantage of such lenses is the possibility to manufacture lenses with simple shapes, such as flat lenses where the optical power is given by the continuous change of refractive index. In addition, this type of optics gives more freedom for the optical design. For example, the use of a specific index profile allows to correct efficiently thermal and chromatic aberrations with a significantly reduced number of lenses compared to a conventional system. While these prospects appear to be quite attractive, and despite years of efforts, actually producing GRIN materials for infrared remains highly challenging. The presentation will shed some light on the strategies to obtain gradient refractive index in the chalcogenide glasses, which exhibit an extended transmission in the infrared range up to 16 μm. We introduce a novel process for producing a radial GRIN in glasses by spatially controlled the formation of nanocrystals in the glassy matrix. The different crystal phases and their proportion ratio were determined by X-ray diffraction and SEM images on the glass-ceramic after treatment. The radial gradient of refractive index of the obtained glass-ceramics has been measured by Phasics at 10.6 μm.

10:50 AM

(ICG-SIV-100-2019) Highly scattering fibers used as sensors

W. Blanc*[1]; D. Tosi[2]; C. Molardi[2]; M. Bellec[1]; F. Mady[1]; M. Benabdesselam[1]; M. Ferrari[3]

1. CNRS, INPHYNI, France
2. Nazarbayev University, Department of Electrical and Computer Engineering, Kazakhstan
3. CNR, IFN, Italy

The use of nanoparticles is gaining large interest in modern photonic technology, mainly because nanoparticles can drastically change the properties of optical media. Here, a custom special optical fiber has been considered for investigation. The fiber presents a MgO-based nanoparticles core, and standard telecommunication size. Modified Chemical Vapor Deposition technique, together with the spontaneous phase separation, permit to grow inside the core a random distributed pattern of nanoparticles. The nanoparticle increases the scattering, which is, in general, an unwanted occurrence. Nevertheless, interesting applications can emerge in sensor field. Interestingly, the fabrication method of these sensors is simplified, since it does not require the inscription of reflective elements such as Bragg gratings. In this work we focus on the distributed sensing applications offered by the enhanced backscattering. The fiber has been characterized by the use of an Optical Backscatter Reflectometer. The backscattered intensity, induced by the nanoparticles, is tens of dB larger than the one shown by standard telecom single mode fiber. During this presentation, we will discuss about the ability of such fibers to be used as refractive index sensors and on a setup for multiplexed distributed optical fiber sensors capable of resolving temperature distribution with a spatial resolution of 2.5 mm over multiple fibers interrogated simultaneously.

11:10 AM

(ICG-SIV-101-2019) Doubly-resonant side-emitting borosilicate glass fibers from modified rod-in-tube preforms

J. Schröder*[1]; L. Wondraczek[1]

1. Friedrich-Schiller-University Jena, Germany

Glass optical fibers with well-defined, light-diffusing properties are of significant interest for a multitude of applications, e.g., photodynamic therapy or specialty lighting, where light needs to be provided to difficult locations, or with specific spectral properties. In this work, we will present a new technique that allows simple tailoring of fibers through versatile incorporation of different active species. Sol-gel techniques and a slurry-based approach were employed to functionalize the interface of borosilicate glass rod-in-tube preforms with Ag and Eu^{3+}, respectively. Fibers with strongly localized Ag metallic nanoparticles and Eu^{3+} ions were obtained by fiber drawing from preforms below liquidus temperature. The structural and fluorescent properties of the produced glass fibers were examined using Raman and fluorescence spectroscopy as well as electron microscopy. The borosilicate fibers show distinct features due to surface plasmon resonance (SPR) and Eu^{3+} luminescence.

11:30 AM

(ICG-SIV-102-2019) New sodo-niobate amorphous thin films: Microscale patterning of strong second order optical response by a thermo-electrical imprinting process

L. D. Karam*[1]; F. Adamietz[1]; D. Michau[2]; V. Rodriguez[1]; T. Cardinal[2]; E. Fargin[2]; K. Richardson[3]; M. Dussauze[1]

1. Institut des Sciences Moléculaires, France
2. Institut de Chimie de la Matière Condensée de Bordeaux, France
3. University of Central Florida, USA

The synthesis of new amorphous thin films in the Nb_2O_5-Na_2O system prepared by radio frequency sputtering is reported. A range of composition from pure Nb_2O_5 up to 10 at% of sodium has been studied. XRD suggests the amorphous character of the films, and Raman and EDS spectroscopies have confirmed the successful introduction of sodium in the niobate matrix. The resulting films are of good optical quality with high refractive index (2.2 at λ=1 μm) and a wide transparency domain spanning from the visible to mid-infrared (to λ=5 μm) with no scattering. A thermo-electrical imprinting process has been used to induce second order optical response in the niobate thin films. Very encouraging results show that the nonlinear response has been successfully patterned at the micrometer scale and that post-poled films exhibit high second order susceptibility ($\chi^{(2)}$) estimated in the range of 5 to 10 pm/V. These results demonstrate the promising potential for a new kind of mid-infrared Nonlinear Optical-Photonic Integrated Circuit (NLO-PIC) based on novel high index amorphous materials.

11:50 AM

(ICG-SIV-103-2019) Broadband Transparent Optical Phase Change Materials for Nonvolatile Photonics Applications

Y. Zhang*[1]; J. B. Chou[2]; J. Li[3]; H. Li[4]; Q. Du[1]; A. Yadav[5]; S. Zhou[6]; M. Shalaginov[1]; Z. Fang[1]; C. Roberts[2]; P. Robinson[2]; S. Deckoff-Jones[1]; C. Ríos[1]; H. Lin[7]; M. Kang[5]; T. Gu[1]; J. Warner[6]; V. Liberman[2]; K. Richardson[5]; J. Hu[1]

1. Massachusetts Institute of Technology, Materials Science and Engineering, USA
2. Massachusetts Institute of Technology, Lincoln Laboratory, USA
3. University of Shanghai for Science and Technology, Shanghai Key Laboratory of Modern Optical Systems, College of Optical-Electrical and Computer Engineering, China
4. Sun Yat-sen University, Sino-French Institute for Nuclear Energy and Technology, China
5. University of Central Florida, The College of Optics & Photonics, Department of Materials Science and Engineering, USA
6. University of Oxford, Department of Materials, United Kingdom
7. Zhejiang University, College of Information Science & Electronic Engineering, China

Optical phase change materials (O-PCMs), a unique group of materials featuring drastic optical property contrast upon solid-state phase transition, have found widespread adoption in photonic switches and routers, reconfigurable meta-optics, reflective display, and optical neuromorphic computers. Current phase change materials, such as Ge-Sb-Te (GST), exhibit large contrast of both refractive index (Δn) and optical loss (Δk), simultaneously. The coupling of both optical properties fundamentally limits the function

and performance of many potential applications. We report a new class of O-PCMs, Ge-Sb-Se-Te (GSST) which breaks this traditional coupling. Guided by first-principle computational designs, the compositionally optimized alloy $Ge_2Sb_2Se_4Te_1$ claims an unprecedented material figure of merit over two orders of magnitude larger than that of classical GST alloys, benefiting from blue-shifted interband transitions as well as minimal free carrier absorptions, as confirmed by Hall measurements. In-situ heating TEM and XRD measurements are also carried out to confirm and understand the crystal structures of $Ge_2Sb_2Se_4Te_1$. The optimized alloy, $Ge_2Sb_2Se_4Te_1$, combining broadband low loss (1 – 18.5 μm), large optical contrast ($\Delta n = 2.0$), and significantly improved glass forming ability, enables an entirely new field of infrared and thermal photonic devices.

12:10 PM

(ICG-SIV-104-2019) Large-area all-dielectric metasurfaces via templated fluid instabilities

L. Martin-Monier*[1]; T. Das Gupta[1]; F. Sorin[1]

1. Ecole Polytechnique Federale de Lausanne, Institute of Materials, Switzerland

Dielectric and plasmonic metasurfaces require the integration of materials with accurate control over position, size and shape for high optical efficiency. They are typically fabricated by the well-established lithographic or chemical processes. Hence, it remains difficult to scale to large-area and unconventional substrates. We propose the template dewetting of thin chalcogenide glasses as a novel approach to self-organize a variety of large index contrast all-dielectric metasurfaces. Given the right dewetting time-temperature settings, initial film thickness and underlying pattern, the breakup of the film can occur at prescribed locations resulting in nano-objects of tunable position and sizes. This control paves the way towards simple fabrication route of advanced 2D and quasi-3D photonic devices over large area substrates. Low processing temperatures enable use of rigid but also unconventional flexible and stretchable substrates. This bears a particular importance as lithographic processes today are limited not only by cost, but also in terms of area and substrate rigidity. Fine control over size and position enables strong electromagnetic field confinement, with a variety of application in sensing (biotection of proteins), light management (resonantly-enhanced photodetecting arrays) and second harmonic generation.

12:30 PM

(ICG-SIV-105-2019) Solution processed nanostructured materials for photonics and energy applications (Invited)

A. Martucci*[1]

1. University of Padova, Industrial Engineering, Italy

Solution processing is a rapidly growing area in the field of materials science owing to the potential to reduce production costs of high-quality thin films and bulk materials at relatively low temperatures. Among the different wet chemistry techniques, sol-gel chemistry is probably the most used for the realization of nanostructured materials. Another very promising technique is the preparation of nanoparticles by colloidal chemistry and their use as nanocrystal inks. Hydrophobic coatings obtained by sol-gel chemistry were used for increasing the efficiency of heat transfer in two-phase heat exchanger. Heat transfer coefficient was increased by several times, substituting the classic film wise condensation with the dropwise condensation. Aluminum-doped zinc oxide (AZO) or gallium-doped zinc oxide (GZO) represent inexpensive alternatives to indium tin oxide. AZO and GZO nanocrystals that show transparency in the visible and absorption in the near-infrared have been synthesized by colloidal chemistry obtaining coating with comparable properties of those prepared by physical techniques. Silk Fibroin, the protein extracted from the silk fiber, has been used successfully during the last few years as a platform for optics and high tech application. Here we report on the synthesis of easy tailored refractive index nanocomposite made of silk and titanate nanosheets.

Session 12: Multi-material Fibers I

Room: Cambridge (4th floor)
Session Chairs: Fabien Sorin, EPFL; Sylvain Danto, University of Bordeaux; Alexander Stolyarov, MIT Lincoln Laboratory

9:30 AM

(ICG-SIV-106-2019) From Moore's Law for Fibers to Fabrics as a Service (Invited)

Y. Fink*[1]

1. Massachusetts Institute of Technology, USA

Since the dawn of civilization, fibers and fabrics have comprised some of our most essential crafts and manufactured products, including clothing, tapestries, blankets, bandages, and shelters. The technological function of these fibers and fabrics has advanced very slowly over thousands of years, especially when compared with other fields such as communications and electronics. Recently, a new family of fibers composed of conductors, semiconductors and insulators has emerged. These fibers can achieve similar basic device attributes as their modern wafer-based electronic and optoelectronic counterparts, yet are fabricated using preform-based fiber-processing methods, yielding kilometers of functional fiber devices. Here we will describe both the integration of a multiplicity of functional components into one fiber, and on the multiple-fiber level, the assembly of large-scale two- and three-dimensional geometric constructs made of many fibers. These emerging fiber technologies formed the basis for Advanced Functional Fabrics of America (AFFOA), a broad new collaboration between industry, academia and government. The goal of AFFOA is to enable the transformation of fiber and fabric materials into highly functional devices and systems that will see, hear, sense and communicate, store and convert energy and change color hailing the dawn of fabrics that deliver services.

10:00 AM

(ICG-SIV-107-2019) Thermal drawing of bulk metallic glasses: Fundamentals and applications

I. Richard*[1]; W. Yan[1]; D. Nguyên[1]; T. Das Gupta[1]; Y. Qu[1]; F. Sorin[1]

1. EPFL, Switzerland

Metallic glasses have attracted lots of interest due to their intriguing physical properties and potential applications since their discovery about sixty years ago. In particular, a singular feature of the bulk metallic glasses (BMGs) is their ability of being processed precisely in their supercooled liquid state thanks to their large resistance against crystallization and relatively low viscosity above the glass transition temperature. Therefore, MGs offer promising opportunities for applications in health care, micro-engineering, optics and electronics. However, so far the fabrication of well-ordered MG micro- and nanoparts have involved complex fabrication methods. Here we propose to use thermal drawing to produce uniform MG objects within a polymer fiber. First, we show the feasibility of this process with the co-drawing of a Pt-based BMG within polyetherimide, resulting in fibers containing MG ribbons of a very wide range of thicknesses, down to 40 nm. We then present an in-situ heating transmission electron microscopy study on drawn ribbons to understand the influence of the thermal drawing process on the crystallization behavior and explain the ultimate size limit. In order to illustrate the potential of this new class of material in comparison to more traditional drawable materials, we show a variety of complex MG nanostructures in a polymer matrix and some potential applications.

10:20 AM

(ICG-SIV-108-2019) Towards in-Fiber Diode Device via Thermal Drawing

S. Chen*[1]; F. Tan[1]; J. Kaufman[1]; A. Shiri[1]; H. Ebendorff-Heidepriem[2]; R. M. Gaume[1]; A. Abouraddy[1]

1. University of Central Florida, College of Optics and Photonics, USA
2. The University of Adelaide, Australia

One of the long-standing goals in the field of multimaterial fibers is to incorporate the functionalities associated with electronic devices, which necessitate conductor, semiconductor, and insulator materials, into thermally drawn optical fibers. Such a task faces severe obstacles from the complicated materials system that may undergo capillary break-up and unstable mixing between adjacent crystalline materials. Silicon and germanium are the two most widely used semiconductor materials. Here, we present a thermally drawn borosilicate glass fiber with germanium, conductive glass composite and metal current collector as core. The fiber architecture was designed to parallel that of a planar diode device, with the semiconducting phase at the fiber center and two electrically conductive components above and below running the length of the fiber. Conductive glass or polymer composite acting as viscous barrier has been commonly used in device fibers during the draw, preventing mixing of functional and electron flowing phases and thereby preserving the preform architecture in the final fiber. Glass fiber with only composite and two metal current collectors has also been fabricated to study the electric and dielectric properties of the composite layer with varied dopant, and its role in the functioning of the diode fiber.

10:40 AM

(ICG-SIV-109-2019) Intermediate-T_g Glasses For Multimaterial Fibers

S. Danto*[4]; D. Boiruchon[4]; C. Strutynski[4]; F. Désévédavy[2]; A. Abou Khalil[1]; M. Dussauze[5]; F. Smektala[2]; Y. Petit[4]; L. Canioni[1]; Y. Messaddeq[3]; T. Cardinal[4]

1. CELIA - CNRS University of Bordeaux, France
2. University of Bourgogne, France
3. University of Laval, Canada
4. ICMCB - CNRS University of Bordeaux, France
5. ISM - CNRS University of Bordeaux, France

Here we present recent progresses in the fabrication of multimaterial fibers using glasses with intermediate T_g. First we report on photosensitive silver-containing phosphate glasses (T_g ~350-450°C). Their drawing into ribbon fibers and subsequent femtosecond laser irradiation leads to remarkable local linear (fluorescence and plasmonics) and nonlinear (SHG, THG) optical properties. We establish that the unique material properties and fiber's geometry allows for the direct, accurate Laser writing of complex luminescent Ag clusters patterns and waveguides. We demonstrate also that laser writing and chemical etching enables to design innovative topology and 2D dimensionality at the glass fiber surface, such phenomena combining photo-chemistry, imprinted stress, and selective surface reaction. Alternatively, we explore tellurite-based glass/metal composite fibers (T_g ~250-300°C). The drawing of architectures merging electrical and optical features in an elongated wave-guiding structure enables to develop new in-fiber sensing functionalities based on hybrid electric/optic effects. Beside, glass-metal-polymer fiber structures are exposed. We believe the implementation of intermediate-T_g oxide glasses within multimaterial fibers will give access to a whole new range of materials properties, and hence of functionalities, in linear/nonlinear optics, photonics, electro-optics or sensing.

11:10 AM

(ICG-SIV-110-2019) Advances in semiconductor-core silica fibers (Invited)

U. Gibson*[1]

1. NTNU, Norway

Silica clad fibers with cores from groups IV and III-V on the periodic table have been made using the molten-core method. Laser treatment has been shown to result in the formation of single crystal cores with low optical loss. Here we report the properties of GaSb core fibers, including room temperature photoluminescence. We will also introduce fibers where the core has a mixture of materials with a eutectic-like phase diagram. Laser treatment is shown to be a valuable method for phase segregation in such systems because of the controllable temperature profile and the optical accessibility of the core. In our experiments, we use the silica-based cladding to absorb the CO2 laser radiation, resulting in local melting of the core. Controlled translation allows homogenization of alloys or compositional structuring of the core.

11:40 AM

(ICG-SIV-111-2019) Single-Crystal Semiconductor Core Fibers for Wearable Electronics (Invited)

L. Wei*[1]

1. Nanyang Technological University, Singapore

The demonstration of flexible functional fabrics will enable the realization of wearable full-body sensing system to monitor various physiological signals. This requires the integration of functional materials such as semiconductors, conductors, and insulators into a single fiber with complex architectures and diverse functionalities. However, the common use of thermally stable amorphous semiconductors in such fibers generally results in a high density of electronic defects, which subsequently leads to the poor electrical properties of the fabricated fiber-based devices. In this talk, I will present our recent progress on the laser-induced directional crystallization to enable the precise control on both the crystal structures and the device density of in-fiber semiconductor devices. Specifically, we have achieved meter-long single-crystal semiconductor-core fibers with the unprecedented control over architecture, composition, size, and functionality, while maintaining the flexibility of fibers. Since this fabrication approach relies on a physical heating mechanism as opposed to the conventional chemical methods, it significantly broadens the repertoire of the accessible materials and geometries. The hierarchical nature of these fibers makes them particularly suitable for the fabrication of wearable electronics for full-body sensing.

12:10 PM

(ICG-SIV-112-2019) High performance optoelectronic fibers: From amorphous bulk to monocrystalline nanowires

W. Yan*[1]; Y. Fink[1]; F. Sorin[2]

1. Massachusetts Institute of Technology, USA
2. EPFL, Switzerland

The integration of semiconducting architectures within thermally drawn fibers is bringing novel opportunities for smart sensors, brain-machine interface, energy harvesting and smart textiles. However, the electronic and optoelectronic performances of these fibers are limited due to the amorphous state of in-fiber semiconductors, which restricts their potential applications. Here we show a newly developed solution-based crystallization schemes to induce monocrystalline semiconducting nanowires transformation from their amorphous bulk in an optoelectronic fiber. The anisotropic surface energy of crystal planes in the solvent modulates the phase and orientation of nanowires that grow along the desired axis. The resulting nanowire-based devices exhibit an unprecedented combination of excellent optical and optoelectronic properties in terms of responsivity, sensitivity and response speed that compare favorably with other nanoscale planar devices. Furthermore, we elucidate the excellent optoelectronic properties via investigating photocarrier dynamics by means of ultrafast spectroscopies. We then demonstrate this nanowire-based optoelectronic fiber for a fluorescence imaging application. This work sheds light on the interplay between the materials microstructure and device performance, and can open new opportunities for increasingly sophisticated functionalities in multimaterials fibers.

SVII: Arun K. Varshneya Festschrift

Arun K. Varshneya Festschrift III

Room: Georgian (mezzanine)
Session Chair: Daniel Swiler, Owens Illinois

9:30 AM

(ICG-SVII-019-2019) Varshneya Glass Science Lecture: Mechanics, Chemistry, and Light: The photoelasticity of glass

J. Zwanziger*[1]

1. Dalhousie University, Chemistry, Canada

Application of mechanical stress to glass causes interesting changes in how it transmits light. This interplay is summarized by the elasto-optic tensor, the key metric for technological applications including zero stress-optic glass, and reduced stimulated Brillouin scattering glass. Fundamentally, these effects are controlled by the glass chemistry, and in particular the nature of the chemical bonds that make up the glass. We will summarize our approach to this problem, which is focused on both an empirical and ab initio approach to the structure-property relations governing the elasto-optic tensor. We will describe the control of the stress-optic response through judicious choice of glass chemistry, and also describe our current progress in understanding and developing glass with reduced stimulated Brillouin scattering. We will include discussion of both average properties and energy-dispersive effects. We will show how these effects may be computed ab initio, with a reasonable trade-off between accuracy and speed, and illustrate a bond-based model we are developing that attempts to put in simple terms the empirical relations we have discovered.

10:30 AM

(ICG-SVII-020-2019) From Alfred to Aalborg: Counting Constraints and Strengthening Glasses (Invited)

M. M. Smedskjaer*[1]; J. C. Mauro[2]

1. Aalborg University, Department of Chemistry and Bioscience, Denmark
2. The Pennsylvania State University, Departement of Materials Science and Engineering, USA

Professor Arun Varshneya's research within glass science and technology has covered a variety of physical properties and glass making and processing techniques. This includes his pioneering work on glass mechanical properties, which overlaps with his role as president for Saxon Glass Technologies, a company that produces a chemically-strengthened glass injector device (EpiPen). Building on Prof. Varshneya's ideas and results in the field, this talk intends to highlight some of our own research on glass strengthening through post-processing and/or topological optimization of the glass network. First, we discuss the use of topological constraint theory to understand and predict the hardness and indentation response of glasses. Second, we demonstrate the unique effects of pressure and thermal history on the strengthening of aluminosilicate glasses through ion exchange. Third, we highlight the importance of understanding glass structure and its response to densification for tailoring the mechanical properties. Specifically, we discuss how certain structural motifs, such as trigonal boron units, can lead to effective chemical strengthening, yet optimal intrinsic damage resistance.

10:50 AM

(ICG-SVII-021-2019) Network Dilation Anomaly and Stress Relaxation in Ion-Exchanged Glasses: The Role of the Network Topology (Invited)

M. Bauchy*[1]

1. University of California, Los Angeles, Civil and Environmental Engineering Department, USA

Prof. Arun Varshneya is at the origin of many advances in the understanding of ion exchange for the strengthening of silicate glasses. It is amazing that his pioneering work has remained so relevant to today's cutting-edge engineering applications involving high-performance glass. In this presentation, I will present some new molecular dynamics findings highlighting the critical role played by the network topology on ion exchange strengthening at different stages, namely, (i) network dilation anomaly, (ii) stress relaxation, and (iii) final extent of strength development.

11:10 AM

(ICG-SVII-022-2019) On the relation between microstructure and flexibility of organic-inorganic silica aerogels (Invited)

S. Urata*[1]; A. Kuo[1]; H. Murofushi[2]

1. AGC Inc., Innovative Technology Research Center, Japan
2. AGC Inc., New Product R&D Center, Japan

Silica aerogel has a variety of excellent properties, but the mechanical brittleness inhibits the practical applications. Recently, many experimental efforts have been made to improve the compressibility and bendability of aerogels by hybridization with organic materials, and, very recently, novel hybrid aerogels composed of aliphatic hydrocarbon chains connected by siloxanes, namely doubly cross-linked aerogels (DCLAs), have been proposed as the most flexible and applicable aerogels [e.g. Zu et al., ACS Nano, 2018, 12, 521]. To understand the origin of brittleness of the ordinal silica aerogel and the mechanism of flexibility of the DCLAs, we performed reactive molecular dynamics (RMD) simulations. The theoretical calculations allowed us to model the hybrid aerogels as a result of dehydration reactions among silanol groups. After polymerizations, deformation simulations and a variety of microstructure analyses, such as Q^n silicon distribution, local deformation and ring size distribution have been conducted, and it was unraveled that the stiffness of brittle aerogels is originated from Q^3 and Q^4 silicons.

11:30 AM

(ICG-SVII-023-2019) In-situ Raman mapping of glass under a Vickers indenter (Invited)

S. Yoshida*[1]; T. Kobayashi[1]; A. Yamada[1]; J. Matsuoka[1]

1. The University of Shiga Prefecture, Japan

The Vickers indentation test has been long used to model cracking in glass. Not only from a technological point of view but from a scientific point of view, the indentation-induced cracking in glass is important to understand the nature of brittle fracture in an amorphous solid. Although it is known that the driving force for cracking in glass is attributed to indentation-induced stress in the glass, limited amount of information is now available on indentation-induced structural changes in glass under the indenter and on a relation between the structural changes and the driving force for cracking. In this study, in-situ Raman measurement of silicate glasses was performed to obtain in-situ Raman maps of the glasses during Vickers indentation. As the result, it was found that the Vickers indentation induces transient and permanent structural changes in glass, and that the structural change varies from point to point of the glass under the indenter.

11:50 AM

(ICG-SVII-024-2019) Analyses of contact damage and fracture mechanism due to dynamic contact on glasses (Invited)

A. Koike*[1]

1. AGC Inc., New Product R&D Center, Japan

Chemically strengthened glasses are widely used for glass products requiring high strength such as cover glass for mobile devices. Chemically strengthening can generate compressive stress on glass surface and increase durability of glass products by increasing mechanical strength. However, chemically strengthened glass has tensile stress inside as well as compressive stress on the surface, and deeper depth of layer causes higher central tension. Once median crack created by contact damage with sharp contact penetrates deep into tensile stress area, crack propagates rapidly and glass breaks catastrophically in case of high central tension especially. Therefore,

contact damage resistance against indentation and impact should be very important to design tough cover glass for mobile devices. Indentation deformation takes place due to shear deformation and densification. If the glass properties change by changing fictive temperature as well as glass composition, indentation deformation characteristics also change. In addition, if the glass has compressive stress on the surface, cracking due to contact can be suppressed. In this study, residual stress and densification after both typical quasi-static indentation and dynamic indentation were quantitatively analyzed. And also, the fracture mechanism in drop tests of chemically strengthened glass are discussed.

12:10 PM

(ICG-SVII-025-2019) Mechanical behaviour and the role of rigidity fluctuation and super-structural disorder (Invited)

L. Wondraczek*[1]

1. University of Jena, Germany

Microscopic deformation processes determine defect formation on glass surfaces and, thus, the material's resistance to mechanical failure. While the macroscopic strength of most glasses is not directly dependent on material composition, local deformation and flaw initiation are strongly affected by chemistry and atomic arrangement. Aside from empirical insight, however, the structural origin of the fundamental deformation modes remains largely unknown. Experimental methods which probe parameters on short or intermediate length-scale such as atom-atom or super-structural correlations are typically applied in the absence of alternatives. Recent evidence from spatially-resolved Raman spectroscopy in the THz-gap highlighted the importance of nanometer-scale structural heterogeneity. From such direct observations of deformation-induced variations on the characteristic length-scale of molecular heterogeneity, we revealed that rigidity fluctuation mediates the deformation process of inorganic glasses. Molecular field approximations which are based solely on the observation of short-range (interatomic) interactions fail in the prediction of mechanical behavior. We will now present direct correlations between spatial fluctuations in shear modulus and the observed macroscopic behaviour.

SIII: Glass Technology and Manufacturing

Session 2: Glass Furnace Operation and Design (TC 21)

Room: Clarendon (mezzanine)

Session Chairs: Aaron Huber, Johns Manville; Daniel Swiler, Owens Illinois

1:20 PM

(ICG-SIII-028-2019) Industrial Process and Product Innovation through Modeling and Simulation (Invited)

M. K. Choudhary*[1]

1. MKC Innovations, The Ohio State University, USA

The lecture describes several case studies to illustrate the application of engineering and scientific fundamentals and advanced simulation approaches for process and product innovations in a manufacturing industry. The lecture focuses largely on glass fiber related processes and products but a polymeric foam system is also discussed to illustrate the verstility of the approach outlined in the lecture. On the process side, the lecture discusses aspects of glass melting, forming, and polymeric foam extrusion. On the product side, the lecture describes developments of a fiberglass insulation product for cold temperature applications and a nano-graphite containing extruded polystyrene product with enhanced thermal and mechanical properties. The case studies show that modeling, after being validated by laboratory measurements and plant trials, and in partnership with engineering and manufacturing can be a highly effective instument for process and product design, development and optimization.

1:45 PM

(ICG-SIII-029-2019) A new approach for modeling the radiative heat transfer in a foam layer

M. Nakamura*[1]; K. Aiuchi[1]

1. Nippon Electric Glass Co., Ltd., Japan

In many industrial glass furnaces, foam layer covers the surface of the glass melt, and reduces the heat transfer between the combustion space and the glass melt. A precise approach for calculating the heat flux in the foam layer is to discretize the foam layer in the thickness direction and solve the radiative transfer equation (RTE) numerically. However, this method is time-consuming when the glass melt region should be solved simultaneously in a 3D furnace model. In this study, a new method for calculating the heat flux in the foam layer without solving RTE has been proposed. A simplified expression for the heat flux in the foam layer can be obtained with the Milne-Eddington approximation, and the expression has been converted to a form of the conventional radiative heat transfer between two gray surfaces, which correspond to the glass melt surface and the crown surface. In this approach, the effects of the absorption of glass melt and the scattering by bubbles in the foam layer are considered by introducing an effective emissivity, where the optical path length of the foam layer is calculated by the Rosseland approximation. This method has been applied for various conditions of optical path length, and the results have been compared with numerical results obtained by the discrete ordinates (DO) radiation model to examine the precision of the proposed method.

2:05 PM

(ICG-SIII-030-2019) Thermal Properties within a Reacting Batch Pile (Invited)

W. W. Johnson*[1]

1. Corning Incorporated, Modeling & Scientific Computing, USA

The batch-to-glass conversion is the "main event" within a glass furnace, yet simulation of the batch pile remains the weakest part of furnace models behind melt convection, combustion and Joule-heating sub-modules. Heat-transfer through reacting batch interplays with melting kinetics as one affects the other. Thermal properties vary widely from room-temperature batch through glass melt at furnace temperature. This talk discusses aspects of heat-transfer in reacting batch and the resulting challenges measuring thermal properties.

2:25 PM

(ICG-SIII-031-2019) Fundamental design aspects of electrical melters that determine fining quality and upscaling limits (Invited)

W. Kuhn*[2]; A. Reynolds[1]

1. Fives Stein Ltd., United Kingdom
2. Fives Stein Glass Division, France

Cold top electrical glass melters have some very interesting advantages over combustion tanks in terms of thermal efficiency, compactness and emission reduction. However, the cold top tanks have the reputation of a limitation in glass quality, flexibility and limitation in tank size. To better understand these limitations, one has to review the melting process steps such as batch heating and melting, glass mixing and grain dissolution, high temperature fining and reabsorption of seeds during cooling. Cold top melter designs that do not fully integrate these considerations will suffer under performance limitations. Tanks like the Fives/Penelectro shelf type melter or the Sorg VSM melter that integrate a vertical segmentation are well better suited for a process step control. But even these types of tanks suffer under the typical problem glass flow shortcuts and minimum residence times well below the piston flow times. The understanding of the melt convection and its driving forces in cold top melters presents the key issue for the design optimisation. Non-dimensional numbers can lead to a better understanding of the impact factors on the melt convection patters and intensity. The

fining performance in terms of bubble rise and absorption of seeds can be improved based of melt convection optimisation. Chances and limits of upscaling of cold top vertical melters are discussed.

2:45 PM

(ICG-SIII-032-2019) Glass Melting Furnace Design with lowered CO2 footprint using renewable resources (Invited)

E. H. Muijsenberg*[1]

1. Glass Service, Czechia

The share and use of Electric melting is today steadily growing again. This is not new, as some decennia's ago it already was quite popular. The first furnace that used electric current was built in 1905 following Sauvageon's design was melting glass for window glass production. Since that time many different designs were tried. In more recent decennia's electric melting became less popular due to low price and wide availability of fossil fuels. Just in recent years with the fear of Global Warming and plans for CO2 reduction the interest in full or partial (Hybrid) electric melting is getting more attention again. The generation of electricity by alternative energy sources is of course a great help here as it brings costs of Electricity finally down and will be CO2 free. In Europe the average generation of electricity is already in range of 38% by renewable resources such as wind, solar hydro and bio. The question for the future is not if we will have more electric energy usage for glass melting, but if the future will be All Electric Melting (AEM) or hybrid that means a balance between using more Bio fuels some amount of fossil fuels and large amount of electric melting step by step to reduce our CO2 footprint. The paper will show some examples of the past & present and some ideas for the future stronlgy supported with mathematical modeling of new furnace designs.

3:05 PM

(ICG-SIII-033-2019) Design of an All Electric Cullet Remelter

N. Chalasani*[1]

1. Johns Manville, Furance Design, USA

Using computational fluid dynamics (CFD) as a design tool along with past and current operations data, an all-electric cullet/marble remelter is designed and optimized. The design and optimization include side entry versus bottom entry electrodes, internal electrode cooling versus external electrode cooling (electrode holder), electrode location inside the melter, electrode immersion depth, distance between the electrodes, number of zones, number of electrodes per zone, bubbler location and melter surface area. Application of CFD for evaluating these design parameters is overviewed and results from these CFD simulations are presented.

3:40 PM

(ICG-SIII-034-2019) Review of Glass Melter Design and Technology Used for Vitrification of Nuclear Waste

W. C. Eaton*[1]; J. Vienna[1]

1. Pacific Northwest National Lab, USA

Vitrification of nuclear waste is a unique application of glass melting technology used to immobilize waste by transforming it into a durable glass waste form. While commercial glass manufacturing and waste vitrification have common considerations, the priority and the degree to which these drive both melter design and operation varies considerably. In the commercial glass industry, melting technology is driven by the ability to produce a desired product in an economically viable way. In the nuclear waste arena, the liability of producing or storing waste and environmental concerns drive the need for processing and converting that waste to a more stable solid form. The emphasis of nuclear waste vitrification is on how much waste can be immobilized per unit product at low operational risk. In the US, and in several other countries, the baseline technology is the liquid-fed joule heated ceramic melter, a technology most similar to cold-top electric melting in the glass industry. There are also induction heated waste vitrification technologies in use today. This presentation gives an overview of nuclear waste vitrification technology as a foundation and context for understanding the many advances and specific developments currently being made in this area of glass research and melter design.

4:00 PM

(ICG-SIII-035-2019) CT imaging of static and dynamic samples for waste-glass modeling

S. A. Luksic*[1]; P. Hrma[1]; W. C. Eaton[1]; T. Varga[2]

1. Pacific Northwest National Lab, EED, USA
2. Pacific Northwest National Lab, USA

X-ray computed tomography (CT) offers a unique method for characterizing the morphology of simulated nuclear waste cold caps and glass melt pools during vitrification. Progress has been made at PNNL in adapting an electric glass-melting furnace to a CT instrument, allowing for in-situ, hot stage imaging of the batch-to-glass conversion. Batch reactions and foaming during nuclear waste vitrification are dynamic, which necessitate short collection times for in-situ CT scans. Various reconstruction methods and image collection approaches, combined with automated post-processing, allow quality three-dimensional reconstructions of these dynamic processes recorded using 1-minute scans. The internal foam structure of melts are discernable in-situ in these scans, and the porosity and geometric volume can be measured. These values are highly reproducible and are in good agreement with the measured volume of feed pellets during heating as determined by photographing the cross-sectional profile at selected intervals during conversion.

4:20 PM

(ICG-SIII-036-2019) Deposition and Evaporation of Condensable Vapors in Thermochemical Regenerators: Self- Cleaning Mechanisms in the OPTIMELT™ system

P. Orawannukul*[1]; S. Kobayashi[1]; O. Verheijen[2]; M. V. Kersbergen[2]

1. Praxair Inc, R&D, USA
2. Celsian Glass & Solar BV, Netherlands

Air heating regenerators used for glass melting furnaces are prone for plugging due to formation of salt deposits in the checker channels. Thermal cleaning to melt deposits is difficult and time consuming. Even with periodic cleaning and heat recovery performance deteriorates significantly with time. The mechanism of deposits formation is well understood. Alkali vapors in flue gas such as NaOH and $NaBO_2$ react with SO_2 and O_2 upon cooling and form Na_2SO_4 and other species, which condense and form liquid and solid deposits on heat exchanger surfaces. In a commercial OPTIMELT thermochemical regenerators little deposit accumulation was observed after two and half years of commercial operation. Due to the cyclic change of checker atmosphere in the thermochemical regenerators Na_2SO_4 deposit is vaporized in the reducing atmosphere during the heat recovery cycle (i.e., reforming cycle). In order to elucidate this "self-cleaning" mechanism chemical equilibrium analysis was conducted to identify stable salt species under oxidizing and reducing conditions. The evaporation rate of the Na_2SO_4 under a simulated regenerator condition was measured in the lab-scaled setup and compared with the theoretical deposition rate of the Na_2SO_4. This paper reports the results of the thermodynamic analysis and the laboratory test.

4:40 PM

(ICG-SIII-037-2019) What and Where Is the Problem with the Regenerator and What Should We Do Next?

M. Bennett*[1]; N. Simpson[2]

1. AMETEK Land, United Kingdom
2. Simpson Combustion & Energy Ltd, United Kingdom

We know there is a regenerator problem but not sure where? This is a problem that is becoming more frequent as the life of a furnace becomes longer. This paper will review thermal data from AMETEK Land's NIR-B Glass, a near infrared thermal imaging

camera, obtained at a cross-fired furnace and an end-fired regenerative furnace. By inspecting the thermal profile of the ports on the cross-fired furnace case study, the higher the temperature at the end of the firing cycle indicates where the higher percentages of furnace gases are flowing. Conversely the colder ports indicate where the reduced flow and plugging is occurring. This enables the appropriate regenerators to be cleaned or replaced/repaired. The end-fired case study identifies which side has the greater problem. In both examples the problem identified by AMETEK Land's NIR-B Glass and the resulting solution will be presented.

5:00 PM

(ICG-SIII-038-2019) New concept to characterize the energy demand for glass production

B. A. Fleischmann*[1]

1. Huettentechnische Vereinigung der Deutschen Glasindustrie e.V. (HVG), Glass Technology, Germany

The objective of this presentation is to develop a concept that allows to understand how different figures, that characterize the energy use, are connected and to show that a more technological approach may also help to come to a modified comprehension regarding the theoretic demand for melting. Looking on characteristic numbers that specify the energy demand and energy consumption, respectively, for production or melting of glass there seems to exist a lot of characteristic numbers in parallel that seemingly show the same quality but are very different in quantity. The unit for example may be kWh per tonne of glass and the values are around 650 or 2052 in Germany. Are these two figures really comparable? Or more provocative: how can one reasonably compare the "theoretic" energy demand for melting a tonne of glass with the energy consumption for producing a tonne of salable glass? To solve these questions a new concept was developed to link the theoretic energy demand with a physically defined temperature that is connected to glass composition as well as the use of additional and "new" system boundaries is recommended.

5:20 PM

(ICG-SIII-039-2019) Application of advanced sensors in the glass industry

A. Faber*[1]

1. CelSian Glass & Solar, Netherlands

The availability of advanced sensors, next to thermocouples, in industrial glass melting furnaces is a prerequisite for further automation in the glass manufacturing industry. These advanced sensors should provide real time, quantitative information about the quality of the glass melt, the position and thickness of the batch and foam layers, the key parameters of the combustion process, the energy flows in the furnace and the status/integrity of the furnace lining (refractories and insulation). In this presentation a survey will be given of available measuring techniques, like in-line chemical analysis of raw materials, redox sensors of the glass melt, laser sensors for combustion gases and batch monitoring cameras. Next, the needs for the development of new, reliable sensors will be discussed.

5:40 PM

(ICG-SIII-040-2019) Fuel-fired Floating Glass melting tank stirring and mixing simulation

X. Zhang*[1]

1. ABB Corporate Research, Power device, Sweden

Glass melting is an energy intensive process. Currently, in fuel-fired floating glass furnaces, a typical operation process is with long retention time of 5 to 10 hours, due to very weak flow circulation and mixing in the large continuous melt tank. It is critical to improve glass making process efficiency. In this work, glass melt stirring is investigated through computational fluid dynamics simulation (CFD and electromagnetic simulation. Optimal flow velocity and flow pattern are selected. Based on the simulation results, a new method of glass melt stirring, and mixing is proposed. By using the new method, the glass melting process will become faster, and it will significantly reduce retention time and thus increasing productivity.

Thursday, June 13, 2019

SI: Glass Structure and Chemistry

Session 3: Metallic Glasses

Room: Terrace (lower level)
Session Chair: Jian Luo, Corning Incorporated

8:00 AM

(ICG-SI-075-2019) TBOD as a fundamental metric to assess the structure and bonding in bulk metallic glasses (Invited)

W. Ching*[1]

1. University of Missouri-Kansas City, USA

In this presentation, I advocate the use of total bond order density (TBOD) as a fundamental quantum mechanical metric to assess the atomic scale structure and internal cohesion of bulk metallic glasses. The first step is to construct appropriate large structure models of sufficient size and fully optimize the structure with no constraints. This is followed by detailed calculation of the electronic structure and interatomic bonding between every pairs of the atoms in the model. The TBOD and is obtained by summing up all bond order values of atoms in the model and normalized by its volume. Results from the calculations on two different BMG models are used to illustrate the efficacy of using TBOD and its partial components (PBOD): (1) Vitreloy $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ and (2) Binary Zr_xCu_{1-x} glass ($x = 0.32 - 0.54$). These results indicate the inadequacy of using only the geometric parameters in analyzing the properties of bulk metallic glasses. Extension to other metallic alloys will also be discussed.

8:30 AM

(ICG-SI-076-2019) Nanoglass: A new class of nanostructured glassy materials (Invited)

S. Singh*[1]; H. Gleiter[1]; H. Hahn[1]

1. Karlsruhe Institute of Technology, Institute of Nanotechnology, Germany

Glasses are considered as one of the most important high-performance materials for scientific research as well as for advanced technology applications. This is because of their interesting structural, thermal, optical, electrical and mechanical properties. Recently, the concept of nanoglasses has been developed, i.e. amorphous structures with nanometer-sized inner structures. Nanoglasses will allow to modify the defects and the chemical microstructures of glasses in a way comparable to the methods that have been used for nanocrystalline materials. It is known that a nanocrystalline material with a high density of defects in the form of grain boundaries is obtained by consolidating nanometer-sized crystals. The idea behind nanoglasses is to apply a comparable synthesis approach as in case of nanocrystalline materials, i.e., consolidation of nanometer-sized glassy particles under high pressure to obtain a high density of interfaces between adjacent glassy regions. In analogy to the nanometer-sized microstructures, such glassy materials have been named nanoglasses. It is believed that the proposed concept of nanoglasses will open a new door to novel properties.

9:00 AM

(ICG-SI-077-2019) Molecular modeling of stress corrosion behavior

S. Basu*[1]; M. LaBranche[2]; L. Huang[2]; Y. Shi[2]

1. Rensselaer Polytechnic Institute, Department of Mechanical, Aerospace and Nuclear Engineering, USA
2. Rensselaer Polytechnic Institute, Department of Materials Science and Engineering, USA

Glass is well known to be susceptible to stress corrosion cracking caused by chemicals in the environment, a phenomenon that can cause delayed failure of glasses due to growth of pre-existing surface defects in the presence of humidity. The complex macroscopic effects of stress corrosion, like fracture, occur due to microscopic interactions, which demand a study to replicate the microstructural interactions within a model, which should reproduce the macroscopic behaviors. The purpose of this research is to study the stress corrosion behavior of a model metallic glass system with a view towards representing the underlying atomic level mechanisms using a molecular dynamics approach. The process is implemented by modeling corrosive interaction between a chemical and the metallic glass components. Crack propagation and fracture due to the effect of the chemical is analyzed using our model with a focus towards understanding the corrosion as a stress activated process. Crack growth velocities in presence of the chemical are computed as a function of stress intensity factor and temperature, with a view towards establishing a physically consistent model that can provide a better comprehension of the complex mechanisms of stress corrosion cracking.

9:20 AM

(ICG-SI-078-2019) Microstructure Design for Ductile Glass Composite

Y. Zhang*[1]; M. Alnaggar[2]; B. Deng[1]; L. Huang[1]; Y. Shi[1]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA
2. Rensselaer Polytechnic Institute, Civil and Environmental Engineering, USA

In this work we use molecular dynamics (MD) simulations to investigate glass composites constituted by two brittle model glasses with different stiffness. We show that tuning the stiffness ratio (SR), shape, volume fraction and distribution of the two brittle glass constituents can trigger a brittle to ductile (BTD) transition. Such composite glasses can exhibit high strength, remarkable toughness and some work hardening. The highest failure strain of 80% can be reached in composite glasses as compared to 7% in monolithic model glasses. We also found that mechanical properties of such glass composites will not be deteriorated by introduction of pre-notch. Excellent load redistribution capability introduced by structural heterogeneity is responsible for high ductility in our composite glasses. Through a systematic analysis, we unveil the design principles that lead to the aforementioned BTD transition. We believe the current approach could enhance ductility and broaden the application of glasses as enabling structural materials.

10:00 AM

(ICG-SI-079-2019) Stress- and temperature-driven structural dynamics in a Zr-based metallic glass (Invited)

R. Maass*[1]

1. University of Illinois at Urbana-Champaign, Department of Materials Science and Engineering, USA

Subjecting a metallic glass to increasing temperature leads to thermally activated relaxation dynamics that is well described with monotonously decreasing relaxation times with increasing temperature. Similarly, relaxation times are known to increase as a function of waiting time (aging) at a given temperature. Here we use x-ray photon correlation spectroscopy (XPCS) to reveal how the structural dynamics of a prototypical Zr-based metallic glass changes markedly due to stresses within the elastic regime and due to strain localization via shear banding. In particular, we discuss how stresses within the elastic regime can cause dramatic deviations from the ubiquitous thermally activated and monotonic structural dynamics: as a function of time at constant temperature, strongly time-dependent fluctuations of the relaxation times are seen. We also show how strain localization into shear bands accelerates the thermally activated relaxation dynamics, leading to a distinctly different aging behavior, as characterized by temperature-specific scaling functions. These observations highlight how stress can cause deviations away from the generally observed monotonous structural dynamics in metallic glasses.

10:30 AM

(ICG-SI-080-2019) A Structural Measure of Effective- (Fictive-) Temperature and its Basis in Statistical Mechanics (Invited)

D. Alix-Williams[1]; M. L. Falk*[1]

1. Johns Hopkins University, Materials Science & Engineering, USA

The concept of fictive-temperature has long been utilized to characterize the processing dependence of glass structure, and has recently been shown to be predictive of metallic glass ductility. Some theories have hypothesized that it is actually a real temperature related to the configurational degrees of freedom of the glass, i.e. an "effective-temperature," notably the shear-transformation-zone (STZ) and soft-glassy-rheology (SGR) theories. Here we derive a thermodynamic integration scheme for calculating effective-temperature based on a 2-temperature hypothesis. To test this scheme we simulate a binary Cu-Zr metallic glass modeled with an EAM potential. Measures of the energy fluctuations associated with both the fast and slow degrees of freedom are measured during the glass quench. The resulting effective-temperature is consistent with estimates of fictive-temperature obtained from simulation in more heuristic ways. The results indicate that effective-temperature can be understood as a purely structural quantity. The method provides a means to measure the effective-temperature in the absence of fluctuations induced by shear and without resorting computationally expensive and impractical methods for explicitly measuring the configurational entropy. NSF DMR 1408685/1409560

11:00 AM

(ICG-SI-081-2019) Near Tip Fields and Transonic Propagation of Shear Band in Metallic Glasses

J. Luo*[1]; Y. Shi[2]

1. Corning Incorporated, USA
2. Rensselaer Polytechnic Institute, USA

In micron-scale molecular dynamics simulations with two independent force fields, we studied the propagation of shear band within a macroscopic tensile strain range from 3.5% to 5%. The strain singularity at the head of the shear band is r^{-1}, independent of the macroscopic strain, which agrees with a recent experiment. When the strain is above 4.5%, the shear band can accelerate beyond the shear wave speed but remain smaller than the longitudinal wave speed. Our results suggest that shear band propagation may have connection with the recently developed weakly nonlinear crack propagation theory.

Session 5: Borate Glasses

Room: Statler (mezzanine)
Session Chairs: Efstratios Kamitsos, National Hellenic Research Foundation; Steve Feller, Coe College

1:20 PM

(ICG-SI-082-2019) Borate Glasses and Their Response to Temperature and Pressure (Invited)

R. Youngman*[1]; M. M. Smedskjaer[2]

1. Corning Incorporated, Science & Technology Division, USA
2. Aalborg University, Denmark

Borate glasses continue to be of significant scientific interest, especially in the development of structural models and rationalization of structure/property relationships. These glasses are well known for substantial structural changes in response to different thermal histories, especially in terms of the boron coordination number. In this work, we study the impact of high temperature compression on the structure and properties of a variety of boron-containing glasses, ranging from simple borates to more complex borosilicate and aluminoborate glasses. The application of pressure at temperatures around Tg enables permanent densification of the glasses, and sizes of the resulting glass pieces are amenable to a variety of characterization approaches. Compression leads to changes in bulk density and short-range structure involving cation coordination, but the structural response to densification is also manifested in alteration of the environment and concentration of superstructural units, a key characteristic of borate glasses. The impact of compression on both structure and glass properties will be described.

1:50 PM

(ICG-SI-083-2019) Borate liquids and synchrotron x-ray diffraction: What can we learn? (Invited)

O. L. Alderman*[1]; C. J. Benmore[2]; A. Tamalonis[1]; E. Clark[1]; R. Weber[1]

1. Materials Development Inc., R&D, USA
2. Argonne National Lab, X-ray Science Division, USA

Accurate, precise, and often unique, information on the structure of borate liquids, glasses and ceramics can nowadays be obtained using high-quality x-ray diffraction measurements. These have been made possible through several improvements in synchrotron x-ray source brilliance, especially in the high-energy (~100 keV) regime, image plate detector technologies and sample environments such as the laser-heated aerodynamic levitation furnace. In this talk I will briefly summarize our published results on B_2O_3 and sodium borate melts, followed by comparison to new measurements on liquids bearing other modifiers such as calcium, barium and lithium. The unique opportunities presented by the singular structural chemistry of borates will be discussed, followed by the merits of the methodology, the challenges, and suggestions for future directions.

2:20 PM

(ICG-SI-084-2019) Thermal, Optical and FTIR Studies of NiO. CoO Substituted $Li_2O.Bi_2O_3.B_2O_3$ Glasses

S. Kumar*[1]; A. Yadav[1]

1. Deenbandhu Chhotu Ram university of Science & Technology Murthal, Physics, India

The (NiO.CoO) substituted $Li_2O.Bi_2O_3.B_2O_3$ glasses were synthesized via melt quench technique. Broad Hamp XRD patterns confirm the glassy phase present in prepared glasses. Density, molar volume and oxygen packing density have been analyzed to study glass structures of samples with a decrease in the Lithium-ions. Two glass transition temperatures T_{g1} and T_{g2} were observed. Stability parameter, reduced glass transition temperature (T_{rg}) has been calculated from DSC curves. With an increasing trend in Tg, an extension of a glass-working region is observed, which confirm the role of mixed TMI content (NiO.CoO) and Bi_2O_3 as a glass network modifier. FTIR studies give a significant shifting and change in area under the curves, suggest the formation of Non-Bridging Oxygens. MTE was observed at 7.0 mol% that causes a slight increase in the concentration of BO^{4-}units which is responsible for a decrease in NBOs. The values of an optical band gap and Urbach energy were determined from the UV-Vis-NIR absorption spectroscopy. The observed sharp absorption peaks having transitions $3A_{2g}(F) \rightarrow 3T_{2g}(F)$ & $3A_{2g}(F) \rightarrow 3T_{1g}(F)$ corresponds to Ni^{2+}(d7-configuration) and transition $4T_{1g}(F) \rightarrow 4T_{1g}(P)$ corresponds to Co^{2+}(d8-configuration) make these glasses suitable for spectral devices. Racah parameter (B), crystal field splitting energy, Nephelauxetic ratio (β) was calculated using the TS-diagrams.

2:40 PM

(ICG-SI-085-2019) Thermoluminescence and structural analysis on calcium and lithium borate glasses doped with Dy^{3+}

S. R. de Souza*[2]; E. S. Bannwart[2]; S. W. Martin[1]; J. E. De Souza[2]

1. ISU, MSE, USA
2. UFGD, Physics, Brazil

Presently, calcium and lithium borate glasses, particularly in the composition of tetraborates, CaB_4O_7 and $Li_2B_4O_7$, are being extensively studied due to their interesting thermoluminescence (TL) response with possible environmental and/or medical applications as radiation dosimeters. Calcium borate glasses present low melting temperature, high thermal and chemical stability and high transparency in the UV region. Moreover, lithium oxide addition to the $CaO\text{-}B_2O_3$ binary system enhances its chemical and thermal properties. In the present work, the influences of $Dy^{3+}$and the substitution of calcium oxide by lithium oxide on optical and structural characteristics of the glasses were evaluated by NMR and IR spectroscopies, UV-Vis absorption, density and thermoluminescence measurements. Different glass compositions in the undoped system were obtained with the effective atomic number (Z_{eff}) changing from that of human tissue (Z_{eff} = 7.42) up to that of human bone (Z_{eff} = 13.17). Nevertheless, thermoluminescence may be greatly affected by Li^+ in concentrations below 10 mol%, while Dy^{3+} can form substitutional complex defect with borates promoting significant changes in the TL emission.

3:00 PM

(ICG-SI-086-2019) X-ray absorption near edge structure (XANES) spectroscopy measurement on multivalence nanoceria in borate glass

K. S. Ranasinghe*[1]; D. E. Day[2]; R. SIngh[1]

1. Kennesaw State University, Physics, USA
2. Missouri University of Science & Technology, Ceramic Engineering, USA

A borate glass containing varying amounts of cerium (IV) oxide was successfully prepared with both trivalent Ce3+ (Ce2O3) and tetravalent Ce4+ (CeO2) state nanoparticles. X-ray absorption near edge structure (XANES) spectroscopy measurement was used to determine the coexistence of the multivalence state in the borate glass. Significant changes in the Ce+3 and Ce+4 amounts were observed when the glass was melted with different melting parameters as well as different raw materials. TEM micrographs confirm the coexistence of Ce2O3 and tetravalent CeO2 nano particles in the glassy matrix with a size range of 2-5nm. FT-IR analysis shows the effect of cerium oxide on bonds formed within the glass network. The effect of the addition of CeO_2 in glass melt, on Borate (BO_3^{-3}) and (BO_4) oxidation was specifically observed. Increasing the concentration of the cerium oxide drove the formation of borate oxygen bonds B-O-B and possibly Ce-O-B bonds.

3:40 PM

(ICG-SI-087-2019) New Developments in the Chemistry of Borates under Extreme Conditions (Invited)

H. Huppertz*[1]

1. University of Innsbruck, Austria

Borates are of great industrial and academic interest due to their excellent physical and chemical properties. The wide variety of applications is based on the great structural diversity of borates, as the physical and chemical properties are closely related to the crystal structure. In the past, we successfully established the finding of edge-sharing BO_4tetrahedra as a new structural motive in the chemistry of borates. Recently, we presented the first thoroughly characterized molybdenum borate $Mo_2B_4O_9$, which is, to our knowledge, the first compound incorporating transition-metal clusters into an anionic borate crystal structure. Interestingly, $Mo_2B_4O_9$connects borate and metal cluster chemistry, two hitherto separated fields of research. The fact that no transition-metal-cluster-containing borates have been reported before emphasizes once again the importance of unconventional syntheses methods.

4:10 PM

(ICG-SI-088-2019) Assessment of Mirragen Advanced Wound Matrix in a Randomised, Controlled, Multicenter Trial (Invited)

S. Jung*[1]; C. M. Zelen[2]; D. Armstrong[3]

1. Mo-Sci Corporation, USA
2. Professional Education and Research Institute, USA
3. University of Southern California, Surgery, USA

Bioactive glass is an emerging technology in treating soft tissue injuries. The first bioactive glass based medical product for use in wound healing applications, Mirragen® Advanced Wound Matrix, was cleared by USFDA in 2016. After proving safety and efficacy, the goal has shifted to determining the mode of action for the bioactive glass in the wound bed. A randomized clinical trial (RCT) comparing the standard of care to the Mirragen® dressing in a diabetic foot ulcer model was completed and is reported presently. The evaluation for the RCT include percentage of wounds healed at 6 and 12 weeks, percent area reduction at 6 and 12 weeks, percent granulation tissue at 6, 12, and 16 weeks, quality of life assessments, histology of sectioned tissue before and during treatment, and a gene expression analysis of the sectioned tissue to determine changes in the local biology. Additionally, Mirragen® has been tested against several strains of bacteria and fungus both planktonic (floating) and in an established biofilm to assess the anti infective properties against these organisms. The outcomes of these studies have contributed significantly to understanding the mode of action for the Mirragen® dressing in a soft tissue injury.

4:40 PM

(ICG-SI-089-2019) Analysis of the reasons for deviation in determination of alumina in pharmaceutical glass by EDTA volumetric method

D. Yang*[1]

1. Beijing Glass Group Company, China

Alumina is a very important component in Pharmaceutical glass. The introduction of a small amount of alumina plays a key role in improving the strength, chemical stability, thermal stability and decreasing the tendency of glass crystallization of pharmaceutical glass. But in the actual alumina composition determination, it is often prone to the deviation of the result of measurement, which is misleading to the actual production control. From the practical point of view, the paper has been analyzed and explained in detail about the reasons for the deviation of the alumina EDTA capacity determination in pharmaceutical glass and its standard determination technique.

5:00 PM

(ICG-SI-090-2019) EPR and optical studies of Calcium Oxychloro Bismuth Borate Glasses doped with V_2O_5

A. Agarwal*[1]; M. Malik[2]

1. Guru Jambheshwar University of Science and Technology, Physics, India
2. DCRUST, Physics, India

The present paper deals with the compositional dependence of optical absorption and Spin Hamiltonian parameters in calcium oxychloride bismuth borate glasses prepared by melt-quench method. X-ray diffraction studies confirm amorphous nature of doped glasses. The variation in molar volume and density with increasing $CaCl_2$ concentration indicates strong structural changes that are taking place inside the glass matrix. The optical absorption data (200-800 nm) is analysed by means of Davis-Mott model to evaluate optical band gaps corresponding to indirect allowed transition (r=2) and indirect forbidden transition (r=3). The optical band gap is lying in the range 2.41–2.60 eV and 2.18–2.35 eV for r=2 and r=3 respectively. Spin Hamiltonian parameters, dipolar hyperfine coupling parameters, covalency rates are calculated from the EPR spectra of vanadyl ions. EPR spectra confirms the octahedral coordination of V^{4+} ion (exists as VO^{2+}). The hyperfine coupling parameter (P) and fermi contact interaction term (K) were calculated by using Kivelson and Lee formulations and obtained values indicated that the term -PK contributes to hyperfine coupling which arises due to interaction of polarized 's' electron with unpaired 'd' electron of vanadyl ion.

5:20 PM

(ICG-SI-091-2019) Composition-Structure-Property Correlations in Rare Earth Doped Heavy Metal Oxyfluoride Glasses

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Rare earth doped oxyfluoride glasses are of great interest for optical applications due to their high emission efficiency and extensive IR and UV transmission windows. A prominent example of RE-doped oxyfluoride glasses is the composition GeO_2-PbO-10PbF_2, which is already used for optical amplifier applications. Replacement of the expensive GeO_2 component by B_2O_3 has been shown to produce glasses with a similar application spectrum while being economically priced. In this work, we report the preparation and characterization of RE-doped (Eu^{3+}, Yb^{3+}) oxyfluoride glasses with the composition (40-x) B_2O_3-xGeO_2-10Al_2O_3-40PbO-10PbF_2 (x=0 to 40), where the addition of Al_2O_3 serves to improve the optical properties. Modern Solid-State NMR and pulsed and cw EPR techniques are used to develop a structural rationale for the design of materials with optimized optical properties. While the NMR spectra of the ^{11}B, ^{19}F, ^{27}Al, and ^{207}Pb nuclear probes give information about the structure of the glassy matrix, EPR studies of the paramagnetic Yb^{3+} dopants give insight into the local environments of the luminescent rare-earth ions. Based on further XRD and DSC measurements as well as UV/vis absorption and luminescence spectroscopies we develop a consistent picture of the structure-property relation in this class of materials. This work was supported by FAPESP, grant number 2013/07793-6 and 2017/06649-0.

5:40 PM

(ICG-SI-092-2019) Ferrite Additive Influence on the Structural, Thermal and Electrical Properties of Lithium Bismuth Borate Glasses Co-Doped Copper Ferrites

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The glass system Li_2O-Bi_2O_3-B_2O_3+$CuFe_2O_4$ were synthesized by melt quench technique. The prepared glasses were characterized using their physical, thermal, optical, electrical properties and structural studies. Two glass transition temperatures T_{g1} and T_{g2} were observed

and glass stability (S) was calculated from DSC curves. The compositional variations in values of all physical (D and V_m) and thermal parameters confirm the role of Bi_2O_3 as a glass network modifier and an increase in its concentration in glass was causing a closely packed arrangement of atoms. The results obtained from IR studies confirm that Bi_2O_3 play dual role as network modifying oxide as well as network forming oxide. Also, the significant shifting in IR bands with increase in Bi_2O_3 content in the glass matrix suggests the formation of new boron–oxygen ring. The presence of sharp cut-off and large transmission in UV–VIS–NIR regime make these glasses suitable for spectral devices. The cut-off wavelength, optical band gap and Urbach's energy were determined from the absorption spectra and were related with the structural changes occurring in these glasses with increase in Bi_2O_3:B_2O_3 ratio. The dc conductivity decreases with increase in Bi_2O_3 content because of blocking effect of the Bi ions on the migration of mobile ions (Li-ions and $CuFe_2O_4$) in glass network.

Session 6: Phosphate Glasses - General

Room: Berkley (mezzanine)

Session Chair: Ladislav Koudelka, University of Pardubice

1:20 PM

(ICG-SI-093-2019) The structure and optical properties of Nd:phosphate glasses (Invited)

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Nd:phosphate glass is widely used as the gain medium for high power laser facility. In this work, the relationship between structure and optical properties of Al_2O_3-$K_2O(Li_2O)$-P_2O_5-Nd_2O_3 glasses with different P/Al ratio has been studied. Glass was prepared by traditional melting and quenching method. Thermal anneal was done at different temperatures around glass transition temperature range. The coordination environment of Nd^{3+} ion in phosphate glass was detected by pulsed EPR and NMR techniques. It is found that the second order of coordination sphere of Nd^{3+} ion was greatly affected by P/Al ratio and thermal history. The relationship between coordination environment of Nd^{3+} ion and optical properties as well as spectroscopic properties of Nd:phosphate glass is discussed.

1:50 PM

(ICG-SI-094-2019) Synthesis of dehydroxylated Nd-doped phosphate and oxynitride phosphate glasses

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The production of Nd-doped phosphate laser glasses requires high chemical and optical homogeneity and absorption coefficients of hydroxyl ions lower than 5 cm^{-1} to avoid quenching of the Nd^{3+} luminescence. Current dehydroxylation methods consist in melting the glasses using a carrier gas, such as O_2, bubbling throughout. In a first study on the synthesis of Nd-doped oxynitride phosphate glasses, we demonstrated that an additional remelting step under reducing N_2 flow using a graphite crucible helped obtaining the glasses with higher Nd^{3+} luminescence lifetime with respect to the original nitrided glasses. Then, the same methodology has been evaluated in the oxide phosphate glasses with composition $15Na_2O$-$15K_2O$-20BaO-$50P_2O_5$ (mol %), that showed to give rise to glasses with high optical homogeneity, very low OH absorption coefficients and an important increase in the luminescence lifetime.

2:10 PM

(ICG-SI-095-2019) Correlation between structural and thermal properties in LiPON and NaPON glasses

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Nitridation of lithium and sodium phosphate glasses, $LiPO_3$ and $NaPO_3$, has been widely studied because of the changes on its properties like glass transition temperature, density and electrical conductivity. In a systematic study for preparing LiPON and NaPON glasses it was possible to achieve samples with high contents of nitrogen (x = N/P rates up to 0.66). $LiPO_3$ and $NaPO_3$ glasses were obtained by the conventional melt/molding method at 800°C using Pt/Au crucible. The nitridation process was carried out by remelting the $LiPO_3$/$NaPO_3$ glasses under NH_3 flow. We find the nitrogen uptake is strongly dependent on temperature and mass of the initial of both $LiPO_3$/$NaPO_3$ charge, as well as if the $LiPO_3$ is a powder or bulk piece. It was possible to determine the nitrogen uptake via weight loss of the sample before and after the ammonolysis and corroborate these estimated values with CNHS measurements. Increases in transition temperature with increasing nitrogen were determined with DSC measurements and are comparable to literature values. We also demonstrate that peak intensities in Raman spectroscopy are very well correlated with nitrogen uptake. With all of these correlations, we are able to produce samples with specific amounts of nitrogen content and calculate the nitrogen content with various simple tests.

2:30 PM

(ICG-SI-096-2019) Investigation of titanium phosphate-tellurite glass for Faraday rotators

L. Boroica*[1]; B. Sava[1]; M. Elisa[3]; S. Iordache[2]; I. Vasiliu[2]; R. Stefan[2]; A. Galca[4]; V. Kuncser[4]; A. Trefilov[1]; R. Pascu[1]; I. Danciu[5]

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5. Automatic Data Processing, Romania

This work is focused on investigation of optical, thermal, magnetic and magneto-optical properties of novel Te-based phosphate glass applied as Faraday rotators. The glass $35Li_2O$ $10Al_2O_3$-$5TiO_2$-$45P_2O_5$-$5TeO_2$ was prepared by a non-conventional wet route of raw materials processing, followed by melting-quenching-annealing. The absorption and the extinction coefficient exhibit a similar descendent trend with wavelength showing in evidence a high optical transmission over 600 nm that recommend this glass as magnetic sensing material. A luminescence band is observed in the blue domain by excitation in UV-range, due to Te_2 clusters formed during the glass melting process which favors the reduction of TeO_2 to Te atoms followed by recombination of these species into diatomic molecules. FTIR absorption reveals specific bands for Te-O-Te bonds as well as for phosphate network. The low T_g of this glass as well as the relative high thermal expansion coefficient disclose a less rigid mixed network composed of P-O-P, Te-O-Te and Te-O-P bonds The magnetization in dependency on applied magnetic field reveals a diamagnetic behavior of the glass. The decreasing of the Faraday rotation angle and Verdet constant with wavelength, in the visible domain, is observed for the investigated glass. In the case of this low TeO_2 content glass, a Verdet constant of about 0.013 min/Oe cm at 650 nm was found.

2:50 PM

(ICG-SI-097-2019) Photoelasticity in phosphate glasses (Invited)

A. Saitoh*[1]; H. Takebe[1]

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We have studied properties and structure in ternary phosphate glasses with small photoelastic constant (PEC). Possible applications are liquid crystal displays and fiber current sensors which require rigorous control of the propagation angle of linearly polarized light for maintaining the color rendering property or sensing property based on the Faraday effect. For display applications, evaluations of wavelength dependence are significant because a difference of PEC causes image distortion. However, the photoelastic effect caused by stress-induced birefringence leads to undesired rotation of the polarized light in glass, reducing the optical performance of the device. The compositional trends in above properties are considered by the short range structures regarding Sn- Ba-, and Zn-polyhedra and anionic phosphate units. In ZnO/SnO containing system, properties fall into some compositional ranges. The diffraction experiments revealed that Zn^{2+} prefers tetrahedral coordination. On the other hand, Sn^{2+} was incorporated in isolated, three-coordinated sites that converted to four-coordinated sites with greater ZnO contents. In the BaO containing systems, some properties monotonically changed. The ^{31}P MAS-NMR presents distributions of phosphate units with increasing BaO oxides.

Session 6: Phosphate Glasses - NMR and Structure

Room: Berkley (mezzanine)

Session Chair: Doris Möncke, Alfred University

3:40 PM

(ICG-SI-098-2019) Network former mixing (NFM) effects in phosphate glasses: Structure/property correlations studied by modern solid-state NMR techniques (Invited)

H. Eckert*[1]

1. University of Muenster, Germany

The use of multiple network formers is an important part of the design strategy of phosphate glasses for applications as photonic, ion transport or bioactive devices. In many glass systems the interaction between the different network formers results in strongly non-linear variations in physical properties (network former mixing (NFM) effects) upon linear changes of the composition, which require a detailed understanding on a structural basis. The issues to be addressed involve both the structural organization and connectivities within the framework, the local environments and spatial distributions of the mobile ions, and possible phase separation or nano-segregation effects. Besides Raman and X-ray photoelectron spectroscopies, solid state nuclear magnetic resonance (NMR) methods are particularly useful for providing detailed answers to such issues. As illustrated by recent results on boro-, fluoro- and silicophosphate glasses some emerging general principles governing structure/property correlations can be identified.

4:10 PM

(ICG-SI-099-2019) Preliminary results of Solid-state NMR analysis of phosphate glasses deposited as thin films

L. Montagne*[1]; F. Mear[1]; O. Lafon[1]; F. Pourpoint[1]; H. Nagashima[1]

1. University of Lille, France

Phosphate glasses are investigated as materials for electrolytes in all solid-state batteries, in which they are designed as thin film of thickness not larger than a few tenth of nanometers. The structure of such glassy thin films is an important parameter to control, since it may affect significantly the performance of the materials. We will present in this communication a structural analysis of phosphate glasses deposited as thin layers on silicon substrates. The compositions were chosen from sodium borophosphate to lead phosphate compositions. Another original point of the work is the development of solid-state NMR methods suitable for the analysis of the thin films. The sensitivity was first improved by the incorporation of paramagnetic ions (Cu^{2+}, Mn^{2+}, Gd^{3+}) which allows reducing the relaxation delay. We also explored the use of Dynamic Nuclear Polarization (DNP) to enhance the NMR signal of the thin film. Our results show that some difference in the local structure of the film is observed in comparison with the bulk films, which depend on the polymerization degree of the bulk phosphate glass network.

4:30 PM

(ICG-SI-100-2019) Using solid state NMR and Raman Spectroscopies to solve short and long-range order in fluorophosphate glasses

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1. Institute of Chemistry- São Paulo State University (UNESP), Inorganic Chemistry, Brazil
2. Physics Institute Universidade de Sao Paulo, Brazil

Fluorophosphate glasses have been studied for using in many optical applications. The addition of BiF_3 in these glasses can provide additional applications as super-broadband near-infrared emission for optical amplifiers and photocatalysis processes. In this work, we used solid state NMR and Raman spectroscopies to characterize the effect of the BiF_3 incorporation and also F/P ratio in the glass system $NaPO_3$-$Ba(PO_3)_2$-NaF-BaF_2. Thermal properties have also been evaluated and the Tg values ranges from 280 to 230°C, suggesting a significant decrease in the glass network connectivity with increasing BiF_3 content. Raman and ^{31}P NMR indicate a progressive depolymerization of the metaphosphate (Q^2 units) backbone with breakage bridges associated with Q^1 and Q^0 units and the formation of P-F in pyrophosphate units, which can be differentiated via homonuclear 2-D J-resolved spectra. The ^{23}Na-^{31}P and ^{31}P-^{23}Na REDOR experiments suggest a linear decrease of the ^{23}Na-^{31}P dipolar coupling due to successive dilution of sodium and phosphate concentrations with increasing BiF_3 content. ^{31}P-^{23}Na dipolar interaction suggest that the sodium atoms are bridged to the oxygen atoms of the pyrophosphate units and this units are in a random distribution in the network matrix. Finally, the ^{19}F NMR data suggests the formation of $P_2(O,F)_7$ dimers in the glass system.

4:50 PM

(ICG-SI-101-2019) Structural Studies of Bi_2O_3-$NaPO_3$ Glasses by Solid State Nuclear Magnetic Resonance and X-ray Photoelectron Spectroscopy

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2. Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Key Laboratory of Materials for High Power Laser, China

Glasses in the system xBi_2O_3–(100-x)$NaPO_3$ were prepared using transitional melting–quenching and characterized using solid state nuclear magnetic resonance (SSNMR), x-ray photoelectron spectroscopy (XPS), and Fourier-transform infrared spectroscopy (FT-IR). Alloying Bi_2O_3 into $NaPO_3$ results in the depolymerization of phosphorus chain of $NaPO_3$ and the evolution of phosphorus species in the process of $Q^{(2)}_{0Bi} \rightarrow Q^{(1)}_{1Bi} \rightarrow Q^{(0)}_{2Bi}$. The SSNMR and XPS results have consistently proved that both the Bi^{3+} and Na^+ ions are bounded by phosphorus tetrahedrons. No linkage was formed between them. The addition of Bi_2O_3 has not changed the average distribution of Na^+ ions around the phosphorus tetrahedron. Different with Ga^{3+} ions which connect with phosphorus tetrahedrons by corner-sharing, Bi^{3+} ions share edges with the phosphorus tetrahedrons, as confirmed based on the deconvolution of the ^{31}P spectra and charge balance calculations. To the best of our knowledge, we first used such simple method to distinguish edge-sharing and corner-sharing structure in phosphate glasses. Such method will promote a deeper insight of glass structures.

5:10 PM

(ICG-SI-102-2019) Structure-Properties Relations in Rare-Earth doped Indium Fluoride Phosphate Glasses Studied by Solid-State NMR, EPR and Optical Spectroscopy Strategy

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Rare-earth doped transparent glasses are established materials for the design of new-generation lasers and photonic devices. Fluoride-phosphate glasses belong to the most promising host matrix systems in this context. The goal is to design a framework structure dominated by bridging oxygen links, resulting in high mechanical stability, while, creating a fluoride-dominated low-phonon energy local environment for the luminescent ions, which favors high fluorescence quantum efficiencies. In this work, a detailed structural investigation of fluoride-phosphate glasses with nominal composition $20BaF_2$-$20SrF_2$-$20ZnF_2$-$10ScF_3$(30-w)$In(PO_3)_3$-wInF_3-zREF_3 (w = 30, 25, 20, 15), doped with 0.2 mole% Yb^{3+} or Eu^{3+}, has been conducted. As indicated by solid state NMR, the network structure is dominated by indium-oxygen-phosphorus linkages. The ligand environment of the rare-earth ions was studied by (1) ^{45}Sc NMR, (2) echo-detected field sweep EPR spectra at the X-band, using Yb^{3+} spin probes, and (3) excitation and emission spectroscopy of Eu^{3+} dopants. They are found in a mixed environment of fluoride and phosphate ions. As a result, it was possible to deduce the associated quantitative ligand distribution (fluoride versus phosphate) in the first coordination sphere of the rare earth ions by the correlated results.

5:30 PM

(ICG-SI-103-2019) Fragility and Rheological Behavior of Metaphosphate Liquids: Insights into their Chain vs. Network Characters

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The viscosity and the shear relaxation behavior of supercooled Ag- and Sn- metaphosphate liquids are measured using parallel plate techniques. The fragility index m of these liquids, when taken together with that of other metaphosphate liquids, shows variation over a rather large range spanning from ~ 30 to 90 and is found to be a sensitive function of the strength and extent of connectivity or coupling between the phosphate chains provided by the modifier-oxygen coordination polyhedra. The high fragility of the Ag-metaphosphate liquid ($m \approx 90$) is a result of the weak inter-chain coupling which is manifested in a polymer-like rheological behavior that is in contrast with the network-liquid like behavior of the metaphosphate liquids with lower fragility.

5:50 PM

(ICG-SI-104-2019) Cation Mixture in Alkali/Alkaline-Earth Phosphate Glasses

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1. Universidade de Sao Paulo, Instituto de Física de São Carlos, Brazil

Incorporation of Sr to Ca-phosphate opened possibilities for clinical applications. Cation release in physiological conditions is influenced by interactions with network groups. Two series of Sr phosphates glasses were studied to determine cationic mixture and bonding: (I) w Na_2O (0.57-w-x)SrO x CaO 0.43 P_2O_5 ($0 \le w \le 0.40$, $0 \le x \le 0.40$), and (II) (0.50-x-y) Li_2O y Cs_2O x SrO 0.50 P_2O_5 ($0 \le x \le 0.40$, $0 \le y \le 0.50$-x). ^{31}P,^{23}Na, ^{7}Li and ^{133}Cs NMR was applied to analyze local structure around phosphates and cation. In (I), transitions in the evolution of properties (molar volume, Tg, Q^1 ^{31}P-NMR) were detected as a function of the alkaline earth content, which can be interpreted in terms of preferential bonding of Sr/Ca to O in $(PO_{3.5})^{2-}$ anions (Q^1), instead of $(PO_3)^-$ (Q^2). This non-statistical bonding to O is possible up to a maximum concentration of the alkaline-earth, calculated as x=0.28, in good agreement with the observed break in properties at x=0.30. A similar behavior seems plausible for Ca^{2+}, but changes in medium range order and progressive structural distortions induced by the stronger ion cause smooth variations of the molar volume. In (II), Sr was introduced to perturb the Li-Cs mixed alkali effect. The ^{7}Li-^{133}Cs dipolar couplings show that both alkalis are randomly dispersed, irrespective of the concentration of Sr. NMR parameters are scaled by the alkali atom concentration, irrespective of the dilution element (Sr,Li,Cs).

Session 7: Silicate Glass Structure II

Room: Berkley (mezzanine)
Session Chairs: Daniel Neuville, IPGP-CNRS-USPC; Randall Youngman, Corning Incorporated

8:00 AM

(ICG-SI-105-2019) Dangling and stretching motions of network-modifier cations in silicate and borosilicate glasses (Invited)

B. Hehlen*[1]; D. R. Neuville[2]; D. Kilymis[3]; S. Ispas[1]

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2. Institut de physique du globe de Paris, France
3. CIRIMAT, University of Toulouse, France

We have shown in a previous study that the Raman spectra of aluminosilicate glasses were sensitive to vibrations of network-modifiers cations. On the contrary, the contribution steaming from charge compensator cations is very weak providing thereby an experimental contrast to differentiate these two structural cation environments. Complementary experiments have been performed in borosilicate glasses and lead to the same conclusions. Sodosilicate and borosilicate glass models have also been obtained using ab-initio numerical simulations and the atomic vibrations have been calculated. The simulations show that two vibrational contributions of network-modifier cations are expected at frequency between ~150cm^{-1} and 380cm^{-1}, in very close agreement with the experimental observations. A vibrational analysis performed in a series of sodosilicate glasses reveals that these modes originate from dangling and stretching motion of the cation relative to its nearest non-bridging oxygen. The same type of analysis is in progress for borosilicate systems.

8:30 AM

(ICG-SI-106-2019) The Nature of Al^V in Aluminosilicate Glasses

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2. Corning Incorporated, USA

Silicon nearly always adopts a tetrahedral configuration in silicate glasses, and simple models suggest that aluminum in aluminosilicate glasses will adopt a tetrahedral configuration as long as charge balancing cations are present (e.g. peralkaline and tectosilicate compositions). However, in many compositions, experiments have shown that Al^V exists in quantities much greater than those predicted by simple models. However, the geometry of Al^V and the nature of the bonding has not been well explored. In this study, we explored several aluminosilicate glass structures prepared using molecular dynamics simulations. We developed a method for calculating the average Al^V configuration and compared those configurations across compositions and interatomic potentials to understand the geometry and bonding of Al^V. We also observe the coordination numbers of surrounding oxygens and next nearest neighbor aluminums which allows us to compare to Lowenstein's aluminum avoidance hypothesis. Understanding the nature of Al^V bonding can inform mechanistic studies like those exploring the nature of diffusion, viscous flow and plastic deformation.

8:50 AM

(ICG-SI-107-2019) Modeling the Structure of Quaternary CaO-MgO-Al_2O_3-SiO_2 Glass by Combining Multiple Computational Tools with X-ray and Neutron Scattering

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2. University of California San Diego, Department of Chemistry and Biochemistry, USA

Quaternary CaO-MgO-Al_2O_3-SiO_2 (CMAS) glasses are important constituents of the Earth's lower crust and mantle; they also have important industrial applications such as metallurgical processes, concrete production and emerging low-CO_2 cement technologies. In particular, for alkali-activated materials (AAMs), a class of low-CO_2 cements, it has been shown that the chemical composition and associated atomic structure of the glassy precursor (i.e., CMAS glass) have dramatic impact on the glass reactivity and subsequent materials properties. However, studies on the composition-structure-reactivity relationships for CMAS glasses relevant to AAM technologies are lacking. Here, we combine molecular dynamics simulations and density functional theory (DFT) calculations with X-ray/neutron scattering experiments to resolve the atomic structure of a CMAS glass. We show that the final structural representation obtained is not only thermodynamically favorable (according to DFT calculations) but also agrees with experiments (including X-ray/neutron scattering and literature data). Analysis of the final structures along with literature data reveals new structural information on the CMAS glass (including medium-range orders and Mg clustering), aiding in our mechanistic understanding on glass dissolution behavior occurring during the formation of AAMs.

9:10 AM

(ICG-SI-108-2019) ZrO_2 addition in SiO_2-CaO-Na_2O-P_2O_5 bioactive glass system: Effects on the network structure and solubility

S. Mokhtari*[1]; A. W. Wren[1]

1. Alfred University, Materials Science and Engineering, USA

The aim of this work is to study the impact of ZrO_2 incorporation in bioactive glass structure to control the solubility of the glass. The structural effects of ZrO_2 addition is investigated when substituted for SiO_2 in the $0.56SiO_2$–$0.25CaO$–$15Na_2O$–$4P_2O_5$–$xZrO_2$ (where x=4, 8, and 12) glass series. Initial characterization on the starting glass powders included X-ray diffraction (XRD) and differential thermal analysis (DTA) to analyze thermal profile of each glass composition. To further investigate the effects of zirconium incorporation in the glass structure, X-ray photoelectron spectroscopy (XPS), magic angle spinning nuclear magnetic (MAS-NMR), and Raman spectroscopy were conducted. Solubility of the glasses were analyzed using Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES), and pH measurements to investigate the ion release profile of the glass powders after 1, 10, 100, and 1000 hours incubation in de-ionized water. To evaluate in-vitro bioactivity, simulated body fluid (SBF) testing was conducted on each glass composition incubated for 1000 hours, and Fourier transform infrared spectroscopy (FTIR) was performed before and after incubation of the glasses in SBF. The chemical and morphological changes were studied using scanning electron microscopy and energy-dispersive X-ray analysis (SEM/EDS).

9:50 AM

(ICG-SI-109-2019) Understanding the structural origin of intermediate glasses (Invited)

S. Jaccani[1]; S. Sundararaman[1]; L. Huang*[1]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA

Intermediate glasses show nearly constant elastic moduli with temperature and/or pressure. These glasses would prove useful in designing a-thermal optical fibers for enhanced telecommunication, fiber sensing applications and in designing glass products for applications where a broad range of thermal and mechanical stimulation is expected. In this study, intermediate glasses belonging to the Na_2O-SiO_2, Na_2O-Al_2O_3-SiO_2 and Na_2O-TiO_2-SiO_2 glass systems were identified from in-situ high-temperature Brillouin light scattering (BLS) experiments. Glasses important for engineering applications like the international simple glass (ISG) and the less brittle glass (LBG) were also found to exhibit intermediate behaviors. In-situ Raman spectroscopy was used to investigate their structural evolution from room temperature to temperatures beyond T_g. Raman spectra along with molecular dynamics simulations revealed common structural signatures that intermediate glasses with different compositions possess. Our study showed that the intermediate elastic behaviors come from a delicate balance between the stiffening effect associated with conformation changes in the medium range flexible rings and the softening effect due to the weakening of short range chemical bonds with temperature.

10:20 AM

(ICG-SI-110-2019) Mixing properties and structure in molten alkali and earth-alkali silicates glasses and melts

D. R. Neuville*[1]

1. IPGP-CNRS-USPC, Géomatériaux, France

The relationship between physical properties and structure of glasses and melts in the system $M'O$-M_2O-SiO_2(with M=Li, Na, K and M'= Mg, Ca, Sr, Ba) are technologically and geologically important, in particular to understand the microscopic origin of the configurational thermodynamic properties. The connection of these elements with the tetrahedral silicate network is fundamental to understand the physical properties of magmatic liquids. The configurational properties of melts and glasses provide fundamental information needed to characterize magmatic processes. A principal difficulty, however is to link the "macroscopic" configurational entropy with the structure of melts. This has been done by combining viscometry with Raman spectroscopic structural studies. From the viscosity measurements at low and high temperatures, we have obtained the configurational entropy. We are using Raman spectroscopy at room temperature between the alkali and alkaline-earth silicate melts. We establish some link between the variation of the viscosity, the configurational entropy as the function of chemical composition and the Q species obtained from the Raman spectroscopy. These structural variations are related to the changes in configurational entropy. It is possible, to understand this variation of viscosity and mixing between alkali and earth-alkaline elements in silicate melts.

10:40 AM

(ICG-SI-111-2019) Relationship between structure and optical properties in thulium doped CaO-Al_2O_3-SiO_2 glass

J. She*[1]; B. Peng[1]

1. Xi'an Institute of Optics and Precision Mechanics of Chinese Academy of Sciences, China

The properties of optical materials rely on their microstructure, i.e., the atomic, molecular and mesoscale arrangement and interaction between chemical species. The investigation on structure and component changing will be useful to understand the optical properties changing. For years, more and more attention has been paid on 2μm region laser which is used as Doppler radar wind sensing atmospheric gases profiling, advanced manufacture, pump sources for optical parametric oscillators, medical instruments, and free-space communications. With the easily obtained commercial diode laser pumped source and 200% theoretical quantum efficiency, the Tm^{3+} doped laser materials are optimal candidate to output 2μm region laser. To the best of our knowledge, few publications dedicated to investigate the structure and optical properties in CaO-Al_2O_3-SiO_2 laser glasses. Here, we provide a systematic study of the structural effect on the thermal, mechanical as well as optical properties of doped thulium ions in CaO-Al_2O_3-SiO_2 glasses with Tm^{3+} concentration up to 10mol%. The proportion of Q^n corresponding SiO_4 units correlated with intensity of 1.8μm emission which arose structure change in glass matrix with increasing Tm^{3+} concentration.

11:00 AM

(ICG-SI-112-2019) Studies of Potassium-Doped Lead Silicates by Laser Ionization Time of Flight Mass Spectrometry

R. Welch*[1]; M. Boyd[1]; M. Martinez-Szewczyk[1]; D. Nonna[2]; M. Affatigato[1]

1. Coe College, Physics, USA
2. Rutgers University, Materials Science and Engineering, USA

Lead silicate glasses have been studied in both industrial and commercial areas for uses in optics, electrical applications, and radiation shielding. However, recent environmental concerns from lead-containing glassware has generated interest on how lead impacts the silicate network, and how additional modifiers can affect these networks. Lead silicate glasses co-doped with potassium were analyzed using Laser Ionization Time of Flight Mass Spectrometry (LIToF-MS), Raman, and Differential Scanning Calorimetry (DSC). The use of LIToF-MS allows for the identification of larger negative and positive ion groupings, and gives insights as to the topology of the glass networks and the role of the modifiers. In the absence of potassium, the lead silicates retain a portion of the lead ions as pure modifiers, but at larger Pb^{2+} concentrations a lead-oxide subnetwork begins to form concurrently. It was shown that potassium ions have a significant effect on the lead silicate network by attacking specific nano-silica units, and by diminishing the formation of any lead oxide subnetworks. Work supported by the United States National Science Foundation under grant numbers DMR-PECASE 9733724, DMR-0904615, DMR-1262315, DMR 1407404, and DMR-1746230.

Session 9: Sol-Gel Glasses

Room: Hancock (mezzanine)

Session Chairs: Lisa Klein, Rutgers University; Andrei Jitianu, Lehman College - City University of New York

1:20 PM

(ICG-SI-113-2019) New insights into the Condensation Kinetics and Structure of Sol-Gel Silicate Glasses by Reactive Molecular Dynamics Simulations (Invited)

M. Bauchy*[1]

1. University of California, Los Angeles, Civil and Environmental Engineering Department, USA

The sol-gel method is an attractive technique to synthesize homogeneous glasses with high purity while relying on lower processing temperatures than in the melt-quench method. However, several fundamental questions remain partially unanswered. How is the condensation kinetics governed by the solution chemistry? What is the nature of the atomic driving force behind the condensation reaction? Are sol-gel glasses different from melt-quenched glasses in terms of structure and/or stability? In this presentation, I will address these questions based on some recent new insights offered by reactive molecular dynamics simulations.

1:50 PM

(ICG-SI-114-2019) Modern NMR Techniques for the Structural Characterization of Sol-Gel Glasses (Invited)

H. Eckert*[1]

1. University of Sao Paulo, Physics, Brazil

Sol-gel glasses are an attractive area for both fundamental and applied research owing to their use as catalysts, bioactive materials, photonic devices, and solid electrolytes. As some of these applications cannot be realized with glasses prepared by traditional melt-cooling, a fundamental understanding of structure-property relations in this research field is an important research objective. Nuclear magnetic resonance (NMR) spectroscopy offers an element-selective, inherently quantitative and experimentally very flexible approach for the structural elucidation of non-crystalline materials. The presentation will focus on the structural characterization of non-siliceous glass components based on the network-former species Al_2O_3, B_2O_3, and P_2O_5 as well as the fluoride ion. By monitoring the structural evolution occurring during the sol->gel->glass transformations NMR can yield important mechanistic information, which is useful for optimizing the synthesis parameters. In addition, detailed structural studies as a function of glass composition reveal the underlying principles of glass formation in these systems. Presentation supported by the Center of Research, Technology and Education (CeRTEV), funded by FAPESP, Process No. 2013/07793-6

2:20 PM

(ICG-SI-115-2019) Highly transparent large-refractive index tellurite glass film via an optimal non-hydrolytic sol-gel synthetic route

X. Pan[1]; J. Zhao[2]; G. Qian[3]; X. Zhang[1]; Y. Wei[1]; Y. Ruan[1]; A. Abell[1]; H. Ebendorff-Heidepriem*[1]

1. The University of Adelaide, School of Physics, Australia
2. Leibniz Institute of Photonic Technology, Germany
3. Flinders University, College of Science and Engineering, Australia

High refractive index thin films have shown great promises in optical applications, such as hybridising with luminescent particles to extract emission of those particles. In comparison to organic-based materials, inorganic materials exhibit superior thermal resistance, enabling application under high-temperature environments. Furthermore, optical applications require high transparency. In this research, high refractive index (n»2.0) TeO_2-based (80TeO_2-10ZnO-10Na_2O, TZN) films were fabricated via non-hydrolysis sol-gel method, together with a systematic study of maximizing the transparency (from 500 nm to 4 mm). Fabrication of TZN glass films was extensively studied by mass-spectrometry, XRD, TG-DSC, UV-Vis, and STA-FTIR to reveal physical and chemical reactions at each step with regards to Te-alkoxide precursor synthesis, sol preparation, gelation, and densification. These fundamental studies have identified the optimal route to achieve the highest quality TZN glass thin film, specifically by suppressing and removing the formation of metallic Te and tellurite-based crystals, respectively. The applicability of this optimized protocol has been experimentally demonstrated using scanning confocal imaging and fluorescence spectral analyses.

2:40 PM

(ICG-SI-116-2019) Luminescent nanocomposites for high-power lasers and scintillators

J. Mrazek*[1]; H. Heskova[1]; I. Kasik[1]; L. Prochazkova[2]; V. Cuba[2]; E. Mihokova[3]; M. Nikl[3]

1. Institute of Photonics and Electronics of the Czech Academy of Sciences, Czechia
2. Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering, Czechia
3. Institute of Physics of the Czech Academy of Sciences, Czechia

Rare earth-doped yttrium aluminium garnets (YAG) represent key photonic materials. However, their crystallization temperature above 800 °C strongly limits their applications. The nanocomposite based on YAG nanocrystals encapsulated inside a sol-gel matrix is a promising way allowing the preparation of thin films that keep optical properties of YAG nanocrystals. We present a versatile sol-gel route to obtain europium-doped yttrium aluminium garnet (Ce:YAG) nanocrystals encapsulated inside a silica glass matrix. Defect-free Ce:YAG nanocrystals with tailored size were prepared by a radiation induced synthesis. The nanocrystals were dispersed in a sol prepared by a controlled hydrolysis of tetramethylorthosilicate. The sol-gel approach resulted in the formation of highly transparent monoliths. The Ce:YAG nanocrystals were homogenously distributed inside a silica glass matrix and they were thermally stable up to 1250 °C. The xerogels exhibited absorption spectra typical for Ce^{3+} ions localized inside a crystalline lattice of YAG. The thermal treatment above 1300 °C resulted to the solid-state reaction between the nanoparticles and the silica matrix. The promising application of prepared nanocomposites in the field of radioluminescent phosphors and high-power laser technology is widely discussed in the contribution.

3:00 PM

(ICG-SI-117-2019) Structural Analysis of Melting Gels during Heat Treatment

S. Kallontzi*[1]; L. Fabris[1]; A. Jitianu[2]; G. Tsilomelekis[3]; L. C. Klein[1]

1. Rutgers University, MS&E, USA
2. Lehman College-CUNY, Chemistry, USA
3. Rutgers University, CBE, USA

Melting gels are hybrid organic-inorganic silica gels with the ability to soften when heated to around 100°C. This is the temperature where the viscosity decreases and allows the material to become fluid. Even when the gel becomes rigid after cooling to lower temperatures, the softening is repeatable. However, at higher temperatures, these hybrid gels reach their reversibility limit, where they become permanently rigid, and the result is a hybrid glass. The unique temperature range that characterizes these gels was studied with FT-IR spectroscopy. The melting gels were synthesized using methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DMDES). Three different precursor molar ratios, 65%MTES-35% DMDES, 70%MTES-30% DMDES and 75% MTES-25% DMDES were studied. A sample doped with gold nanoparticles, and an undoped sample were analyzed for each ratio. FT-IR spectra were collected while increasing the temperature at a steady rate until the consolidation temperature. The evolution of the molecular structure showed changes in the complexity of the hybrid network. Structural differences were evident during the heat treatment related to the development of the 3D character of the melting gel. The doped melting gels developed less 3D structure than the undoped gels.

3:40 PM

(ICG-SI-118-2019) Sol-gel derived materials for solid-state lighting (Invited)

R. M. Almeida*[1]

1. Instituto Superior Técnico, Engenharia Química / CQE, Portugal

White light emitting diodes (WLEDs) based on lanthanide (Ln)-doped phosphors still have efficiency limitations, namely because the Stokes shift from UV/blue LED excitation to the emitted lower frequency visible light converts some of the pump energy into heat. However, if white light generation (WLG) is achieved through IR-pumped up-conversion (UC) instead, the cost of the LED lamp will be reduced, while the energy loss from Stokes shift can be minimized and UV/blue light leaks may be avoided. Sol-gel (SG) synthesis of Ln-doped oxide phosphors for UC in WLG has been achieved by two different approaches: (1) Ln ion mixing in suitable proportions and (2) Ln ion incorporation into photonic crystal structures, namely Bragg mirrors or Fabry-Perot microcavities. The SG-derived matrix was either aluminosilicate (AS) glass or titania. The active Ln elements were Yb (as a sensitizer for 980 nm pump absorption), Er (red and green emitter), Tb (green emitter) and Tm (blue emitter), to obtain the right proportions of the three primary colors, based on the CIE chromaticity diagram coordinates. The color temperature and color rendering index were also calculated. One of the best results was obtained via the first approach for a Tm/Yb-doped AS glass (x = 0.365, y = 0.313, CCT = 3963 K). While the second approach allows UC control by an optical structure independent of the specific phosphor, it still needs further optimization.

4:10 PM

(ICG-SI-119-2019) Sol-Gel Derived Inks for 3d Printed Glass Optics (Invited)

R. J. Dylla-Spears*[1]; K. Sasan[1]; T. Fears[2]; J. Destino[3]; N. Dudukovic[2]; M. Johnson[2]; D. Nguyen[2]; T. Yee[2]; O. Herrera[1]

1. Lawrence Livermore National Laboratory, Optics and Materials Science & Technology, USA
2. Lawrence Livermore National Laboratory, USA
3. Creighton University, USA

Techniques for three-dimensional (3d) printing of glass have opened the door to novel glass optics with both unconventional structures and tailored compositions. In the direct ink writing (DIW) approach, rheologically tuned silica-containing pastes are first extruded through a nozzle at room temperature and deposited in the geometry of interest, forming low density green bodies. The green bodies are then converted to full density, optically homogeneous glass by a series of heat treatments. The 3d-printed glass components have material and optical properties that rival conventionally prepared optical grade fused silica. However, to fully realize the potential of this technique for preparing novel optics requires the development of a library of ink formulations that lead to glasses with different properties. Several sol-gel approaches to ink preparation leading to refractive index control in 3d printed silicate glasses will be presented. In addition, efforts to blend and thermally process these inks into gradient composition optics will be described. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 within the LDRD program 16-SI-003 and 19-ERD-020. LLNL-ABS-765937

4:40 PM

(ICG-SI-120-2019) Preparation of Cu_3N thin films on glass substrate by nitridation of solution process-derived CuO thin film with urea

Y. Ohigashi[1]; A. Miura[1]; N. Rosero Navarro[1]; K. Tadanaga*[1]

1. Hokkaido University, Japan

Copper nitride (Cu_3N) thin films have received attention to the application to optical storage devices and microscopic metal lines. Cu_3N thin films have been prepared by RF magnetron sputtering or Molecular Beam Epitaxy process. However, preparation of Cu_3N thin films using solution-based process should be important for the practical application of these films. In the present study, thin films of Cu_3N on glass substrate were prepared by nitridation of CuO thin films using urea as a nitrogen source. First, CuO thin films were prepared by a solution process using cupper acetate as a starting material. Then CuO thin film and urea were placed downstream and upstream side in a tube furnace, respectively, and heated under a nitrogen flow. X-ray diffraction patterns and absorption spectra showed that Cu_3N were formed with a heat-treatment at 400°C for 12 h under the nitrogen flow. FT-IR and Raman spectra suggested that Cu_3N was produced by the reaction of CuO and decomposition products of urea.

5:00 PM

(ICG-SI-121-2019) Sol-Gel modified upconversion nanoparticles: Energy and biomedicine applications (Invited)

S. J. Ribeiro*[1]; C. Hazra[1]; S. Ullah[1]; Y. E. Correales[1]

1. São Paulo State University- UNESP, Institute of Chemistry, Brazil

Lanthanides compounds have been widely used in energy conversion processes (down-shifting, down-conversion and up-conversion). In particular, upconversion nanoparticles (UCNP) have been used since the 60's of the last century in several different applications. Infrared pumping and emission spanning the UV-Vis region up to the infrared is very attractive from the technological point of view. In this presentation we will show 3 may examples where light activated processes like photodynamic therapy, photocatalysis and temperature measurements can benefit from the spectral properties of UCNP modified at the surface sílica and titânia through sol-gel methods. Acknowledgments: Brazilian agencies FAPESP, CNPq and CAPES are acknowledged for financial support.

5:30 PM

(ICG-SI-122-2019) Corrosion protection of Al and Mg alloys using integrated self-healing systems

A. Durán*[1]; Y. Castro[1]

1. Instituto de Ceramica y Vidrio (CSIC), Glasses, Spain

Aluminum and magnesium alloys are called "light alloys" due to be their favorable strength to weight ratio. One drawback is their susceptibility to localized corrosion. Hybrid inorganic-organic SiO_2 sol-gel coatings have been proposed as good barrier systems because

they combine the properties of organic components with those of the inorganic components. However, corrosive ions can still diffuse through micro-pores and attack the metallic substrates. Using hybrid silica coatings with systems based on cerium or organic inhibitors is one way to combine passive and active corrosion protection and self-healing. This work describes a smart multilayer system that combines an anodizing process, followed by the infiltration and deposition of cerium coatings and a final hybrid silica coating with or w/o inhibitors. The anodized coating acts as a reservoir of corrosion inhibitors. If the system is damaged, these substances are released in a controlled way to passivate the substrate, thus inhibiting further corrosion. Acknowledgements. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 739566

5:50 PM

(ICG-SI-123-2019) Melting Gels and their corresponding hybrid gasses for protection against corrosion of AZ31B

M. Aparicio[2]; J. Mosa[2]; G. Rodriguez[1]; J. Guzman[1]; M. Jitianu[3]; L. C. Klein[4]; A. Jitianu*[1]

1. Lehman College - City University of New York, Chemistry, USA
2. Instituto de Cerámica y Vidrio, Consejo Superior de Investigaciones Científicas (CSIC), Spain
3. William Paterson University, Department of Chemistry, USA
4. Rutgers University, Department of Materials Science and Engineering, USA

Magnesium alloys, with a density two-thirds that of aluminum, are very attractive for industry. These alloys are extremely susceptible to corrosion in the presence of aggressive electrolytes such as NaCl. Here, we designed hybrid coatings obtained by the consolidation of organically modified "melting gels" for the corrosion protection of AZ31 magnesium alloy in NaCl solutions. Melting gels are silica-based hybrid gels that are rigid at room temperature, but soften around 110ºC. They are prepared, starting with a mono-substituted siloxane, methyltrimethoxysilane (MTMS), and a di-substituted siloxane, dimethyldimethoxysilane (DMDMS). Four gel compositions were prepared with concentrations between 50% MTMS-50% DMDMS and 70% MTMS-30% DMDMS. The methyl groups are retained into the gels, and in the hybrid glasses when these heated to temperatures between 140 and 170ºC. The thermal behavior of the gels was investigated using TG/DTA and DSC. The T_g noted on DSC decreased from -7.1 to -55.9ºC with a decrease in the amount of MTMS. To follow the evolution of the molecular structure, oscillatory rheometry studies were employed. The T_g obtained from oscillatory rheometry decreases from -6 to -50ºC with a decrease in the amount of MTMS. From anti-corrosion properties point of view, the main focus was to study the interaction between hybrid glass coatings and AZ31B substrate.

SII: Glass Physics

Session 1: Glass Transition and Relaxation II

Room: Hancock (mezzanine)
Session Chairs: Ozgur Gulbiten, Corning Incorporated; Walter Kob, University of Montpellier

8:00 AM

(ICG-SII-127-2019) Stretched and compressed exponentials in the relaxation dynamics of a metallic glass-forming melt (Invited)

W. Kob*[1]; Z. Wu[2]; W. Wang[3]; L. Xu[4]

1. University of Montpellier, France
2. Beijing Normal University, China
3. Chinese Academy of Sciences, China
4. Peking University, China

The hallmark of the dynamics of glass-forming liquids is that it is slow and stretched. In contrast to this one finds for the same material below its glass-transition temperature a relaxation dynamics that is compressed, i.e. a Kohlrausch-Williams-Watts exponent larger than one. The reason for the occurrence of such different dynamics is not clear nor does one know how it is connected to the microscopic structure of the system. In this talk I will present the results of large scale molecular dynamics simulations of a metallic glass-former to establish such a connection. By probing the temperature and wave-vector dependence of the intermediate scattering function we find that the relaxation dynamics of the glassy melt is directly related to the local arrangement of icosahedral structures: Isolated icosahedra give rise to a liquid-like stretched exponential relaxation whereas clusters of icosahedra lead to a compressed exponential relaxation that is reminiscent to the one found in a solid. Our results show that in metallic glass-formers these two types of relaxation processes can coexist at the same temperature and give rise to a relaxation and vibration dynamics that is surprisingly complex.

8:30 AM

(ICG-SII-128-2019) Flexible, intermediate and rigid glass-forming liquids : An atomic scale insight (Invited)

M. Micoulaut*[1]

1. Sorbonne Université, France

Glasses can be quantified according to their degree of bond density and in network glasses, such a concept appears to be useful for the characterization of non-monotonic physical properties which underscore the flexible, intermediate or rigid nature of the network structure. Here, we will review how molecular simulations of chalcogenide glass-forming liquids are able to substantiate such notions and experimental observations. We will essentally focus on dynamics and relaxation behavior of typical binary chalcogenides (Ge–Se, As-Se) and related ternaries. It is found that the relaxation behaviour of the supercooled liquid is strongly correlated to the variation of rigidity with different variables such as temperature or composition.

9:00 AM

(ICG-SII-129-2019) Knocking at the bottom of the energy landscape: Extended Kob-Andersen model

A. D. Parmar*[1]; M. Ozawa[1]; A. Ninarello[2]; L. Berthier[1]

1. University of Montpellier, France
2. CNR-ISC, Uos Sapienza, Italy

The glass state is associated with the astronomical large relaxation timescales and often related to the "entropic crisis." This nature of the glassy state makes the equilibrium sampling very challenging in experiments and simulations. In this work, we present an "Extended Kob-Andersen (KA)" model, a perturbation to the standard KA model. In addition to binary Kob-Andersen system, we introduce "α" particles, which opens a new pathway to employ efficient swap algorithm for the perturbed system. Our approach extends the observational window into the physics of low-temperature liquids and suggests the in-silico system corresponds to lower entropic state compared with the standard KA model.

9:20 AM

(ICG-SII-130-2019) Topological Control on Glass Relaxation

X. Li[1]; Y. Hu[1]; M. M. Smedskjaer[2]; J. C. Mauro[3]; M. Bauchy*[1]

1. University of California, Los Angeles, Civil and Environmental Engineering Department, USA
2. Aalborg University, Denmark
3. Pennsylvania State University, USA

Understanding, predicting, and controlling glass relaxation is of primary importance for the manufacturing of substrate glasses used in display applications, as any small variation in volume can result in undesirable pixel misalignment. However, no clear atomistic mechanism of structural and stress relaxation is available to date, which limits our ability to identify optimal glass compositions featuring low relaxation. Here, based on molecular dynamics simulations, we study the relaxation of a series of alkali-free calcium aluminosilicate (CAS) and sodium silicate (NS) glasses with varying compositions.

We observe that select glass compositions exhibit minimal relaxation. We investigate the structural origin of this behavior by means of topological constraint theory. Based on this analysis, we demonstrate that minimal relaxation is achieved for isostatic glasses, which are both free of eigenstress and floppy modes. This highlights the crucial role of the atomic topology in controlling the propensity for relaxation.

10:00 AM

(ICG-SII-131-2019) Relaxation Dynamics of Ge-Se Glasses

O. Gulbiten*[1]; P. Lucas[2]

1. Corning Incorporated, Science & Technology Division, USA
2. University of Arizona, USA

Ge-Se glass system is one of the most studied families of chalcogenides. However, there is still no consensus on the structure of Ge-Se glass system, and the validity of different structural models have been debated. Since the low-temperature structure is still being investigated understanding of dynamic processes in the vicinity of the glass transition can help shed light on the structural origins of this behavior. Here we present a calorimetric study of Ge-Se glasses in the temperature and frequency spectrum throughout the glass transition. Heat capacity spectroscopy and differential scanning calorimetry were utilized to probe the dynamic behavior of structural motifs. Investigation of relaxation dynamics of Ge-Se glasses will help reduce the ambiguity in the structural understanding of Ge-Se glasses.

10:20 AM

(ICG-SII-132-2019) Observation of Rigidity Percolation in the Viscoelastic Properties of Chalcogenide Glass-Forming Liquids

S. Sen*[1]; W. Zhu[1]; Y. Xia[1]; M. Lockhart[2]; B. Aitken[2]

1. UC Davis, USA
2. Corning Incorporated, USA

The viscoelastic properties of supercooled $As_xSe_{100-x}$and Ge_xSe_{100-x} ($0 \leq x \leq 30$) liquids are studied using oscillatory parallel plate rheometry. In addition to the low-frequency bond scission/renewal based relaxation process, the shear relaxation of the liquids with selenium chains longer than 3 to 5 atoms is also characterized by a high-frequency segmental chain dynamics. The temporal decoupling of the high-frequency chain mode from that of the bond scission/renewal process is a unique function of the average selenium chain length. The floppy chain mode abruptly vanishes for liquids with average chain lengths shorter than ~ 3 to 5 Se atoms, thus implying a dynamical rigidity transition. Moreover, the shear modulus associated with the low-frequency mode shows a rapid increase with shortening of chain length as the average network connectivity <r> increases beyond ~ 2.2. To the best of our knowledge, these results provide the first direct evidence of rigidity percolation in viscoelastic glass-forming networks.

10:40 AM

(ICG-SII-133-2019) Dynamical-gap and viscoelasticity of glass forming fluids: The role of rigidity

J. Toledo[1]; G. Naumis*[1]

1. Instituto de Física, Mexico

Rigidity plays an important role in the relaxation properties of glasses yet is usually determined from the average coordination number through the chemical composition. In this talk we will discuss how viscoelasticity can be used as an alternative to determine the rigidity. In particular we show that the dynamical structure factor of dense glass forming fluids, as well as rheological experiments, contains information about rigidity that we can relate with the presence of a dynamical-gap. In the case of non-directional bonds, we present simulations in simple fluids which show how rigidity affects the dynamical-gap. For the case of directional bonding, viscoelasticity is affected by steric effects that slow down relaxation.

10:50 AM

(ICG-SII-134-2019) Complex Shear Relaxation in As_xSe_{100-x} Supercooled Liquids – Competition between Slow and Fast Processes

W. Zhu*[1]; M. Lockhart[2]; B. Aitken[2]; S. Sen[1]

1. UC Davis, Materials Science Engineering, USA
2. Corning Incorporated, USA

Shear relaxation behavior in supercooled As_xSe_{100-x} liquids ($0 \leq x \leq 30$) near their glass transition is studied using oscillatory parallel plate rheometry. While liquids with $x \geq 20$ display a single relaxation process, samples with $x < 20$ demonstrate the presence of a slow, Debye-like, short range process and a fast cooperative process that are attributed, respectively, to the Se-Se bond scission and renewal and the segmental motion of selenium chains. Both processes display a non-Arrhenius temperature dependence and the difference between the two relaxation time scales become increasingly small with the addition of As. The combined contribution from both processes to viscosity is estimated using the Maxwell relation. While at higher temperatures the slow process is predominantly responsible for viscous flow, the fast process becomes a more important contributor to viscosity, and hence, to fragility near T_g. This dynamical crossover is likely a fundamental characteristic of fragile liquids that represents a temperature dependent evolution of their free energy landscape. The fragility of supercooled selenium liquid appears to be remarkably closely linked to the temperature dependence of the shear modulus of the slow process, thus validating the prediction of the elastic shoving model.

11:10 AM

(ICG-SII-135-2019) The Relativistic Glass Transition: A Thought Experiment

C. Wilkinson*[1]; J. C. Mauro[1]

1. Pennsylvania State University, USA

In order to quantify the viscosity of glass-forming systems at relativistic speeds, the Deborah number is analyzed incorporating the Maxwell relation for relaxation time. Using the time dilation coefficient proposed by Einstein for special relativity, the new observation times are then calculated, and the corresponding shear modulus is used to determine the shift in the glass transition range behavior. The new glass transition temperature is then incorporated in the MYEGA expression to calculate the relativistic viscosity curve. B_2O_3 glass is used as an example to show the impact of relativistic time scales on viscosity and the glass transition.

Session 2: Nucleation, Crystallization, and Phase Separation

Room: Terrace (lower level)
Session Chairs: Edgar Dutra Zanotto, Federal University of Sao Carlos; Kenneth Kelton, Washington University

1:20 PM

(ICG-SII-136-2019) What determines the glass-forming ability of a liquid? (Invited)

H. Tanaka*[1]; J. Russo[2]; F. Romano[3]

1. University of Tokyo, Japan
2. University of Bristol, United Kingdom
3. Universit'a Ca' Foscari, Italy

If a liquid is cooled with a certain cooling rate, it will be either crystallized or vitrified depending upon the rate. However, it has been unclear what physical factors control the fate of the liquid. We found that crystal-like angular order grows in both size and lifetime when the degree of supercooling is increased. Furthermore, we revealed that such structural order plays a crucial role in not only crystal nucleation but also polymorph selection. This indicates the importance of pre-ordering in a supercooled liquid, which acts as

precursor for crystal nucleation and thus also plays an important role in the selection of polymorphs. On the basis of this physical picture, we study the glass-forming ability of liquids with competing orderings, where an increase in the glass forming ability is signaled by a depression of the melting temperature towards its minimum at triple or eutectic points. We find that the enhancement of glass-forming ability is caused by an increase in the structural contrast between liquid and crystal: stronger competition in orderings towards the melting point minimum makes a liquid structure less similar to crystalline structures. This increase in the liquid-crystal structural difference leads to a rapid increase of the free-energy barrier for crystallization towards the glass-forming region.

1:45 PM

(ICG-SII-137-2019) The Development of the Implicit Glass Model

M. E. McKenzie*[1]; S. Goyal[1]; L. Cai[1]; I. Dutta[1]; D. Baker[1]; T. Loeffler[2]; J. C. Mauro[3]

1. Corning Incorporated, Science & Technology, USA
2. ANL, USA
3. The Pennsylvania State University, USA

Understanding the glass-ceramic nucleation behavior is important to create new materials for high-tech applications. The complex nature of nucleation and growth processes makes studying the emerging crystal structure a challenge. We introduce an implicit glass model (IGM) which, through the application of a Generalized Born solvation model, effectively replaces the background glass with a continuous medium. This permits the computational efforts to focus on the nucleation event. Three different systems (barium silicate, soda lime silicate, and lithium disilicate) are studied. Experimental validation was found using SEM measurements and solubility of different possible crystals are compared with known phase diagrams. IGM is generally applicable to crystal nucleation in any liquid or glassy system. Being an advanced modeling technique, this talk will cover the implicit models, IGM's assumptions, and the advantages and disadvantages of its use.

2:05 PM

(ICG-SII-138-2019) The Impact of Dynamical Heterogeneity on Crystal Nucleation and Growth (Invited)

G. C. Sosso*[1]; M. Fitzner[2]; S. J. Cox[3]; A. Michaelides[2]

1. University of Warwick, Chemistry, United Kingdom
2. University College London, United Kingdom
3. University of Cambridge, United Kingdom

When dealing with the nucleation and growth of crystals from supercooled liquids or supersaturated solutions, we often focus exclusively on structural changes. After all, the most obvious difference between a crystal and his parent phase is the long-range order of the former compared with the disordered network of the latter. However, dynamics does matter as well: atoms and/or molecules move around to some extent in liquids, but barely if at all in crystals. It is thus not unreasonable to ask ourselves whether the dynamical properties of the parent liquid phase may have an impact on the kinetics of crystal nucleation and growth. Here, we show that this is precisely the case: supercooled liquids which exhibit dynamical heterogeneity, i.e. the coexistence of spatially extended domains of slow- and fast-moving particles in the liquid network, display a strong tendency to generate crystalline nuclei within specific regions of the liquid, which differ in terms of both structural and dynamical aspects. In particular, we consider the prototypical case of ice nucleation from supercooled water: our findings offer a long-awaited point of view on the nucleation process, harnessing some concepts traditionally bound to the dynamics of glassy solids to shed new light on the molecular-level details of crystal nucleation and growth.

2:30 PM

(ICG-SII-139-2019) Crystal Nucleation in nBaO.mSiO$_2$ glasses

K. F. Kelton*[1]; X. Xia[2]; M. E. McKenzie[3]

1. Washington University, Physics, USA
2. Washington University, Institution of Materials Science & Engineering, USA
3. Corning Incorporated, USA

Understanding and controlling crystal nucleation are critically important for the manufacturing of glass and glass ceramics. Most nucleation data are analyzed within the classical theory of nucleation (CNT), a phenomenological theory developed more than a century ago. Many of the fundamental assumptions of CNT have been questioned and fits to the data rely on adjustable parameters that cannot be independently checked. To explore further, CNT and non-classical theories are fit to new time-dependent nucleation data for BaO.2SiO$_2$ and 5BaO.8SiO$_2$ glasses. Two non-classical theories are examined, the diffuse interface theory and a semi-empirical density functional theory, which have been shown earlier to be equally best in describing nucleation in metallic liquids and silicate glasses. For the two BaO-SiO$_2$ glasses studied all of these models give a good fit to the steady-state nucleation rates at temperatures above the temperature of the maximum in the nucleation rate. For CNT, a positive temperature dependent interfacial free energy must be assumed, with parameters that are determined from the fit; this factor emerges directly from the two non-classical theories. Which of the theories is the most valid will be discussed.

2:50 PM

(ICG-SII-140-2019) Thermodynamic pathways for the nucleation nBaO-mSiO$_2$ glasses

M. E. McKenzie*[1]; K. F. Kelton[2]; X. Xia[2]

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2. Washington University, Physics, USA

Studies in silicate glasses show that while the classical nucleation theory (CNT) can be fit to experimental nucleation data at high temperature, it fails dramatically for temperatures below the peak in the nucleation rate. This failure could signal a change in the sign of the temperature dependence of the interfacial free energy between the glass and the nucleating crystal, a reversal in the change of the driving free energy with temperature, or a crossover in the kinetics of long range diffusion and interfacial attachment. This talk will explore the work of cluster formation pathways for two different barium silicate systems (1BaO-2SiO2 and 5BaO-8SiO2) and three different temperatures (above, at, and below the maximum nucleating temperature). The variations in the pathways to nucleate a new phase seems to provide a first clue into why CNT breaks down at lower temperatures.

3:30 PM

(ICG-SII-141-2019) Time-dependent crystal nucleation of silicate liquids at deep and shallow undercooling (Invited)

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Liquid-to-crystal transformation kinetics are generally triggered by nucleation processes which impede spontaneous crystallization of glasses. As a result, crystal nucleation in undercooled liquids, which have been heated from below the glass transition, reaches its steady state only after a characteristic period of time. Delayed nucleation is also evident if glasses are cooled from temperatures above liquidus. Theory claims that the delay originates from three contributions: Firstly, the time it takes the system to establish a steady-state cluster size distribution for clusters with sizes up to the critical cluster size, secondly the average time of formation of the first supercritical nucleus at steady state nucleation, and thirdly the time for the

growth of supercritical clusters to detectable sizes. The paper aims in collecting experimental evidence for the existence of the three characteristic times that govern time-dependent crystal nucleation in silicate glasses in both homogeneous and heterogeneous nucleation processes. In particular, light will be shed on the question to what extent the time dependence in nucleation results from inherent effects and from artifacts of the thermal experiment.

3:55 PM

(ICG-SII-142-2019) Reanalyzing crystal nucleation data: A step back to move forward (Invited)

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2. Tempered Glass Division, Pilkington Brasil Ltda, Brazil

The quest to understand and control crystal nucleation in supercooled liquids sparkled the interest of the glass science community for more than half of a century. An unfathomable amount of time and energy was devoted to building the foundation that is now used to test theories and guide the development of new glass-ceramics. Recently, some attention has been directed towards an alleged failure of the Classical Nucleation Theory (CNT) to describe the temperature-dependence of the homogeneous crystal nucleation rates, reported to happen around and below the temperature of maximum nucleation. Some physical explanations for this apparent failure have been proposed. Here, however, we decided to step back and reanalyze available nucleation data (crystal number density versus time at several temperatures) following good statistical practices. This is the first time that some of these "classical" data have been revisited. Besides, we propose and use a test to check whether a given dataset has a significant probability to have not reached the steady-state condition. Four different compositions were considered in this work, namely $Li_2Si_2O_5$, $BaSi_2O_5$, $Na_2Ca_2Si_3O_9$, and $Na_4CaSi_3O_9$. Within the uncertainty of the analysis, we did not observe the mentioned CNT failure when using only the reanalyzed data that passed the steady-state test. In our view, this was a necessary step back to move forward based on solid ground.

4:20 PM

(ICG-SII-143-2019) Nucleation growth of mullite, sapphirine and cordierite phases from magnesium aluminosilicate melts by in-situ high-tempreature observation

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2. Nippon Sheet Glass Co., Ltd., Japan

Magnesium aluminosilicate (MAS) is one of the intersting glass forming systems in which various charactersitic crystal phases such as mullite, sapphirine, cordierite, enstatite and forsterite appear. Glass and glass-ceramics of MAS system has been known as the unique materials with small thermal expansivity for structural, thermal and optical uses. For control of crystallization behavior in this system, fundamental knowledge of crystallization is important. In this study, in-situ techniques were applied to MAS melts in order to understand their crystallization behavior and their glass composition dependence during cooling process. Crystal precipitation and growth were observed clearly against temperature and the information about the nucleation, crystal shape and growth rate of mullite, sapphirine and cordierite could be obtained. It was found that glass composition difference affects much against crystallization behavior of this system.

4:40 PM

(ICG-SII-144-2019) Phase Selective Crystallization of Ln^{3+}-Based Fluoride Crystals from Phase Separated Aluminosilicate Glass: A Molecular Dynamics Simulation Study

J. Zhao*[1]; X. Xu[1]; X. Li[2]; J. Du[4]; D. Chen[3]; X. Fan[1]; X. Qiao[1]

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3. Fujian Normal University, College of Physics and Energy, China
4. University of North Texas, Department of Materials Science and Engineering, USA

Oxyfluoride glass-ceramics with LnF_3 or $NaLnF_4$ nanocrystals are considered as favorable hosts for luminescence applications. However, owing to the lack of detailed structural understandings, the preparation of such materials with targeted crystal phase is still experience driven through a trial and error approach. Here, applying molecular dynamics simulations with effective pair-wise partial charge potential, a series of aluminosilicate glass with Ln-F, Na-F-Ln, or Na-F rich region is presented. These fluoride-rich regions are the precursor for LnF_3, cubic and hexagonal $NaLnF_4$, and NaF crystals' precipitation. By various analyzing methods, this simulation study shed more light on the general structural features as a function of Al/Si ratio. The results confirm that the concentration of Na^+ in fluoride phase plays a key role in determining the crystalline phase (LnF_3, $NaLnF_4$, NaF) and phase transition (cubic and hexagonal $NaLnF_4$). Therefore, MD simulations can provide insights on atomic scale of the phase separation behavior that is useful in predicting potential crystalline phase and phase transition, which can help to explore novel luminescent oxyfluoride glass-ceramics.

5:00 PM

(ICG-SII-145-2019) Compositional changes of phase-separated nanoparticles in silicates

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2. CAMECA, USA
3. Université d'Angers, LPhiA, France
4. Université de Bordeaux, BIC, France
5. Université de Paris, IPGP, France
6. Harvard Medical School, Center for NanoImaging, USA

The study of amorphous phase-separated Dielectric Nano-Particles (DNPs) smaller than 10 nm is a great challenge for the materials community. In conjunction with Transmission Electron Microscopy (TEM) and Electron-Probe Micro-Analysis (EPMA), we took advantage of a recent technology, Tri-Dimensional (3D) Atom Probe Tomography (APT) to investigate the variations of the chemical composition in sub-20-nm oxide nanoparticles, grown in silicate glass through heat treatments, at their early stages of nucleation. More precisely, we are investigating the core of an optical fiber drawn from a preform prepared according to the Modified Chemical Vapor Deposition (MCVD) process. We provide here a comprehensive set of experimental data obtained from direct measurements of the concentration for P, Mg, Ge and Er within amorphous dielectric nanoparticles (DNP) of radii ranging from 1 nm to 10 nm. We report on an increase of the concentration of Mg and P with the size of the DNPs. Most importantly, we also demonstrate that erbium ions are partitioned in these small DNPs and their environment changes with the size of the nanoparticles. Molecular dynamics simulations were also implemented to discuss the structural modifications of the Er environment. This presentation highlights the trade off on the size of the DNPs: smaller to reduce light scattering vs bigger to modify luminescence properties.

5:20 PM

(ICG-SII-146-2019) Phase Separation and Fluorescence Properties of Rare-Earth Doped Borosilicate Glasses

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2. Otto-Schott-Institut für Materialforschung, Jena University, Germany

Nowadays, there is a high demand for materials being suitable for photonic applications. Rare-earth doped glasses and glass-ceramics are promising candidates to meet the demands of photonic materials. At the moment, research is mainly focused on oxyfluoride glass-ceramics as well as borate glasses. However, their applicability is limited by the evaporation of fluorine during glass preparation, low concentration of rare-earth ions in the crystals or in case of borate glasses, their poor chemical glass stability. To overcome the issue of chemical durability, borosilicate glasses are a decent choice. This paper is focused on the characterization of rare-earth doped borosilicate glasses showing phase separation in borate-rich droplets embedded in a silicate matrix. The structural evolution during the phase separation process is studied using Raman and infrared spectroscopy. By means of scanning transmission electron microscopy, it is shown that there are structural changes upon phase separation. While the as-cast glass consists of irregularly formed particles with already preferred local sites of the rare-earth ions, a heat treatment leads to spherical-shaped droplets of larger size with an evident enrichment of the rare-earth ions in the phase separation droplets. Moreover, the fluorescence properties of the phase separated glasses are correlated with their microstructures

5:40 PM

(ICG-SII-147-2019) Kinetics of phase separation in SiO_2-BaO-B_2O_3 glass thin films

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Liquid/liquid phase separation has already been studied in bulk glasses where morphological evolution and growth during the coarsening stage are of particular interest. It is known that growth law highly depends on the mechanism and can be limited either by diffusion or by hydrodynamic transport. From a process point of view, industrial glass surfaces are often functionalized by magnetron sputtering to add new optical, morphological or mechanical properties. That's why in this study we investigate phase separation in glass thin films as a surface nanostructuring method. In order to understand kinetics and mechanisms, thin layers of a model glass for phase separation, barium borosilicate, are deposited by RF magnetron sputtering. Layers between 20 and 800nm thick were studied after different annealing time at high temperature around 900°C. Images obtained by SEM and AFM have been compared using homemade Python image processing. From statistical data, growth kinetics in barium borosilicate glass thin films are found significantly slower compared to the bulk. As in bulk glasses, composition, temperature and annealing time impact the final morphology of phase separation. Besides we have observed that droplets growth in thin films is also influenced by additionnal parameters such as initial layer thickness or hygrometry. All these parameters allow to control morphologies and size of objects obtained by phase separation.

6:00 PM

(ICG-SII-148-2019) Effects of Electric Field on the Laser-fabrication of Single Crystals of Ferroelectric Sb_2S_3 in $84Sb_2S_3$-$16SbI_3$ Glass

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2. Lehigh University, Physics, USA

Spatially selective fabrication of single crystal architectures in glass through laser irradiation offers the potential to create photonic devices with new functionality for optical communication. Full realization of this potential will require an increased level of control over the growth and orientation of these optically active crystals. By perturbing the crystallization process through the application of an external field (e.g. electric or mechanical), the environment around the growth front is affected. Therefore, we are exploiting such perturbations to control the crystal formation. In this paper, we will specifically report on the effect of an electric field on the formation of single crystals in a recently established model system, viz. Sb_2S_3 ferroelectric crystals in $84Sb_2S_3$-$16SbI_3$ glass with a 639 nm continuous wave laser. Using scanning electron microscopy and electron backscattered diffraction techniques, the effects of the electric field on the nucleation and growth process, particularly crystal orientation, are investigated.

6:20 PM

(ICG-SII-149-2019) New thermostable luminescent materials based on iron-containing nanoporous silicate glass matrices: Synthesis and spectral properties

M. Konon*[1]; T. Antropova[1]; M. Girsova[1]; I. Anfimova[1]; L. Dikaya[1]; E. Semenova[1]

1. Institute of Silicate Chemistry of Russian Academy of Science, Russian Federation

Porous glasses (PGs) derived from phase-separated alkali borosilicate glasses are well known as host matrices for composite materials with various functional properties. For example bismuth-containing composites with luminescence in a wide range from the visible to the near infrared region of the spectrum were obtained on the basis of such PGs. Giving new unique properties to the composites is possible not only by filling the pores of the PGs with different dopants, but also by modifying the matrix itself. Sodium borosilicate glass forming system was modified by adding Fe_2O_3 at the synthesis stage. The leaching behavior (in HCl acid solution) of heat-treated phase-separated iron-containing glasses was studied. Glass compositions suitable for producing mesoporous glasses and their structural parameters were determined. These PGs were used as host matrices for new high-silica luminescent composite materials, produced by impregnating them with bismuth nitrate solution and the following sintering till the closure of the pores. The spectral optical and luminescent properties of obtained composite materials were studied. This work was supported by the Russian Foundation for Basic Research (project no. 18-03-01206).

Session 3: Glass under Extreme Conditions I

Room: Clarendon (mezzanine)
Session Chairs: Bernard Hehlen, University of Montpellier; Sushmit Goyal, Corning Incorporated

1:20 PM

(ICG-SII-150-2019) Role of oxygen in the polyamorphism of lithium borates (Invited)

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Alkali borate glasses are considered as strong glass-formers, and they exhibit an increasing fragility as the alkali oxide content increases. This fragile behavior indicates a rapid raise in the configurational entropy above Tg, contrary to what it is observed in the strong B_2O_3

liquid. However, it is not well understood in which manner the structural mechanisms are involved in the entropy increase, partly due to the lack of data on the structural reorganization when going from the glass to the liquid. Structure and electronic information can be obtained from K-edges spectra that are usually measured using energy-loss spectroscopy (EELS) or X-ray absorption spectroscopy (XAS). These techniques have been recently extended by the use of X-ray Raman Scattering (XRS) that can yield to similar information. All these techniques are chemically selective and can probe the local environments of Li, B and O atoms in alkali borate glasses. Unlike EELS and XAS, XRS allows measurements in complex sample environments (high-pressure, high-temperature, …) By coupling XRS with the aerodynamic technique, we probed the local environment of B and O in the glassy and liquid states. We will present results on the evolution of B and O K-edges spectra as a function of temperature for an extended range of composition, from pure B_2O_3 up to 67mol% Li_2O. The BO_4 -> BO_3 conversion will be followed and its impact on the O environment will be discussed.

1:50 PM

(ICG-SII-151-2019) Ultrahigh pressure polyamorphism in GeO_2 and SiO_2 glasses with coordination number >6 (Invited)

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2. HPCAT, USA
3. The University of Chicago, USA

Knowledge of pressure-induced structural changes in network forming glasses is of great interest not only in condensed matter physics, geoscience, and materials science, but also in engineering and industry. As prototype network-forming glasses, silica (SiO_2) and germania (GeO_2) have been the most extensively studied. Our recent development of double-stage large volume cell combined with multi-angle energy dispersive X-ray diffraction at the beamline 16BMB in the Advanced Photon Source (USA) opened way to investigate structure of oxide glasses under ultrahigh pressure conditions of >100 GPa (Kono et al., 2016, PNAS, 113, 3436-3441; Kono et al., 2018, PNAS, 115, 1742-1747). The new experiment revealed existence of ultrahigh pressure polyamorphism in GeO_2 glass with coordination number larger than 6 (Kono et al., 2016). Here we introduce our recent development of the structure measurement of oxide glasses under ultrahigh pressure conditions of >100 GPa and show ultrahigh pressure structure changes in GeO_2 and SiO_2 glasses with coordination number larger than 6.

2:20 PM

(ICG-SII-152-2019) Structure of high-temperature liquid oxide

S. Kohara*[1]; Y. Onodera[2]; S. Tahara[3]; C. Koyama[4]; H. Tamaru[4]; A. Masuno[5]; J. Okada[6]; A. Mizuno[7]; H. Oda[4]; Y. Watanabe[8]; Y. Nakata[8]; K. Ohara[9]; T. Ishikawa[4]; O. Sakata[1]

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2. Kyoto University, Japan
3. University of the Ryukyus, Japan
4. Japan Aerospace Exploration Agency, Japan
5. Hirosaki University, Japan
6. Tohoku University, Japan
7. National Institute of Technology, Hakodate College, Japan
8. Advanced Engineering Services Co., Ltd., Japan
9. Japan Synchrotron Radiation Research Institute, Japan

Investigation of the liquid state at high temperatures is very challenging, because chemical reactions with containers are very difficult to avoid at high temperature. In addition, the contribution of diffraction from a crystalline container makes it difficult to obtain high quality diffraction data from liquids. However, the use of levitation and containerless methods can overcome these problems and, in many cases, enable deep undercooling and enhanced glass formation owing to the elimination of extrinsic heterogeneous nucleation. Recently, studies on liquids and the formation of glasses from supercooled liquids using levitation techniques have been of particular interest in understanding the structure of these materials and the process of glass formation. Quantum beam measurements especially X-ray and neutron diffraction techniques combined with density and viscosity measurements at the International Space Station are a powerful tool to study the structure and dynamics in glasses and liquids. We have been working on high-temperature glass-forming liquid oxides, *e.g.* SiO_2 and non-glass-forming liquid oxides, *e.g.* Al_2O_3, ZrO_2 to uncover the relationship between glass-forming ability and atomistic structure in liquid oxides. We review our previous studies and report recent study on liquid Er_2O_3 by X-ray diffraction and density measurements, and reverse Monte Carlo – molecular dynamics simulations.

2:40 PM

(ICG-SII-153-2019) Permanent densification of silica glass and hypervelocity impact loading conditions: Experimentation and MD simulation

J. Guin*[1]; C. Dereure[1]; R. Renou[2]; D. Loison[1]; E. Lescoute[2]; M. Nivard[1]; J. Sangleboeuf[1]; L. Berthe[3]; L. Soulard[2]

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2. CEA-DAM DIF, France
3. Arts et Metiers ParisTech, PIMM, France

Mechanical behavior of materials under extreme conditions (pressure, loading rate (up to 10^9 s^{-1}) is of interest for practical applications in aeronautical or planetology fields. Futhermore such experiments, due to their time scale, offer a real opportunity for comparison with molecular dynamic simulation. For silica, when experimental conditions are well mastered, shock waves may induce permanent deformation in the glass (phase change, densification) without any or rather limited fracture damage. Laser driven shock loading tests were performed to generate such loading conditions. Compared with other shock-generating methods such as plate impact, the benefit of laser impulses is that the shock pressure is only applied to the laser-impacted zone, which allows to reach high pressures without damaging the glass in a way that it is no more recoverable for post- mortem investigation such as Raman spectroscopy. Shock induced structural modifications were explored by Raman spectroscopy both at the impacted surface and as a function of depth. In this work the Raman signature of the impacted zone was compared to: 1) other Raman signatures of permanently densified silica glass structures resulting from different thermo-mechanical path (plate impact, press belt, Diamond anvil cell, laser engraving). 2) MD simulations results obtained for similar loading conditions.

3:00 PM

(ICG-SII-154-2019) Pressure-induced structural changes in Na_2O-B_2O_3-Al_2O_3-SiO_2 glasses at high pressure up to 9 GPa: Insights from multinuclear (^{11}B, ^{17}O, ^{23}Na, ^{27}Al, and ^{29}Si) solid-state NMR

A. Lee*[1]; S. Lee[1]

1. Seoul National University, Republic of Korea

Probing the structural changes and the extent of disorder in Na_2O-B_2O_3-Al_2O_3-SiO_2 glasses at high pressure remains elusive in geochemistry and glass science. Since the degree of polymerization of silicate melts expects to decrease with pressure above 5-8 GPa, unraveling the glass structure above that pressure range is required to predict and explain the change in melt properties with pressure. To establish a relationship between pressure and glass structures, we report multinuclear NMR results for $2Na_2O$-B_2O_3-Al_2O_3-$4SiO_2$ glasses at high pressure up to 9 GPa. $^{[4]}B$ and $^{[5,6]}Al$ fractions increase by ~30% and ~40% at 9 GPa, respectively, indicating that Al is more susceptible to pressure-induced structural change than B. $^{[5,6]}Si$ also increases with pressure. A decrease in quadrupolar coupling constant of ^{23}Na from ~2.4 to ~1.9 MHz with pressure indicate less disorder around Na at high pressure. The effect of pressure on the network connectivity in the glasses is manifested in an increase in

$^{[4]}$Si-O-$^{[5,6]}$Al and $^{[4]}$Si-O-$^{[4]}$B fractions and a decrease in Na-O-$^{[4]}$Si fraction, leading to an increase in the degree of polymerization of the glasses. The current results provide an improved understanding of the change in melt properties of sodium boroaluminosilicate glasses from the atomic configurations at high pressure.

Session 3: Glass under Extreme Conditions II

Room: Clarendon (mezzanine)
Session Chairs: Thomas Bennett, Cambridge University; Mathieu Bauchy, University of California, Los Angeles

3:40 PM

(ICG-SII-155-2019) Network formation in ultra-high pressure carbonate liquids

M. C. Wilding*[1]; M. Wilson[2]; Y. Kono[3]; R. Brooker[4]; J. Drewitt[4]; P. A. Bingham[1]; J. B. Parise[5]

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2. University of Oxford, Department of Chemistry, United Kingdom
3. Ehime University, Geodynamics Research Center, Japan
4. University of Bristol, Earth Sciences, United Kingdom
5. Stony Brook University, Chemistry, USA

The change in the structure and structural properties of glasses with pressure is of interest to scientists from a wide range of disciplines and there have been many recent studies that have investigated the evolution of traditional network-forming glasses as a function of pressure. The influence of pressure on exotic glass-forming systems remains relatively unexplored. In this contribution we present the results of an high pressure X-ray diffraction study of a rare carbonate glass using a newly-developed, double stage Paris-Edinburgh large volume press, which enables ultra-high pressures of up to 45GPa to be achieved. We have combined the diffraction data with molecular dynamics simulations of the equivalent liquids in which the carbonate anions are allowed to be flexible. Although carbonates are expected to be simple, relatively structure-less, inviscid liquids, we show that changes in the total structure factor in response to ultra-high pressures are directly related to the emergence of ordering on new length-scales and formation of a carbonate network arising as a direct result of the flexibility of the carbonate anion. This has significant implications for properties of the carbonate liquid and results in an unexpected increase in the viscosity with pressure by at least three orders of magnitude.

4:00 PM

(ICG-SII-156-2019) Effect of pressure and temperature on viscosity of a borosilicate glass

L. Ding*[1]; M. Thieme[2]; S. Demouchy[2]; B. Kaus[3]; C. Kunisch[4]

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2. Universite de Montpellier & CNRS, France
3. Johannes Gutenberg University, Germany
4. SCHOTT AG, Germany

During industrial glass production processes, the actual distribution of stress components in the glass during scribing remains, to date, poorly quantified, and thus continues to be challenging to model numerically. In this work, we experimentally quantified the effect of pressure and temperature on the viscosity of SCHOTT N-BK7 glass, by performing in situ deformation experiments at temperatures between 550 and 595°C and confining pressures between 100 and 300 MPa. Experiments were performed at constant displacement rates to produce almost constant strain rates. The resulting net axial stresses range from 81 to 802 MPa, and the finite strains range from 1.4% to 8.9%. The mechanical results show that the SCHOTT N-BK7 glass is viscoelastic near the glass transition temperature at 300 MPa of confining pressure. To elucidate the data, we incorporated both 1-element and 2-element generalized Maxwell viscoelastic models in an inversion approach. Results show that the 2-element Maxwell model fits the experimental data well. The stress decreases with increasing temperature at 300 MPa and the temperature dependence yields a similar activation energy to a previously reported value at 1-atm. The SCHOTT N-BK7 glass shows a limited linear increase in viscosity with increasing pressure of ~0.1 $\log_{10}$ (Pa*s)/100 MPa, which is in agreement with the most recent 2-internal- parameter relaxation model (based on experiments).

4:20 PM

(ICG-SII-157-2019) Pressure-induced densification of vitreous silica: Insight from elastic properties

C. Weigel[1]; M. Mebarki[1]; R. Vacher[1]; M. Foret[1]; B. Ruffle*[1]

1. Montpellier University, Physics Department, France

In situ high-pressure Brillouin light scattering experiments along loading-unloading paths are used to investigate the compressibility of vitreous silica. An accurate equation of state is obtained below 9 GPa using sound velocities corrected for dispersion. Conversely, huge inelastic effects are observed in the range 10-60 GPa, unveiling the reversible transformation from the fourfold-coordinated structure to the sixfold one. We find that the associated density changes fully correlate with the average Si coordination number. Decompression curves from above 20 GPa reveal abrupt backward coordination changes around 10-15 GPa and significant hysteresis. Further, contrary to common wisdom, the residual densification of recovered silica samples can be figured out from the pressure cycles.

4:40 PM

(ICG-SII-158-2019) Pressure induced network collapse of amorphous As_2Se_3 from First Principles molecular simulations

M. Micoulaut*[1]

1. Sorbonne Université, France

First principles molecular simulations at pressures up to 14.4 GPa is used to characterize the modification of cold-compressed As_2Se_3 glass. The simulations give a good account of the neutron diffraction results at zero pressure and also permits to provide an atomic scale picture of the pressure induced network collapse. The evolution with pressure departs from the usual behavior observed in chalcogendes upon densification such as bond length and coordination number increase which occur between 5 and 10 GPa. Here, both As-Se and As and Se coordination numbers remain constant over an extended pressure range and conversely to most network glasses As_2Se_3 is found to densify with constant strain up to elevated pressures. On the basis of the molecular dynamcis results, these suprising features are found to be linked with an angular reducation and the presence of a certain number if intermediate coordinated spaces such as As4, As5 and Se3.

5:00 PM

(ICG-SII-159-2019) Time-resolved Ablation Dynamics of Silicate Glasses with Few Cycle Laser Pulses

N. Talisa[1]; S. T. Locker[2]; A. AlShafey[1]; M. Tripepi[1]; B. Harris[1]; S. K. Sundaram[2]; E. Chowdhury*[1]

1. The Ohio State University, Physics, USA
2. Alfred University, Ultrafast Materials Science and Engineering Laboratory, USA

We studied various single shot femtosecond ablation process in silicate glasses (soda-lime silicate, aluminosilicate, boroflat and ZnO-glass) under intense 10 fs pulses with nominal a wavelength 760 nm at 45° angle of incidence at p-polarization to capture the time-resolve ablation dynamics, which is critical to understanding of control of glass structure and properties under intense laser irradiation. The glass compositions were melted, cast into disks, annealed, and characterized for their density, glass transition temperature, and crystallinity, using water displacement, differential scanning calorimetry (DSC), and x-ray diffraction, respectively. Then the sample disks were polished flat to prepare for laser studies. We

performed time-resolved high resolution surface microscopy from 0-10 ns range in a pump probe setup, where the probe, at 400 nm with 150 fs pulse duration, passed through the back of the sample and captured ablation at front surface. We used shadowgraphy to record Ionization, recombination and material removal during ablation. We characterized the morphology and chemical gradient in the region of laser study using scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS), respectively. We will present these results and detailed ablation dynamics of these glasses.

Session 8: Optical Properties of Glass VI

Room: Statler (mezzanine)
Session Chair: Shi Ye, South China University of Technology

8:00 AM

(ICG-SII-160-2019) Optical Functional Nanocrystal-Doped Glass and Fibers (Invited)

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1. South China University of Technology, State Key Laboratory of Luminescent Materials and Devices, and Guangdong Provincial Key Laboratory of Fiber Laser Materials and Applied Techniques, China
2. Zhejiang University, State Key Laboratory of Modern Optical Instrumentation, College of Optical Science and Engineering, China

Optical glass and fiber working in near/middle-infrared (NIR/MIR) region are extensively investigated owing to their various potential applications. Quantum dot (QD, such as PbS) doped glass with tunable broadband NIR emission and rare-earth-ion (such as Er^{3+}) doped glass ceramics with enhanced MIR emission are well suitable for the above-mentioned applications. Importantly, we use "melt-in-tube" method to fabricate the QD/nanocrystal-doped glass fibers. Furthermore, thermal and optical properties between fiber core and cladding glass are well matched, which ensure that the structure of the precursor fiber is well preserved during the fiber-drawing process. The excellent spectroscopic characteristics and well-preserved structure suggest that the obtained QD/nanocrystal-doped glass fiber may be a promising gain fiber material.

8:30 AM

(ICG-SII-161-2019) Ultra-short-pulsed laser filamentation in soda lime silicate glass: Probing the roughness of the cut surface

F. Werr*[1]; A. Veber[1]; D. Werner[2]; J. Betz[2]; U. Eppelt[3]; L. Müllers[3]; D. de Ligny[1]

1. Friedrich-Alexander-University, Institute of Glass and Ceramics, Germany
2. Flabeg Deutschland GmbH, Germany
3. Coherent Munich GmbH & Co. KG, Germany

Ultra-short-pulsed laser micromachining is an emerging process to cut glass. The possibility to generate cuts on a micrometre scale, the benefit of free shape cuts and the minimal invasive impact to the surrounding material make the process advantageous to conventional methods. Further understanding of the laser-glass interaction and the mechanism of the glass failure will lead to an optimisation of the process and enhance the quality of cut glass. As a link between mechanical properties and quality of the cut, the roughness of broken surfaces will be investigated. Commercially available OptiWhite™ silicate glass was laser treated with changing power and analysed in this study. The surfaces at the laser-entrance and laser-exit side were observed with SEM to check for visible changes. On both sides a viscous flow of the ejected glass is evidenced showing a large variety of deformation features. Imaging of the broken surface revealed that micro-cracks are forming. With a Laser-Scanning-Microscope (LSM) the topography of the broken surface is scanned and linked to the SEM images of the laser-entrance and laser-exit side to survey if a relation between roughness and deformation features can be drawn. The study of the dependence with the laser parameters gives an orientation to cut optimisation.

8:50 AM

(ICG-SII-162-2019) Application of Glass Phase Separation Technology in Fabrication of Optical Fiber Materials

L. Yang*[1]

1. Huazhong University of Science and Technology, Wuhan National Laboratory for Optoelectronics, China

The main factors restricting the application of silica glass in luminescent materials are concentration quenching of rare earth ions in silica glass and impurities of transition metals which are difficult to remove. We have studied the phase separation characteristics of borosilicate glass. Based on the phase separation characteristics of borosilicate glass, we have prepared a series of nanoporous quartz glass, studied the adsorption characteristics of nanoporous silica glass and the distribution characteristics of transition metal impurities in nanoporous silica glass. The results show that nanoporous quartz glass exhibits very high relative area and can absorb a large number of rare earth ions without clusters. The results also show that the distribution of transition metal elements in borosilicate glasses is selective, and the high valence transition metal impurities tend to be selectively distributed in boron-rich phase. Using this characteristic, we can effectively control the impurity content of transition metal elements in nanoporous silica glass. Based on the above research, we have prepared a series of rare earth ion doped luminous silica glasses using nanoporous silica glass, and prepared rare earth ion doped optical fibers, and demonstrated their optical properties.

9:10 AM

(ICG-SII-163-2019) Optical properties of palladium-doped Sol-gel-derived ZrO_2 thin films for multi-resonant surfaces

R. Sajzew*[1]; L. Müller[1]; S. Fuhrmann[1]; H. Ebendorff-Heidepriem[2]; L. Wondraczek[1]

1. Otto Schott Institute of Materials Research, Germany
2. University of Adelaide, Institute of Photonics and Advanced Sensing, Australia

One possibility to modify coupling efficiencies of light in optical materials is to utilize resonance effects, such as the surface plasmon resonance (SPR) of metallic nanoparticles (NP). By choice of metal species, particle shape and surrounding matrix, characteristic SPR frequencies can be achieved. Utilization of more exotic metal species, e.g., palladium, expands the SPR frequency range which can be covered by well-established metals like gold and silver. The aim of this study was to verify the existence of the SPR effect of metallic palladium NPs embedded in transparent oxide glassy and ceramic thin films. In particular, a synthesis method for the preparation of palladium-doped zirconia thin films by sol-gel method was developed. Structural characterization by Electron Microscopy, X-Ray diffraction and Raman spectroscopy revealed that the obtained material consists of tetragonal zirconia and palladium oxide or metallic palladium, depending on processing parameters like atmosphere, treatment temperature and cooling rate. With the help of Mie-theory simulations and UV-Vis spectroscopy optical activity of metallic NPs in the thin films was shown.

Session 8: Optical Properties of Glass VII

Room: Statler (mezzanine)
Session Chairs: Xusheng Qiao, Zhejiang University; Guoping Dong, South China University of Technology

10:00 AM

(ICG-SII-164-2019) Structural Modifications of Lanthanum Aluminosilicate Glasses using Femtosecond Laser Irradiation

D. K. Dobesh*[1]; S. K. Sundaram[1]

1. Alfred University, Glass Science, USA

Ultrashort laser irradiation enables the precise modification of glasses with minimal thermal penalty. Irradiation may alter structural connectivity and composition of the base glass both spatially and temporally. Investigations of tailoring the base glass

composition of lanthanum aluminosilicates were conducted to enable high contrast refractive index modifications. Lanthanum rich (11-24mol%) aluminosilicate glasses were studied in combination with high repetition rate femtosecond (about 40 fs) laser in order to locally modify the optical refractive index. Network polymerization were examined in irradiated regions to correlate ion polarizability and the optical linear refractive index. Optical properties and structural associations with rare-earth content will be the basis of our analysis for the effects due to coupling with the laser source. Optical and terahertz measurements were used to investigate the refractive indices in various frequencies. Structural polymerization were investigated using 27Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR), Raman, Fourier-Transform Infrared (FTIR) spectroscopy, and Differential Scanning Calorimetry (DSC). We will present our results on the structural-optical property correlations of ion polarizability and connectivity as a function of ultrafast laser modification of the glasses.

10:20 AM

(ICG-SII-165-2019) PbS quantum dots in one glass rod for multi-wavelength emissions

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1. Pohang University of Science and Technology(POSTECH), Department of Materials Science and Engineering, Republic of Korea

Lead chalcogenide quantum dots (QDs) have been intensely studied as promising candidates for near-infrared lasers, light-emitting diodes, fiber-optic amplifiers and mode locked quantum dots laser because of their size-dependent optical and electronic properties. The average size of QDs inside glass can be controlled using thermal treatment, incorporation the third elements and changes in the host glass composition. Recently, the plasmon-assisted precipitation of PbS quantum dots using continuous-wave (CW) laser in glasses were reported. However, the bulk glass was easy to have cracks and the size distribution of PbS QDs was broad due to the nonuniform intensity of laser. In this work, glass rods with a diameter of 0.5 mm were prepared using conventional melt-quenching method. After Ag ion exchanged, 532 nm CW laser with a different intensities were irradiated along its length to induce the precipitation of PbS QDs with different sizes. TEM images combined with electron energy loss spectroscopy (EELS) showed the formation and size distribution of PbS QDs. Photoluminescence of 1.2 μm~1.8 μm were recorded from each different regions in one glass rods depending upon the power and duration of the laser irradiation.

10:40 AM

(ICG-SII-166-2019) Round-Robin on optical and emissivity measurements of coated float glass samples according to EN 410 and EN 12898: A technical report of ICG TC10

C. Kermel*[1]; S. Timmermans[2]; H. Wilson[3]; P. A. van Nijnatten[2]; I. Marenne[4]

1. Belgian Ceramic Research Centre - INISMa, Belgium
2. OMT Solutions, Netherlands
3. Fraunhofer Institute for Solar Energy Systems ISE, Germany
4. AGC Glass Europe, R&D Centre, Belgium

Two important parameters that characterize a window are the U value (heat loss through a window) and the g value (quantity of solar heat entering through a window). For standard glazing units, consisting of flat planes of non-scattering glass, they can be obtained by calculation from the emissivity, the direct solar energy transmittance and reflectance and thermal properties of the glazing unit components. Much progress has been made in recent years to decrease the emissivity of coated glass to values that reach the measurement limit. Thus, after previous round robin tests in 1988 and 2003, ICG TC10 conducted a new round robin test in 2017-2018 intended to: Determine the measurement uncertainties for solar and luminous characteristics (according to EN 410:2011) and normal emissivity (according to the procedure that will be published as EN 12898:2019) obtained by different users with different equipment on the same sample series: a set of 6 different glass samples covering an emissivity range from 0.89 (float glass) down to 0.01 (glass with a low-emissivity coating). 21 participants from 13 countries ran the round robin test with a dozen different UV-visible-NIR and MIR instruments. The results are presented and compared with those of the previous round robin tests on optical properties and emissivity conducted by the ICG TC10.

11:00 AM

(ICG-SII-167-2019) The glass-forming region and physical property of fluoro-sulfo-phosphate glass

Y. Xiao*[1]; W. Wang[1]; Y. Ji[1]; Q. Zhang[1]

1. South China Univesity of Technology, State Key Laboratory of Luminescent Materials and Devices, China

Poly-anionic glass with rich ligands has attracted increasing interest for their potential applications in hosting optically active cations. Here the glass-forming regions (GFR) of RFPS systems (R_2SO_4–AlF_3–RPO_3, R = Li, Na, K) are predicted via the thermodynamic calculation and subsequently determined by experiments. It is simple and practicable to explore new glass system based on the thermodynamic method and the calculated GFR provides a significant guidance for experimental exploration. Based on this, the physical properties of such glasses are further investigated in detail. The results suggest that RFPS glasses exhibit typically low linear refractive index n_d (1.48 ~ 1.52) and nonlinear refractive index n_2 (0.86 ~ 1.05 × 10^{-13} esu), high Abbe's number ν (69 ~ 72), and moderate elasticity modulus E (50 ~ 75 GPa), which might be promising candidates for optics and laser glasses.

11:20 AM

(ICG-SII-168-2019) Terahertz time-domain spectroscopy and low-frequency Raman scattering of Alkali Borate Glass

T. Mori*[1]; Y. Iijima[1]; Y. Fujii[2]; S. Kitani[3]; A. Koreeda[2]; H. Kawaji[3]; S. Kojima[1]

1. University of Tsukuba, Division of Materials Science, Japan
2. Ritsumeikan University, Department of Physical Sciences, Japan
3. Tokyo Institute of Technology, Materials and Structures Laboratory, Japan

We performed terahertz time-domain and low-frequency Raman spectroscopies on lithium borate glasses to investigate the boson peak dynamics which universally appears in glassy materials. We discuss the lithium composition dependence of the boson peak frequency and relationship between the boson peak and first sharp diffraction peak of the lithium borate glasses.

11:40 AM

(ICG-SII-169-2019) Effect of heat treatment on the luminescent properties of optical glass fibers doped with bismuth

S. Firstov*[1]; A. Kharakhordin[1]; S. Alyshev[1]; K. Riumkin[1]; E. Firstova[1]; M. Melkumov[1]; V. Khopin[2]; A. Guryanov[2]; E. Dianov[1]

1. Fiber Optics Research Center, RAS, Russian Federation
2. Institute of Chemistry of High-Purity Substances, RAS, Russian Federation

Bismuth-doped glass fibers are very promising active media for optical devices (CW and pulse lasers, amplifiers etc.) which can operate in almost entire near IR spectral region starting from 1140 nm and ending at 1800 nm. This became possible due to unique chemical and thermodynamic features of bismuth resulting in the formation of specific active centers with various gain bands. The origin of the unusual properties of bismuth-doped materials which have drawn much attention is still under debate. Recently, it was found that a heat treatment of the high-germania-core glass fibers doped with bismuth can significantly affect the amount of the bismuth-related active centers and the non-active centers responsible for unsaturable losses. In this talk, we report experimental results regarding the effect of heating and cooling rates on the luminescent characteristics of the active fibers. Also, experiments on the isochronal and isothermal annealing of Bi-doped fibers have been

performed. The observed behaviors of the optical properties in bismuth-doped fibers subjected to heat treatments will be discussed. These experimental data can be a reliable foundation for better understanding the nature of the bismuth-related active centers. Funding. This work was supported by the Russian Foundation for Basic Research (Grant 18-32-20003)

Session 9: Glasses under the Indenter (TC 06)

Room: Arlington (mezzanine)
Session Chair: Lothar Wondraczek, University of Jena

8:10 AM

(ICG-SII-170-2019) Understanding the Deformation and Cracking Behavior of Glass under Indentation (Invited)

L. Huang*[1]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA

Indentation is often used to study the deformation and cracking behavior of glass. However, it is not easy to delineate the individual contribution of deformation modes (densification, shear flow and network structure changes) underneath an indenter due to experimental difficulties associated with in-situ investigations at a local scale (tens of microns) under non-uniform stresses. Given the stress field under an indenter is largely compressive, hydrostatic compression and decompression in a diamond anvil cell (DAC) was used in this work to help understand the response of glass to indentation during the loading and unloading process. To this end, an optical microscopy technique was developed to measure volume of glass under pressure in the DAC by using liquid argon as a pressure transmitting medium. This provided the densification and recovery of glass under hydrostatic compression and decompression. In-situ Brillouin light scattering experiments were carried out to measure the elastic response of glass to pressure. A few multicomponent glasses with vastly different indentation cracking behaviors were selected to study in this work. Our experiments revealed that glass networks with a high ability to undergo reversible structure changes in response to compression and decompression show a high cracking resistance under indentation, which was confirmed by our molecular dynamics simulations.

8:40 AM

(ICG-SII-171-2019) Indentation Fracture Toughness Measured with Diamond Tips of Various Sharpness

T. M. Gross*[1]; H. Liu[2]; Y. Zhai[3]; L. Huang[4]; J. Wu[1]; J. Luo[1]; B. Meenakshi Sundaram[1]

1. Corning Incorporated, USA
2. Penn State, USA
3. Carnegie Mellon, USA
4. Rensselaer Polytechnic Institute, USA

The Vickers indentation fracture toughness measurement is intended to be an easy technique that can be used to quickly determine the toughness values of glasses. However, it is often observed that this measurement technique does not provide reasonable values for intermediate to anomalous glass types, i.e. glasses that deform with a signficant densification component. In a $xCaO\text{-}xAl_2O_3\text{-}(100\text{-}2x)SiO_2$ glass family that deforms with a larger densification component as SiO_2 content is increased, it was observed that the trends in fracture toughness with SiO_2 content go in opposite directions when comparing Vickers indentation with chevron notch fracture toughness measurements. However, as we change the indenter tip to sharper angles and reduce the densification component for all glass types, we observe that the indentation and chevron notch methods trend in the same direction enabling the determination of the indentation toughness calibration constants for sharper tips. The new sharper indenter toughness measurement technique was further applied to a variety of commericial glasses to demonstrate its potential as a simple method to determine toughness of all glass types including normal, intermediate, and anomalous glasses.

9:00 AM

(ICG-SII-172-2019) Observation of Crack-Free Vickers Indents at 500 N in Annealed Caesium Aluminoborate Glass

K. Januchta*[1]; M. Stepniewska[1]; Y. Yue[1]; L. Jensen[2]; Y. Zhang[3]; S. Munch[3]; M. Somers[3]; M. M. Smedskjaer[1]

1. Aalborg University, Department of Chemistry and Bioscience, Denmark
2. Aalborg University, Department of Materials and Production, Denmark
3. Technical University of Denmark, Department of Mechanical Engineering, Denmark

Crack-resistant oxide glasses are increasingly important in modern day society due to the demand for materials that exhibit excellent mechanical performance, yet maintain transparency and acceptable chemical durability. This is currently achieved through post-processing, but such processes could cause undesirable side effects and/or additional cost. There is thus an interest in improving glass mechanics through composition optimization. In the search for crack-resistant glasses, i.e., glasses requiring high loads to initiate cracking during sharp contact loading, we have recently focused on aluminoborate glass compositions. Although this glass system suffers from poorer chemical durability and lower hardness compared to the industrially favored silicate-based compositions, their resistance to crack initiation is superior to that of the latter family. In this work, we present a caesium aluminoborate glass, which can withstand loads as high as ~500 N during Vickers indentation without forming any radial cracks. This exceeds the highest crack resistance previously reported for untreated, annealed oxide glasses by one order of magnitude. In addition, the created indents exhibit a time-dependent shrinkage, analogous to self-healing, which has never been reported to our knowledge. We discuss the origin of these observed behaviors in terms of a proposed molecular-scale deformation mechanism.

9:20 AM

(ICG-SII-173-2019) Relationship between mechanical properties and network structure of the aluminoborosilicate glasses of $20Na_2O–xB_2O_3–(20\text{-}x)Al_2O_3–60SiO_2$

T. Murata*[1]; Y. Kato[1]; S. Nakane[1]; H. Eckert[2]

1. Nippon Electric Glass Co., Ltd., Fundamental Technology Division, Japan
2. University of Sao Paulo, Brazil

Aluminoborosilicate glasses are widely used for a variety of glass products, and their mechanical properties are relevant in technological applications. As they contain multiple network former cations, their glass structure is interesting and related to their mechanical properties. In a previous study of borosilicate and aluminosilicate glasses, we observed that the coordination number of B or Al affects mechanical properties. In this study, the relationship between mechanical properties and network structure of a group of sodium aluminoborosilicate glasses ($20Na_2O–xB_2O_3–(20–x)Al_2O_3–60SiO_2$) were investigated. By increasing the B_2O_3 content, the four coordination unit BO_4 increased while the Q^n state of Si and the coordination number of Al remained constant measured by NMR. The Young's modulus, hardness and fracture toughness increased with increasing B_2O_3 content, which can be explained by the increased atomic packing density due to the increasing the amount of BO_4 units. The effect of B_2O_3 on the crack resistance of sodium aluminoborosilicate glasses will be compared with that of borosilicate glasses and discussed.

10:00 AM

(ICG-SII-174-2019) Crack Fraction and Indentation Fracture Threshold in Calcium-Aluminosilicate Glasses

H. Kuo*[1]; Y. Fu[1]; C. Cohen[1]; J. Loven[1]; N. T. Wiles[1]; S. P. Baker[1]

1. Cornell University, Materias Science and Engineering, USA

The indentation fracture threshold is an important concept in glass surface durability. Below this load, a pointed indenter pressed into a glass surface produces only plastic deformation; above it, cracks are formed which may later grow and cause failure. To quantify this, Vickers indentations are made at a given load. The number of

indentation corners at which radial cracks appear divided by the total number of corners is the crack fraction. The fracture threshold is defined as the load where the crack fraction is 50%. By making many indentations at each of a series of loads, good statistics can be obtained. We attempted to use this method to study tectosilicate calcium-aluminosilicate glasses with SiO_2 contents from 40 to 100%, but found that the results were influenced by cracks other than radial corner cracks as well as the time-dependence of crack formation. We developed methods to account for these phenomena and found that the crack resistance varies strongly with composition in this series. However, when the glasses were repolished, the results were completely different. Subsequent work has shown the crack fraction to be much more sensitive to surface preparation and surface conditions than to composition for these samples. The effects of roughness and environmental exposure on crack fraction will be discussed.

10:20 AM

(ICG-SII-175-2019) Mechanical properties of enamel and sintered silver deposited onto glass by nanoindentation methods

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1. Institute of Mineral Engineering - RWTH University, Germany

Bi_2O_3-B_2O_3-ZnO-SiO_2 enamel is used as a protective coating in various applications, such as glassware, automotive and architectural glass. For specific products, an additional sintered silver layer is required for the electrical functionalities. The main drawback of theses layers is their weakening effect on the mechanical strength of the complete system. Characterization of the mechanical behavior of the layers provides a deeper comprehension of the in-service failure mechanisms. In this work, the fracture toughness of the layers and glass has been investigated by nanoindentation using a corner cube tip. The layers present relatively high surface roughness compared to the indentation depths, therefore, the analysis is done onto polished cross section. The length of radial cracks are evaluated onto high resolution topography mapping images using the indentation tip, and by scanning electron microscopy (SEM). The model for determining the indentation fracture toughness requires the local elastic and plastic properties such as the young modulus and hardness. Silver and enamel layers have a multiphase microstructure, hence, the average value of E and H have been assessed by surface indentation mapping using a berkovich tip. Finally, correlation between the layers mechanical behavior, residual stress state and defect size enables to understand the in-service failure mode.

10:40 AM

(ICG-SII-176-2019) Mapping of the plastic zone under nanoindentation imprints: Toward a better ductile to brittle transition insight in oxide glasses

G. Trenvouez*[1]; K. Han[1]; M. Nivard[1]; V. Keryvin[2]; C. Bernard[2]; J. Guin[1]

1. Univ Rennes CNRS, Physics Institute Rennes, France
2. UBS Université Bretagne Sud - CNRS, IRDL, France

In order to study the regime of nanoindentation for which plasticity (shear flow and densification) is the only responsible for the creation of the residual imprint (i.e. no crack). We have developed a technique allowing for the 3-dimensional probing of the plastic zone, with a nanometer scale resolution underneath nanoindentation imprints. Nonetheless this regime is quite difficult to study experimentally as it requires the application of ultra-low indentation loads (below 50 mN) in order to minimize as much as possible the occurrence of cracks. This leads to a plastic zone size of the order of tens to hundreds of nanometers, which makes conventional methods such as Micro Raman or Brillouin Spectroscopies inappropriate to study this zone. The experimental approach is nonetheless necessary for the validation of the constitutive law implemented in numerical simulations. This method based on AFM and image 3D image treatment is sensitive to the structural modifications in the glassy network resulting from the densification and allows for the 3-dimensional reconstruction of the plastic domain. We will present the robustness of the developed method as well as experimental results such as the effect of load, loading rate. This method is also very promising for studying the first steps of crack nucleation under sharp contact.

11:00 AM

(ICG-SII-177-2019) In Situ X-ray Phase Contrast Imaging of Crack Evolution during Dynamic Indentation in Glass

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1. Johns Hopkins University, USA
2. Argonne National Laboratory, USA
3. Corning Incorporated, USA

Dynamic indentation of glass is believed to induce strain rate dependent crack initiation and propagation behaviors. Confirming and understanding such behaviors is important in many applications such as in developing multiscale fracture models and designing fracture-resistant glasses. However, cracks evolve over extremely small timescales, making it difficult to visualize their behavior in real-time. Therefore, we employ X-ray phase contrast imaging (XPCI) to observe in situ crack growth during indentation of chemically strengthened aluminosilicate, using the high brilliance synchrotron X-ray source at the Advanced Photon Source, Argonne National Laboratory, to provide sufficient contrast. Indentation is performed with a custom-built, piezo-driven Berkovich indenter that is capable of indentation velocities of 0.1~0.5 m/s. Initiation of a median crack is observed during loading, consistently across samples, at some distance below the surface. The crack is prone to initiate and propagate more easily under higher indentation velocity. This provides some of evidence the strain rate dependent behavior of cracks during dynamic indentation.

11:20 AM

(ICG-SII-178-2019) Experimental Investigation of the Indentation Size Effect

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2. University of California Los Angeles, Civil and Environmental Engineering, USA

Many glass compositions exhibit the so-called Indentation Size Effect (ISE), where the indentation hardness depends on the maximum vertical indentation force. In this study, we perform microindentation on Fused silica ($\nu = 0.16$) and Soda Lime ($\nu = 0.22$). Seven different peak loads were selected and the tests were run in force control. The indentation curves were analyzed with the Oliver and Pharr method to get the indentation hardness (H_{IT}). Yoshida's method, consisting of AFM and annealing techniques, was then used to determine the volume ratio of annealing recovery (V_R) and volume of plastic flow (V_P) for each maximum load. Initial results show that as the peak load was increased, V_R stayed approximately consistent while the V_P increased, suggesting that this is a mechanism that controls the ISE. This phenomenon was seen on both glasses. Additionally, the V_P of soda lime is greater than the V_P of fused silica when compared at the same max force, which is supported by the observations of Rouxel, the higher the Poisson's Ratio, the more plastic accumulation and the less effect of densification. Based on these results, we demonstrate that the ISE is governed by the extent of viscous shear flow occurring upon indentation. We propose that this effect arises from a shear-thinning behavior of the glass under high values of shear stress.

11:40 AM

(ICG-SII-179-2019) 3-D densification measurement of Vickers-indented glass using digital holographic tomography

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1. University of Wisconsin-Milwaukee, USA
2. Nippon Electric Glass, Japan
3. University of Shiga Prefecture, Japan
4. Rutgers University, USA

Although the strength of defect-free glass is surprisingly high, it can be significantly compromised due to surface damage. Indentation is often used to model the contact damage responsible for strength reduction in oxide glasses. Contact damage induces plastic shear flow and densification that result in crack-producing stresses. Measuring the interplay of the two under different loading conditions and material compositions provides fundamental insight into the process of crack nucleation as well as new strategies to strengthen a glass. In this work we study the densification of Vickers-indented glass using digital holographic tomography (DHT), which is direct, is sensitive, and can provide high spatial resolution. Previous works have used predominantly micro-Raman imaging which is not nearly as direct nor nearly as high resolution as the present technique and therefore must be done at a higher load usually where cracking has already occurred. Using the density maps for three types (silica, soda-lime, and aluminoborosilicate) of glass, we describe the current state-of-art, challenges and potential of DHT for glass research.

Session 9: Post-treatment Strengthening (TC 06)

Room: Arlington (mezzanine)

Session Chair: Morten Smedskjaer, Aalborg University

1:20 PM

(ICG-SII-180-2019) GPa-class yield stress of chemical strengthened soda-lime glass sheet prepared by multi-treatment of field-assisted ion-exchange method

T. Yano*[1]; S. Nagai[1]; N. Matsushita[1]; T. Kishi[1]

1. Tokyo Institute of Technology, Department of Materials Science and Engineering, Japan

Mechanical strength of glass products have continuously been gathering much attension in many application fields. In order to make glass tough to the external stress and impact, the formation of compressive stress layer in glass surface is knwon to be very effective to suppress the crack growth from surface. For the thin glass sheet, the chemical strengthening technologies using ion exchange have been developed and utilized widely. In this study, the electric-field assisted chemical strengthening is applied to obtain the soda-lime glass sheet with GPa-class yield stress for both sides. Our group has developed 3-step strengthning method to introduce potassium ions uniformly into two sides of surface. The obtained flat glass sheets with the shickness of 1.5 mm showed the yield stress about 1GPa and Weibull (shape) paramters k were ~20 for two sides. In this study, the stress profile of the chemically strengthened glass sheets are measured using the surface stress meter. From the analyses of the obtained stress profiles, the fracture toughness of the strengthened glass sheets is evaluated to understand the fracture behavior. Especially, the origin of high Weibull parameter of the obtained samples is discussed.

1:40 PM

(ICG-SII-181-2019) Explore the effect of stress on the anti-destruction strength of chemical strengthened glass

D. W. Hu*[1]; G. B. Tan[1]; A. W. Qin[1]; B. F. Chen[1]

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Chemical strengthened glass (CSG) has high anti-destruction strength due to surface compressive stress (CS) via ion exchange, but the central tension (CT) has a negative effect on the CSG strength. This paper introduced a tension release experiment, to study CT effect on CSG cracking, by the stress profile and the section state of the CSG through 'scattered light photoelastic' stress meter and optical microscope. The research shows, damaging-trail appears in the middle of the section of CSG and becomes dense with the increasing CT; the damaging-trail becomes wider and the damaging degree of CSG becomes more serious with the further increasing CT. 'Crack bifurcation' in CSG was studied, the relationship between crack bifurcation and stored CT energy was pointed out; when the CT exceeds a certain threshold, the damaging-trail eventually extends to the whole section, corresponding to the crack bifurcation, this process repeats and finally forms many small fragments. In this paper, different thick CSG was further studied, and the safety threshold of 'linear density of central tension' (LD_ct) was defined; the CSG presents stable and safe within the LD_ct threshold. Finally, this paper compared the LD_ct effect on anti-destruction strength of sodium-aluminosilicate and lithium-aluminosilicate CSG, the mechanism of CS and CT to increase the CSG anti-destruction strength was further analyzed.

2:00 PM

(ICG-SII-182-2019) Novel evaluation method of local stress in chemically strengthened glass by using micro-Raman spectroscopy

R. Sasaki[1]; N. Terakado*[1]; Y. Takahashi[1]; T. Fujiwara[1]; S. Orihara[2]; Y. Orihara[2]

1. Tohoku University, Japan
2. Orihara Industrial Co., Ltd, Japan

Recently, strengthening methods and applications in chemically strengthened glass have been diversified, and accordingly novel stress evaluation methods are strongly required. Therefore, we propose an all-optical method in which the micro-scale, local stress can be evaluated by using micro-Raman spectroscopy. Chemical strengthening in the glass can be explained by the stuffing effect, in which suppressed volume expansion dominates the compressive stress. Here, the suppressed volume expansion can be estimated from the ion exchange rate and structural relaxation rate and we show that these two parameters are introduced from three modes in micro-Raman spectra, i.e., A_1, D_2, and Boson peaks. Consequently, we succeeded to determine a depth dependence of the compressive stress and found that the value and the depth dependence are approximately equal to those measured by means of a commercial equipment based on photoelastic effect.

2:20 PM

(ICG-SII-183-2019) Boron effects on glass modulus and ionic inter-diffusivity of chemically strengthened glasses

J. Wu*[1]; C. Smith[1]; T. M. Gross[1]

1. Corning Incorporated, USA

Boron can exist as three- or four-coordinated state in glass, and the coordination can be affected by chemical composition. We designed an experiment with two series of glasses, one is $15Na_2O15Al_2O_3xB_2O_3(70\text{-}x)SiO_2$, where x=0, 5, 10 and 15 and all boron cations are three-coordinated, the second is $15Na_2O(15\text{-}x)Al_2O_3xB_2O_370SiO_2$, where x=0, 5, 10 and 15 and all boron cations are four-coordinated. Such coordination changes have different effects on Young's modulus; as x increases, Young's modulus decreases for the former, but it increases for the latter. Also in the former case, the density decreases as boron content is increased, but it increases in the latter. This result is consistent with a simple packing density approximation, i.e. the glass with higher density has higher Young's modulus. All glasses were ion-exchanged in a potassium salt bath at 380 °C. Both series of glass shows the K^+ inter-diffusivity decreases as the amount of boron is increased, and the oxygen number densities (the number of oxygen atoms in a unit volume) increase linearly with boron. The higher density of oxygen atoms may block the pathway for alkali inter-diffusion, which causes lower diffusivity. When the inter-diffusivity is plotted against oxygen number density, it decreases as an exponential function.

2:40 PM

(ICG-SII-184-2019) Strengthening of Soda Lime Glass by Ion Exchange Using Dual Salt Baths

I. Erdem*[1]; S. Aydin[1]

1. Istanbul Technical University, Metallurgical and Materials Engineering, Turkey

Chemical tempering is applied to achieve high mechanical performance in glasses that are used in applications requiring high strength. Conventionally it is realized with an ionic exchange process that takes place between the ions in the original glass surface and in the salt bath it is in contact with. Hardness, cracking behavior, strength and mechanical properties as such are improved by the compressive stress generated on glass surface through the incorporation of larger ions. There are different ion exchange methods and a variety of salt baths to incorporate these larger ions to generate compressive stress. One method is to use a combination of salts depending on the glass transition temperature of glasses and the melting temperature of the salts. In the present study, Corning® 2947 soda-lime glass slides were submitted to conventional ion exchange process using a dual salt bath containing KNO_3 . $RbNO_3$ in varying ratios. The process is applied under varying temperatures that are below the glass transition temperature and varying durations. Mechanical properties of the ion exchanged glasses were studied in terms of hardness and strength. Investigation of the concentration profile of ions incorporated into the ion exchanged glasses were performed by using energy dispersive X-ray spectroscopy (EDS).

3:00 PM

(ICG-SII-185-2019) The application of acoustic emission technique for detecting indentation crack formation in chemically strengthened glasses

E. D. Kaçar*[1]; L. Šimurka[1]; B. Ogut[1]; L. Václavek[2]; J. Tomáštík[2]; I. Sokmen[1]; R. Čtvrtlík[2]

1. Sisecam Science Technology and Design Center, Coating Technologies Directorate, Turkey
2. Palacky University and Institute of Physics Academy of Sciences of the Czech Republic, Joint Laboratory of Optics, Czechia

Usage of acoustic emission is one of the emerging techniques in glass research for the detection of sub-surface micro-cracks, which is impossible for any other conventional methods. In this research, indentation tests coupled with a novel ultra-high sensitivity acoustic emission method were applied onto chemically strengthened glass types. The effect of time and temperature on the efficiency of chemical tempering process were detected from the various stress profiles derived as the result of the experiments. In order to simulate different contact conditions, the indentation was performed with Berkovich, cube corner and spherical indenter types. Moreover, glass strain-rate sensitivity was explored by varying the length of indentation intervals. The signals were processed in time and frequency domain to identify different types of cracks. The experiments prove that as the time intervals get shorter during loading-creep-unloading state of indentation experiment while load is kept constant, the probability of visible crack formation increases. In addition, the type of indenter has also been shown to have an effect on the amount of acoustic emission signal received. In particular, the experiments show that acoustic emission gives an additional hint to understand the effect of sub-surface cracks on the failure mechanism of chemically strengthened glass.

3:40 PM

(ICG-SII-186-2019) Effects of Thermal Histories on Physical and Ion Exchange Properties of Glasses

L. Zhang*[1]

1. Corning Incorporated, Corning Glass Technology, USA

Some alkalie glasses can be chemically strengthened to develop a compressive stress (CS) on the glass surface. The CS can improve glass damage resistance. For the same glass composition, the manufacturing process or treatment, i.e. glass thermal histories can affect the magnitude and depth of the CS generated during ion exchange. In this study, some alkali containing glasses were studied for the impact of thermal history on glass physical properties and ion exchange related properties. Glasses were made through fusion draw process. Thermal treatments were done to rewrite some glass thermal histories. Glass density and refractive index change with process and glass thermal histories. With changing glass fictive temperature, stress relaxation behavior and ion exchange related properties change.

4:00 PM

(ICG-SII-187-2019) Numerical Simulation for Fracture of Thermally Tempered Glass Sheets by Dynamic Loading

S. Hirobe*[1]; Y. Kato[4]; K. Yoda[4]; K. Yanagihara[4]; Y. Kitajima[3]; S. Urata[2]; K. Oguni[1]

1. Keio University, Japan
2. AGC Inc., Innovative Technology Research Center, Japan
3. AGC Inc., Asia General Division, Automotive Company, Japan
4. AGC Inc., Production Technology Division, Japan

The residual stress field in thermally tempered glass sheets should be well controlled to avoid large sharp fragments from the point of user's safety. While the fracture pattern of thermally tempered glass sheets is strongly affected by the residual stress field and the elastic wave, the release process of the residual stress due to fracture and the effect of the interference of the elastic wave are still not clear. The aim of this research is therfore simulating the crack propagation process to understand the mechanism for the fracture of thermally tempered glass sheets. We propose an effective numerical analysis method for the dynamic fracture process in thermally tempered glass sheets by using Particle Discretization Scheme Finite Element Method (PDS-FEM). We perform the simulation for the fracture of thermally tempered glass sheets by dynamic loading. To ensure that our method properly captures the effect of the residual stress field on the fracture pattern, the simulations are performed on the thermally tempered glass sheets with two types of in-plane residual stress distribution: homogeneous and inhomogeneous distribution. The fracture pattern obtained from the simulations coincide with the experimental observations. This indicates that the proposed numerical analysis method has the ability to predict the dynamic fracture process of thermally tempered glass sheets.

4:20 PM

(ICG-SII-188-2019) Mechanical properties of metal-nanoparticle-implanted sodalime silicate glass

M. Ono*[1]; S. Miyasaka[1]; Y. Takato[1]; S. Urata[1]

1. AGC Inc., Research Center, Japan

A novel framework for toughening brittle oxide glass originated from enhanced ductility by implanting a soft secondary material is proposed. To do this experimentally, copper-metal nano-particles are implanted in the surface layer of commercial sodalime silicate glass by using the electrofloat method. Using a bath of molten tin with dissolved metal, on-line implantation of Copper is done in the surface layer with thickness of 300 μm. Fracture toughness of the Cu-implanted glass obviously improves while hardness decreases. The crack initiation load of the implanted glass is found to be compatible with the glass chemically strengthened in ordinary tempering conditions. The origin of the suppression in crack propagation and advantageous stress distribution are discussed based on experimental observation from cross-section, together with molecular dynamics calculations, and Peridynamic simulation.

4:40 PM

(ICG-SII-189-2019) Non-stoichiometric Annealing of CVD'ed ZnSe Transparent Ceramics for Hardness Improvement

C. Goncalves*[1]; X. Chen[1]; K. Richardson[1]; R. M. Gaume[1]

1. University of Central Florida, CREOL, USA

Zinc selenide (ZnSe) has long been recognized as an important infrared material for both passive and active optical components due in parts to its high transmission over a wide spectrum (0.2 - 14 μm), its good thermal stability, and the possibility to manufacture large optics using chemical vapor deposition (CVD). Various methods have been proposed to satisfy the demand for improved durability in harsh environments while maintaining good optical performance. This work reviews some of these approaches and investigates novel non-stoichiometric heat-treatments producing hardened solid-solutions or controlled precipitates in CVD-grown ZnSe ceramics. The experimental protocols and the mechanisms by which hardness increases are discussed and considerations for optimization and scale-up are proposed.

Session 9: Stress Fields (TC 06)

Room: Arlington (mezzanine)
Session Chair: Morten Smedskjaer, Aalborg University

5:00 PM

(ICG-SII-190-2019) Flow stress and the micromechanics of silicate glasses, 50 years after Marsh

E. Barthel*[1]; J. Teisseire[2]; V. Keryvin[3]; G. Kermouche[4]

1. CNRS/ESPCI, SIMM, France
2. Saint-Gobain Recherche, France
3. UBS, France
4. EMSE, France

The origin of the poor resistance of silicate glasses to surface damage has long been a matter of concern and potential strategies for improvement have motivated a lot of research. In the 60s, Marsh investigated the assumption that the mechanical resistance of silicate glasses is related to the flow stress, concluding that "flow stresses are likely to play an important role in fracture". Recently, through progress in micromechanic experiments, the plastic response of silicate glasses could be explored with an unprecedented level of details, so that realistic constitutive models can be proposed and constantly refined through new small scale experiments. In this contribution, we reevaluate Marsh's assumption and reformulate his viewpoint within this improved understanding. We compare the results with the known phenomenology of glass micromechanics: hardness, pile-up or sink-in and indentation crack patterns, and conclude on the significance of flow stress for a good understanding of damage mechanisms in silicate glasses.

5:20 PM

(ICG-SII-191-2019) Stress-Strain Field Dependencies in the Continuum Mechanics Response of Silicate Glasses to Sharp Indentation

B. C. Davis*[1]; I. Reimanis[1]; S. Glaesemann[2]

1. Colorado School of Mines, Metallurgical and Materials Engineering, USA
2. Corning Incorporated, USA

The stable crack systems observed at sharp indentation sites in silicate glasses are an area of considerable interest. These crack systems develop when a shear crack in the plastic-zone grows into the linear-elastic-zone in Mode I loading, making maximum principal stress a potential indicator of sharp indentation damage. In a sharp indentation event, there are numerous boundary conditions and material properties which can be considered input variables to the mechanical response of a silicate glass. In this research, an axisymmetric FEA model was used to perform an extensive sensitivity study with 10^2-10^3 unique solutions. In select cases, experimental indentation results were used to validate the FEA model. The results of this sensitivity study indicate specific input variable ranges which have significant effects on the maximum principal stress field, as well as the size and shape of the plastic-zone. In contrast, the results also indicate variable ranges which have surprisingly little effect on the stress-strain field response.

5:40 PM

(ICG-SII-192-2019) Residual Stress Measurements around Indentations in Sintered Soda-Lime and Borosilicate Glasses

A. Assmann[1]; C. E. Foerster[1]; F. C. Serbena*[1]

1. State University of Ponta Grossa, Brazil

In this work, the stress field around 10N Vickers indentations in sintered borosilicate (BS) and soda-lime (SL) glasses with 10 vol% Al_2O_3 were measured by fluorescence microscopy. Porosity, surface morphology and microstructure were characterized by optical and scanning electron microscopies. The probe response function was fitted to the fluorescence data taking into account the iteraction of the laser beam within the sample and effects of light absorption, refraction, scattering by alumina particles and pores and stresses gradients. The experimental fluorescence shift as a function of the distance from the indentations was compared with the models of Yoffe and using the PRF function. It was found the experimental blister field strength is a factor of 10 smaller then that predicted by Yoffe's model, event taking into account the densification of the glass underneath the indenter. Indentation residual stress were also measured for SL glass using the modified Zeng and Rowcliffe model. Stress profiles were measured around 50N and 100N Vickers indentations performed at temperatures from -196°C to 400°C. The blister field strength increased with temperature and could be explained by the variation of the E/H ratio with temperature. This work contributes for the understanding of the mechanisms responsible for the indentation residual stresses in glasses.

6:00 PM

(ICG-SII-193-2019) Interpreting Stress Fields and Plastic Deformation under Indentations in Vitreous Silica using Raman Spectroscopy

N. T. Wiles*[1]; G. G. Moore[2]; S. P. Baker[1]

1. Cornell University, Materials Science, USA
2. Corning Incorporated, Characterization Sciences, USA

Indentation methods using pointed indenters are often used to characterize the resistance of silicate glasses to plastic deformation (hardness). However, it is difficult to determine specific structure-properties relationships because (a) the stress field under such indentations is highly inhomogeneous, and (b) plastic deformation occurs by an unknown combination of shear and densification that depends on composition and stress state. Furthermore how deformation mechanisms change with strain is unknown. In this study, we attempted to determine how deformation mechanisms depend on strain (densification) by collecting Raman spectra from within Vickers indentations at a range of loads in vitreous SiO_2. The sampled volume for Raman spectroscopy was about 1 μm in diameter and indentation diagonals varied from 1 to more than 60 μm. By considering the sampled volume as a fraction of the expected stress distribution as a function of the indentation load, our analysis reveals that structural evolution with load is not linear, and that different structural changes gradually evolve simultaneously with deformation rather than one after another as suggested by other studies. These results reveal the sophisticated deformation response of the glass to indentation and shows that future work of this kind is necessary to understand how plastic deformation occurs under indentations.

Session 11: Thermal Properties of Glass I

Room: Clarendon (mezzanine)
Session Chairs: Limin Wang, Yanshan University; Frederic Affouard, University of Lille

8:00 AM

(ICG-SII-194-2019) Clarifying the glass transition through heat capacity of metal, nitrate salt and silicate glasses (Invited)

P. Wen*[1]

1. Institute of Physics, Chinese Academy of Sciences, China

Focusing on a fundamental issue, the glass transition, we have measured systematically excess heat capacity DC_P of supercooled liquid relative to glass around the glass transition temperature in a serial of glasses including metal, nitrate salt and silicate glasses. A universal model is proposed to explain the excess DC_P in all glasses considered here, in which the DC_P arises merely from translational motion with same nature of "random walk" in Einstein's liquid. The consistence between theoretical calculation and experimental data provides an opportunity to clarify the essence of the glass transition, i.e., the dynamic frozen of translational motions. The result might be meaningful not only to uncover a shady corner of the glass transition, but also to understand further the mysterious liquid state.

8:30 AM

(ICG-SII-195-2019) Multiple relaxations and their influences on magnetic properties of metallic glasses (Invited)

J. Wang*[1]

1. Ningbo Institute of Materials Technology of Engineering, Chinese Academy of Science, China

Isothermal annealing is a very useful strategy in modulating the properties and structures of metallic glasses, which has been regarded as a single relaxation progress. In this talk, I will introduce our recnet work on the enthalpy relaxation of Au- and Fe-based metallic glasses. An intriguing transition from β relaxation to α relaxation was confirmed during isothermal annealing. Energy landscape model is proposed to quantitatively explain how the relaxation modes transform. The magnetic properties are enhanced predominantly during β relaxation stage but don't change very much during a relaxation stage. The plasticity doesn't change very much during β relaxation stage but gets deteriorated during α relaxation stage. The micro-structural origin of the influence of β relaxation on magnetic properties is studied. These results propose an optimum thermal anneling protocol to fabricate metallic glasses with both excellent magnetic properties and mechanical properties.

9:00 AM

(ICG-SII-196-2019) The role of liquid–liquid transition in glass formation of CuZr alloys

L. Hu*[1]

1. Shandong University, China

Some glass-forming liquids have different liquid phases that have the same composition but different structure, density and entropy. Based on experimental and molecular dynamics simulation, we here report thermodynamic, dynamic, and structural evidence of the liquid–liquid transition (LLT) in ten Cu–Zr glass-forming liquids well above the liquidus temperature. We find that for Cu–Zr alloys, the LLT is beneficial to glass formation, and there is a close relationship between the relative transition strength (RTS) of the LLT and the critical thickness representing the glass forming ability (GFA): the bigger the value of the RTS parameters, the stronger the GFA of Cu–Zr alloys. This work not only uncovers the role of the LLT of melts in the glass formation of solids, but also sheds light on the inheritance of properties of glassy solids from the aspect of the detectable dynamics of high-temperature melts.

9:20 AM

(ICG-SII-197-2019) Anomaly on the relationship between coefficient of thermal expansion and cooling rate

S. Inaba*[1]; J. Endo[1]; K. Hayashi[1]

1. AGC Inc., Japan

Precise control of the coefficient of thermal expansion (CTE) of glass is important for semiconductor packaging applications. On the other hand, it is well known that glass structure is influenced by a cooling rate, resulting in the physical property changes. Here we investigated the cooling rate dependence of CTE between 50 and 200 °C of several alkali/alkaline earth aluminosilicate glasses, and revealed that the cooling rate dependence of CTE was closely related with glass composition: some glasses show positive relation between CTE and cooling rate and others show negative relation. The effect of cooling rate on CTE will be discussed from the viewpoint of the mixed effect of alkali and/or alkaline earth ions.

Session 11: Thermal Properties of Glass II

Room: Clarendon (mezzanine)
Session Chairs: Liming Wang, Yanshan University; Jakob König, Jozef Stefan Institute

10:00 AM

(ICG-SII-198-2019) Investigation from experiments and simulations of glasses obtained by different thermal/athermal routes: Are there true physical differences? (Invited)

F. Ngono Mebenga[1]; J. Willart[1]; G. Cuello[2]; M. Jimenez[2]; F. Affouard*[1]

1. University of Lille, Department of Physics, France
2. Institut Laue-Langevin, France

In practice, the glassy state can be actually reached by many different routes: i) the classical thermal route by cooling the liquid state sufficiently rapidly to avoid crystallization, ii) the mechanical route (milling) that consists in the progressive mechanical destruction of the crystalline order and iii) the concentration of a diluted liquid form such as encountered in the freeze-drying and the spray-drying processes. These different routes exhibit marked specificities and involved very different sources of physical stresses: "classical" such as temperature or pressure but also milling or fast/slow dehydration. Given the reported differences on the kinetic of recrystallization and also knowing the existence of polyAmorphism situations (water, selenium), it is legitimate to ask whether amorphous products produced by different techniques have discernible characteristics. In this work, disaccharide lactulose glasses obtained by four different amorphisation methods (milling, quenching of the melt, spray-drying and freeze-drying) have been investigated using a broad range of experimental (X-Ray, DSC, NMR, neutron scattering) and numerical (molecular dynamics) tools. Structural, dynamical, and thermodynamical properties have been obtained to clarify the impact of the amorphisation techniques on the nature of the glassy state.

10:30 AM

(ICG-SII-199-2019) Thermal conductivity of glass foams (Invited)

R. R. Petersen*[1]; J. König[3]; M. B. Ostergaard[2]; Y. Yue[2]

1. Skamol, Department of R&D, Denmark
2. Aalborg University, Dept. of Chemistry and Bioscience, Denmark
3. Jozef Stefan Institute, Advanced Materials Department, Slovenia

Glass foams are light weight cellular glasses with many applications in civil engineering and the petrochemical industry. A mix of properties such as low thermal conductivity, high strength and closed porous structure make the glass foam an attractive thermal insulating material. The thermal conductivity is a key parameter of glass foam performances since energy saving is increasingly important for our society and climate. Through the production process, glass

foams with controlled chemistry can be created, giving the possibility to understand the heat transport mechanism and, thereby, to optimise the production condition to lower the thermal conductivity. In this presentation, we review recent work on the thermal properties of glass foams, with focus on the heat transport through the glass foam. We demonstrate the importance and ways of controlling gas composition and glass chemistry in respect to foam structure, crystallinity and bulk conductance. Some design criteria for producing low conducting glass foam will be outlined.

11:00 AM

(ICG-SII-200-2019) Thermal behaviors in two-glass-transition miscible glass-formers: Experimental evidence of continuous mobility gradients

L. Wang*[1]

1. Yanshan University, China

Two glass-transitions have been observed in calorimetric measurements in some miscible molecular mixtures. Explanation of the phenomena has been puzzling with diverse structural models involving homogeneous mixing or phase separation. We performed calorimetric studies of the two glass-transition mixtures composed of tripropyl phosphate and polystyrene. Special inspection is taken to monitor the thermal behaviors in the regions between the two glass transitions. Two glass temperatures T_g are found to be composition dependent. Compared with glasses quenched at a higher rate, excess heat capacity is detected in the whole temperature range from low T_g to high T_g in glasses quenched at a slow cooling rate. Ageing between the two transitions generates endothermic peaks in reheating calorimetric measurements with the onset temperatures located invariantly ~4 K above the corresponding ageing temperatures. Thermal cycles around the endothermic peaks operated by the heating-cooling-reheating measurements can remove the ageing effect. The results unambiguously suggest the remarkable non-equilibrium and equilibrium behaviors are involved between two T_g's. Based on the results, continuous mobility gradients can be confirmed experimentally between the two glass-transitions, indicting a different case from phase separation.

11:20 AM

(ICG-SII-201-2019) Effects of pore structure and gas phase on thermal conductivity of glass foams

M. B. Ostergaard*[1]; R. R. Petersen[1]; J. König[2]; Y. Yue[1]

1. Aalborg University, Chemistry and Bioscience, Denmark
2. Jozef Stefan Institute, Slovenia

Glass foams are an interesting material with various applications such as lightweight filling in road embankments and insulation material. For thermal insulation, the thermal conductivity is a crucial property. In general, thermal conductivity decreases with decreasing density, thus a simple way to improve the insulation value is to decrease the density. However, at low density some characteristics such as the cellular structure and the gas composition become important. The pore structure is important, as the heat transfer through the solid phase around one big pore is faster than between many small pores due to the tortuosity factor. The influence of gas composition becomes more pronounced with decreasing density due to a higher relative contribution of gaseous conductivity to overall thermal conductivity. Therefore, it is essential to generate closed pores in order to entrap a low conducting gas, such as CO_2 rather than O_2. In this presentation, we illustrate and discuss the effect of the pore structure and the gas composition on the thermal conductivity of glass foams.

11:40 AM

(ICG-SII-202-2019) Porous Glass Insulator Properties Understanding through Microscopy Characterization and Machine Learning Image Segmentation

A. Stratulat*[1]

1. Carl Zeiss Microscopy, United Kingdom

The development of new advanced foam glass insulators for industrial applications (cavity walls, roofs, piping, etc.) relies on the understanding of the material structure (porosity), material properties (thermal conductivity) and process optimization. In order to solve some of the industrial challenges (achieve homogeneity of pore size distribution, minimize defects, lower thermal conductivity), advanced characterization techniques are required to better understand the performance of these materials. 3D X-Ray Microscopy (XRM) provides methods for imaging and analysis of ceramics such as porosity measurement throughout the volume of interest, identification and segmentation of different phases and non-destructive observations of internal defects, inclusions or voids. In addition, real 3D structures are generated that can be imported into simulation models to predict thermal properties. This presentation will overview the advantages of coupling XRM with simulations to better understand and improve the materials properties of foam glass insulators.

SIII: Glass Technology and Manufacturing

Session 1: Raw Materials, Batch Melting, and Fining (TC 18)

Room: Cambridge (4th floor)
Session Chairs: Mathieu Hubert, Corning Incorporated; Jaroslav Klouzek, University of Chemistry and Technology, Prague; Jennifer Rygel, Corning Incorporated

1:20 PM

(ICG-SIII-041-2019) Effect of Microstructure and Phase Distribution on Thermal Conductivity of Reacting Batch (Invited)

I. Peterson*[1]; J. Wright[1]; N. LeBlond[1]; E. Fairchild Law[2]; R. Iurilli[2]; E. Stapleton[3]; W. W. Johnson[4]

1. Corning Research and Development Corporation, Process Research, USA
2. Corning Research and Development Corporation, Manufacturing Technology and Engineering, USA
3. Corning Research and Development Corporation, Characterization Science and Services, USA
4. Corning Research and Development Corporation, Modeling and Simulation, USA

The thermal conductivity of reacting batch is important for heat transfer in both industrial melting and nuclear waste vitrification. Measurements of the high-temperature thermal conductivity are challenging for several reasons, including the behavior of the measurement systems at high temperature, and the evolving microstructure and phase distribution in the batch. This talk will review approaches from the literature on how to measure thermal conductivity and relate it to the microstructure, along with the results of recent experiments.

1:50 PM

(ICG-SIII-042-2019) X-ray imaging of High Temperature furnace applied to glass melting

D. Boloré[2]; F. Pigeonneau*[1]

1. Mines-Paristech, Centre for Material Forming, France
2. Saint-Gobain SEFPRO, USA

Melting of glass former liquid is done by heating at high temperature raw materials composed of carbonaceous components like Na_2CO_3, $CaCO_3$. To reduce the amount of CO_2 which produces a large quantity of bubbles dispersed in a high viscous liquid, the raw materials are

substituted by recycling glasses (cullet). Nevertheless, even with recycling glasses, a large population of bubbles is created. In order to study the first steps of the bubble creation, we develop an experimental tool to observe bubble creation and fluid motion. The experimental set-up is composed by a X-Ray source, a furnace in which a cylindrical crucible in alumina contains the recycling glass under granular powder. By increasing the temperature up to 1100°C, the glass reaches the glass transition and becomes liquid. A large amount of bubbles are produced by mainly two effects: i) collapse of granular media leading to a bubble size close to the initial size of the glass powder, ii) heterogeneous nucleation of bubbles at the contact of the crucible producing bubbles during over a large time range. Bubble size distributions have been determined for three initial glass powder sizes. To study the bubble and liquid motion, an optical flow technique has been used to observe the liquid motion. Liquid motion exhibits a complex structure due to the momentum transfer between the two phases.

2:10 PM

(ICG-SIII-043-2019) Rheological characterization of calcium- and iron-rich silicate slags during solidification

C. Giehl*[1]; M. Kleindienst[1]; P. Quirmbach[2]; H. Koerber[2]; Y. Hemberger[2]

1. Anton Paar, Rheometry, Austria
2. DIFK Deutsches Institut für Feuerfest und Keramik GmbH, Germany

High temperature rheometry is a sensitive technique to monitor changes in visco-elasticity of molten materials like slags, silicate and metal melts. These may involve subliquidus formation of crystals, crystal ripening, degassing, redox and contamination processes. Concentric cylinder rheometry is a means to discriminate viscous and elastic components of the visco-elastic behaviour in a partially molten systems. Multicomponent silicate melts are, in contrast to e.g. single oxide melts or pure metals, usually characterized by a crystallization temperature interval, within which the system can be termed a suspension. Here, we present rotational and oscillatory concentric cylinder measurements on a calcium- and iron-rich silicate slag with shear-rate dependent behaviour at different super-liquidus to sub-liquidus temperatures. Shear-thinning becomes more pronounced with decreasing temperatures, likely as a result of the increasing solid fraction. Slag viscosity is known to exert controls on exchange reaction rates with coexisting e.g. steel melts during refining and has also been suspected to influence the composition of inclusions in the steel melt.

2:30 PM

(ICG-SIII-044-2019) Modeling of batch-to-glass conversion – State of the art and beyond? (Invited)

R. Pokorny*[1]; P. Hrma[2]; S. Lee[2]; J. Klouzek[1]; M. J. Schweiger[2]; A. Abboud[3]; D. P. Guillen[3]; A. A. Kruger[4]

1. University of Chemistry and Technology Prague, Czechia
2. Pacific Northwest National Lab, USA
3. Idaho National Lab, USA
4. U.S. Department of Energy, Office of River Protection, USA

Without an exact model of the cold cap, where the batch-to-glass conversion takes place in Joule-heated electric melters, it is impossible to reliably predict the melting rate and the melter performance. Regrettably, "the batch melting subdomain still represents a weak part in the glass furnace modeling and optimization effort" (Choudhary). Why is it so? Why we can easily simulate and predict the apparently analogous melting of an ice sheet floating on a surface of hot water, while simulating melting of a batch sheet on a surface of molten glass seems to be so challenging? The reason is of course the complex phenomena that take place at the interface, and specifically, the lack of their complete understanding. Such phenomena include the dissolution of solid particles and the growth, coalescence, and collapse of bubbles coming from the batch and melt, as well as the motion of large bubbles (cavities) emerging from collapsing foam. This contribution will review the current state-of-the-art of mathematical modeling of glass batch melting and ponder the outstanding milestones on our way to a physicochemical model.

3:00 PM

(ICG-SIII-045-2019) Physico-chemistry and mineralogy of the Mayo Tsanaga sand (Maroua, Cameroon): Potentialities in the glass and ceramics industry

E. Yanné*[1]

1. National Advanced School of Engineering of Maroua, Cameroon

In order to promote the local materials, we have characterized the sand of Mayo Tsanaga taken on his bed of Makabaye in Maroua. For this, X-ray diffraction, X-ray fluorescence, scanning electron microscopy, particle size, bulk density and melting temperature were used. The modulus of fineness measured is 2. The coupling chemical and mineralogical analysis allowed an average quantification: quartz (79.32%), albite (12.01%) anorthite (5.20%) and sanidine (3.17%). The melting temperature is obtained at 1568 °C. and the apparent density is 1400 kg/m^3. Sand, highly rich in quartz, can be valorized in the manufacture of the silica glass and enter in the composition of the silico soda-lime glass. The ceramic industry could consume this sand especially for the production of porcelain which requires raw materials free of coloring oxides. The absence of coloring oxides and the value of the fineness module eliminate systematically magnetic purification and grinding operations in industry. This sand of a large deposit, hitherto unexploited, has a mineralogical and chemical composition close to a vitrifiable mixture. It is therefore an ideal raw material for the glass and ceramic industry.

3:40 PM

(ICG-SIII-046-2019) Expected energy saving of float furnaces by briquette/cullet preheating (Invited)

T. Maehara*[1]; Y. Doi[1]; T. Enomoto[1]; A. Lankhorst[2]

1. AGC Inc., Production Technology Division, Japan
2. CelSian Glass & Solar B.V., Netherlands

Batch/cullet preheating by waste heat from the flue gas is one of the solutions to reduce the energy consumption of a glass melting furnace. Considering its application for float glass furnaces however, several challenges are still remaining. For instance dust and carry-over issues due to a high batch ratio and the relatively high investment cost. One of the solutions for these issues is the application of glass-batch-briquettes as a waste heat recovery medium. A mixture of briquettes and cullet can be preheated up to 500°C by direct heat exchange without dust and clogging issues. About 1GJ/t of energy saving was expected, even without taking further benefits into account due to improved melting kinetics. The loading of hot briquettes into the furnace will cause a large improvement of the batch to melt conversion speed due to its lower tangible heat and higher thermal conductivity. Laboratory experiments have quantified these effects and the results suggested the possibility of pull increase. By applying CFD modelling to a 500t/d float furnace, the total benefit of the briquette/cullet preheating has been determined.

4:10 PM

(ICG-SIII-047-2019) Briquetting of waste glass cullet fine particles for energy saving manufacture and improved melting behavior

W. Deng*[1]; R. Wright[2]; C. Boden-Hook[2]; P. A. Bingham[1]

1. Sheffield Hallam University, United Kingdom
2. Wright Engineering Ltd, United Kingdom

Fine particles of glass cullet arising during glass recycling cannot presently be recycled into glass manufacture, due to the potential for foaming issues during re-melting. Consolidation of glass fines into briquettes could enable their reintroduction into furnaces, reducing waste and glass melting energies. Properties of briquetted cullet fines and their melting behavior in SLS glass batches are presented. Briquette mass and mechanical properties were analyzed. With slight modifications to maintain the same final glass composition, up to 15 wt% briquettes were successfully added to a representative container glass batch and melted. Results confirm that briquette

additions can provide equivalent final glass, supporting their industrial uptake. The decomposition kinetics of batches, representing typical container glass batches up to 15% briquette additions, were calculated using the Ginstling Brounstein and Arrhenius equations. The briquette additions accelerated the decomposition reactions and silicate reaction kinetics by decreasing the activation energy for carbonate decomposition. Silica sand was shown to melt at lower temperatures with the briquette addition. The positive effects of briquette additions to SLS glass batches are demonstrated by this study.

4:30 PM

(ICG-SIII-048-2019) Batch, glass melt, melt flow and their mutual relationship

M. Jebava*[1]; L. Nemec[1]; J. Brada[2]

1. Laboratory of Inorganic Materials, joint workplace of the University of Chemistry and Technology Prague and the Institute of Rock Structure and Mechanics of the ASCR, Czechia
2. Glass Service, Inc., Czechia

Batch-to-glass conversion needs its time and energy, and homogenization processes occurring in the melt (bubble removal, sand dissolution) also needs specific conditions to be accomplished – these are following phenomena. From the point of view of the energy we know that the batch-to-glass conversion and heating of primary melt consumes most of total energy (up to 95%); then we also have to compensate structural heat losses. So, by proper energy distribution in the space we can partially control a melt flow character and thus achieve higher space utilization and higher melting performance. Melting performance can be increased so far that the homogenization process related to glass quality – bubble removal, sand dissolution – is no more the limiting part of melting process but batch-to-glass conversion starts to be the limiting one. The change of character of the melt flow also changes a way of heat transport to the batch from beneath – from mostly convective heat transport given by strong melt circulation to the combination of convective and radiative one supported by a presence of heating electrodes underneath the batch. All mentioned effects on melt flow character and melting performance were modelled mathematically; electric boosting was used as a tool for various energy distribution in the melting furnace.

4:50 PM

(ICG-SIII-049-2019) Residence time distribution analysis of a container glass furnace

S. Ceola*[1]; E. Alejandro[2]

1. Stazione Sperimentale del Vetro, Research and Development, Italy
2. Vidrala S.A., Glass Technology Manager, Spain

In glass container production there are context or problems that, for their interpretation, require a knowledge of the real situation of the glass flows in the furnace, as presence of stones and undissoved silica, or strategy for an effcient color change. The study of flow regime in glass furnace is then of paramount importance. One of the few experimental fluid-dynamic observable is the Residence time distribution (RTD) curve. This curve tells when and how glass comes out from the furnace, and the analysis of its shape could give insight on the actual mixing regime of the furnace. After elaboration of the RTD, several experimental fluid-dynamic parameters are accessible, as the characteristic mixing time of the furnace, the show-up time and the time at which the variation after a color change step is maximum. In this paper the experimental strategy for the determination of the RTD is described. The case presented is a furnace for container glass with two doghouses and two canals (Vidrala Corsico plant, Italy), where two differentracer have been used at the same time. The RTD curves obtained are interpreted and elaborated to analyze the flow regime, and the distribution of the tracers from the two doghouses over the canals. Eventually, different possible applications of the RTD analysis will be explained.

5:10 PM

(ICG-SIII-050-2019) Insight into nuclear glass synthesis: Experimental and modelling approach (Invited)

S. Schuller*[1]; E. Sauvage[1]; S. Hocine[1]; K. Paraiso[1]; T. Charpentier[2]; A. Mesbah[3]; M. Toplis[4]

1. CEA, DEN/DE2D/SEVT Marcoule, France
2. NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, France
3. ICSM, UMR 5257 CEA/CNRS/ENSCM/ Université de Montpellier, Site de Marcoule, France
4. Institut de Recherche d'Astrophysique et Planétologie, Université de Toulouse, Centre National de la Recherche Scientifique (CNRS), Université Paul Sabatier, France

Basic research dedicated to the nuclear glass synthesis supported by a modelling approach, is conducted from laboratory-scale and mock-up, to full-scale non-radioactive facilities in the French Nuclear Energy Division (CEA Marcoule). The glass melt and the vitreous material obtained after cooling are produced by a succession of physical and chemical interactions between a solid waste (calcine) and a alumino-borosilicate glass precursor (glass frit) through a high-temperature vitrification process under optimal parameters (temperature, stirring, feeding rate). From macroscopic to an atomic scale, mechanisms are studied to determine the thermo-activated reactions and the key parameters (kinetic and thermodynamic) responsible for the formation, dissolution of precursors and homogenization of the glass melt. This talk will be focus on academic research conducted to characterize and to model the vitrification process. Experimental results (XRD, SEM, microprobe, DTA/TGA, MAS NMR) and thermal, chemical (0D) models generalized to thermo-hydraulic simulations (3D) will be presented. These simulations can be valuable tools to give furnace capacities and to better determine how and where the precursor's transformation (due to diffusion, advection, viscosity, thermal transfer) into glass occurs in the vitrification furnaces. This work is support by CEA, ORANO and EDF.

5:40 PM

(ICG-SIII-051-2019) Effect of sucrose on foaming and melting behavior for low-activity waste melter feed

S. Lee*[1]; C. Appel[1]; N. Jani[1]; D. Dixon[1]; P. Hrma[1]; J. Klouzek[2]; R. Pokorny[2]; M. J. Schweiger[1]; A. A. Kruger[3]

1. Pacific Northwest National Lab, USA
2. University of Chemistry and Technology Prague, Czechia
3. U.S. Department of Energy, Office of River Protection, USA

Nuclear waste is mixed with glass-forming and -modifying additives in a slurry form, charged into an electric melter, and converted to glass for vitrification. During feed-to-glass conversion, chemical reactions and physical transitions occur in a cold cap which is a reaction layer floating on the molten glass. A considerable amount of gases evolves and some residual gases develop foam in the cold cap. Sucrose is used as a reducing and anti-foaming agent. To investigate sucrose effect on foaming and melting behavior during feed-to-glass conversion, various amounts of sucrose were added to a simulated low-activity waste melter feed at carbon to nitrogen (C/N) mole fraction ratios of 0.05, 0.55, 0.74, 1.02, 1.12, and 1.42. The feed volume expansion test showed that foaming was suppressed as the C/N ratio increased. Sucrose reacted mostly with nitrate and nitrite, not with other chemicals in the feed. By evolved gas analysis, NO and O_2 gas evolution decreased while, CO_2 and N_2 gas evolution increased. Interestingly, high sucrose addition induced feed bloating at low temperatures.

6:00 PM

(ICG-SIII-052-2019) Foam under cold cap

P. Hrma*[1]; S. Lee[1]; J. Klouzek[3]; R. Pokorny[3]; A. A. Kruger[2]

1. Pacific Northwest National Laboratory, USA
2. DOE Office of River Protection, USA
3. University of Chemistry and Technology, Czechia

Conversion of glass batch (melter feed) to glass melt occurs in the cold cap (batch blanket) that floats on the melt pool. In the final stage of conversion, the batch turns to foam that eventually collapses releasing gas to the atmosphere (on the top surface of the batch pile) or into the glass melt below (at the batch-melt interface). In either way, the heat for the conversion process is transferred through the foam layer. An intricate relationship exists between the foaming response and the heat delivered to the cold cap that determines the rate of melting. While the foam layer thickness is influenced by the heat flowing through it, the temperature at which foam collapses influences the heat flow received. This has been demonstrated for electric melters, where virtually all melting heat flows through the foam layer at the cold-cap bottom. Even for this simpler situation, foam behavior cannot be monitored "in situ," i.e., directly, in glass melters, but was observed and investigated on laboratory samples of several melter feeds (formulated for nuclear waste vitrification) known to exhibit a broad range of melting rates under identical melter operating conditions. This allowed us to assess the foam layer thickness, foam (cold cap) bottom (the melt/cold-cap interface) temperature, and even the rate of melting.

Session 5: Towards Carbon-free Glass Production

Room: Tremont (4th floor)

Session Chairs: AJ Faber, CelSian Glass & Solar; Oscar Verheijen, CelSian Glass & Solar

1:20 PM

(ICG-SIII-053-2019) The Challenges and Potential Opportunities of Glass Manufacturing Operations Toward Carbon Neutrality

S. Bhaduri*[1]

1. Owens Illinois, Inc., USA

During the last couple of years, it has become evident that there has been a surge in global manufacturing businesses embracing climate science by reducing carbon emission. Even though glass is considered as a preferred packaging material, glass manufacturing process involves considerable energy consumption. Carbon dioxide (CO_2) emission, one of the major contributors to global warming is a significant component of waste gas in the glass manufacturing process. Realizing this objective, most glass companies are creating their own strategies, trying to ramp up the technologies to overcome this challenge. In this presentation, a state-of-the-art of various decarbonization strategies in the glass manufacturing process will be elaborated. Unfortunately, there is no silver bullet solution for this problem because each strategy has its own challenges. To overcome these challenges, a concerted plan must be in place involving a holistic approach starting-off with evaluating the entire environmental footprint throughout the whole value chain and imposing an integrated approach in the entire operation. Finally, to be a pioneer in this effort in overcoming this challenge, a cross-disciplinary approach is needed involving glass manufacturers, major gas suppliers, renewable energy developers, electric and hybrid furnace manufacturers, etc.

1:40 PM

(ICG-SIII-054-2019) The Transition of the Chinese Glass Industry toward Zero Emission (Invited)

S. Peng*[1]

1. China Triumph International Engineering Co., Ltd, China

The paper introduces the basic status quo of the Chinese glass industry. Under the guidance of global low carbon concept and the green development policy of the Chinese government, the Chinese glass industry independently developed the core technology of zero emission, setting up the zero emission standards of the Chinese glass industry, which gradually propelled the transition of the Chinese glass industry toward zero emission. In the future, the Chinese glass industry will strengthen the international technical cooperation and make contributions to the energy saving and emission reduction of the world.

2:10 PM

(ICG-SIII-055-2019) Sustainable glass furnace technologies

A. Faber*[1]

1. CelSian Glass & Solar, Netherlands

An update will be given of a previous review on CO_2-neutral glass melting technologies, at ICG2018. Specific attention will be paid to the main technological bottlenecks for the energy transition in the glass manufacturing industry. Next to this, new low-carbon heating technologies which are developed in other high temperature industrial processes, particularly in the steel industry, are addressed.

2:30 PM

(ICG-SIII-056-2019) Research projects concerning glass within the Kopernikus initiative in Germany (support code: Federal Ministry of Education and Research 03SFK3M0)

B. A. Fleischmann*[1]

1. Huettentechnische Vereinigung der Deutschen Glasindustrie e.V. (HVG), Glass Technology, Germany

To decrease the CO2 emissions significantly when producing glass, different technologies are up for discussion. Currently HVG works mainly on two aspects: flexibility potential of the process chain for glass production with reference to the unsteady availability of renewable electric power what are the technical needs and what are the expenditures to create a CO2 circular flow around a glass melting furnace with durable fuels and what to do, to be more insensitive compared to fluctuating renewable energy sources. Both projects will be described. While the project to determinate the flexibility regarding the fluctuating electric power is more or less completed and results are shown, the work concerning the CO2 cycle will start soon and the concept is introduced in its principal technical details.

2:50 PM

(ICG-SIII-057-2019) Heat Oxy-combustion, for a clear efficiency

L. Jarry*[1]; C. McCrea[2]; T. Kang[3]

1. AIR LIQUIDE, GLASS AND METAL, China
2. AIRGAS, USA
3. D.I.C, R&D, USA

This paper will introduce the latest achievements of Heat Oxy-combustion in terms of hight thermal performance for energy saving and also Air Liquide/AIRGAS new development for oxy-combustion based glass melting furnaces. Carbon-Free Glass production for fossil fuel-based industries has proven to be challenging. Although there are alternative energy sources or innovation-based solutions available, there is no single solution fit for all as each of them carries advantages and at the same time downsides. Fuel saving through melting efficiency gain can be achieved in various methods such as waste heat recovery, hydrogen combustion, and electrical melting. Heat Oxy-Combustion is one of such technologies based on oxy-combustion. Unlike conventional oxy-fuel

technologies, which do not take advantage of the waste energy from combustion fumes, Heat Oxy-Combustion recovers a significant portion of the heat, that is otherwise lost through flue gases, by indirectly preheating fuel and oxygen. This Heat Oxy-Combustion has been rapidly improved so that fuel savings can be achieved from 10 to 15 % compared to traditionnal Oxy-combustion and its competitive equipment cost makes ROI even more favorable. Through perfecting oxy-combustion processes and e-services, Air Liquide innovations lead to game-changing ways to increase efficiency.

3:10 PM

(ICG-SIII-058-2019) Upgrading of Existing Emission Control Equipment by Thoughtful Integration of State-of-the-Art Technology

M. Schroeter*[1]

1. Durr Systems Inc, USA

Many glass furnaces historically have been equipped with emission control systems compliant with environmental legislation for particulate matter, SO_2, HCl, HF and NOx at the time of their installation. With changing legislation or site emission conditions, existing equipment might no longer be able to meet design performance. While state-of-the-art technology, like Dürr's Multi-pollutant Ecopure® Catalytic Candle Filtration (CCF) system, easily achieves emission standards of tomorrow, the presentation shows ways of holistic integration of state-of-the-art technology with existing emission control equipment in order to save capital expenditures. The presentation will explain the basics of Dürr's state-of-the-art Multi-pollutant Ecopure® Catalytic Candle Filtration (CCF) technology. With reference to example cases the presenters will show the principle of holistic integration of Dürr's Multi-pollutant Ecopure® Catalytic Candle Filtration (CCF) technology with existing emission control equipment and qualitatively refer to performance improvements of the complete system. Additionally, the paper will present, how foresighted engineering can even form the basis for compliance with more stringent future emission standards.

3:45 PM

(ICG-SIII-059-2019) An all-encompassing and radical view on a carbon-free glass production

C. Roos*[1]

1. RWTH Aachen University, Glass, Germany

The glass industry faces fundamental challenges with actual CO2 regulations. Most actions focus on reducing the CO2 emission in fossil firing. And many efforts are done in overcoming the issues of all-electric melting which is commonly seen as the future melting technique for mass-glasses. Nevertheless it seems to be of lesser interest to tackle the CO2 emissions that are coming from the batch itself. A simple calculation shows that at a cullet ratio of 50% about 25% of total CO2 is coming from the batch and hence dissociation of the carbonate-based raw materials. This clearly shows that also the batch itself should be included in a total CO2-emission reduction concept. Pros and cons of different approaches to such an all-encompassing concept will be discussed.

4:05 PM

(ICG-SIII-060-2019) Calcination of soda-lime glass batch briquettes

Y. Doi*[1]; T. Maehara[1]; T. Yano[2]

1. AGC Inc., Japan
2. Tokyo Institute of Technology, Japan

Fining of bubbles in molten glass is one of the most important issues for the efficiency of glass manufacturing process. The initial melt just after the batch to melt conversion contains a plenty of CO_2 bubbles and become oversaturated with CO_2. The origin of CO_2 are both carbonates in the glass batch and the combustion air. Therefore, "melting of CO_2-free glass batches in the CO_2-free atmosphere" would be effective to reduce not only bubbles in the initial melt but also the required time/temperature for the fining process. As previously reported, we can obtain the CO_2-free soda-lime glass batch by heat treatment (calcination) of glass batch briquettes at 900°C for several hours. Combination of calcined briquette and cold-top melting made it possible to test the idea of CO_2-free batch to melt conversion process. When we fed fully calcined briquettes into the laboratory scale continuous cold-top furnace, the bubble density of the obtained glass was 1,000 times lower than that of the glass from normal briquettes without calcination. Here, we investigated the influence of degree of calcination for briquettes on bubble density in cold-top melting system. The degree of calcination were adjusted by changing heat treatment condition of briquettes. The dependency of the CO_2 bubble density on the degree of calcination will be discussed from the quantitative analysis results of the dissolved CO_2 amount in glass samples.

4:25 PM

(ICG-SIII-061-2019) How glass minerals can contribute to glass manufacturing with a low carbon footprint

H. van Limpt*[1]; R. Dorscheidt[1]; B. Wilms[1]; A. Petitjean[1]

1. Sibelco, T&I, Belgium

In the near future the glass industry is facing a main challenge: SUSTAINABLE PRODUCTION with a low carbon footprint. Glass manufacturers will use alternative furnace concepts and more secondary, recycled materials. Glass furnaces using traditional fuels (natural gas, oil) will be replaced by full electric furnaces and/or hybrid furnaces using electricity and alternative fuels like hydrogen and bio fuels. The melting behavior of minerals and cullet in these types of furnaces might be completely different. Next to this, there will be a great social pressure to switch to secondary materials and legislation will be in place to achieve these goals. The pressure to minimize waste and losses will increase. To anticipate on these developments Sibelco launched a research program in which alternative and optimized materials and solutions are developed for future glass production. In the framework of this program Sibelco develops new models and methods to evaluate the melting behavior of glass batches varying from laboratory tests to thermodynamic models. New materials reducing the reject levels and increase the production efficiency of the glass production process are developed. Alternative secondary materials are processed into new, consistent glass minerals with a low carbon footprint and ultra-pure minerals enabling the production of new sustainable glass products are evaluated.

4:45 PM

(ICG-SIII-062-2019) New Raw Materials for Use in Glass Production

D. Backhouse*[1]; W. Deng[1]; C. Spathi[1]; M. Marshall[2]; R. Ireson[2]; P. A. Bingham[1]

1. Sheffield Hallam University, Materials and Engineering Research Institute, United Kingdom
2. Glass Technology Services Ltd (GTS), United Kingdom

The industrial manufacture of glass products is both an energy-intensive (6500 GWh a^{-1} in the UK for furnaces alone) and CO_2-generating (2.2 MT a^{-1} in the UK) process[1]. As public awareness of climate change has increased, so has the drive towards greater energy efficiency and lower CO_2 release. To this end, the use of ashes from biomass power plants as a raw material for glass production was investigated. These ashes were found to be particularly rich in K and Ca, whilst being low in carbonate content compared to conventional raw materials such as soda ash (Na_2CO_3) and limestone ($CaCO_3$). In addition to the benefit of reduced CO_2 content, the partial replacement of Na_2O with K_2O invokes the mixed-alkali effect, reducing the melting temperature. Float and clear container (flint) glass samples with biomass ash in replacement for soda ash and limestone were produced and analysed by XRD, FT-IR spectroscopy, UV-Visible

spectroscopy, DTA-TGA and SEM-EDS. They were then compared to benchmark float and flint glass samples. We present data from this investigation, highlighting the feasibility of biomass ashes as raw materials for glass production, and outline the proposed future development. 1. 'Industrial Decarbonisation & Energy Efficiency Roadmaps to 2050: Glass', Report to Department of Energy and Climate Change and the Department for Business, Innovation and Skills, March 2015.

5:05 PM

(ICG-SIII-063-2019) All-Electric Melting: Recent Developments (and improved understanding)

A. Reynolds*[1]

1. Fives Stein Limited, United Kingdom

This paper relates to all-electric melting technology (via direct resistive heating) which today gives a viable energy-efficient solution to glass melting without producing CO_2 (from combustion). The high cost of electricity has tended to limit electric furnaces to applications where specific compositions favour the use of cold-top furnaces and these in general are of relatively small capacities compared to those required for commodity glasses (container and float). Application of the technology into the container sector has been hampered by the conservative nature of the industry, understandable acknowledging some well-publicised failures, and misperceptions that electric furnaces inevitably have high capex and opex, short lives and are difficult to operative. This presentation aims to give background into why all-electric melting has a part to play in the future of Glass Melting; we will review advantages and limitations, with a view to dispel myths surrounding the technology. An overview will be provided of the current technologies offered by Fives including the latest 'state-of-the art' units operating now in Europe. Finally, we introduce how Fives is supporting the container sector in investigations of electric melting; how to identify and control the risks of designing and operating large scale units (200 - 400+ TPD). We will look at elements such as output flexibility, redox control and furnace life.

5:25 PM

(ICG-SIII-064-2019) Electric Melt Furnaces

E. W. Ferreira*[1]

1. TECO, USA

The current solution to reduce the carbon footprint of industrial scale glass production lies in minimizing fossil fuel combustion. This is achieved by improving efficiencies within the melting / combustion systems. Another method is replacing fuel firing with electric boosting (heating the melt with electrical energy), typically up to 15% to 25%. The future sees electric boosting increasing significantly. Fully electrical glass furnaces do currently exist. It would be prudent to understand how these furnaces function; learn from their limitations and to engineer solutions that are scalable to applications that traditionally do not use electricity. TECO has a production proven full electric melt furnace called the TECO Double Square Cold Top Electric Melter. This paper highlights the benefits of using this TECO technology through the use of CFD modeling.

5:45 PM

(ICG-SIII-065-2019) A commercial and technical feasible future for all-electric commodity glass manufacturing

R. Meuleman*[1]

1. Eurotherm by Schneider-Electric, Global Business Development, Netherlands

The lecture will try to cover the todays' technology of innovative power supply systems that we made available to the furnace designers. Today's electrical furnace boosting power supplies need to become energy efficient, highly flexible, real-time controllable, process intelligent, molybdenum and tin-oxide friendly, achievable and standardized. Old fashioned oil filled stepped and variable transformers don't meet does requirements anymore and therefore we have designed solid state based power supplies that meet the requirements of new all-electric furnace designs. The lecture will cover an energy efficiency comparison in between fossil fuel fired and all-electric furnaces and will also cover the three different aspects of CO_2 emissions by having a look at the whole food and beverage supply chain and the impact glass, as a preferred packaging material, has on it. It intends to stimulate glass manufactures, their customers and their suppliers to re-thing their todays melting technology and start to consider "all-electric" melting in near future.

6:05 PM

(ICG-SIII-066-2019) CO_2 reduction on large furnaces (> than 400 tons/day) with superboosting and hybrid all-electric furnaces: An update on current experience and the future

S. C. Hakes*[1]

1. F.I.C. (UK) Ltd, United Kingdom

This paper will examine how the use of electrical energy (if from renewables) through molybdenum electrode boost systems can dramatically reduce the amount of carbon dioxide produced during glass melting process. The paper will look at the experience of 6MW boost installations and proposals for large electric furnaces (300 to 1,000 tons plus) in carbon reduction. It will examine potential pitfalls and offer solutions by showing examples of Superboosting and 'H' Electric furnaces. The paper will examine how large electrical furnaces suitable for Float Glass manufacturing can be operated to achieve the holy grail of low specific energy consumption and dramatically reduce carbon dioxide emissions. Examples of superboosting and furnace designs and their relevance will be demonstrated together with the results of modelling.

SIV: Emerging Applications of Glass

Session 1: Solar Applications and Insulation Properties

Room: White Hill (4th floor)
Session Chair: Joachim Deubener, Clausthal University of Technology

1:20 PM

(ICG-SIV-113-2019) Large-area fluidic windows (Invited)

L. Wondraczek*[1]

1. University of Jena, Germany

The building sector represents one third of the global final energy use, and a corresponding fraction of anthropogenic CO_2 emissions. At the same time, roughly 80 % of our life are spent indoors, creating a strong demand for enhanced comfort levels. Here, we adress this subject through two aspects. First, while providing a very large surface for potential functionality, the building skin is used mostly for passive insulation. Second, low-temperature latent heat provides a very large reservoir of presently unused energy, e.g., low-temperature process heat such as emitted from electronic devices, or ambient heat surrounding the building. A new generation of materials was developed by which buildings can be wrapped into a layer of insulating liquid. This liquid circulates within the (transparent or opaque) building's envelope, transforming the passive skin into an organic component for functional interaction with HVAC facilities. Large-area fluidic devices were produced for implementation with façades and smart windows by combining a series of novel glass processing technologies. Ensuring compatibility with existing production lines and logistics of state-of-the-art windows, fully functional windows were fabricated and tested during indoor and outdoor operation for heating, cooling and shading in various demonstration scenarios.

1:50 PM

(ICG-SIV-114-2019) The future development of cover glass for efficient harvesting of solar energy (Invited)

S. Karlsson*[1]

1. RISE Research Institutes of Sweden, Glass, Sweden

Glass as a cover material for solar energy harvesting constitutes a significant part of the cost. Furthermore, is glass an important component for efficient light capture and protection to the environment. Research and development of cover glass is needed to increase the service lifetime and to reduce the cost per watt peak. Recent research efforts have provided knowledge of which properties that needs to be optimized balancing efficiency, service lifetime and cost. Challenges with the development of cover glass for efficient harvesting of solar energy will be discussed. Some recent results related to optimization of the glass composition for enhancing properties for the purpose and the deposition of functional thin films will be presented. The failure modes for PV modules and how glass can improve the resistance to failure will be discussed. Developments of transparent and robust multifunctional coatings that provide anti-reflective and anti-soiling properties on the outer glass surface are desired. On the interior surface are anti-reflective and chemical barrier multifunctional coatings desirable to increase transmission and reducing potential induced degradation (PID). Replacing the conventional silver strings in PV modules with transparent conductive materials and back-reflecting backsheet materials are among the promising techniques for further maximizing the efficiency.

2:20 PM

(ICG-SIV-115-2019) Photocatalytic activity of germanosilicate glassceramics containing Ga_2O_3 nanostructures

R. Lorenzi*[1]; N. V. Golubev[2]; I. S. Ignat'eva[2]; V. Sigaev[2]; A. Paleari[1]

1. University of Milano-Bicocca, Department of Materials Science, Italy
2. Mendeleev University of Chemical Technology of Russia, Sarkisov International Laboratory of Glass-based Functional Materials, Russian Federation

Photocatalysis is a crucial process in sustainable environmental technologies and in the development of next generation hydrogen production lines. The opportunity of having photocatalytic activity in glasses and glassceramics may open the way to the design of novel photocatalytic systems based on optical fiber geometry as well as self-cleaning windows and containers. Here we show the photocatalytic performances of nanostructured glassceramics with an amorphous germanosilicate matrix embedding nanoparticles of gallium oxide. The latter is a wide band gap oxide with known photocatalytic activity. In this study we have investigated melt-quenched glasses with molar composition 7.5%Li_2O-2.5%Na_2O-20%Ga_2O_3-25%SiO_2-45%GeO_2. The nanocrystallization has been achieved with a two-step thermal treatment (18 h at 570 °C followed by 30 m at 651 °C) which maximize the number of nanoparticles per volume with an average size of less than 10 nm. Photocatalytic degradation of rhodamine dye in water under UV light was performed using powdered samples. The results evidence a photocatalytic activity which follows a mixed kinetics of the 0^{th} and 1^{st} order. Interestingly, the performances of the recovered powders after the first cycle show better results with respect to pristine sample. The formation of defects probably responsible of such an enhancement has been detected by photoluminescence.

2:40 PM

(ICG-SIV-116-2019) Influence of thermal annealing conditions and N_2 flow rate on the properties of N doped TiO_2 films

Y. Yang*[1]; T. Wang[1]; X. Cao[1]; Y. Sun[1]; Z. Zhang[1]; L. Ma[1]; S. Peng[1]

1. State Key Laboratory of Advanced Technology for Float Glass, China

In this paper, we studied the effect of thermal annealing conditions and N_2 flow rate on the properties of N doped TiO_2 films. The results indicated that the crystallinity of the as-deposited films become poor with the increase of the N_2 flow rate and is amorphous in nature when the N_2 flow rate≥2 sccm. As N_2 flow rate increases, the band gap decreases from 3.21eV to 2.85 eV. The crystallization of the films after vacuum annealing become poor. With the increase of annealing temperature, the defects on the surface of the film increased, the content of N in the film decreased, and the band gap increased to 3.02-3.21eV. After normal pressure annealing the crystallinity of the film becomes better, the grain size becomes larger, the content of N in the film decreases, and the band gap increases to 2.93eV.

3:00 PM

(ICG-SIV-117-2019) Comparison of open- and closed-porous foamed glass

J. König*[1]; U. Hribar[1]; P. Cimavilla[2]; A. Lopez-Gil[2]; M. Rodrigues-Perez[2]; R. R. Petersen[3]; Y. Yue[3]

1. Jozef Stefan Institute, Advanced Materials, Slovenia
2. CellMat Technologies S.L., Spain
3. Aalborg University, Section of Chemistry, Denmark

Foamed glass is a lightweight material mainly used for thermal insulation in the construction and chemical industry. Its excellent combination of properties is related to closed pores filled with CO_2 gas and low density (i.e. high porosity). In order to obtain superior insulation properties several parameters need to be tuned in relation to the composition of the glass used for the synthesis. For acoustic insulation, however, open porosity is preferred. Despite straightforward application in acoustics the reports on this aspect are scarce. In this contribution, we present the results of our work focused on development of closed and open porous foamed glass for thermal and acoustic insulation. Open and closed-porous foamed glasses were prepared from cullets of different chemical composition. For closed-porous samples CRT-panel glass was used, while for open-porous samples bottle glass was used. The closed and open porosity of both samples was further tuned by specific additives for adjusting surface tension or crystallization. Thus we were able to prepare samples with 95 % closed or open porosity at a density of 100–120 kg/m^3. The synthesis, and thermal and acoustic properties will be discussed.

Session 1: Battery Applications and Metallizations

Room: White Hill (4th floor)

Session Chairs: Ana Rodrigues, Federal University of Sao Carlos; Steve Martin, Iowa State University

3:40 PM

(ICG-SIV-118-2019) Structural dependence of electrical transport in mixed network former glasses

A. Mogus-Milankovic*[1]; K. Sklepić Krehač[1]; L. Pavić[1]; G. Tricot[2]; L. Koudelka[3]

1. Ruder Boskovic Institute, Department of Materials Chemistry, Croatia
2. University de Lille, France
3. Iniversity of Pardubice, Czechia

Sodium ion containing have attracted increasing attention because of their potential applications as a solid electrolytes in ion batteries. Sodium batteries provide an appealing substitute for lithium batteries by decreasing cost since sodium is more naturally abundant than lithium. In this study two series of sodium mixed network former glasses are investigated: $40Na_2O$-xGeO_2-(60-x)P_2O_5 and $40Na_2O$-$10B_2O_3$-(50-x)P_2O_5-xGeO_2, x-0-30 mol%. By mixing network formers and keeping modifier concertation constant the structure changes having an effect on the ionic conductivity enhancement. The increased mobility of modifier cations, Na^+, is correlated with the interlinkage of depolymerized phosphate network and incorporated various germanate units which form an easily conductive pathways for sodium ions jump. Using 1D/2D MAS NMR technique the structural units formed in the network are determined and quantified. The analysis of local environment and links between Ge/B/P units are crucial for determining the sodium ion transport mechanism.

This study reveals that the increase in ion conductivity is controlled by the modifications of structure as a function of GeO_2 addition. These results are in close correlation with the those obtained for similar lithium (boro)phosphate glass systems.

4:00 PM

(ICG-SIV-119-2019) Structure/Property correlations on new $Li_{1.5}M_{0.5}Ge_{0.5}(PO_4)_3$ (M = Sc, Ga, Y) NASICON glass-ceramics by impedance spectroscopy and solid state NMR

I. d'Anciães Almeida Silva*[1]; A. C. Rodrigues[2]; H. Eckert[1]; A. Nieto Munoz[2]

1. University of São Paulo, São Carlos Institute of Physics, Brazil
2. Federal University of Sao Carlos, Materials Engineering Department, Brazil

The design of all-solid-state batteries requires optimized materials with high ionic conduction and appropriate chemical stability as solid electrolytes. These materials can be synthesized through controlled crystallization of specific precursor glasses into glass-ceramics with a Na-Super Ion Conductor (NASICON) phase. This research aims the aliovalent substitution of Ge^{4+} by Sc^{3+}, Ga^{3+}, and Y^{3+} ions in the NASICON unit cell of the LGP precursor using the glass-ceramic route to synthesize these new materials. Impedance spectroscopy and modern solid state NMR techniques were employed to probe their structure and ion dynamics. FAPESP grants 2017/17800-0 and 2013/07793-6 (CeRTEV - Center for Research, Technology, and Education on Vitrous Materials) are acknowledged.

4:20 PM

(ICG-SIV-120-2019) Vanadium oxyfluoro phosphate glasses: A possible new cathode for solid state battery

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4:40 PM

(ICG-SIV-121-2019) Melt-Quenched Glasses as Solid-State Electrolyte for Lithium Metal Battery

R. Zhao*[1]; S. Kmiec[1]; G. Hu[1]; S. W. Martin[1]

1. Iowa State University, Materials Science and Engineering, USA

Solid-state batteries using solid-state electrolytes (SSE) are promising options toward safer and higher energy density batteries due to the utilization of inorganic electrolyte and metallic lithium as anode. Sulfide glassy materials are good candidates for SSE with their promising properties. However, the most well-studied sulfide SSE are Li_2S-P_2S_5 and their analogues made by ball-milling method and then pressed into pellets, and the cell made with the SSE pellet may short when the lithium dendrite grow along the interparticle boundaries. In this work, we demonstrate the application of melt-quenched glasses as solid-state electrolyte. Sulfide glass Li_2S-SiS_2-P_2S_5, and oxysulfide glass Li_2S-SiS_2-P_2O_5 were made by melt-quenched method, and then characterized using XRD, Raman and NMR. To investigate the electrochemical properties of the glasses, symmetric cells with metallic lithium as electrodes were made and tested by EIS and galvanostatic measurements. These results provide a promising group of glass with SiS_2 that can be applied to lithium metal battery.

5:00 PM

(ICG-SIV-122-2019) Synthesis and Characterization of Alumina-doped Lithium Borovanadate Glasses with Applications to Lithium Batteries

M. L. Kindle*[1]; S. Kmiec[2]; I. d'Anciães Almeida Silva[3]; S. W. Martin[2]; M. Song[1]; J. McCloy[1]

1. Washington State University, School of Mechanical and Materials Engineering, USA
2. Iowa State University, Materials Science and Engineering, USA
3. University of São Paulo, São Carlos institute of Physics, Brazil

The desire for scalable energy storage technologies with higher specific energy densities is critical for numerous technologies. Glass electrodes can have a capacity of 500 mAh/g and can be created in facile melt quench procedures. Many vanadate glasses have been shown to have improved performance compared to their crystalline counterparts. However, the difference in performance between glass systems and their respective structures still needs investigation. The $LiBO_2$-V_2O_5 system is reported as a possible high-performing cathode material. However, the $LiBO_2$-V_2O_5 glass system shows inconsistent glass formability at high vanadium content, which is the electroactive species. An analysis of the effect of $LiBO_2$ and Al_2O_3 on the vanadate glass system has been performed. X-ray photoelectron spectroscopy (V) and nuclear magnetic resonance (B-11) data show that alumina stabilizes and increases the BO_3 coordinated species and decreases V^{4+} concentration which promotes VO_4 chains to form with BO_3 units, which is a stable glass structure according to literature. This is likely due to the $[AlO_4]^-$ species, which requires lithium for charge compensation and reduces the amount of $[BO_4]^-$ units that can form. This extension of the borovanadate glass forming region and structural analysis could improve the energy density of lithium metal batteries with further study.

5:20 PM

(ICG-SIV-123-2019) Lithium Ion Diffusion Pathways and Defect Behaviors in Crystalline $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ Solid State Electrolytes from atomistic simulations

P. Kuo*[1]; J. Du[1]

1. University of North Texas, Material Science and Engineering, USA

By replacing commonly used liquid electrolytes with Li-conducting glass or glass-ceramics, solid state lithium ion battery can provide higher specific power and energy density, as well as stability with reduced cell volume and weight. Lithium-Aluminum-Germanium-Phosphate (LAGP) is a promising electrolyte material that allows low activation energy (E_a) and anisotropic diffusion for Li^+. Despite the amount of Al^{3+}/Ge^{4+} defect can strongly effect the hopping distance, local environment and the energy barrier of Li^+, the atomic scale information is difficult to acquire from experimental approach. In this study, the defect and dynamic behaviors in of $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ ($0.1 \leq x \leq 0.8$) crystal were studied by static and molecular dynamic atomistic simulation methods. Defect cluster energy, structural change, E_a and diffusion mechanism were investigated. Redistribution of Li^+ into the interstitial 36f site were confirmed, and a model of the variation of Li^+ potential on the diffusion path was proposed. This investigation links the static analysis of the glass-ceramic to its ion diffusion behavior, which provides an insight to LAGP as the future electrolyte material in SSLB.

5:40 PM

(ICG-SIV-124-2019) Properties and metallization behaviors of $50B_2O_3$-30BaO-(20-x)ZnO-xBi_2O_3 glass frits

L. Chen[1]; Y. Lai*[1]

1. National United University, Materials Science and Engineering, Taiwan

Glass frit compositions of $50B_2O_3$-30BaO-(20-x)ZnO-xBi_2O_3 oxide are fabricated and characterized in this study. The glass frits, aluminum powders, and organic vehicle are mixed together to form an aluminum paste. Followed by screen printing on SiN/Al_2O_3, the aluminum paste is fired from 700°C to 900°C. Experimental results show that the glass transition temperature decreases whereas the coefficient of thermal expansion increases with the increase of Bi_2O_3 content. The reaction mechanism at the interface is analyzed by scanning electron microscopy and transmission electron microscopy. The current-voltage curve is measured to realize its electrical performance.

Session 5: Glass for Buildings and Transportation I

Room: Stuart (4th floor)
Session Chairs: Mehran Arbab, PPG; Andriy Romanyuk, GlasTrösch AG

8:00 AM

(ICG-SIV-125-2019) Reimaging Windows – Innovations in Glass with the Potential to Transform the Built Environment (Invited)

K. Sawyer[1]; C. Harris[2]; M. LaFrance*[1]

1. Department of Energy, Building Technologies Office, USA
2. National Renewable Energy Laboratory, USA

Buildings account for more than 40% of the nation's total energy demand and 70% of electricity use, resulting in an annual national energy bill totaling more than $380 billion. DOE's Building Technologies Office (BTO) is working to develop innovative, cost-effective energy saving technologies that could lead to a significant reduction in building energy consumption and enable sophisticated interactions between buildings and the power grid. BTO's goal is to reduce aggregate building energy use intensity by 45% by 2030, relative to 2010 energy-efficient technologies. The rapid development of next-generation windows are vital to meeting BTO's building energy use reduction goals. Windows are our connections to the outdoors and their thermal and optical performance directly impacts occupant comfort and building energy consumption. Next-generation window technologies such as dynamic solar control and highly insulating windows, have the capability to transition windows from being energy "consumers" to being energy neutral or even energy positive in some climates. DOE continues to invest in materials discovery, development and characterization R&D to achieve affordable technologies with higher performance thermal and optical properties. Ultimately, tomorrow's windows have the potential to outperform today's walls, fundamentally transforming the energy impact of windows in buildings.

8:30 AM

(ICG-SIV-126-2019) A circular building system out of interlocking cast glass units

F. Oikonomopoulou*[1]; T. Bristogianni[2]; F. A. Veer[1]

1. Delft University of Technology, Architectural Engineering + Technology, Netherlands
2. Delft University of Technology, Materials, Mechanics, Management & Design (3Md), Netherlands

A novel structural system made of interlocking, dry-assembled cast glass components has been developed by the Glass Group of TU Delft, aiming at altering our design and construction philosophy towards a sustainable, circular application of structural glass in buildings. Instead of the commonly applied float glass, solid interlocking cast units of the desired cross-section are proposed. A dry, transparent interlayer is used as intermediate, evading the use of adhesives and allowing for even loading. The proposed system offers multiple engineering advantages such as inherent redundancy, reversibility and increased fracture toughness. Preliminary research on interlocking geometries and interlayer materials showed that osteomorphic blocks and polyurethane interlayers are the most promising for further development. This work presents the experimental investigation of the proposed system. To explore the effect of the interlock's geometry to the system's structural performance, series of assemblies with osteomorphic units of varying wave amplitudes are made and tested in shear. Then, to examine the structural behaviour of the entire system, a plate-like assembly is constructed of multiple osteomorphic blocks restrained by a rigid metal frame and tested under concentrated load at various pre-compression rates. The results exhibit the engineering advantages of the segmented system, highlighting its structural potential.

8:50 AM

(ICG-SIV-127-2019) Magnetron Sputtered Coatings on Glass for Buildings and Transportation: Current Applications and Future Opportunities (Invited)

A. Polcyn*[1]

1. Vitro, USA

Magnetron sputtered thin film coatings applied to large area glass substrates is a very broad field, with applications in not only the building and transportation industries, but also in electronics and various specialty markets (e.g. furniture and appliances). In this presentation, current technology for transparent coatings on soda lime silicate glass for building and transportation applications will be reviewed. Applications to reduce heating and cooling load for buildings and automobiles, to heat the glazing itself for defrost and defog applications, and to enable generation of energy and light, will be considered. In addition to the functional characteristics of the coatings, aesthetic challenges related to the coatings will be addressed. Finally, future opportunities for further improvements in the current coatings, as well as potential breakthrough opportunities with new coatings, will be explored.

9:20 AM

(ICG-SIV-128-2019) ACTILAZ® Technology: A Rapid Thermal Treatment to enhance thin film coatings performances (Invited)

P. Reutler*[1]

1. Saint-Gobain, France

Saint-Gobain has created ACTILAZ, a unique, proprietary laser irradiation technology, developed and industrialized with its partners Trumpf, manufacturer of high power laser systems, and Manz, integrator of specialized industrial equipment. The result of 10 years of R&D activities, ACTILAZ is installed on a Saint-Gobain's coater, at the exit of the thin film sputtering line based on magnetron technology. The glass runs by at full speed under a high-power laser line narrower than 100 micrometers and 3.3 meters long to boost the performances of the thin film coatings. This breakthrough innovation has already been successfully launched for an insulation product, Saint-Gobain's ECLAZ® glazing. An outlook on further coating applications will also be given.

10:10 AM

(ICG-SIV-129-2019) Light-Weight Glass Laminates for Automotive Industry with Enhanced Toughness and Superior Opticss (Invited)

V. Bhatia*[1]

1. Corning Incorporated, Automotive Glass Solutions, USA

The advent of thin, chemically-strengthened glass has the opportunity to revolutionize the automotive glazing industry. Gorilla® Glass is a fusion-formed, ion-exchanged aluminosilicate glass that has found widespread adoption in the consumer electronics industry.

The higher retained strength of this glass allows it to be thinner but stronger than conventional float glass. We propose hybrid laminates made of a PVB layer sandwiched between one ply of Gorilla Glass and a second ply of float glass. This configuration reduces the weight over a standard laminate made of two plies of float glass by 30%, and improves the resistance to rock-strike by 2x. In addition, the superior optical attributes and reduced thickness can be leveraged for better heads-up display performance and improved night vision. We further show that the hybrid configuration is ideally suited to integrate additional functionality, such as dynamic tinting and transparent displays, inside the laminate structure. The addition of such functionality is typically limited in standard float glass laminates owing to the already-existing thicker stacks, but hybrid laminates relax that restriction. The value of the hybrid window is further reinforced by the improved protection and enhanced optics such laminates provide to the added functional elements.

10:40 AM

(ICG-SIV-130-2019) Accelerating Strengthening in Silicate Glasses (Invited)

S. K. Sundaram*[1]

1. Alfred University, Inamori School of Engineering, USA

Notable progress has been made in use of external fields, e.g., electric field, microwaves, and laser pulses to accelerate strengthening of silicate glasses. An overview of the progress made in this area will be presented followed by a summary of recent studies on effects of DC electric field and ultrashort laser pulses on strengthening. In the case of direct current (DC) field, three aluminosilicate glasses (Al_2O_3-SiO_2) were selected for the experimental work and four variables, composition, voltage, temperature, and time, were tested. Our results showed that an applied voltage did not affect the depth of layer (DOL) or the compressive stress (CS) that occurs during an ion exchange process. In the case of laser irradiation, we successfully altered the surface hardness of three silicate glasses of commercial interest, aluminoborosilicate (ABS), borofloat (BF), and soda-lime silicate (SLS), using femtosecond laser pulses. The laser system generated < 40 fs pulses with an energy of 500 nJ with a central wavelength of 800 nm. Using a peak power of 2.2 W, we observed an 18-20% increase surface hardness in glasses with low-modifier content and 16.6% decrease in glasses with high-modifier content. These results show promise for selective or local strengthening of silicate glasses.

11:10 AM

(ICG-SIV-131-2019) Glass Bending Process Using Microwave Beam

M. Shevelev*[1]

1. Gyrotron Technology Inc., USA

A new process of glass heating has been developed by GTI. It is based on the gyrotron - the source of high frequency microwave beam having power up to a few hundred kilowatts. Glass can be heated by microwave due to the existence of dipole molecules, which tend to re-orientate under electric field. Microwave is significantly more efficient than any common heat source including infrared, hot gas, and electric resistance due to the microwave's ability to penetrate inside material and heat selectively. Microwaves are able to heat glass volumetrically and create controllable heat distribution. Heating glass with a microwave beam has been successfully applied commercially for glass gravity bending. The beam is scanned over the glass surface by moving metal mirrors to provide the necessary heating profile. The present paper contains the results of modeling of glass heating with a moving microwave beam. It was shown that almost any temperature profile can be achieved on the glass by selecting the optimal microwave beam trajectory and diameter. The certain criteria should be met when high accuracy of sharp heat distribution is required. The paper also contains estimation of resulted bending profile. The results were used in a commercial glass bending application. The heating profile with a temperature difference of about 100°C and accuracy of 2°C was achieved during the heating of windshield glass to over 650°C.

11:30 AM

(ICG-SIV-132-2019) Hardness, indentation fracture toughness, wear resistance of soda lime silicate float glass (Invited)

S. H. Kim*[1]

1. Pennsylvania State University, Chemical Engineering, USA

Soda lime silicate (SLS) flat glass is used as architectural materials for windows and transparent external walls in buildings. From the moment it is manufactured, the float glass surface is exposed to ambient air and surface reactions involving water molecules impinging and adsorbing from humid air takes place all times. This talk will cover how thermal treatments of SLS float glass alters the humidity dependence of mechanical and tribological properties of SLS float glass surfaces. Two treatments will be discussed in this talk – one is thermal tempering commercially used for strengthening of float glass panels and the other is thermal poling which has been explored in laboratories as a means to alter the surface chemistry (especially, sodium concentration profile). The effects of humidity on indentation hardness, indentation fracture toughness, and mechanochemical wear behaviors of thermally-tempered surfaces (both air- and tin-sides) and thermally-poled surfaces (both anodic and cathodic treatments of the air-side only) will be discussed in light of chemical and structural changes of the treated glass surfaces. This study may provide insights into strategies to further improve the durability of SLS float glass.

Session 5: Glass for Buildings and Transportation II

Room: Stuart (4th floor)
Session Chairs: Mehran Arbab, PPG; Andriy Romanyuk, GlasTrösch AG

1:20 PM

(ICG-SIV-133-2019) Multifunctional Coatings on Glass for Construction and Automotive Industries (Invited)

S. Oktik*[1]

1. SISECAM, Research and Technological Development, Turkey

The global flat glass market in 2017 is estimated to be around ~82 billion$ and it is projected to reach ~112billion$ in 2022 (6% CAGR). Continuous improvement of the optical, mechanical, electrical and chemical properties of bulk glass and glass surfaces together with functions provided by passive and active layers on glass has resulted in an annual production capacity of 20 million tons in 2016 which has a market value of 6 billion $. It is anticipated that the CAGR of capacity and market would be ~6,1% and ~%5,9 respectively. The manufacturing technologies currently is dominated by: PVD technologies (~60%), pyrolytic coating technologies (~35%). Coated glass with soft or hard-coated low-e and solar low-e layers are the most popular products. Besides those coatings technologies depositing multiple thin films on glass for fabricating active or passive systems (smart coatings) which change the light and heat transmission/emission properties by applied voltage or by light or heat intensity variation have been maturing for large volume productions. The global market for smart coatings in construction and transportation sectors is predicted to be around ~4 billion $ in 2018 and expected to grow by CAGR of ~20% to over 8 billion $ in by 2022. This brief review is aimed to summarize the worldwide distribution of technologies products and market for multifunctional coatings on glass.

1:50 PM

(ICG-SIV-134-2019) Enhanced vacuum glazing bonding strength by anodic bonding assisted sealing method

H. Li*[1]

1. Wuhan University of Technology, China

A novel sealing method is introduced in this study. Anodic bonding technology was used for sealing vacuum glazing to enhance the bonding strength. Vacuum glazing is a unique fenestration technology which has excellent thermal and sound insulation properties. Two sheets of plane glass were sealed using anodic bonding assisted low-temperature sintering that employs V_2O_5-P_2O_5-B_2O_3 low-melting glass powder. Through Shear Strength test, Super-depth Microscopy, SEM, and EDS, the best bonding treatment schedule was determined. As the result shows, anodic bonding has a dramatic influence on sealing performance. When the sealing temperature and bonding time are kept constant, the shear strength of sample increases with increasing bonding voltage. When the bonding temperature is 470°C and the voltage is 600V, the sealing sample air tightness is 3.9×10-9 Pa•m^3/s. The improved bonding strength enhances life-time of vacuum glazing.

2:10 PM

(ICG-SIV-135-2019) Design of ITO and Glass Substrate for Heating Aircraft Windshields

E. Sasse*[1]

1. PPG, USA

Glass has been an important part of aircraft transparencies for many decades. Many commercial aircraft windshields contain indium tin oxide (ITO) coated glass that serves as a de-fog and de-ice heater. The window must heat enough to prevent ice from building up on the outer surface of the windshield and fog from building up on the inner surface, while not getting too hot to adversely affect form, fit, or function of the aircraft transparency. There are many design factors to consider when manufacturing a heated aircraft windshield. In this paper the design considerations of the glass substrate and the ITO coating itself will be discussed.

2:30 PM

(ICG-SIV-136-2019) Glass Surface Chemistry in Processing and Properties of Automotive and Security Glass (Invited)

W. LaCourse*[1]; T. Amodei[2]

1. Alfred University, Inamori School of Engineering, USA
2. Armoured One, USA

Security glass applications range from retrofitted polymer films for "Active Shooter" protection to multi-layer glass/polymer laminates. Many are produced by secondary processors, after shipping and most require strongly adherent polymer coatings. The role of glass surface chemistry, particularly surface hydroxyls is critical in primary processing, and subsequent handling, storage, coating formation and long term performance of the products. Surface hydroxlys, together with physisorbed water, can strongly influence "weathering" and "contact damage resistance", both of which affect optical properties, polymer adhesion and loss of adhesion in use. Methods for enhancing or reducing these effects via post-forming, and pre-coating treatments will be reviewed.

Session 8: Challenges with Vitrification of Low Activity Waste

Room: Whittier (4th floor)
Session Chairs: Tetsuji Yano, Tokyo Institute of Technology; John Vienna, Pacific Northwest National Lab

8:00 AM

(ICG-SIV-137-2019) Effect of network modifiers on iodine redox equilibrium and on glass properties

M. Cicconi*[1]; E. Pili[2]; D. R. Neuville[1]

1. Institut de Physique du Globe de Paris, Géomatériaux, France
2. CEA, DAM, DIF, France

Understanding the solubility and redox equilibria of halogens in glasses and melts is a key point in many areas, from Earth to Materials science to Waste Management. Recently, we evaluated the iodine solubility limits depending on the $SiO_2/(B_2O_3+SiO_2)$ molar ratio, in two ternary glass systems - Na_2O-B_2O_3-SiO_2 and K_2O-B_2O_3-SiO_2 - and a strong composition dependence was observed [1-2]. In this study, the effect of different types of network modifier cations on iodine redox equilibrium and glass properties have been investigated in borosilicate glasses. Structure, thermal properties, and iodine oxidation state have been characterized via Raman spectroscopy, DSC, and iodine LIII-edge X-ray Absorption Spectroscopy (XAS). In particular, the complementary use of Raman and XAS points to the presence of iodine with different stable valences within the glass network, and that the iodine redox equilibrium is influenced by the modifier cations field strength. Examples on the study of iodine in amorphous materials and on the parameters influencing its oxidation states will be provided.

8:20 AM

(ICG-SIV-138-2019) Rhenium Speciation, Solubility, and Redox Effects in Sodium Borosilicate Melts

H. Gan*[1]; D. A. McKeown[1]; X. Xie[1]; I. L. Pegg[1]

1. Catholic University of America, Vitreous State Laboratory, USA

Retention of Tc^{99} in nuclear waste glass is challenging due to its high volatility and low solubility at high temperature. Re is often used as a Tc surrogate due to their similar chemical behavior. This work was focused on the determination of Re speciation and solubility in a molten Na-borosilicate waste glass under controlled oxygen fugacity. The base glass was loaded with excess Na-perrhenate in a Pt crucible under controlled atmosphere. Glass was analyzed for redox state, Re concentration, and excess crystalline phases. The glass was also analyzed by Raman spectroscopy and XAS to identify the structural characteristics of the Re species in the glass matrix. Re solubility in borosilicate melt depends strongly on redox conditions at 1150ºC, was stable from ambient air to about 10^{-8} atm f_{O2}, then dropped precipitously, becoming virtually zero at 10^{-10} atm f_{O2}, where all of the Re is in metallic form. Raman spectra indicate that the population of Na-perrhenate species in the glass correlates with Re solubility. XAS identified Re present as $[ReO_4]^-$, Re metal, or as a $[ReO_4]^-$ and Re metal mixture, depending on f_{O2}. No Re^{4+} was detected, in stark contrast to Tc, which exhibits transitions from Tc^{7+} to Tc^{4+} to Tc^0 with decreasing f_{O2}. These and other chemical behaviors of Re and Tc in nuclear waste glasses will be compared.

8:40 AM

(ICG-SIV-139-2019) Tc/Re Volatilization during Nuclear Waste Vitrification (Invited)

K. Xu*[1]

1. Wuhan University of Technology, State Key Laboratory of Silicate Materials for Architectures, China

The high volatilization of Tc-99 at elevated temperatures is one of the primary concerns in vitrifying Tc-containing nuclear wastes. Although recycling volatilized Tc back to the melter could manage

its volatilization, other volatile components such as sulfur could be also recycled back to the melter with Tc, thus resulting in the reduction of the waste loading in the glass. Therefore, it is crucial to understand the mechanism of Tc volatilization from nuclear waste feed and glass melt at elevated temperatures, in order to control its loss during vitrification. Accordingly, this talk will discuss several vital effect factors, such as nitrate/nitrite and sulfate salts, foaming of the feed and REDOX of the melt on the volatilization of Tc/Re (Re is considered as Tc surrogate), and the mechanism Tc volatilization during nuclear waste vitrification through analyzing previous literatures and performing series of tests in simplified feeds. Finally, strategies proposed to manage Tc/Re volatilization will be compared.

9:10 AM

(ICG-SIV-140-2019) Crystallization in Statistically-Designed Low-Activity Waste Glasses

C. Lonergan*[1]; C. H. Skidmore[1]; S. Sannoh[1]; J. Vienna[1]

1. Pacific Northwest National Lab, USA

Low-activity waste (LAW) glasses are of interest for a wide variety of compositions. This flexibility is beneficial for waste vitrification but requires an understanding of material behavior for a broad range of chemistries. Twenty LAW glasses were statistically designed within established bounding conditions, prepared with mixtures of oxides and carbonates, and then were characterized for properties such as viscosity, chemical durability, and electrical conductivity. One glass showed sub-micron scale crystallization that was un-anticipated and persistent regardless of varying melting temperatures. The crystallization was further explored using microscopic analysis to understand its origin and determine ways to mitigate its presence in the future. It was determined to occur upon cooling and different quenching approaches resulted in a reduced impact of crystallization but did not achieve complete removal. Compositions were varied to eliminate the crystallization and it was found to be heavily impacted by chromium oxide concentrations and, to a smaller extent, boron oxide concentrations. The results are presented in this work.

Session 8: Turning Nuclear Waste to Glass

Room: Whittier (4th floor)

Session Chairs: Cristina Leonelli, University of Modena and Reggio Emilia; Scott Kroeker, University of Manitoba

10:00 AM

(ICG-SIV-141-2019) Gas Release and Foaming Behavior in Low Activity Waste Glasses: How Reducing Agents Affect Melting Rates

J. George*[1]; P. Hrma[1]; R. Pokorny[2]; J. Klouzek[2]; M. J. Schweiger[1]

1. Pacific Northwest National Lab, USA
2. University of Chemistry and Physics, Czechia

At the Waste Treatment and Immobilization Plant at the Hanford Site, radioactive waste will be mixed with glass forming and modifying additives to form slurry that is fed into electric melters and converted to glass. Sucrose and other reducing agents may be added to the slurry feeds to reduce foaming and increase the melting rate. Reacting feeds form a cold cap on the surface of the glass pool. Gases that evolve during the melting process form foam in the cold cap, which can lead to difficulties in melting. The effect of two reducing agents, sucrose and iron (II) oxalate, are studied on two simulated low-activity waste feeds: a high nitrate composition, AN-102, and a low nitrate composition, AZ-102. Feed expansion tests show few differences in the amount of foaming for both feeds prepared with or without sucrose, though pore size distribution in the foams vary after quenching. Addition of iron (II) oxalate results in significantly less foaming than the no-sucrose and sucrose feeds for both compositions studied. Evolved Gas Analysis shows that reducing agents resulted in NO evolution at lower temperatures. Iron (II) oxalate results in an increase in sulfate evaporation at melter operating temperatures.

10:20 AM

(ICG-SIV-142-2019) Nuclear Waste and Simulant Vitrification in a Laboratory-Scale Melter with Off-Gas Sampling

D. Dixon*[1]; W. C. Eaton[1]; C. Stewart[1]; J. Lang[1]; D. Cutforth[1]; M. Hall[1]; J. Venarsky[1]

1. Pacific Northwest National Lab, USA

The path for immobilizing Hanford tank waste for long-term storage is to mix these liquid/solid mixtures with additive chemicals and minerals and then vitrify the resulting melter feed slurries in an electrically-heated melter vessel. Small-scale melter tests are typically useful for gathering information about melter feed processing without requiring high volumes of slurry as used for large-scale melter tests and limit the committed resources for testing while providing dynamic information that can be difficult to acquire from crucible tests. An externally heated, laboratory-scale melter (LSM) with glass pouring capabilities and a unique off-gas treatment and sampling system has been fabricated at Pacific Northwest National Laboratory. The off-gas system design allowed the total off-gas stream to be diverted to a sampling loop consequently preventing the inherent issues related to required off-gas piping geometry for slip-stream sampling. Multiple low-activity waste simulants, real supernatant from Hanford tanks, and a projected high-alumina, high-level waste simulant were vitrified in the LSM. Selected melter feed, glass, and off-gas product samples from these LSM tests were sent for chemical analysis and the results were used to determine the retention in the glass product of desired chemicals (Re, Ru, and technetium-99) and the recovery of chemicals through the system.

10:40 AM

(ICG-SIV-143-2019) Effect of water vapor on nuclear waste feed conversion to-glass

J. Marcial*[1]; R. Pokorny[1]; J. Klouzek[1]; M. Vernerova[1]; P. Hrma[2]; A. A. Kruger[3]

1. University of Chemistry and Technology, Prague, Laboratory of Inorganic Materials, Czechia
2. Pacific Northwest National Lab, USA
3. Department of Energy, USA

To vitrify Hanford nuclear waste, waste slurry will be mixed with glass-forming and -modifying constituents and charged into an electric melter where a layer of reacting and melting feed material (the cold cap) is floating on molten glass. The morphology and properties of the cold cap, especially the foam layer at the cold cap bottom, effect the melting rate. Laboratory studies of feed melting behavior, including the feed expansion experiments, are commonly performed with dried feed, whereas the vitrification of feed slurry, which contains more than 50% of water, proceeds at high partial pressure of H_2O in the plenum space. According to published studies, the presence of water influences the melting behavior of commercial batches. To examine the effect of water on the melting of low-activity (LAW) and high-level (HLW) waste feeds, we performed a series of feed expansion experiments using (i) dried HLW and LAW feed samples in dry atmosphere, (ii) dried HLW and LAW samples in humid atmosphere, and (iii) HLW and LAW slurry samples under humid and dry atmospheres. The effect of feed sample preparation and the effect of water vapor will be discussed in relation to the feed melting rate.

11:00 AM

(ICG-SIV-144-2019) International experience in radioactive waste glass

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Glass is the overwhelming world-wide choice for the immobilisation of high-level waste (HLW) resulting from nuclear fuel reprocessing and an excellent solution for low and intermediate level waste as well as hazardous waste of various nature (M.I. Ojovan, W.E. Lee, S.N. Kalmykov. An Introduction to Nuclear Waste Immobilisation,

Elsevier, 3rd Edition (2019)). Glass defined as "a solution of different substances one in another" by Michael Faraday is selected due to its high physical and chemical durability, tolerance to varying waste chemical composition, as well as to high doses of irradiation inherent to nuclear waste. Borosilicate glass is the formulation of choice in most applications although phosphate and other glass compositions are used and/or investigated. The durability of glass ensures a high degree of environment protection both during storage/transportation and final disposal. The overall cost of vitrified radioactive waste is usually lower compared with alternative options accounting for transportation and disposal costs. Vitrification technologies are used on industrial scale and novel approaches are deployed to widen glass utilization as an immobilization matrix for radioactive and toxic elements. This report is based on international experiences and focuses on utilization of in-can melting and disposable ceramic containers that further decrease processing costs and facilitate technological approaches.

11:20 AM

(ICG-SIV-145-2019) Rokkasho Melters and Glasses - Lessons Learned

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1. Japan Nuclear Fuel Limited, Japan

The vitrification active tests were started at Rokkasho Reprocessing Plant (RRP) in 2007. We experienced serious operational difficulties in glass pouring primarily due to Yellow Phase (YP) formation and Noble Metals (NMs) sedimentation in the glass melts. Minor troublesome elements like sulfur/molybdenum/organics and lower waste oxides contents of Rokkasho wastes were brought about the unstable formation of the cold cap on Liquid-Fed Joule-Heated Ceramic Melter (LFCM) process. We have investigated the causes and found out that sulfate/molybdate clustering, NMs clustering, and foaming would be occurred in the transformation and glass reaction layer of the cold cap. We have successfully established the two major countermeasures. One is the heat balance control to form a stable cold cap along with the glass chemistry control to suppress YP formation and the bottom rinsing operation to prevent NMs sedimentation. Another one is the development of the new glass formulations for higher waste loading to adjust the glass frit portion with vanadium oxide addition. The advanced LFCM process for more stable operation and higher throughput capabilities is also actively in progress. Integration of glass formulations with melter engineering is crucial for advanced nuclear waste vitrification.

11:40 AM

(ICG-SIV-146-2019) Comparison of DOE Melter Model and Commercial Glass Furnace Model to Data from a Pilot-Scale Melter Test

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1. Idaho National Laboratory, Materials Science and Engineering, USA
2. UCT Prague, Czechia
3. Pacific Northwest National Lab, USA
4. U.S. DOE, USA

Simulations were conducted to compare the results from a computational fluid dynamics and heat transfer model developed by the U.S. Department of Energy Office of River Protection glass science team and those from a commercial glass furnace model to data from a pilot-scale waste glass melter test. Advances in high performance computing capability have enabled the realization of high-fidelity, coupled simulations with unprecedented resolution and increasingly realistic physics. Having well-tested and validated computational models of the nuclear waste melters is essential for the support of the operations at the Hanford Waste Treatment and Immobilization Plant. Such models provide valuable information to assist with the prediction of melting rate and other process parameters (e.g., electrode power, off-gas temperature and composition, glass residence time distribution, etc.) to optimize production and aid operational troubleshooting; avoid the negative impacts of spinel particle settling and silica dissolution to ensure long melter life and high product quality; and ensure glass homogeneity to support product qualification. By performing this experiment-to-models comparison, various operational details and practices were learned and accounted for in the glass science model to improve its predictive accuracy.

Session 8: Challenges with Vitrification of High–level Waste I

Room: Whittier (4th floor)

Session Chairs: Ashutosh Goel, Rutgers University; William Ebert, Argonne National Lab

1:20 PM

(ICG-SIV-147-2019) Redox behavior of Ruthenium in nuclear glass melt

C. Laurin[1]; E. Regnier*[1]; S. Gosse[2]; M. Toplis[3]; A. F. Laplace[1]; J. Agullo[1]; V. Legrand[1]; O. Pinet[1]

1. CEA, DE2D, France
2. CEA, DPC, France
3. IRAP, France

In France, nuclear spent fuel is reprocessed. The remaining highly radioactive solution, containing fission products (among them ruthenium) and minor actinides, is calcined and mixed with a sodium-borosilicate glass at high temperature (≈1100°C) to confine radioelements. Unlike the majority of transition metals present in waste, ruthenium is poorly soluble in glass (around 100 ppm at 1200 °C). It forms mainly RuO_2 needles and tends to aggregate with Pd-Te beads. In specific cases, Ru^0 can also be observed. Understanding the equilibria involving the different ruthenium redox states is of great interest. Because of the very low solubility of ruthenium in the vitreous matrix, the ruthenium redox behavior is generally considered to be independent of the surrounding glass matrix. In this case, ruthenium is exposed to the surrounding glass matrix O_2-fugacity. Thus, according to the oxygen fugacity of the glass, thermodynamic calculations (CALPHAD method) are performed to determine the ruthenium phases expected at the thermodynamic equilibrium, as a function of temperature. In parallel, oxidation kinetics of Ru^0 in air and in glass melt are compared in order to determine if glass melt introduces further kinetic limitation. The combination of both experiments and thermodynamic calculations finally allows to propose a reactive pathway explaining the existence of small amounts of Ru^0 in certain oxygen fugacity and temperature conditions.

1:40 PM

(ICG-SIV-148-2019) The Influence of Glass Chemistry on Caesium Volatility in Glass Systems Being Considered for Nuclear Waste Immobilisation

J. T. Radford*[1]; C. R. Scales[2]; C. L. Corkhill[1]; R. J. Hand[1]

1. University of Sheffield, Material Science and Engineering, United Kingdom
2. National Nuclear Laboratory, United Kingdom

The current UK stockpile of intermediate level waste is 99,000 m^3 and is expected to rise to 191,000 m^3 by 2125. Currently cementation is the preferred treatment route. However, thermal processing such as vitrification offers significant volume reductions, up to 75% for some wastestreams. For vitrification to be accepted as the preferred treatment option, the issue of volatility during the vitrification process must be addressed as volatile components of ILW such as ^{137}Cs and ^{90}Sr account for almost 50% of the current total radioactivity in the UK's ILW stockpile. This study has employed a bespoke off-gas system to investigate the volatility of caesium during the vitrification process. A series of borosilicate glasses containing a range of Ca and Zn additions and a series of iron phosphate based glasses containing B, Mn and Zn additions have been produced. All additives in both series range from 2.5 – 10 mol%. All compositions have been analysed using a suite of glass characterisation techniques before being doped with ~2wt% Cs_2O and re-melted. An in-situ Raman system has been incorporated into the experimental design

to determine the speciation of the Cs bearing vapour species released from the glass melt as a function of melt composition. This information will be used to optimise caesium retention.

2:00 PM

(ICG-SIV-149-2019) Development of High Level Liquid Waste loading glass

T. Ishio*[1]; Y. Miura[1]; T. Horimai[1]; K. Owaku[1]; H. Mitsuhashi[1]; N. Kanehira[1]; T. Hoshino[1]

1. Japan Nuclear Fuel Limited, Japan

The basic research programs of vitrification technology for waste volume reduction, which are commissioned project from Ministry of Economy, Trade and Industry of Japan (METI) to IHI Corporation, Japan Nuclear Fuel Limited (JNFL), Japan Atomic Energy Agency and Central Research Institute of Electric Power Industry, have been implemented from 2014 for developing the advanced vitrification technology of low level wastes and high level liquid wastes (HLLW). In this project, JNFL is primarily concerned with the high waste loading glass focused on solubility of Mo which may cause the formation of undesirable secondary phase (yellow phase) in the case of HLLW vitrification. And, we have collaborated with various universities to study the above programs. Furthermore, we have uniquely investigated the effects of several constituents to keep a good performance with high waste loading, which are conflicting with each other, of simulated HLLW glasses. Through this investigation, we had obtained candidate borosilicate glass composition ranges until FY2016. And, we have narrowed these ranges from the point of view of physical & chemical properties and melter operating requirements until FY2018. We will summarize these results until FY2018 and the next term development planning. This work was carried out as a part of the basic research programs of vitrification technology for waste volume reduction supported by the METI, Japan.

2:20 PM

(ICG-SIV-150-2019) Network Structure of Nuclear Waste Glasses at Canister Centerline Temperatures

A. Krishna Murthy[1]; S. Kroeker*[1]

1. University of Manitoba, Chemistry, Canada

Commercial and prototype glasses for the immobilization of high-level radioactive waste have been comprehensively studied by a vast array of chemical and physical techniques. However, most of this work has been done at ambient temperatures, leaving relatively unexplored the higher-temperature regime at which radioactive glasses exist in the near term. Considering the importance of glass network structure in critical properties such as chemical durability and devitrification, we have used laser-heated nuclear magnetic resonance (NMR) spectroscopy to characterize several model nuclear glasses at temperatures up to 400°C. Compositions have been selected to evaluate the role of temperature in molybdenum retention within the glassy phase, encompassing simple borosilicates as well as more complex aluminoborophosphates and borosilicophosphates, which have been shown to significantly improve molybdenum and sulfur solubility. Magic-angle spinning NMR of ^{29}Si, ^{31}P, ^{27}Al, ^{11}B, ^{23}Na and ^{95}Mo provide complementary perspectives on the structural evolution of these glasses with temperature, revealing the limitations of studies done at ambient laboratory temperatures and providing a basis for more relevant property predictions.

2:40 PM

(ICG-SIV-151-2019) Characterisation of in-situ vitreous products for higher activity waste in the UK

S. Walling*[1]; L. J. Gardner[1]; M. Kauffmann[1]; D. Bailey[1]; C. L. Corkhill[1]; N. C. Hyatt[1]

1. University of Sheffield, Materials Science and Engineering, United Kingdom

Alternative vitrification techniques utilising in-situ and in-container melting of radioactive wastes and contaminated soils have been proposed and trialled over the past decade. Characterisation and chemical durability assessments were undertaken of several glasses produced via in-container melting technology. These glasses combine simulant wastes with structural and chemical similarities to UK nuclear waste streams, combining magnesium rich materials, plastics, cement and steel, along with glass forming materials and tracer elements. The resultant heterogeneous glassy wasteforms contain pyroxene and olivine crystallites (Mg-Fe), with a degree of ionic substitution from Ca, Al and other minor constituents. Sr and Re, along with most lanthanides added into the melts as U/Pu surrogates (La, Ce, Pr, Nd, Eu) appear to split between crystalline and glassy phases. These vitrified wasteforms have demonstrated chemical durability under PCT test conditions, and the ability to retain non-active tracer elements within both glassy and crystalline phases. This suggests that in-container vitrification has the capability to produce wasteforms with long-term durability and warrant further investigation into their applicability in nuclear waste management.

3:00 PM

(ICG-SIV-152-2019) Optimisation of the new Ca/Zn base glass formulation for enhanced operability

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1. National Nuclear Laboratory, WM&D, United Kingdom

The new Ca/Zn base glass for the immobilisation of highly active waste in the UK has recently been tested at the Waste Vitrification Plant (WVP), Sellafield. Although developed specifically for storage tank wash-out feeds containing high molybdenum concentrations, the intention is to move across completely to the new 'Ca/Zn-½Li' formulation for all wastes, including standard reprocessing liquors. During the initial trial campaign, the opportunity for improving the performance of the new Ca/Zn base glass by optimising the lithium content was identified. This will enhance the operability of WVP by: 1) Increasing its softening temperature to reduce the risk of melter neck blockages. 2) Ensuring the maximum possible waste loadings are achievable. 3) Allowing greater flexibility in Li-dosing of the waste liquor feed to minimise the loss of dust to the off-gas system. Hence, a series of laboratory-scale trials were carried out to investigate the vitrification and product performance of Ca/Zn base glasses with reduced lithium content. As well as the effect of re-distributing the lithium to the waste stream, the study also investigated the envelope of acceptable total Li_2O content in the vitrified product as well as the deviation from the ideal 1:1 Li:Na ratio.

Session 8: Challenges with Vitrification of High–level Waste II

Room: Whittier (4th floor)
Session Chairs: Albert Kruger, US Department of Energy; John McCloy, Washington State University

3:40 PM

(ICG-SIV-153-2019) Characteristics of vitrification process of borosilicate glasses with simulated high-level radioactive wastes as a function of glass composition

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2. Japan Nuclear Fuel Limited, Japan

Cold cap formation and vitrification behavior are investigated using borosilicate glass beads and simulated high-level radioactive wastes (HLW) using high-temperature X-ray CT. Slight compositional difference in borosilicate glass are found to affect much the structure of cold cap on heating, and also the dissolution of waste components into glass melt. Spatial separation of Mo-containing phase from molten glass phase appears to suppress Mo dissolution and accelerate the aggregation of Mo-bearing compounds, which finally leads the formation of yellow phase (YP) in melt. Microscopes and

composition analyses are used to understand the mechanism and path to suppress YP. Development of the glass compositions for high-level radioactive wastes has been carried out by slurry-based combinatorial method. Couples of fine glass powders with different composition are dispersed in water and form stable slurries. Robotic dispensing system prepares their mixtures with various ratios in the arrays of Teflon® container. After mixed with simulated HLW and dried, the obtained pellets are melted at 1200 °C for the systematic investigation of glass for high loading of HLW. This work was carried out as the basic research programs of vitrification technology for waste volume reduction supported by the Ministry of Economy, Trade and Industry, Japan.

4:00 PM

(ICG-SIV-154-2019) Impact of glass structure on ruthenium solubility in sodium aluminosilicate and borosilicate glasses

H. Hah*[1]; A. Tyryshkin[2]; A. Yaremchenko[4]; H. Eckert[3]; A. Goel[1]

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4. University of Aveiro, CICECO – Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, Portugal

The U.S. Department of Energy currently plans to immobilize nuclear waste in borosilicate glass at the Hanford site. The operating temperature of the Joule-heated ceramic melters (JHCM) used in this vitrification process will be 1150 C. Ruthenium, which is present in high level waste, provides unique challenges to vitrification. Firstly, the limited solubility of ruthenium in borosilicates causes sedimentation of ruthenium in the JHCM due to its higher density relative to the borosilicate melt. Secondly, given that ruthenium oxide tends to volatilize at around 1200 C some of it volatilizes during vitrification, creating toxic fumes. In this study, the effect of glass structure on the solubility of ruthenium in alkali aluminosilicate and borosilicate glasses has been investigated. Accordingly, baseline glasses in the system Na_2O–Al_2O_3–SiO_2 and Na_2O–B_2O_3–SiO_2 have been designed and synthesized over a broad composition space with distinct structural features. The structure of glasses has been studied using ^{11}B and ^{27}Al MAS-NMR spectroscopy. Ruthenium solubility in baseline glasses has been followed by ICP-OES, Raman, and EPR spectroscopies along with XRD, DSC-TGA, and electrical conductivity measurements. The results will be discussed in the presentation.

4:20 PM

(ICG-SIV-155-2019) Impact of ruthenium on the crystallization behavior of molybdenum-containing high-level waste glasses

H. Kamat*[1]; A. Yaremchenko[2]; B. I. Arias-Serrano[2]; A. Goel[1]

1. Rutgers - The State University of New Jersey, Department of Materials Science and Engineering, USA
2. University of Aveiro, Department of Materials and Ceramic Engineering, Portugal

U.S. DOE is designing a multicomponent aluminoborosilicate based glass-ceramic (GC) with a targeted crystalline phase assemblage to immobilize the projected secondary waste generated by the proposed Transuranic Extraction (TRUEX^{plus}) process. RuO_2 is one of the components of the waste stream which exhibits low solubility in the GC matrix. Above its solubility limit, it is known to precipitate and crystallize as needle-like RuO_2 crystals. Apart from that, RuO_2 can also provide nucleating sites for undesirable crystal phases in the GC waste form affecting its long term chemical durability. Therefore, understanding the impact of RuO_2 on the crystallization behavior of the proposed GC waste form is highly relevant for the design of advanced glassy waste forms with high waste loading. In this study, a series of glasses based on the proposed GC waste form (GC-Mo-6.25) have been synthesized by incorporating increasing amounts of RuO_2. Crystallization behavior has been studied using a suite of characterization techniques including DSC, XRD, Raman spectroscopy, SEM-EDS, and electrical conductivity measurements. The results will be discussed in the presentation.

4:40 PM

(ICG-SIV-156-2019) Impact of mixed network former effect on spinel crystallization in high-level nuclear waste glasses

N. Balasubramanya*[1]; P. Florian[2]; A. Scrimshire[3]; P. A. Bingham[3]; M. Ahmadzadeh[4]; J. McCloy[4]; A. Goel[1]

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2. CNRS, CEMHTI, France
3. Sheffield Hallam University, Materials and Engineering Research Institute, United Kingdom
4. Washington State University, Materials Science and Engineering, USA

The vitrification of nuclear wastes containing high fractions of Fe, Ni, and Cr often results in the undesirable crystallization of spinels in the melter, which poses a threat to the efficiency of the melter and can limit the waste loading. This study aims to understand the impact of the mixed network formers in the system Na_2O-Al_2O_3-B_2O_3-SiO_2-Fe_2O_3-MnO-NiO-Cr_2O_3. In particular, the effect of varying Al_2O_3/SiO_2 and B_2O_3/SiO_2 ratios on the propensity of spinel crystallization has been evaluated. While x-ray diffraction and vibrating sample magnetometry (VSM) suggested that the presence of spinels in glasses during simulated idling conditions, there were no spinels in the glasses during simulated melter conditions. VSM along with energy dispersive was used to understand the nature and composition of spinels in glasses. The tendency of a transition element to enter the spinel structure is affected by its coordination environment, which in turn is influenced by the short – to – medium range order in the glass structure. Despite the challenges of performing nuclear magnetic resonance (NMR) on iron-containing systems, we successfully obtained high-quality high-field ^{11}B and ^{27}Al magic angle spinning-NMR spectra. NMR, along with Raman and Mössbauer spectroscopies, have been employed to study the structural coordination of boron and aluminum and redox chemistry of iron in the glasses.

5:00 PM

(ICG-SIV-157-2019) Impact of crystallization on chemical durability of simplified nuclear waste Li_2O-Na_2O-Al_2O_3-B_2O_3-SiO_2 glasses

A. A. Deshkar*[1]; B. Parruzot[2]; J. Reiser[2]; J. Vienna[2]; A. Goel[1]

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2. Pacific Northwest National Lab, USA

Vitrification of sodium and alumina-rich high-level radioactive waste (HLW) into borosilicate glasses faces the problem of nepheline ($NaAlSiO_4$) precipitation during canister-centerline cooling (CCC), which is potentially detrimental to the durability and long-term stability of the final waste form. The current model used for immobilization of HLW drastically limits waste loadings. Since it is important to determine the effects of composition on glass properties for improving waste loadings of high-alumina wastes in glass, the present study aims towards understanding the impact of crystallization of nepheline and similar phases on the chemical durability of simplified HLW glasses designed in the Li_2O-Na_2O-Al_2O_3-B_2O_3-SiO_2 system. Accordingly, glasses have been designed in the meta-aluminous, peralkaline and per-aluminous regimes and CCC heat-treatments were conducted on these glasses which were further analyzed using X-ray diffraction to calculate the crystal fractions. Product Consistency Tests (PCT) were conducted on both the quenched glasses and multi-phase CCC heat-treated samples for 100 days to analyze the impact of crystallization on long-term chemical durability of these glasses. Modifications were made in the PCT experiments to include 1 cm^3 cubes of respective samples into each vessel in order to observe altered surfaces using optical and electron microscopy.

5:20 PM

(ICG-SIV-158-2019) A spectroscopic investigation to understand the impact of melt chemistry and environment on spinel crystallization in high-level waste glasses

N. Balasubramanya*[1]; M. Naji[2]; M. Ahmadzadeh[3]; E. T. Nienhuis[3]; D. P. Guillen[4]; J. McCloy[3]; A. Goel[1]

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3. Washington State University, and Materials Science and Engineering Program, USA
4. Idaho National Lab, Advanced Process and Decision Systems Department, USA

The study focusses on the fundamental understanding of the effects of melt chemistry and melt environment (oxygen fugacity) on nucleation and crystallization of spinels in HLW glasses. The formulated compositions of the Na_2O-Al_2O_3-B_2O_3-SiO_2-Fe_2O_3-$M_{1x}O_y$ system are studied in ambient and reducing atmospheres to understand the tendency of a transition metal ion to enter into spinel along with Fe. In the Na_2O-Al_2O_3-B_2O_3-SiO_2-Fe_2O_3-$M_{1x}O_y$-$N_{1x}O_y$ system, the influence of the presence of the second transition element is studied. The glasses, made under both ambient and reducing conditions were subject to a panoply of techniques such as X-ray diffraction, Raman spectroscopy, near edge X-ray absorption spectroscopy XANES at the Fe-K(edge), magnetic measurements and electronic microscopy. Although the changes with transition metals and melt environment are seen to be very subtle, the addition of transition metals to the melt at ambient conditions did not induce any crystal formation or structural changes. While the reducing atmosphere had a significant impact, it was found that the formation of spinel is determined by the cation's ability to get readily reduced which we explain with the help of crystal field stabilization energy.

5:40 PM

(ICG-SIV-159-2019) Formulation of High-Al_2O_3 Waste Glasses from Projected Hanford Waste Compositions

J. Vienna*[1]; J. Kroll[2]; Z. Nelson[1]; C. H. Skidmore[1]; D. Dixon[1]

1. Pacific Northwest National Lab, USA
2. Western Frontier Services, USA

High alumina high-level waste (HLW) is stored at the Hanford Site. This waste will be vitrified into borosilicate glasses at the Hanford Tank Waste Treatment and Immobilization Plant (WTP). The efficiency of the WTP operation will be strongly influenced by the loading of high Al_2O_3 wastes in HLW glass and the melter processing rate. A study was performed to formulate glasses with high loading of Al_2O_3-rich HLW and demonstrate their processability. Glasses with Al_2O_3 concentrations ranging from 30 to 35 wt% were designed and tested. One example glass with Al_2O_3 loading of 34 wt% was processed in a small-scale continuous melter. These compositions showed promising properties and good processability, suggesting that Hanford HLW glasses loaded with excess of 30 wt% Al_2O_3 can be successfully produced at the WTP. The ability of existing glass property-composition models to predict the properties of HLW glasses with high Al_2O_3 content was evaluated. Viscosity and electrical conductivity model predictions appeared reasonably close to measured values, while crystallization and product consistency test model predictions were found to be significantly different from measured values.

6:00 PM

(ICG-SIV-160-2019) Thermodynamic and kinetic assessment of nepheline crystallization in Na_2O-Al_2O_3-B_2O_3-SiO_2 glasses: Impact of mixed network former effect

A. A. Deshkar*[1]; O. Gulbiten[2]; R. Youngman[2]; A. Goel[1]

1. Rutgers University, Materials Science & Engineering, USA
2. Corning Incorporated, USA

Vitrification of sodium and alumina-rich high-level radioactive waste (HLW) into borosilicate glasses faces the problem of nepheline ($NaAlSiO_4$) crystallization, which is detrimental to the durability and long-term stability of the final waste form. Studies show the suppressing effect of B_2O_3 on nepheline crystallization, but its precise mechanism has not yet been fully understood. It is anticipated that the change in glass viscosity and fragility arising from the variation of B_2O_3 might be helpful in elucidating the drivers behind nepheline crystallization in aluminoborosilicate glasses. Therefore, the present study aims towards understanding the thermodynamic-kinetic behavior governing the crystallization of nepheline based Na_2O-Al_2O_3-B_2O_3-SiO_2 glasses. Accordingly, the crystallization behavior of the synthesized glasses has been studied by conducting non-isothermal and isothermal heat treatments, while the thermodynamic-kinetic behavior has been investigated by probing the temperature-dependence of viscosity using rotational viscometry and 3-point beam bending method. Utilization of MAS-NMR spectroscopy on glasses and glass-ceramics has been useful in establishing a correlation between fragility and the boron speciation in the as-studied glasses.

6:20 PM

(ICG-SIV-161-2019) Crystallization behavior of HLW glasses: Impact of non–framework cation mixing

Z. Sun*[1]; N. Balasubramanya[1]; S. Kamali[3]; M. Ahmadzadeh[2]; J. McCloy[2]; A. Goel[1]

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2. Washington State University, Materials Science and Engineering, USA
3. University of Tennessee Space Institute, USA

Abstract: This study focuses on understanding the relationship between iron redox, composition, and spinel crystallization tendency in a simplified high–level nuclear waste. Glasses in the Na_2O–M_xO_y-Al_2O_3–B_2O_3–Fe_2O_3–SiO_2 system (M=modifier cation, in this case Li or Ca), with varying CaO/Na_2O and Li_2O/Na_2O ratios, have been synthesized by melt–quench technique and studied for their crystallization behavior. The aim is to understand the impact of non–framework cation mixing on the glass structure and the interplay between Fe^{3+} and other tetrahedrally coordinating elements (Si, B). The spinel–forming tendencies have been studied as a function of the ionizing potentials of the alkali and alkaline–earth cations. While Raman and infrared spectroscopies have been used to understand the glass network structure, x-ray diffraction and vibrating sample magnetometry are used to confirm and quantify the crystalline phases. Differential scanning calorimetry has been used to determine the heat capacity changes and the glass transition temperatures. The iron redox from Mössbauer spectroscopy and the viscosity from rotational viscometer experiments have been used to understand mass transfer and the probable redox reactions taking place at high temperatures. An attempt has been made to understand the compositional dependence of spinel crystallization based on thermodynamic and kinetic parameters.

Session 9: Nano-Crystals in Glasses

Room: Tremont (4th floor)
Session Chairs: Takumi Fujiwara, Tohoku University; Heike Ebendorff-Heidepriem, University of Adelaide

8:00 AM

(ICG-SIV-162-2019) Thermal processing of transparent oxyfluoride glass-ceramics: Fabrication of planar waveguides (Invited)

Y. Ledemi*[1]; K. Venkata K.[2]; L. Maia[3]; E. Veron[4]; M. Allix[4]; R. Kashyap[2]; Y. Messaddeq[1]

1. Universite Laval, COPL, Canada
2. Ecole Polytechnque de Montreal, Department of Engineering Physics, Canada
3. Universidade Federal de Goiás, Instituto de Física, Brazil
4. Conditions Extrêmes et Matériaux: Haute Température et Irradiation, CEMHTI-CNRS UPR3079, France

The incorporation into specialty optical glasses of nanocrystals of desired composition and crystalline phase, size and spatial distribution is attracting a large interest over the last 25 years. Thermal processing of such materials is critical not only to tailor their nucleation/growth process of particles to achieve enhanced optical properties, but also to give them specific shape adapted for the targeted applications (i.e. fiber drawing, optics molding). In this work, we will report on the fabrication of planar waveguides produced during the ceramization process of oxyfluoride glass-ceramics. An appropriate design of chemical glass composition, relying on a mixing of halide and oxide components, allows to modify the refractive index at the bulk surface, giving rise to a planar waveguide. This phenomenon, never reported to our knowledge, has been observed in several mixed glass-compositions and has been studied in more details in lead-silicate oxyfluoride glass-ceramics from optical and structural points of view. The simplicity of this processing technique, in comparison with conventional methods used to produce planar waveguides (e.g. film deposition, ion-exchange, etc.) paves the way for the development of glass-ceramics-based optical devices and components.

8:30 AM

(ICG-SIV-163-2019) Spatially designed assembly of nanocrystals in glasses by laser

T. Komatsu*[1]

1. Nagaoka University of Technology, Japan

The design and control of the morphology and orientation of nanocrystals in glasses are extremely important for the basic science and also practical applications of glasses with nanocrystals. One of the most attractive techniques for the spatially designed assembly of nanocrystals is the laser-induced crystallization. We focus on the spatial assembly of Er^{3+}-doped CaF_2 nanocrystals in CaF_2-Al_2O_3-SiO_2 based oxyfluoride glasses by continuous wave Yb:YVO_4 laser (λ=1080 nm) laser irradiations (e.g., power 1.5 W, scanning speed 2 μm/s). The size of CaF_2 nanocrystals present in the region close to the center of lines was larger than that in the region close to the edge of lines. The correlation between the morphology and dispersion state of CaF_2 nanocrystals and photoluminescence properties of Er^{3+} ions incorporated into in CaF_2 nanocrystals was clarified. The formation mechanism of CaF_2 nanocrystals in the laser irradiated part was discussed from the temperature distribution model. We emphasize that the chemical composition of the base glasses and also the interfacial free energy between nanocrystals and the glassy phase are important for the design of nanocrystals by lasers.

8:50 AM

(ICG-SIV-164-2019) Precipitation of Pd nanoparticles in phosphate glasses for UV plasmon resonance

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1. University of Jena, Otto Schott Institute of Materials Research, Germany
2. University of Erlangen-Nuremberg, Department of Materials Science, Germany
3. South China University of Technology, The China-Germany Research Center for Photonic Materials and Devices, The State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Fiber Laser Materials and Applied Techniques, China
4. University of Adelaide, ARC Centre of Excellence for Nanoscale BioPhotonics (CNBP), Institute for Photonics and Advanced Sensing (IPAS), School of Physical Sciences, Australia

Surface plasmon resonance (SPR), a collective oscillation of free carriers in a confined nanostructure, can lead to local electric field enhancement. This characteristic has been exploited for photonics, optics-based sensing, and photovoltaic devices. However, representative mateirlas such as gold, silver, and copper are limited to the visible or near-infrared spectral ranges, whereas Palladium holds promise for UV SPR. Because Palladium nanoparticles and molecular complexes have optical activity in UV spectral region, it has further useful traits such as in hydrogen storage, water disinfection, and catalysis. We investigated the optical properties of Pd^{2+} in selected solutions to identify plasmonic responses of Pd nanoparticles experimentally and under DFT simulation of Pd^{2+} complexes. The solutions were chosen considering the ligand field strength in phosphate and fluorophosphate glass. In metaphosphate glass, plasmonic responses were obtained at 355 nm, which corresponds to 50-nm diameter of Pd nanoparticles after precipitation of Pd nanoparticles by thermal reduction.

9:10 AM

(ICG-SIV-165-2019) Opticalliy Transparent glass-ceramics in the system Na_2O-FeO-MnO-SiO_2 (Invited)

T. Honma*[1]; M. Terasawa[1]; T. Komatsu[1]

1. Nagaoka Univeristy of Technology, Department of Materials Sciencs and Technology, Japan

Sodium oxide is essential materials for glass industries as well as secondary batteries in order to develop sodium ion batteries. Present authors group propose a new concept to fabricate sodium ion batteries by meand of glass-ceramics technology. $Na_2FeP_2O_7$ and $Na_2MnP_2O_7$ can be obtained by heat treatment of precursor glass which prepared by melt-quenching method. While searching for a new system, optically transparent glass-ceramics in the system Na_2O-FeO-MnO-SiO_2have been successfully prepared via conventional heat-treatment of glass. We introduce our strategy to develop active materials for sodium ion batteries and discuss crystallization behavior of new transparent glass-ceramics.

10:00 AM

(ICG-SIV-166-2019) Photoluminescence and Crystallization Process of Rare Earth co-doped Oxyfluoride Glass Ceramics Containing Fluoride Nano-crystals

J. Zhang[1]; L. Jia*[1]; Q. Tian[1]; L. Meng[1]; X. Zhao[1]

1. Wuhan University of Technology, China

Rare earth doped oxyfluoride glass ceramics containing fluoride nano-crystals have attracted much attention due to their good mechanical and chemical stability, and low phonon energy local surroundings for rare earth ions, resulted in high efficiency luminescence. In this research, Tm^{3+}/Ho^{3+}, Er^{3+}/Ho^{3+} co-doped oxyfluoride glass ceramics containing $NaYF_4$, or PbF_2 nano-crystals were fabricated by conventional melt-quenching and subsequent heat-treatment method. Energy transfer induced visible upconversion and infrared luminescence from Ho^{3+} ions were observed

under 800 nm laser excitation. The luminescence were enhanced due to nano-crystal formation and growth, which shortened the distance between rare earth ions and decreased the effect maximum phonon energy. Moreover, the energy transfer rate from Tm^{3+} (Er^{3+}) ions to Ho^{3+} ions was greatly increased. The nano-crystals in glass matrix were confirmed by XRD, TEM and Electron Energy Loss spectroscopy (EELS). The results showed rare earth ions were preferentially precipitated into fluoride nano-crystals. In addition, the crystallization processes of fluoride nanocrystals in glass matrix were investigated. Rare earth ions clusters were observed in glass matrix before crystallization. These phenomena confirmed that rare earth ions acted as nucleation agent for fluoride nanocrystal formation.

10:20 AM

(ICG-SIV-167-2019) Crystallization of nano-sized $Bi_2Ti_2O_7$ phase and its formation mechanism in Na_2O-Bi_2O_3-TiO_2-SiO_2 glass

O. Kwon*[1]; C. Baek[3]; N. Terakado[1]; Y. Takahashi[1]; T. Fujiwara[1]; Y. Yang[2]

1. Tohoku University, Applied Physics, Japan
2. Pusan National University, Nanoenergy Engineering, Republic of Korea
3. Pusan National University, Nano Fusion Technology, Republic of Korea

Glass-ceramics obtained by heat treatment has been widely researched on applying it from structural materials to photonics devices. As the photocatalytic material, anatase-type TiO_2-nanocrystallized glass-ceramics demonstrates the hydrogen generation by water splitting, leading us to expect the application in energy sustainability material with mass productivity. $Bi_2Ti_2O_7$ crystal is reported to have a relatively high dielectric constant and is expected to photocatalytic material with band-gap of 2.8 eV. However, the synthesis of the $Bi_2Ti_2O_7$ phase accompanies some difficulties, and therefore it leads to obstruct the property investigation of $Bi_2Ti_2O_7$ phase and its application. In this study, we have succeeded in fabricating the $Bi_2Ti_2O_7$-nanocrystalline material based on nanocrystallization in $10Na_2O$–$10Bi_2O_3$–$40TiO_2$–$40SiO_2$ precursor glass, and examined the crystallization mechanism in order to utilize as nanostructured-photocatalyst.

10:40 AM

(ICG-SIV-168-2019) Impact of additives on nanocrystallization of BaF_2 in fluoroborate system

K. Shinozaki*[1]

1. AIST, Inorganic Functional Materials Research Institute, Japan

Fluoride nanocrystals in oxide glass matrix have recieved much attention due to its excellent features of luminescence and formability. In this work, a siries of oxyfluoride glasses with 1Ln2O3-20BaF_2–40ZnO–40B_2O_3 were prepared by using conventional melt-quenching method. DTA curves was obtained and heat-treatment temperature was determined. Cubic BaF_2 nanocrystals were formed by heat-treatment of the glass samples, and the crystal size decreased with increasing rare earth ion content: particle sizes of 32 and 8 nm were obtained for the non-doped sample and the sample doped with 1 mol% Er_2O_3. The non-doped glass sample was opaque, but the 1Ln_2O_3-doped glass sample showed high optical transparency. Also, the crystalline size was depended on the ionic radii of rare earth ion: particle size of 5 nm for La_2O_3 and 8nm for Er_2O_3. Upon continuous-wave laser excitation at 980 nm, both of the glass and glass-ceramic samples with Er-doping showed upconversion luminescence. Even though borate has high phonon energy, we observed upconvesion luminescence in the glass sample, indicating the formation of a BaF_2-like structure in the as-quenched glass sample. These results indicate that rare earth ion act as nucleation sites of BaF_2 nanocrystals.

11:00 AM

(ICG-SIV-169-2019) Effect of CdSe and ZnSe on Spectroscopic Properties of White Light Emitting Dy^{3+}-Doped Tellurite Glasses

O. Kibrisli*[1]; A. Ersundu[1]; M. C. Ersundu[1]

1. Yildiz Technical University, Metallurgical and Materials Engineering, Turkey

Among trivalent lanthanide ions, Dy^{3+} offers promising features for white light emitting solid-state lighting applications due to its yellow and blue emission bands in the visible region. The position of rare earth energy levels is identical for different hosts while the intensity of the emissions change with the local crystal field of the host. Therefore, tellurite glasses are considered as promising luminescent materials due to their several advantageous properties. It is well-known that doping of nanoparticles into glass matrix along with rare earth ions enhances luminescence properties due to nanoparticle-light interactions induced by surface plasmon resonance. In this study, the effect of CdSe and ZnSe nanocrystals on luminescence efficiency of Dy^{3+} doped tellurite glasses were investigated. Conventional melt-quenching was applied to synthesize as-cast samples and controlled heat-treatment procedures were realized for the growth of nanoparticles in glass matrix. UV-Vis absorption, photoluminescence, X-Ray diffraction and Raman scattering techniques were applied. CIE color coordinates, lifetime values and J-O parameters were determined for the evaluation of tellurite glasses as solid-state lighting materials. The authors gratefully acknowledge The Scientific & Technological Research Council of Turkey (TUBITAK) for the financial support under the project numbered 117M206.

Session 10: Glass Modifications by Femtosecond Interactions (TC 20)

Room: Beacon Hill (4th floor)
Session Chairs: Setsuhisa Tanabe, Kyoto University; Marcelo Nalin, Institute of Chemistry - UNESP

8:30 AM

(ICG-SIV-170-2019) Femtosecond laser irradiation in yttrium aluminosilicate glass optical fibers (Invited)

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1. Paris-Sud University, ICMMO, France
2. University of Illinois at Urbana-Champaign, Electrical and Computer Engineering, USA
3. Clemson University, Materials Science and Engineering, USA

Femtosecond (fs) lasers enable high peak powers and ultrashort pulse durations, making them attractive and versatile tools for a wide variety of applications (e.g., 3D integrated photonic devices). To-date, most studies on fs-laser irradiation effects in optical fibers have been dedicated to silica and silica-like (i.e., slightly doped silica) compositions. This is due to the relatively restricted doping levels achievable in preforms, hence fibers, fabricated using conventional chemical vapor deposition techniques. However, recent fiber fabrication techniques, such as the molten core method (MCM), broaden the available fiber core dopants and their doping concentrations into silica. Such flexibility makes the MCM a formidable testbed to investigate the relationships between glass composition (and glass structure) with fs-laser induced modifications. In this context, an yttrium aluminosilicate core – silica clad glass optical fiber is fabricated using the MCM, and is then irradiated by fs-laser. The core composition effect on the nanogratings formed in the irradiated regions, as well as their thermal stability compared to conventional silica fibers, are investigated. Findings suggest a high thermal stability of nanogratings in the 600-1000 °C temperature range, possibly attributed to the higher coordination of Al in these glass compositions, making them potential candidates for high temperature sensors.

9:00 AM

(ICG-SIV-171-2019) Customized Side-Emitting Fiber: Controlled Decoupling of Light via Femtosecond-Laser Induced Microstructures

A. Reupert*[1]; M. Heck[2]; S. Nolte[2]; L. Wondraczek[1]

1. Friedrich Schiller University Jena, Otto Schott Institute of Materials Science, Germany
2. Friedrich Schiller University, Institute of Applied Physics, Germany

This paper investigates the possibility of transforming a commercial optical fiber into a line- shaped optical light diffuser with a customized emission profile by the means of femtosecond laser-written scattering centers. Such line-shaped light diffusors have many applications in the homogeneous and volumetric illumination of turbid media, i.e., media which are strongly scattering and absorbing such as in, e.g., interstitial light delivery for phototherapy where light is needed to cause a photochemical reactions, or in photo-bioreactors where optimal photosynthetic conditions have to be achieved in concentrated suspensions. Here, the relevant aspect for optimal illumination conditions is the controlled decoupling of light from the fiber into the surrounding so as to create flat or otherwise customized emission profiles. So far, most commercially available light diffusing fibers have an exponentially decaying emission profile. Little research has been conducted on methods which allow for customization. We argue that with an adequate theoretical understanding, femtosecond induced scattering centers can be used as building blocks to construct an arbitrary emission profile at low cost.

9:20 AM

(ICG-SIV-172-2019) Investigating femtosecond laser interaction with $Ge_{23}Sb_7S_{70}$ chalcogenide glass

G. Torun*[1]; K. Saadi[1]; K. Richardson[2]; Y. Bellouard[1]

1. EPFL, Galatea Lab, IMT/STI, Switzerland
2. Univ. Central Florida, CREOL and College of Optics and Photonics, USA

Focusing ultrafast laser pulses inside transparent materials induces localized permanent structural modifications, such as increased refractive indices or self-organized nanogratings that are of particular interest for photonics applications. Among materials of interest, chalcogenide glass is an attractive candidate for mid-infrared applications due to its broad-transparency from 0.593 um to 8.3 um. So far, our knowledge on how these substrates behave under ultrashort pulses is limited. Here, we investigate structural changes inside the $Ge_{23}Sb_7S_{70}$ glass exposed to various pulse durations, ranging from 50 fs to about 300 fs, and at low pulse energies. Our preliminary results, obtained with compositional elemental analysis (EDAX) coupled with Raman spectra suggest an increase of number of $GeS_4/2$ and $Ge_2S_6/2$ units in the glass network, and the subsequent formation of bridging S–S linkages in the formation of latter species. This observation could lead to possible densification effects that in turn, may lead to interesting waveguiding properties. Further, we report the influence of various laser parameters such as polarization, net fluence and repetition rate, and in particular, how these parameters affect the morphology of laser affected zones, in the context of photonics applications.

Session 10: Rare Earth Doped Glasses (TC 20)

Room: Beacon Hill (4th floor)

Session Chairs: John Ballato, Clemson University; Giancarlo Righini, Enrico Fermi Center

10:00 AM

(ICG-SIV-173-2019) Super Broad Band NIR emission from Yb/Ho/Tm triply doped oxyfluoride glass

S. Balaji*[1]; S. Annapurna[1]

1. CSIR-Central Glass and Ceramic Research Institute, Glass Division, India

Broad band NIR emission sources are immensely required for number of technological advancements like broad band data communication, real time environmental monitoring laser based sensors, moderate to high energy Q-switched lasers for tissue engineering or surgery etc. Rare earth doped glasses are being explored for such kind of applications considering their impactful advantages. In the present work, we have demonstrated a super broad band NIR emission in the range 1650 to 2100nm from $Yb^{3+}/Ho^{3+}/Tm^{3+}$ triply doped low phonon thermally stable fluorotellurite glass. Interestingly, its non-linear upconversion (UC) emission losses are few thousand factors less than the Yb^{3+}/Ho^{3+} and Yb^{3+}/Tm^{3+} co-doped samples. Population at different excited states were dynamically controlled by tuning the concentrations of individual rare earth ion so that the unfavourable UC and MIR emission transitions from Ho^{3+} as well as Tm^{3+} ions were significantly restricted to get super broad band NIR emission. Structural stability of the parent glass allows one to use these glasses for development of broad band tuneable NIR emitting fiber laser sources.

10:20 AM

(ICG-SIV-174-2019) Study of fluoro-phosphate glasses with a high terbium content for magneto-optical applications

B. Bellanger*[1]; Y. Ledemi[1]; Y. Messaddeq[1]

1. University of Laval, Chemistry, Canada

The development of glass preforms heavily doped with terbium in order to produce optical fiber shows a strong interest in the field of telecommunications. Indeed, the single crystals currently used as a Faraday rotator are susceptible to misalignment. In this study, we explored fluoro-phosphate glasses according to the following composition law: $(1-x)(70NaPO_3 - 30BaF_2)-xTbF_3$ with x = 50 mol%, the largest content of Tb^{3+} successfully dissolved in these glasses without observing crystallization which corresponds to an ionic density of $9.98x10^{21}$ cm^{-3}. Bubble-free vitreous rods about 5 cm long, 4 mm in diameter and containing from 35 to 50 mol% of TbF_3 were successfully prepared by the convention melt-quenching technique. Thermal, thermo-mechanical and optical properties of the prepared glasses were characterized respectively by DSC, TMA, viscosity measurements, UV-Visible-NIR spectroscopy and prism coupling technique. Glass transition temperatures and refractive index at 1538 nm vary from 352 to 390°C and 1.5412 to 1.5466 respectively. As the conventional fiber drawing of glasses with such a high concentration of terbium has led to crystallization, alternative approaches to produce fibers based on the crucible technique are being explored. The potential of these fluoro-phosphate glasses and fibers for magneto-optical applications will be discussed.

10:40 AM

(ICG-SIV-175-2019) Heavy metal oxide glasses containing luminescent rare-earth single crystals

E. Souza[1]; D. F. Franco[1]; S. J. Ribeiro[1]; M. Nalin*[1]

1. Institute of Chemistry - UNESP, Inorganic and General Chemistry, Brazil

Transparent glasses containing high luminescent crystals are of great interest in photonics. This work reports the synthesis of luminescent cubic single-crystals using germanate based glasses as precursors. The crystals were prepared by controlling the cooling process from a supersaturated solution of composition

97(40PbO-20GeO_2-25Bi_2O_3-15Ga_2O_3)-2Yb_2O_3-0.5-Er_2O_3-0.5Tm_2O_3 (in mol %). Cubic crystals with dimensions ranging 100 μm were obtained. The crystalline phase was characterized by means of X-Ray diffraction, micro Raman spectroscopy, Transmission electron microscopy and EDS measurements while optical properties were evaluated using UV-Vis and luminescence spectroscopy. The crystalline phase was characterized as $Yb_3Ga_5O_{12}$ with spacial group Ia-3d. Both Er^{3+} and Tm^{3+} were also supposed to be present in the crystalline phase, probably substituting Yb^{3+} ions. Such statement is supported by optical measurements once the stark levels, arising from Er^{3+} emission in crystalline phases, were observed in both infrared (1550 nm) and visible (~550 nm) regions when the sample was excited with 980 nm. The glass presents intense green up-conversion emission under IR excitation. Weak blue emission, $^1G_4$-->$^3H_6$, from Tm^{3+} was also observed at 480 nm

Session 12: Multi-material Fibers II

Room: Cambridge (4th floor)

Session Chairs: Fabien Sorin, EPFL; Sylvain Danto, University of Bordeaux; Alexander Stolyarov, MIT Lincoln Laboratory

8:20 AM

(ICG-SIV-176-2019) Preform Drawing of Glass-coated Sn Microwires

J. Zhao*[1]; J. Benner[1]

1. Western New England University, Mechanical Engineering, USA

Thermal drawing from a preform is a versatile manufacturing tool for the scalable production of glass-coated microwires containing a crystalline core. In this paper, experimental investigations are conducted to reveal the governing process parameters for the successful preform drawing of glass-coated Sn microwires. Capillary instabilities have been identified as the main challenges and different modes of break-up have been observed and underlying physics examined. Scaling analysis is conducted which suggested the dimensionless numbers that govern the mode transitions.

8:40 AM

(ICG-SIV-177-2019) Substantiation of 3D architectural control in crystalline-semiconductor fiber-embedded microelectronic systems

C. Faccini de Lima*[1]; M. Zheng[1]; V. Koraganji[1]; L. van der Elst[1]; A. Gumennik[1]

1. Indiana University, Intelligent Systems Engineering, USA

Fibers are universally ubiquitous, from textiles to optical-fiber networks. However, the integration of high-performance microelectronic systems within a thin fiber remains a major challenge. Addressing it, our laboratory develops a technique for controlling the fiber's 3D architecture. First, additive manufacturing and thermal draw of a preform define the cross-sectional geometry of the fiber device. The fiber is then axially patterned by a spatially coherent, material-selective capillary breakup, resulting in assembly of initially continuous, separate cores into arrays of discrete devices contacted in parallel. Since the intricacy of the final devices correlates to the complexity of the preform cross-section, free-form fabrication of preforms enables fiber device functionalities unattainable otherwise. Segregation-driven control of doping in post-breakup semiconducting particles was demonstrated, allowing to control an individual device's internal architecture. We present recent advances in 3D printing of silica preforms and in obtaining the windows of parameters in the Navier-Stokes equation for which capillary breakup behavior is deterministic through numerical simulations. We argue that those developments substantiate VLSI-Fi as a scalable method for fabrication of high-performance fiber-embedded microelectronic systems.

9:00 AM

(ICG-SIV-178-2019) Chalcogenide materials inside microstructured silica fibers: A new base for nonlinear photonics (Invited)

M. Schmidt[1]; H. Ebendorff-Heidepriem*[2]

1. Leibniz Institute of Photonic Technology, Fiber Photonics, Germany
2. University of Adelaide, Australia

Hybrid optical fibers include sophisticated materials which are traditionally not used within fiber optics. As a result, fiber-based devices with unprecedented photonic properties can be envisioned which are particular important for the field of nonlinear light generation, which is the topic of this talk. In the first part of the presentation I will concentrate on liquid chalcogenides based nonlinear optofluidics – a strongly growing field within fiber optics research. Here I will report on our latest results on supercontinuum generation within CS_2 filled fibers. Using femtosecond optical pulses we observe for the first time noninstantaneous soliton-driven infrared octave-spanning supercontinuum generation with exceptionally high coherence. The second part of the talk is dedicated towards nonlinear light generation in solid chalcogenide nanowires inside silica fibers. I will first introduce the technology of pressure-assisted melt infiltration, which allows studying the flow of glassy materials inside small silica bores. Despite device implementation, I will also discuss Non-Newtonian flow of chalcogenide glasses inside micrometer-size silica bores. We fabricated As_2S_3/silica fibers with aspect ratios > 2000 and nanospikes at both ends of the device and demonstrate octave spanning supercontinuum generation extending out to 4μm at moderate pulse energy.

10:00 AM

(ICG-SIV-179-2019) Advances in multimaterial fibers: New physics, enhanced functionalities, and boosted scalability (Invited)

A. Abouraddy*[1]

1. University of Central Florida, CREOL, The College of Optics & Photonics, USA

I will review the recent progress my group has made in the field of multimaterial fibers. We have explored new physics related to thermally induced fluid instabilities and tensile-induced mechanical instabilities that lead to unexpected phenomena at the interfaces between materials along the fiber axis. Novel material combinations are leading the way to the possibility of introducing semiconductor devices along the fiber, and robust and low-cost midinfrared optical fibers. Finally, I will review our recent investigation of multi-component melt-spinning as a route towards scaling up the production level of multimaterial fibers for the consumer market, particularly for functional fabrics.

10:30 AM

(ICG-SIV-180-2019) Nano-enabled multifunctional fibers for electrical, optical and chemical communication with neural circuits (Invited)

X. Jia*[1]

1. Virginia Tech, Bradley Department of Electrical and Computer Engineering, USA

The development of neural interface devices in the past decades, although has significantly expedited the understanding of neural circuits and the treatment of neurological disorders, is facing a bottleneck. Most of the existing neural interface devices are either based on hard materials such as metal or silicon that can cause long-term tissue damage, or based on flexible film substrates which is difficult to reach deep tissues in the brain. Furthermore, few devices are able to incorporate optical, chemical or other functionalities into electrical recording probes in order to establish two-way communication with neural circuits in vivo. To overcome these problems, here I present a nano-enabled multifunctional fiber based platform

for interrogation of neural circuits in vivo. These fibers are capable of simultaneous electrical, optical and chemical communication with neural circuits in the deep brain regions. These miniaturized devices are integrated with nanomaterials which significantly enhanced their sensing performance. Their small feature size and low bending stiffness lead to high biocompatibility and minimum tissue damage in the brain. This fiber-based platform could facilitate both fundamental understanding of the functional neural networks as well as clinical applications in treating brain-related diseases.

11:00 AM

(ICG-SIV-181-2019) Multimaterial Fibres in Robotic Surgery: Fibres in Robots to Fibre Robots

B. Temelkuran*[1]; M. E. Abdelaziz[1]; G. Yang[1]

1. Imperial College, Hamlyn Centre, United Kingdom

At the beginning of the new millennium, a polymer sheet coated with a chalcogenide glass, rolled around a sacrificial mandrel and drawn into a fibre presented a number of novelties: A new way of guiding light, a waveguide not limited with its materials' optical properties and hence having the ability to transmit light at any chosen wavelength, nanometre scale control of features and geometries at kilometre length scales, and last but not the least, baby steps of the field of multimaterial fibres that changed the way we think about fibres. The resulting fibre, although had an interesting potential in the field of communications, found its immediate application in a completely different field, and served few hundred thousand patients up to date in various surgical specialities as a precise optical scalpel. The enriched choice of materials and ability to achieve exotic geometries with the development of technologies such as 3D printing, we have focused to explore further potential contribution of multimaterial fibres to medicine. The ability to integrate and miniaturize various functions on a single fibre underpins the fibrebot we are developing, a fibre robot that can navigate through the natural lumens of the body equipped with imaging, sensing and therapeutic capabilities thanks to multimaterial fibre technology.

11:20 AM

(ICG-SIV-182-2019) Bioresorbable microstructured phosphate glass optical fiber for theranostic applications

D. Pugliese*[1]; N. Boetti[2]; D. Gallichi Nottiani[1]; O. Podrazký[3]; P. Peterka[3]; D. Milanese[1]; D. L. Janner[1]

1. Politecnico di Torino, Italy
2. Fondazione LINKS – Leading Innovation & Knowledge for Society, Italy
3. Czech Academy of Sciences, Institute of Photonics and Electronics, Czechia

In recent decades, optical fibers have raised increasing interest in the field of theranostics due to their easy integration in catheters and other medical instrumentation and to their ability to transmit light and act as drug delivery systems in capillary form. Optical fibers are also desirable since they can be drawn into kilometers starting from a single preform, thus allowing their production scalability. In this scenario, phosphate glass optical fibers can be regarded as great candidates thanks to their mechanical reliability both in dry and humid environments, radiation durability and biocompatibility. Furthermore, phosphate-based glasses can become biocompatible and resorbable materials, upon properly tailoring their compositions. We report on the design and fabrication of a multifunctional bioresorbable microstructured phosphate glass optical fiber. Different glass compositions were tested and their reabsorption time in a simulated body fluid was found to be tailored by finely dosing MgO and CaO. These features make such fiber suitable for implantation-e.g. after a surgery-for localized treatment. In addition, we show the application of the multifunctional fiber to deliver a photosensitive drug and its activation by light carried with the same fiber. We also report on in-vivo tests of the bioresorbable fiber on male laboratory rats, showing no clinical signs of adverse effects.

Session 13: Open Session on Glasses for Pharma I (TC12)

Room: White Hill (4th floor)

Session Chairs: Daniele Zuccato, Stevanato Group; Holger Roehl, Roche

8:00 AM

(ICG-SIV-183-2019) New challenges for Pharma glasses: Characterisation updates, elemental impurities detection and data quality improvement (Invited)

E. Guadagnino*[1]

1. Professional Glass Expert, Italy

The complexity of drug molecules, the addition of excipients, chelating agents and buffers, requires additional stability studies to ascertain the glass surface compatibility vs new medicines. The need to reduce particle formation and to prevent delamination phenomena has pushed the industry to explore other types of glass besides the conventional borosilicate. Literature data concerning the use of aluminosilicate glasses and quartz are very promising but more data seem to be necessary to explore the spectrum of their application under the most different conditions. The present structure of Pharmacopeia based on neutrality tests seems to be not fully adequate to characterise these new glasses, some consideration on the modernisation of the actual tests and on the alternative use of etching test and XRF and are made. Pharma and research labs are encouraged to collaborate for the preparation and testing of standard procedures and to improve the performances of participating labs. On a future perspective, the production and certification of dedicated reference materials would be of great benefit for the entire community to guarantee a proper quality level of the measurements. Some examples of existing CRM's and basic rules for the implementation of a collaborative intercomparison for the certification of a candidate reference material will be shortly described.

8:30 AM

(ICG-SIV-184-2019) Dependency of Drug-Container-Interaction on filling volume

V. Rupertus*[1]

1. Schott AG, Pharmaceutical Systems, Germany

Today the standard measure for the chemical durability for parenteral packaging is based on the hydrolytic resistance test (ISO 4802; USP<660>; Ph.Eur 3.2.1) for which the vial is filled with purified water for testing purposes to 90% of its brimful volume. However, nowadays an increasing amount of innovative drugs e.g. high-potent drugs will have a low filling volume (<50% of its brimful volume). Consequently, the determined hydrolytic resistance test might not represent the amount of leached glass elements for those volumes. This is attributed to two main contribution factors: One is an increasing ratio of the wetted inner container surface to filled volume. The other contributing effect is an increased leaching tendency typically observed with borosilicate glass of the wetted wall near bottom area. The phenomenon itself will be explained for standard and reduced filling volume. Using accelerated testing conditions (24 weeks at 40°C) results will be presented for some prominent glass elements and different filling volumes, wet solutions and glass compositions (Borosilicate and Alumosilicate glass).

8:50 AM

(ICG-SIV-185-2019) Investigating the effects of the chemical composition on glass corrosion. A case study for Type I vials

N. Bessegato*[1]; S. Panighello[1]; O. Pinato[1]

1. Nuova Ompi S.r.l. unipersonale, SG Lab Analytics, Italy

From the beginning of the 20th century, borosilicate glass is still the material of first choice for the primary packaging of parenteral drugs and especially of biopharmaceuticals because of its high chemical resistance. Type I borosilicate glass is worldwide accepted and

used at this scope, but it may have some issues related to corrosion, delamination and breakage that might compromise the drug efficacy, quality and safety. These issues can be mitigated and avoided approaching the rationale selection of the most suitable raw material from the early stage of the glass container design. In this study, Type I borosilicate glass vials manufactured starting from two glass tubing having different chemical compositions, were investigated and compared in terms of resistance to corrosion. Testing design was applied with the purpose to select the best practice approach comparing different storage simulation conditions: ageing treatment by autoclaving and stability testing (real-time and accelerated). Substantial differences were observed between the different glass types in terms of hydrolytic and corrosion resistance that put in evidence the relation between chemical composition and glass chemical durability and between the different storage conditions applied.

9:10 AM

(ICG-SIV-186-2019) Glass corrosion principles applied to pharmaceutical containers to predict extracted metal concentrations (Invited)

R. Schaut*[1]

1. Corning Incorporated, S&T, Glass Research, USA

The corrosion of glass surfaces by aqueous solutions has been studied for several hundred years. The scientific community has built a comprehensive understanding of the individual mechanisms of attack and continues to refine physics- and chemistry-based models to describe the kinetics and thermodynamics of the corrosion process. Yet, to many in the pharmaceutical sciences, the evolution of glass extract concentrations over time, temperature and pH appear unpredictable and random. Here, we will review the corrosion principles that are pertinent to understanding pharmaceutical containers, including a focus on differences between acidic, basic, and neutral pH environments. We will then describe how the individual principles combine to yield a smoothly-varying corrosion response and predictable behavior. Extractables from tubular borosilicate and Valor® Glass will be shown as examples. Special causes for variations from this response will be highlighted (chelators, surface heterogeneities, etc.).

Session 13: Open Session on Glasses for Pharma II (TC12)

Room: White Hill (4th floor)
Session Chairs: Volker Rupertus, Schott AG; Carol Flynn, Corning Incorporated

10:00 AM

(ICG-SIV-187-2019) Delamination in pharmaceutical glasses: An update

M. Guglielmi*[1]

1. University of Padova, Dipartimento di Ingegneria Industriale, Italy

The detachment of glass flakes from the inner surface of containers is a serious phenomenon, which caused the recall of several drugs, and a warning by the U.S. Food and Drug Administration in 2011. Several studies have been published in the last years, and many progresses have been done in the scientific comprehension of the delamination process, although the exact mechanism and the role of the different parameters are not yet fully understood. The attention of the glass producers and pharma users communities was mainly devoted to predict the propensity of glass vials to delaminate, in order to reduce the risk for patients and the need of very expensive recalls. The technical committee of ICG, TC 12 – Pharma Packaging was created in 2012, with members from glass and pharma companies and from research and services centers. Its main objective, up to now, was to find a suitable and reliable testing method to evaluate the probability of vials to delaminate. The work of TC12 will be shortly reviewed after describing the problem of glass delamination, its complex phenomenology, the relationships with glass composition and vials manufacturing processes, and the possible mechanisms.

10:20 AM

(ICG-SIV-188-2019) TC12 "Pharma Packaging": An update on the activities looking for a Delamination propensity predictive test

D. Zuccato*[1]

1. Stevanato Group, Italy

ICG TC 12 was created in 2012 involving the most important glass vials producers and pharma companies, with the objective of studying the issues related to pharma packaging. The first task of TC12 was to address the problem of predicting the propensity of glass vials to delamination, leaving the study of the mechanisms of flakes formation as a possible future activity. This presentation reports on the latest results obtained in a series of round robin tests which involved all the labs of the companies represented in the Technical Committee. Vials with different expected delamination propensity were tested using a protocol which includes different analytical techniques. Although no flake formation was observed, the results shown that the combination of results coming from different techniques is correlated to an observable morphological modification/corrosion of the inner surface of vials especially at the bottom region. The test protocol is therefore suitable for checking the quality of vials with respect to the propensity to corrosion and the likelihood of delamination. The method allows catching differences in the corrosion behavior mainly between sets of vials with comparable surface/volume ratio. The most recent results, using a different test method, will be discussed during the session.

SVII: Arun K. Varshneya Festschrift

Arun K. Varshneya Festschrift IV

Room: Georgian (mezzanine)
Session Chair: Madoka Ono, Asahi Glass Company

8:00 AM

(ICG-SVII-026-2019) Varshneya Glass Technology Lecture: Structure-Property Relationships in Halide Containing Bioactive Glasses

R. Hill*[1]

1. Queen Mary University of London, DPS, United Kingdom

This talk will discuss structure-property relationships in Fluorine and Chlorine containing bioactive glasses. This will include the use of ^{29}Si, ^{31}P and ^{19}F solid state NMR spectroscopy to elucidate the detailed chemical structure of these bioactive glasses. It will be shown how a structural understanding of the role of phosphorus and the halide in conjunction with Network Connectivity (NC) calculations can be used to predict dissolution rates/bioactivity as well as other properties such as refractive index and hardness. Phosphrus exists largely as orthophosphate species, whilst F anf Cl exist as F-M(n) species. Network connectivity plays an important role in determining dissolution rates and the abilty of the glass to form apatite (bioactivity). Both fluoride and chloride ions are released along with Ca^{2+} and PO_4^{3-} ions and in the case of fluoride containing glasses fluorapatite is formed upon immersion. The design of glasses suitable: i) for re-mineralizing toothpastes, ii) for self repairing dental fillings and iii) for air abrasives for cutting or polishing teeth will be outlined. The talk will then discuss in depth the two toothpastes BioMinF® - based on a fluoride based bioactive glass and BioMinC® - a chloride based bioactive glass.

9:00 AM

(ICG-SVII-027-2019) Fabio celebrates Arun (Invited)

F. Nicoletti*[1]

1. Stevanato Group, Italy

In this contribution to the celebration of Prof. Arun K. Varshneya, a longtime friend of him, Dr. Fabiano Nicoletti, Honorary President of the International Commission on Glass, describes Arun's particular scientific and professional success in the field of ion exchange in glass. After having cited Arun's publications on the subject, the author recalls the important industrial application by him, which allowed the realization of the first self-injector for the rapid administration of drugs, initially used in the military environment, saving a lot of human lives. The author concludes reminding that the great technological improvement in the production of glass cartridges for auto-injectors has certainly been induced and favored by the studies of Arun.

9:20 AM

(ICG-SVII-028-2019) Arun Varshneya: A Guru, A Mentor, A Force to Reckon (Invited)

A. Goel*[1]

1. Rutgers University, USA

I had known Dr. Arun Varshneya since 2004, i.e., when I was an M.S. student in India. However, that does not mean that he knew me too. I had never had an official or formal connection with him, i.e., officially I was never his student or his collaborator, and I don't think, I dare to refer him as a friend of mine. Still, he had a profound impact on my career as he has been the one to whom I have looked up to as an inspiration while building my career in the field of glass science. My presentation will present a rough sketch of an unusual and invisible bond that I have shared with him during the past 15 years and the way he still mentors me and inspires me to succeed in both personal and professional life.

10:00 AM

(ICG-SVII-029-2019) The Guru and Chalcogenide Glass (ChG) materials (Invited)

K. Richardson*[1]

1. University of Central Florida, CREOL, USA

From a leader in glass science and technology, to an academic at Alfred University, we trace the evolution of the glass guru from the world of silica to the 'dark side' of non-oxides. Highlights of the outstanding contributions made to all things chalcogenide are reviewed. Presented are key take-aways that all future ChG-ers need to consider for following in these infrared transparent footsteps.

10:20 AM

(ICG-SVII-030-2019) A Guru in Glass – from the Outside In (Invited)

M. Richardson*[1]

1. University of Central Florida, CREOL, USA

Occasionally one is afforded the chance to open a door into a world that is new, inviting yet comfortable. It is an honor to provide a perspective on the late-career and impact of a swami in the field of glass science. As a fundamental scientist in optics, lasers and light interaction, I have long valued the potential of new materials. But my association with both young and venerable experts in glass science has opened the door to this rich field of science and splendor. Arun Varshneya is not just a pioneer in glass science, but to this outsider looking in, he is a personality who has brought charisma and camaraderie to the field. In this talk this outsider, who is perhaps now an insider, will illustrate his own perspective on the contributions Arun Varshneya has made to glass science.

10:40 AM

(ICG-SVII-031-2019) Loose Ions on a Disordered Landscape: An Enabling Paradigm for Strong Glasses and Fast Ionics (Invited)

S. W. Martin*[1]

1. Iowa State University, Materials Science & Engineering, USA

Normally, glass engineers prefer the chemical species, especially the cations, that make up glass to be rigidly bonded among each other. Such rigid bonding promotes strong glass forming tendencies by frustrating diffusional processes leading to crystal nucleation and crystallization. Vitreous silica with its strong Si-O bonding is archetypical of this paradigm. Likewise, strong bonding imparts improved mechanical strength and chemical durability. However, there are important properties of glass that depend upon more loosely bonded cations. This is the case for mobile cations such as Li^+, Na^+, and K^+. When Li^+ and Na^+ cations are loosely bound in glass, these glasses can be used as solid electrolytes that are enabling to an entirely new class of solid state Li and Na batteries. Similarly, loosely bound Na^+ ions can be chemically exchanged for larger, but less mobile, K^+ to dramatically increase the mechanical strength and toughness and thereby enable an entirely new class of super strong glasses that likewise enable entirely new industries of portable communication devices. In this talk, the authors nearly 40 year study of such loose alkali ions and the devices and systems they enable will be described. Special attention will be paid to the ion exchange process that has been the subject of our most respected Symposium Honoree, Professor Arun Varshneya.

11:00 AM

(ICG-SVII-032-2019) Fracture of Sodium-Silicate Glasses: Insights from computer simulations (Invited)

W. Kob*[1]; Z. Zhang[1]; S. Ispas[1]

1. University of Montpellier, France

Although understanding the process of fracture is important for many applications, not much is known on it on the microscopic level. For example the role of the network modifiers on the fracture dynamics is not clear since on one hand they can locally weaken the glass but on the other hand they also increase the local stiffness of the sample. In this talk I will present some recent results of large scale computer simulations of sodium-silicate glasses for which we have investigated the linear and non-linear elastic properties and found that the latter has a marked dependence on the sodium content. For samples with low sodium concentration we find that the presence of a scratch on the surface will strongly affect the fracture toughness, whereas glasses with high sodium content have a fracture behavior that is less influenced to such surface defects. The sodium concentration also strongly affects the nature and propagation of the fracture front giving hence rise to glass surfaces with distinct structural properties.

11:20 AM

(ICG-SVII-033-2019) Structure and dynamics of ion-exchanged glasses (Invited)

E. I. Kamitsos*[1]

1. National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute (TPCI), Greece

Ion exchange is a well-known process for chemical strengthening of commercial silicate glass and for altering the optical properties of glasses for photonics applications (e.g., waveguides, micro-optics). Despite the numerous reports on ion-exchanged glasses there are still fundamental questions concerning structure and ion transport in the ion-exchanged layer. While most previous studies have focused on commercial soda-lime silicate glasses, this presentation addresses also structure and dynamics of ion exchanged borate glasses. We acknowledge support of this work by the project "National Infrastructure in Nanotechnology, Advanced Materials and Micro - / Nanoelectronics" (MIS 5002772) which is

implemented under the Action "Reinforcement of the Research and Innovation Infrastructure", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

Arun K. Varshneya Festschrift V

Room: Georgian (mezzanine)
Session Chair: Kathleen Richardson, University of Central Florida

1:20 PM

(ICG-SVII-034-2019) Observations related to the free volume theory of glass formation (Invited)

A. Wright*[1]

1. University of Reading, United Kingdom

Quenching to the vitreous state is discussed from the point of view of the inherent fluctuations in both density and composition. Three examples are considered, viz. a random packing of hard spheres, vitreous silica, and "normal" glasses, for which the structure of the super-cooled liquid is defined by one or more chemical equilibria. For single-component glasses (e.g. SiO_2), the true measure of the ("free") volume available for the mechanism of viscous flow (bond switching) lies with the mean square number density fluctuation $<Dr^2>$, whereas, for glasses having more than one component, it is essential to take into account the temperature dependence of the various chemical equilibria, for which the equilibriation time is in general much longer than the times for bond switching and structural relaxation. It is also concluded that the presence of spatial fluctuations in both number density and composition has an important effect on the bulk (macroscopic) physical and chemical properties of the vitreous state.

1:40 PM

(ICG-SVII-035-2019) Aircraft Transparency Technology (Invited)

K. Lakdawala*[1]

1. PPG Aerospace, USA

Aircraft transparences have evolved from flat to complex curved features with various choices of material. The typical material evolution has been – glass, high strength glass, stretched acrylic, chemically strengthened glass and polycarbonate. Each of the materials have their inherent advantages and disadvantages. Every transparency deign involves balancing critical factors such as weight, fuel efficiency, birdstrike capability, service life and cost. There can be rigid framing around the windshield such that the windshield is isolated from fuselage loads alternately the windshields can be subjected to direct fuselage loads (hoop tension). Most commercial and general aviation aircrafts have a conductive heater film or a mesh embedded in an interlayer for deicing and or defogging. Military aircraft transparencies will have various coatings on the inner our outer surface for specific application. Section 25.775 requires windshields and their supporting structure withstand, without penetration, impact with a four-pound bird at VC (design cruising speed) at sea level. This regulation has been in place and is unchanged since part 25 was introduced in 1965.

2:00 PM

(ICG-SVII-036-2019) Sheffield model of viscosity: From Douglas to nowadays (Invited)

M. I. Ojovan*[1]

1. The University of Sheffield, Materials Science and Engineering, United Kingdom

In 1949 Ronald W. Douglas has devised a model of viscous flow based on dual role of oxygen in glasses that resulted in a two-exponential equation for the temperature dependence of viscosity. Arun K. Varshneya in his fundamental monograph refers to this pioneering work clarifying our understanding of viscosity. Although Douglas equation was giving a very good description of viscosity it has not become popular compared VFT and other models currently used. Meantime it is considered that namely two-exponential equations can mathematically most exactly describe the viscosity of amorphous materials. A two-exponential equation $\eta(T) = AT \exp(B/RT) [1 + C \exp(D/RT)]$, where A, B, C and D are material specific constants, has been derived in 2000's in the University of Sheffield using the notion of configurons – broken bonds in an amorphous material. This equation was tested for many inorganic and organic materials and proved valid universally at both low (for glasses) and high (for liquids) temperatures giving a good description of viscosity of both glasses and melts. Within intermediate ranges of temperatures, the Sheffield model gives practically the same description of viscosity as the most frequently used VFT model.

2:20 PM

(ICG-SVII-037-2019) Understanding the effects of compositional changes in ion exchanged glasses

H. Gover[1]; R. J. Hand*[1]

1. University of Sheffield, Materials Science & Engineeering, United Kingdom

The primary method of consistently improving the strength of silicate glasses is the use of thermally or chemically introduced residual stresses, with the latter technique having become increasingly important in recent years. Commonly the focus is on the level of stresses that can be introduced by ion exchange, with relatively little attention being paid to other structural and property changes that arise from the compositional changes inherent in ion exchange. We have undertaken a study in which we examine the effects of compositional changes arising from ion exchange by making bulk glasses with equivalent compositions to glasses produced by ion exchange. The structures of these bulk glasses have been assessed using Raman and IR spectroscopies and the results compared to those obtained on the ion exchanged glasses. In addition the mechanical properties, including fracture toughness, of the bulk glasses have also been assessed. The primary focus has been Na/K ion exchange but Li/Na ion exchange has also been examined.

2:40 PM

(ICG-SVII-038-2019) Rare-Earths Doped Glass and Ceramic Materials for Telecommunication and Lighting (Invited)

S. Tanabe*[1]

1. Kyoto University, Japan

Following the development of optical fiber networks of low-loss silica fiber and needs of large-capacity telecommunication by the wavelength-division multiplexing (WDM) technology, various kind of rare-earth doped fiber amplifiers were invented for different wavelength regions from O- to U- bands. Erbium, praseodymium and thulium were three representative active center ions, where the 4f-4f luminescent transitions at each key band require different properties for their host glasses, which are strongly correlated with the 4f energy level structures. There have been various scientific advances of concerted development in glass science and luminescence physics. After the invention of InGaN-based blue LED, the white LED lamps were invented in the very late 1990s, which has also driven the revolution in the lighting technologies in this 21st century. Most of LED lamps are a phosphor-converting type, in which the 5d-4f transitions of Ce^{3+} or Eu^{2+} doped phosphors play critical role, which can achieve broad and widely tunable luminescence in the whole visible range with large cross section. This talk will review the development histories of rare-earth doped materials for these two different technologies on the basis of required properties and design concepts as well as their future prospects.

3:00 PM

(ICG-SVII-039-2019) Reaction between Glass and Molten Salt in Chemical Strengthening Process (Invited)

Y. Fujiwara*[1]; I. Kashima[1]; T. Yamada[1]; Y. Sera[1]; D. Kobayashi[1]

1. AGC Inc., Japan

Glass surface reaction during a series of processes including chemical strengthening is discussed. Chemical strengthening process is widely applied for cover glasses of mobile display devices to enhance the strength and scratch resistance and so on. It is well-known that the contamination of molten salt causes ion exchange inhibition in the chemical strengthening process. In order to suppress the influence of the contamination, various additives have been investigated. However, there is an issue that an additive of a basic salt erodes the glass. In this study, aluminosilicate glasses which were suitable for chemical strengthening were focused. A specific reaction between glass and molten salt was found when controlling the molten salt to an appropriate pH (measured by dissolving the solidified salt in water) by the type and concentration of the additive. The reaction leads to forming modified layer of about several hundreds of nanometers thickness on the glass surface. The feature of this layer is that alkali metal ions are released and the density is lowered. Furthermore, it was found that the effect of either transmittance increase (reflectance reduction) or strength improvement could be obtained through additional processes such as acid treatment and alkali treatment which prompted surface modification.

3:40 PM

(ICG-SVII-040-2019) Tiny Bubbles: Unique Porous Wall Hollow Glass Microspheres and Applications in Medicine, Energy, Security, Environmental Remediation and Consumer Goods (Invited)

G. Wicks*[1]

1. Applied Research Center, USA

Tiny Bubbles or Porous Wall Hollow Glass Microspheres (PWHGMs), are glass micro-balloons about 1/3 the diameter of a human hair. They range in size from a few to 100 microns in diameter, and have thin outer shells 1-2 microns thick. The most unique feature of PWHGMS is that they contain a continuous, through-wall nano-porosity, induced via phase separation and thermal/ chemical processing, and controlled on a scale of 100 to 1,000 Angstroms. This provides an opening or pathway for materials of interest to be loaded inside the microspheres or glass micro-capsules. These cargos can take the form of solids, liquids and/ or gases, which can subsequently be released on demand. PWHGM technology was originally developed at the Savannah River National Laboratory for nuclear applications and is now being further advanced and tailored for a multitude of new uses in other fields and disciplines. This work is being performed at the Applied Research Center (ARC) in Aiken SC, as well as at a new biotech spin off company, SpheroFill, LLC. Among the interesting initiatives and uses being studied are PWHGM products for medicine, energy, environmental remediation and specialized consumer goods. The development of these unique materials, their capabilities, and few of their exciting new applications will be presented.

4:00 PM

(ICG-SVII-042-2019) Maximizing ion conductivity and minimizing interface resistance of inorganic electrolytes (Invited)

U. G. Fotheringham*[1]; K. Hofmann[1]; M. Reich[1]; A. Roters[1]; W. Schmidbauer[1]; M. Schneider[1]

1. SCHOTT AG, Germany

In general, high performance ionic conductors are equal to what one would expect considering basic physics. First, the fluctuation-dissipation theorem indicates the particular suitability of ordered structures as host systems for the ions. Second, continuum approaches for the energy levels of the ions, in particular Born's solvation energy expression and Debye-Hückel theory, indicate the particular suitability of high permittivity materials. Combining said considerations with the request of a 100% dense material directly leads to high permittivity glass ceramics, e.g., Lithium Lanthanum Zirconium Oxide (LLZO). Indeed, LLZO based materials have turned out to be one of the most promising materials for future batteries, combining both high ionic conductivity and stability versus metallic lithium. Remarkably, the above continuum approaches also indicate how to minimize the interface resistance between neighbouring electrolytes, i.e. by impedance matching which in return is achieved by matching the permittivities. The latter can be demonstrated considering complex impedance measurements at the combination of one solid and different liquid electrolytes with different permittivities.

4:20 PM

(ICG-SVII-043-2019) Kinetics of chemical strengthening and trends in effective diffusion coefficients (Invited)

S. Karlsson*[1]; L. Wondraczek[2]; S. Ali[3]; B. Jonson[3]

1. RISE Research Institutes of Sweden, Glass, Sweden
2. University of Jena, Otto Schott Institute of Materials Research, Germany
3. Linnaeus University, Department of Built Environment and Energy Technology, Sweden

Alkali cation exchange has received significant attention with respect to introducing compressive stress in the glass surface, a process frequently called chemical strengthening. Besides mechanical properties may also other properties such as optical, electrical and chemical properties be modified using ion exchange of various monovalent ions. The mobility of monovalent ions varies and the relations of structural and effective diffusion coefficients may help to understand how to improve the ion exchange kinetics of soda lime silicates. We discuss the trends in the effective diffusion coefficients when exchanging Na+ for various monovalent cations (K^+, Cu^+, Ag^+, Rb^+ and Cs^+) by their correlations to physico-chemical properties. The most significant correlations were found to be the bond dissociation energy and the electronic cation polarizability, indicating that electron localization and the rupture of bonds are of importance for the ion exchange rate.

4:40 PM

(ICG-SVII-044-2019) Strengthened glass by Ion Exchange: Residual stress profile nagging issues

G. Macrelli*[1]; A. K. Varshneya[2]

1. Isoclima SpA, R&D, Italy
2. Saxon Glass Technologies, USA

Strengthened glass by ion exchange is a wide studied topic with remarkable applications for transportation, pharmaceuticals, architectural and consumer electronics. Despite the increased production, there are still some nagging issues to be fully resolved. One of the major anomalies, that the observed surface compression magnitude is a factor of 3 to 5 lower than that predicted by Cooper coefficient, was recently explained by Varshneya et. al. (2015). A second anomaly which remains a nagging issue is the observation that the maximum surface compression observed is often sub-surface. Some Li2O-MgO-Al2O3-SiO2 glasses after ion exchange exhibit conversion of the surface compression to tension over a period of time followed by a buried inner compression, changing to the usual central tension (Donald & Hill 1988). Donald & Hill ascribed this to a large differential thermal contraction of surface layers upon cooling. Varshneya's students refuted this by showing that the relaxation occurred even at temperature of ion exchange. We propose a new explanation. Our approach is based on the calculation of residual stress profile taking into account relaxation effects incorporating fast beta and the slow alpha relaxations. We show that a mathematical model of stress build up and relaxation in the ion exchanged glass can be versatile in the prediction of even unusual stress profiles.

5:00 PM

(ICG-SVII-045-2019) Effect of typical impurities in ion-exchange process of silicate glasses

V. M. Sglavo*[1]

1. University of Trento, Italy

Ion-exchange process has gained remarkable interest during the last years for chemical strengthening silicate glasses. During a typical industrial process, sodium atoms contained in the glass are substituted by potassium ions diffusing from a molten potassium nitrate at temperatures below the strain point of the glass, thus creating a residual compressive stress in the surface layers which strengthens the component. Several variables like glass composition, molten bath composition, temperature and time can affect the efficiency of the ion-exchange process. An interesting aspect regards the presence of impurities in the bath, introduced with the raw salt or accumulated during the process; these have been limitedly considered in the past as responsible for the resulting chemical, physical and mechanical performance. In this work soda lime silicate float glass and sodium borosilicate glass were considered and the effect of variable sodium, magnesium and calcium concentration in the molten bath was analyzed as fundamental parameters affecting the ion exchange process efficiency. Commercial potassium nitrate salts from different sources were also considered. The chemically strengthened samples were characterized in terms of potassium penetration profile, residual stress and mechanical strength. The addition of limited quantities of silica was also studied as possible remedial action for non-efficient baths.

5:20 PM

(ICG-SVII-046-2019) Enlightenment to become a Glass Science Instructor (Invited)

M. Orhon*[1]

1. Sisecam (Retired), RTD, Turkey

How the career of a Turkish AU Glass Science Graduate Student has improved after meeting with Arun Varshneya 35 years ago is described. A chemical engineering undergraduate has been transformed into a Glass Scientist after spending 2,5 years at AU and started to work at the R&D Department of Turkish Glass Works (SISECAM). During all the years she has kept contact with Alfred people both professors and fellow graduates and met them at ICG confrences. In 1986 ICG was held at New Delhi India and it was the first time she has seen Arun again. This encounter had become the beginning of a new kind of friendship other than professor/student relation to glass persons collaboration which has continued till now and will forever. In time she has been asked to write the chapters of Mechanical Strength and Chemical Durability subjects for the "Advanced Glass Technology Educational Notes" book prepared for the production engineers of the company. In writing these parts Arun Varhsneya's book became the only hand book she had used more than any other literature available on these subjects. She had given so many lessons throughout the factories with the slides prepared by utilizing his data which helped her to become a very known and respectable person in the company. She even became Instructor at the Universities of which she will continue to be after her recent retirement from the company. She fully thanks To Arun Varshneya for enlightening her.

Friday, June 14, 2019

SI: Glass Structure and Chemistry

Session 2: Glass and Melt: Macroscopic Properties and Structure of Melt at High Temperature (TC03 & TC26)

Room: Statler (mezzanine)
Session Chairs: Daniel Neuville, IPGP-CNRS-USPC;
Efstratios Kamitsos, National Hellenic Research Foundation

8:00 AM

(ICG-SI-124-2019) Structure and Dynamics of High-Temperature Strontium Aluminosilicate Melts (Invited)

P. Florian*[1]; A. Novikov[1]; L. Hennet[1]; V. Sarou-Kanian[1]; T. Charpentier[2]; D. Massiot[1]; D. R. Neuville[3]

1. CEMHTI-CNRS, France
2. NIMBE-CEA, France
3. IPGP-CNRS, France

We report the study of high-temperature melts (1600–2300°C) and related glasses in the $SrO–Al_2O_3–SiO_2$ phase diagram considering three series: (i) depolymerized ($R = [SrO]/[Al_2O_3] = 3$); (ii) fully polymerized ($R = 1$); and (iii) per-aluminous ($R < 1$). Based on high-temperature ^{27}Al NMR and neutron diffraction, we demonstrate that the structure of the polymerized melts is controlled by the Al/Si distribution in the tetrahedral sites, while the depolymerized melts show smaller rings with a possible loss of non-bridging oxygens on AlO_4 units during cooling for high-silica compositions. Only few five-fold ^{V}Al sites are present except in per-aluminous compositions, in glasses as well as melts with complex temperature dependence. In high-temperature melts, strontium has a coordination number of 8 or less, i.e. less than in the corresponding glasses. The dynamics of high-temperature melts were studied from ^{27}Al NMR relaxation which provides correlation times in close agreement with macroscopic shear viscosity data. At very high temperatures, the NMR correlation times can be related to the oxygen self-diffusion coefficient which shows a decrease with increasing Si/(Al + Si) ratios for polymerized melts with no compositional dependence for depolymerized ones. The dominant parameter controlling the temperature dependence of the aluminum environment of all melts is the distribution of $Al–(OSi)_p(OAl)_{(4-p)}$ units.

8:30 AM

(ICG-SI-125-2019) Structural transition and its effect on crystallization behavior of Alumino-Boro-Silicate glass

J. Cho*[1]; J. Baek[1]

1. Pohang University of Science and Technology, Republic of Korea

The glass network structure governs various thermos-physical properties such as viscosity, thermal and electric conductivities, and crystallization kinetics. We investigated the effect of temperature on structural changes in a Na_2O-CaO-Al_2O_3-SiO_2-B_2O_3 glass system using 27Al MAS NMR spectroscopy. Around the glass transition temperature, most of aluminate structures exist as AlO_4, acting as a glass former. When the temperature is above the melt crystallization temperature, the AlO_4 structure is drastically decreased and glass structures are mainly composed of AlO_5 and AlO_6, acting as glass modifiers. Thermodynamic assessment based on Gibbs energy minimization was used to confirm the dependency of aluminate structure's amphoteric characteristic on temperature by calculating the site fraction of aluminate molecular structures at different temperatures. Temperature-induced aluminate structural variation can also influence silicate and borate structural changes, which have been confirmed by the 29Si and 11B NMR spectra.

8:50 AM

(ICG-SI-126-2019) Rare-Earth Elements Redox kinetics in melts (Invited)

M. Cicconi*[1]; D. R. Neuville[1]

1. Institut de Physique du Globe de Paris, Géomatériaux, France

Rare-Earth Elements (REE) have very distinctive electronic, optical, and magnetic properties. Among REE, Ce and Eu are stable in many systems, with two different valences (Ce^{3+}/Ce^{4+} and Eu^{2+}/Eu^{3+}). Understand the parameters affecting their oxidation states, coordination and bonding environments provides the understanding of the factors controlling the elements speciation both in simplified and multicomponent systems and in turn, the possibility to improve current models and to develop novel technologies/applications. The redox kinetic studies at high temperature allowed defining the element behavior depending on temperature, oxygen activity, and element diffusion. Some examples on the study of Ce and Eu in amorphous and molten materials and on the parameters influencing their oxidation states will be provided.

9:20 AM

(ICG-SI-127-2019) Rare-earth titanate melt structure and glass formation

O. L. Alderman*[1]; C. J. Benmore[2]; A. Tamalonis[1]; R. Weber[1]

1. Materials Development Inc., R&D, USA
2. Advanced Photon Source, X-Ray Science Division, USA

Titanate melts are important in smelting processes, the formation of high-index optical glasses, growth of ferroelectric and functional materials, and potentially for understanding natural magmatic phenomena. In this talk I present structural investigations of rare-earth (RE) titanate melts, some of which form TiO_2-rich binary oxide glasses. In-situ Ti K-edge x-ray absorption near-edge structure (XANES) spectroscopy reveals Ti-O coordination numbers (n_{TiO}) close to five in the melts above their liquidi. Furthermore, n_{TiO} is seen to decrease with increasing RE cation radius, from the non-glass-forming Sc and Y titanates to the glass-forming Nd and La titanates. This is similar to trends observed for alkali titanate glasses, and highlights the benefits arising from in-situ studies of melts, whereby glass-forming and non-glass-forming compositions can be treated on equal footing. Moreover, the RE cation effect on n_{TiO} is suggested to play a key role in the glass forming ability. Both XANES spectroscopy and in-situ high-energy x-ray diffraction indicate an increase in n_{TiO} during cooling and glass formation, toward a value of about 5.5. Such continuous structural transformations are similar to those observed by us in Ba titanate glasses and are expected to increase melt fragility and have a strong impact on phase selection and other melt properties.

10:00 AM

(ICG-SI-128-2019) The temperature dependence of the structure of zinc chloride (Invited)

A. Zeidler*[1]; P. S. Salmon[1]

1. University of Bath, Department of Physics, United Kingdom

The structure of zinc chloride was measured using both neutron and high-energy x-ray diffraction for the glass at 298(1) K and for the liquid over the temperature range 601(1)–977(2) K. In addition neutron diffraction with isotope substitution (NDIS) was use to obtain partial structural information for the glass and the liquid at 605(5) K. Reverse Monte Carlo (RMC) modelling was also employed. The models show temperature dependent structural variability in which there is an interplay between the fractions of corner-sharing versus edge-sharing ZnCl4 tetrahedra. At increasing temperature the system changes from a predominantly corner-sharing glass to a liquid with a significant proportion of edge-sharing motifs at the highest temperatures.

10:30 AM

(ICG-SI-129-2019) The relation between structure, thermodynamics, and properties of oxide glasses

R. Conradt*[1]

1. uniglassAC GmbH, Germany

A continued challenge consists in understanding the relation between the structure of a glass and its macroscopic properties. Technologically, the challenge consists in rendering such understanding useful to the design of glasses with desired properties. The present contribution focuses on macroscopic properties resting on phononic states. These are, first, the properties derived from the heat capacity c_p, in specific: enthalpy, entropy, and Gibbs energy. Above room temperature, c_p is determined by short-range order (SRO, the nature of cation-anion coordination polyhedra) alone. On spatial average, one-component glasses and their crystalline counterparts exhibit identical SRO. This observation is extended to the liquid state and to multicomponent systems. The elastic properties are determined by elastic waves in the acoustic range. Such waves probe both the short-range order and the medium-range order (MRO, the nature of linkage among the cation-anion polyhedra). One-component glasses behave like low-density polymorphs of a given composition. The presence or absence of translational atomic order does not play any role. For multi-component systems, the elastic properties are obtained from a linear superposition of MRO entities the stoichiometry of which is determined by the constitutional phases of the polycrystalline state. Findings are supported by ab-initio DFT calculations.

10:50 AM

(ICG-SI-130-2019) In situ multi scale approach of the glass transition: Linking thermal and mechanical properties to short and mid-range order (Invited)

D. de Ligny*[1]; M. Bergler[1]; F. Werr[1]; A. Veber[1]; P. Benigni[2]

1. University Erlangen-Nürnberg, Materials Sciences and Engineering, Germany
2. IM2NP-CNRS, France

The glass transition is an atomic cooperative process involving a set of relaxations acting at different atomic scale. Collecting in the same time with a high resolution the enthalpic signal coming from a DSC and elastic and/or structural information deduced from spectroscopic observations, allows a more detailed investigation how properties and structure are linked within the glass transition. Since a couple of years a new experimental facility coupling DSC, Raman and Brillouin spectroscopy were implemented. Typically glasses are quenched in the DSC with different cooling rates and are investigated close to the glass transition temperature during heating at a constant rate. The Brillouin spectroscopy data give access to the long range structure since it is related to the elastic and volume properties. The different parts of the Raman spectra are representative of the mid and short range order. A complementary doping of the glass by Eu, allows using the red luminescence of Eu^{3+} which is very sensible to its local structure. This large set of data, representative for different scales of the glass network, is then fitted using a same relaxation formalism. Reliable correlations can be observed. The results presented here will mostly focus on soda-lime glass results and will be compared to previous results of phosphate and borosilicate glasses.

11:20 AM

(ICG-SI-131-2019) Investigation of Liquids and Glasses by Extended Range X-ray Pair Distribution Function and in-situ Property Measurements

R. Weber*[1]; O. L. Alderman[1]; C. J. Benmore[2]; A. Tamalonis[1]; E. Clark[1]

1. MDI, USA
2. Argonne National Lab, Advanced Photon Source, USA

This talk outlines recent advances in the development and use of extended range x-ray pair distribution function measurements. These measurements enable the investigation of nearest neighbor

atomic bonding and mesoscale structure in near real time. In combination with containerless methods, the technique can be applied to deeply supercooled liquids as they approach the glass transition or crystallize. The new capability provides a powerful tool to study phase separation, phase changes, and development of nanoscale heterogeneities. In addition, the prospects for making in-situ measurements of properties (e.g. density and viscosity of supercooled liquids) will be discussed. The application of laboratory-based containerless methods and development of microgravity experiments will also be briefly described. The presentation will be illustrated with examples and results of experiments on a variety of oxide materials. This work is funded by the Department of Energy grant numbers DE-SC-001645, DE-SC0018601 and NASA grant number 80NSSC18K0059.

11:40 AM

(ICG-SI-132-2019) Mixing effect of non-framework cations on viscosity of aluminosilicate glasses and melts

S. Sukenaga*[1]; S. Baba[1]; K. Kanehashi[2]; K. Shinozaki[3]; H. Shibata[1]

1. Tohoku University, Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Japan
2. Nippon Steel & Sumitomo Metal Corporation, Japan
3. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Most of glass materials contain several kinds of non-framework cations, e.g., alkali and alkaline-earth cations, as well as framework cations which construct the network structure. Mixing effect of the non-framework cations on physical properties of aluminosilicate melts and their glasses is important knowledge for estimating the properties of the multicomponent system. In the present study, viscosity of the (30-x)CaO-xR_2O-15Al_2O_3-55SiO_2 (R = Li, Na or K, x = 0-30 mol%) melts was measured using a rotating cylinder method at temperatures above their liquids. The viscosity increases when CaO is replaced by Na_2O or K_2O while the viscosity decreases by replacing CaO by Li_2O. The viscosity at temperatures close to glass transition (T_g) by an indentation method shows that the viscosity decreases with replacing CaO by Li_2O, Na_2O or K_2O. Mixing effect of calcium and alkali cations depends on the temperature range of the melts. Plotting all the viscosity data against normalized temperature by T_g, the fragility (the slope at $T_g/T = 1$) of calcium aluminosilicate melts decreased with replacing CaO by the alkali oxides. This fragility variation will be explained by the change in the local structure of aluminum cations.

12:00 PM

(ICG-SI-133-2019) Thermal expansion of binary and ternary silicate melts in relation to the Q^n distribution

J. Matsuoka*[1]; M. Tsujisaka[1]; J. Katsuki[1]; T. Sugawara[2]; A. Yamada[1]; S. Yoshida[1]

1. The University of Shiga Prefecture, Department of Materials Science, Japan
2. Akita University, Cooperative Major in Life Cycle Design Engineering, Japan

Density of 33Li_2O-67SiO_2 (2L4S), 33Na_2O-67SiO_2 (2N4S), 33(0.5Na_2O-0.5MgO)-67SiO_2 (NM4S), and 33(0.5Na_2O-0.5CaO)-67SiO_2 (NC4S) glass melts were precisely measured from glass transition region to 1668K by TMA and Pt double-bob Archimedean densitometry. Thermal expansion coefficient of 2L4S melt is almost constant against temperature. On the other hand, that of 2N4S decreases with increasing the temperature. It is known that Q^n distribution in lithium disilicate is almost constant among the wide temperature range, and the equilibrium of $2Q^3 \leftrightarrow Q^2 + Q^4$ in sodium disilicate shifts to the right side by increasing the temperature. Therefore, the difference of thermal expansion behavior can be attributed to the difference in Q^n distribution. Temperature dependence of the thermal expansion coefficient of NM4S is nearly the same as that of 2N4S, while that of NC4S is smaller than these. Thermal expansion coefficient as a function of the fraction of Q^3 shows the same slope in these four compositions. This means that the coefficient is strongly affected by the Q^n distribution.

Session 6: Phosphate Glasses and Intermediates

Room: Berkley (mezzanine)
Session Chair: Doris Möncke, Alfred University

8:00 AM

(ICG-SI-134-2019) Glass-forming ability, structure and crystallization of glasses in the ternary system BaO-WO_3-P_2O_5

L. Koudelka*[1]; P. Kalenda[1]; P. Mosner[1]; L. Montagne[2]; B. Revel[2]

1. University of Pardubice, General and Inorganic Chemistry, Czechia
2. University of Lille, France

Tungsten-oxide based materials are known for their electrochromic and photochromic properties resulting in a wide range of applications. This contribution deals with glasses of the ternary system BaO–WO_3–P_2O_5 containing 0-60 mol% WO_3. Fifteen glassy samples from this system were prepared and their basic characteristic parameters were determined. Glasses containing WO_3 are characterized by a good chemical stability. Glass-forming region in this system was determined and glass structure was investigated in four compositional series (100-x)[0.5BaO-0.5P_2O_5]-xWO_3, 50BaO-yWO_3-(50-y)P_2O_5, 40BaO-zWO_3-(60-z)P_2O_5 and (60-u)BaO-uWO_3-40P_2O_5 by Raman and ^{31}P NMR spectroscopies. Changes in the ^{31}P MAS NMR spectra and Raman spectra in all four compositional series are presented and discussed. Crystallization of glasses was studied by XRD and Raman spectroscopy and crystalline products were identified by both methods. Most glasses containing WO_3 crystallize on heating within the range of 650-750°C, with the exception of glasses with 20-30 mol% WO_3, which are thermally stable. Crystallization of glasses revealed the existence of a new compound $Ba(WO_2)_2(PO_4)_2$ prepared by the heat treatment of the glass with composition 25BaO-50WO_3-25P_2O_5.

8:20 AM

(ICG-SI-135-2019) Insights into the structure, chemical bonding and electronic properties of lithium-vanadophosphate glasses from First-Principles Molecular Dynamics simulations

G. Ori*[1]; C. Massobrio[1]; M. Boero[1]

1. IPCMS - CNRS / Université de Strasbourg, France

Glass-based materials containing transition metal (TM) oxides with TM in different oxidation states and modifier ions give rise to a multifunctional platform with tunable ionic-electronic conductivity properties, which are particularly suitable as electrolytes and high capacity cathodes. Glass systems containing vanadium oxides (phosphate and tellurite for instance) are receiving a renewed attention in this field due to their tunable conductivity properties on the basis of the employed synthesis conditions. With this contribution, we show how first-principles molecular dynamics combined with density functional theory can foster our comprehension of the chemical order and chemical bonding properties of the building blocks constituting lithium-vanadophosphate glasses. The output of this work complements the structural knowledge obtained by classical molecular dynamics and represents a key step in order to disentangle the factors governing the complex scenario of the structure - conductivity properties relations for this type of glasses.

8:40 AM

(ICG-SI-136-2019) Redox effects on the structure and properties of Na-Mo-Fe-phosphate glasses

J. Bai*[1]; J. Hsu[1]; R. Brow[1]; C. Kim[2]

1. Missouri University of Science & Technology, USA
2. MO-SCI Corporation, USA

Iron phosphate glasses have been developed as hosts for radioactive wastes, not only because of their excellent chemical durability, but also for their ability to incorporate large concentrations of species like MoO_3 that have lower solubility in conventional borosilicate waste glasses. In the present study, Na-Mo-Fe-phosphate glasses

were prepared with reducing ($NH_4H_2PO_4$) and oxidizing (H_3PO_4) raw materials and the effects of the resulting changes in the Fe^{2+}/Fe^{3+} and Mo^{5+}/Mo^{6+} ratios on glass structure and properties were determined. Two series of Na-Mo-Fe-phosphate glasses were prepared with the different phosphate raw materials: Series A ($xNa_2O•(100-x)•(15MoO_3•22.5Fe_2O_3•62.5P_2O_5$), x=0, 7.5, 15.0, 22.5) and Series B ($15Na_2O•yMoO_3•(28.75-y)Fe_2O_3•56.25P_2O_5$, y=0, 5.75, 11.50, 17.25, 23.00, 28.75). Mössbauer spectrometry reveals much greater fractions of Fe^{2+} in glasses prepared with $NH_4H_2PO_4$ (>50%) than with H_3PO_4 (<10%). Raman spectroscopy reveals the presence of highly-distorted $Mo^{5+}O_6$ sites in Mo-rich glasses prepared with $NH_4H_2PO_4$. The loss of oxygen from the glasses produced under more reducing conditions leads to average phosphate anion sizes, as characterized by high-pressure liquid chromatography. These differences in Fe- and Mo-redox and P-anion distributions are used to explain compositional trends in properties, including glass transition temperatures and aqueous dissolution rates.

9:00 AM

(ICG-SI-137-2019) Antimony phosphate based glass containing alkali metal oxides

O. Boily*[1]; S. Messaddeq[1]; D. Bernier-Marceau[1]; S. Santagneli[2]; Y. Messaddeq[1]

1. Laval University, Canada
2. UNESP, Brazil

The Sb2O3-SbPO4 binary glass system was previously studied, in an attempt to obtain antimony phosphate based glasses with a high homogeneity and a low devitrification tendency. Nevertheless, samples belonging to this glass system may only be prepared with a low thickness of about a millimeter, and have so far restricted widespread applications. Adding alkali metal oxides, specifically a mixture of sodium and potassium oxides, is observed to improve glass formation in this system. Large, transparent and homogeneous bulk samples may be easily obtained with a high alkali metal oxide content. Furthermore, losses by sublimation during glass melting may be entirely suppressed. The Sb2O3-SbPO4-K2O-Na2O quaternary glass system was explored and shows a large glass formation region. This glass system was characterized using Raman and NMR spectroscopy. A profound structural modification, mainly regarding the local environment around phosphorous atoms, is observed when SbPO4 content becomes mostly predominant.

9:20 AM

(ICG-SI-138-2019) Insights on ion and polaron dynamics in phosphate glasses from model-free conductivity scaling

L. Pavić*[1]; A. Šantić[1]; J. Nikolić[1]; R. D. Banhatti[2]; P. Mosner[3]; L. Koudelka[3]; A. Mogus-Milankovic[1]

1. Rudjer Bošković Institute, Division of Materials Chemistry, Croatia
2. Rudjer Bošković Institute, Division of Physical Chemistry, Croatia
3. Faculty of Chemical Technology, University of Pardubice, Department of General and Inorganic Chemistry, Czechia

A deep understanding of electrical transport in mixed conductive glasses is necessary for the development of these materials as cathodes in battery technologies. In this study, we report on the dynamics of polarons and ions in six glass series of composition WO_3/MoO_3-$Li_2O/Na_2O/Ag_2O$-ZnO-P_2O_5 by examining their frequency-dependent conductivity using simple model-free scaling procedures proposed by Summerfield and Sidebottom. The validity of Sidebottom scaling for each glass confirms that the time-temperature superposition principle is satisfied implying that the basic conduction mechanism for individual glass does not change with temperature. However, Summerfield scaling is not valid for all glasses. Deviation observed for purely ionic Li_2O glass and mixed Li_2O-WO_3/MoO_3 glasses where Li^+ conductivity dominates, originates from the specific interaction of Li^+ ions with the local glass network. In addition, the deviation is also observed for particular WO_3-based glasses in which the contribution of ionic conductivity is comparable to polaronic one. The cause of this phenomenon lies in the significant amount of both types of charge carriers and their different thermally activated mobility. We show how very fine differences in conductivity spectra, deduced solely from the experimental data, contain valuable insights into the dynamics of mixed ion-polaron transport.

Session 6: Phosphate Glasses - Bioactive and Weathering

Room: Berkley (mezzanine)
Session Chair: Delia Brauer, Friedrich-Schiller-Universität

10:00 AM

(ICG-SI-139-2019) Oxyfluorophosphate bioactive glasses (Invited)

J. Massera*[1]

1. Tampere University, Faculty of Medical Sciences and Technology, Finland

Fluoride containing bioactive glasses have attracted interest in dental and orthopedic application, as they precipitate fluorapatite which has higher hydraulitic resistance than hydroxyapatite. However, introducing fluoride in silicatete bioactive glasses lead to an increase in the network connectivity, in turn decreasing the glass bioactivity. Furthermore, in orthopedic applications, the optimal bone graft is a 3D scaffolds with controlled porosity. However, common silicate bioactive glasses are prone to crystallization, during sintering, which drastically reduces their bioactivity. Alternatives are the phosphate glasses. Invert phosphate glasses are bioactive and possess thermal properties enabling hot forming. However, little is known on the impact of fluorine on the structure, thermal and in vitro dissolution properties. In this presentation, the $75NaPO_3$-(25-x)CaO-xCaF_2 invert phosphate glass, will be introdcued. With increasing fluorine content an increase of the P-F bond is reported. The structural changes, associated to the increase in F ions, leads to an increase in dissolution rate. The thermal properties were measured using DTA and a crystallization study revealed that upon substitution of CaO for CaF_2 a progressive change from surface to bulk crystallization occurred. The impact of F content as well as crystallization on MC3T3 pre-osteoblastic cell viability was studied using extract and the cytotoxicity index quantified.

10:30 AM

(ICG-SI-140-2019) The role of metal complexes in phosphate glasses hydrolysis

D. A. Avila Salazar*[1]; P. Bellstedt[1]; D. S. Brauer[1]; T. Kasuga[2]; A. Miura[2]

1. Friedrich-Schiller-Universität Jena, Germany
2. Nagoya Institute of Technology, Department of Frontier Materials, Japan

Structural changes in phosphate glasses tune glass degradation, which is of interest for therapeutic applications such as drug delivery. ^{31}P MAS NMR characterization of P_2O_5–(x-y)CaO–Na_2O–CoO glasses was correlated with dissolution kinetics by time-dependent ^{31}P NMR analysis. Here, the paramagnetic nature of Co^{2+} was exploited, as broadening of the ^{31}P resonance provided direct information about the role of metal complexes during hydrolysis. Glasses dissolved congruently and attributing the first dissolution stage to the hydration of phosphate polymers, long chains were identified in EDTA; the mild initial rise in the pH was ascribed as protonation of the two terminal phosphate groups from the original 8-9 polymer chains. Trimetaphosphate and orthophosphate as predominant structures in solution, indicated fast hydrolysis of chains and exhibited paramagnetic broadening, thus suggesting that the phosphate group may be directly coordinated to Co^{2+}. Hydrolysis rate was proportional to phosphate complex stability, with stronger complexes for chains than for rings. A competition between solvent and phosphate for the metal ion occurred in the order: EDTA>Tris(pH: 7.9)>Tris(pH: 7.4)>deionised water. Coordination of phosphate species by metal ions appears to play a catalytic role in the hydrolysis mechanism and may consist in turning phosphorus into a suitable electrophile, for a subsequent nucleophilic attack by water.

10:50 AM

(ICG-SI-141-2019) Structure and dissolution behavior of alkali borophosphate glasses for biomedical applications

P. Freudenberger*[1]; R. L. Blatt[1]; M. Schlesinger[1]; R. Brow[1]

1. Missouri University of Science & Technology, USA

The purpose of this work was to understand borophosphate glass structure and dissolution mechanisms, particularly with respect to resulting pH, for biological applications. Several series of borophosphate glass compositions, $16Na_2O$-(24-y)CaO-ySrO-xB_2O_3-(60-x)P_2O_5 where x = 0, 10, 20, 30, 40, 50, and 60 and y = 0, 12, 24 were prepared. Quantitative High Pressure Liquid Chromatography (HPLC), Raman Spectroscopy, and ^{11}B Magic Angle Spinning-Nuclear Magnetic Resonance Spectroscopy (MAS-NMR) were used to characterize the types and concentrations of phosphate and borate structures of the original glass. The initial addition of B_2O_3 decreases dissolution rates, although with additional B_2O_3, dissolution rates increase. This is due to the formation a tetrahedral borophosphate network at lower B_2O_3 contents, which then transitions to mixed trigonal and tetrahedral borate structures as the B_2O_3 content is increased. The replacement of CaO by SrO reduces the electronic asymmetry associated with the non-bridging oxygens in the phosphate tetrahedra, making the glasses more resistant to hydration. Dissolution behavior was initially estimated using FactSage®, and was compared to calculations similar to work by Ma et al., which considers the types of phosphate species as characterized by HPLC to estimate solution pH.

11:10 AM

(ICG-SI-142-2019) Physical and structural properties of MgO-SiO_2-$PO_{5/2}$ invert glasses prepared by a levitation technique

A. Masuno*[1]; S. Sasaki[2]; Y. Yanaba[3]; H. Inoue[3]

1. Hirosaki University, Graduate School of Science and Technology, Japan
2. Hirosaki University, Faculty of Science and Technology, Japan
3. The University of Tokyo, Institute of Industrial Science, Japan

MgO-SiO_2-$PO_{5/2}$ ternary glasses were fabricated in bulk form by using containerless processing. Densities of 50MgO-(50−x) SiO_2-x$PO_{5/2}$ glasses changed moderately with an increase of x as well as those of 67MgO-(33−x)SiO_2-x$PO_{5/2}$ glasses. Both glass transition temperature and crystallization temperature decreased with an increase of x for 50MgO-glasses and 67MgO-glasses, while ΔT did not changed significantly. Raman scattering spectra showed that connectivity fragmentation of local structure Q^n of SiO_4 and PO_4 units progressed more with in crease of MgO content. It is expected that MgO-rich glasses exhibit excellent mechanical properties because of their characteristic glass structure. Thermal, optical, mechanical and structural properties of MgO-rich MgO-SiO_2-$PO_{5/2}$ ternary glasses will be reported.

11:30 AM

(ICG-SI-143-2019) Structure and weathering of SiO_2 contained phosphate glass

H. Ikeda*[1]

1. Nippon Electric Glass Co., Ltd., Fundamental Technology, Japan

Phosphate glass is an important glass system as host materials for photoluminescent dopants. Although phosphate glass has excellent properties, it is difficult to be applied to a commercial product because of low weathering. In order to improve the weathering, we focused on optimization of phosphate glass network structure by addition of SiO_2. Glass samples with nominal molar compositions of (59-x)P_2O_5 - 13Al_2O_3 - 28Na_2O - xSiO_2 were prepared and investigated. When x is up to 6, the weathering of the phosphate glass was improved, but then it worsened. Glass transition temperature (Tg) showed maximum at x=6, which indicates SiO_2 should participate in the phosphate glass network structure by up to x=6. Raman spectra showed P-Q^2 of phosphate glass decreased while P-Q^1, Q^3 increased. Increasing of P-Q^3 could be explained by forming P-O-Si in the network structure.

11:50 AM

(ICG-SI-144-2019) Efficacy of high-field-strength cation additives in improving Mo solubility in borosilicate glasses

A. Krishna Murthy*[1]; S. Kroeker[1]

1. University of Manitoba, Chemistry, Canada

Despite the attractiveness of sodium borosilicate glasses for radioactive waste immobilization, they have low affinity for certain fission products such as molybdenum, where the high cation-field-strength of Mo^{6+} competes with network-forming cations to induce MoO_4^{2-} clustering and concomitant sequestration of radioactive ions such as ^{137}Cs and ^{90}Sr into water-soluble crystalline molybdate phases. We have explored the use of cation additives with carefully selected field-strengths to influence the structural chemistry of molybdenum. For example, magnesium, with its relatively high field-strength, can be considered an intermediate network former, performing the dual functions of preferentially charge-balancing molybdate units and anchoring them to the silicate network, thereby preventing phase separation. The high field-strength P^{5+} forces Mo^{6+} into high-coordinate environments within the glass network, mitigating against devitrification. Multinuclear NMR spectroscopy and x-ray diffraction of several series of glasses are used to determine the network structure and homogeneity of Mo-loaded sodium borosilicate glasses with added MgO and P_2O_5. These distinct but related strategies successfully increase the Mo loading capacities by at least a factor of three, without molybdate devitrification.

Session 11: Glass-Organic Adhesion

Room: Terrace (lower level)
Session Chairs: Aravind Rammohan, Corning Incorporated; Eunseog Cho, Samsung

8:30 AM

(ICG-SI-145-2019) Computational approaches for understanding adhesion behavior at organic-inorganic interface (Invited)

K. Min*[1]; A. Rammohan[2]; H. Lee[1]; J. Shin[3]; S. Lee[4]; S. Goyal[2]; H. Park[4]; J. C. Mauro[5]; R. Stewart[2]; V. Botu[2]; H. Kim[4]; E. Cho[1]

1. Samsung Advanced Institute of Technology, Autonomous Material Development Lab, Republic of Korea
2. Corning Incorporated, USA
3. Nano Electronics Lab, Samsung Advanced Institute of Technology, Republic of Korea
4. Corning Technology Center Korea, Republic of Korea
5. Pennsylvania State University, USA

Investigating adhesion behaviors at organic-inorganic interface provides fundamental understanding on their functional performance. This is because underlying nature of adhesion can determine the structural stability at such interface during manufacturing and usage. From experiments, pulling and peeling methods are widely applied to measure the degree of adhesion but they cannot provide the microscopic view on how structural deformation is affected under different types of mechanical loading. In this study, we suggest a computational approach to examine adhesion properties depending on different environment by providing quantitative properties and atomic snapshots. As a proof of concept, aromatic and aliphatic type of polyimides placed on top of silica glass are constructed. To quantity the adhesion, we implement three methods of pulling, peeling, and sliding using steered molecular dynamics simulations. Upon those tests, force and detachment distance is measured and compared for those two structures. In order to expand current methods to practical applications, we apply those to design a polymeric binder attached to lithiated silicon based anode for improving its structural integrity during electrochemical cycling. The role of different functional groups is investigated to confirm which of them is the most effective to prevent the cohesive failure in the polymeric binder.

9:00 AM

(ICG-SI-146-2019) Characterizing the fundamental adhesion of Polyimides on glass surfaces using atomistic simulations (Invited)

S. Goyal*[1]; H. Park[1]; J. C. Mauro[2]; A. Rammohan[1]

1. Corning Incorporated, USA
2. Pennsylvania State University, Material Science and Engineering, USA

Understanding the interaction between polyimide and inorganic surfaces is vital in controlling interfacial adhesion behavior. The study present uses molecular dynamics simulations to study the adhesion of commercially relevant polyimides on crystalline and glassy silica surfaces. The talk will focus on the effects of surface hydroxylation, glass structure, and polyimide chemistry on adhesion. The results reveal that polyimide have stronger adhesion on hydroxylated surfaces compared to bare surfaces. Also, adhesion of polyimide onto silica glass is stronger compared to the corresponding crystalline surfaces. Finally, we explore the molecular origins of adhesion to understand why some polyimide monomers like Kapton have a stronger adhesion per unit area (adhesion density) than others like BPDA-APB, allowing us to tailor glass-polymer interfaces.

9:50 AM

(ICG-SI-147-2019) Computational Analysis on the Adhesion Mechanism between Organic Coatings and Glass by Molecular Dynamics Simulations (Invited)

H. Park*[1]; S. Lee[1]; D. F. Acquard[2]; G. Agnello[2]; J. Banerjee[2]

1. Corning Precision Materials, Corning Technology Center Korea, Republic of Korea
2. Corning Incorporated, USA

Fundamental understanding of organic-inorganic interfaces is critical for the modulation of adhesion or process improvement. Thus, we investigate adhesion and failure mechanisms between organic coatings and glass in this work. Molecular dynamics simulations are employed to study adhesion between two kinds of organic films – copolymer and surfactant – and the silica glass, and to analyze failure mechanisms as a function of the adhesion test modes and relative humidity. Under anhydrous conditions, the interface between the copolymer (containing polar/dispersive components) and fully-hydroxylated silica surface undergoes a cohesive failure and the adhesion force at sliding test is smaller than at pulling test. However, the introduction of humidity induces a shift to adhesive failure and a decrease in adhesion energy. The micelle structure of n-Hexadecyltrimethylammonium Chloride (CTAC) surfactant in the hydrated state collapses during the dehydration process, and a monolayer-like film is formed on a silica surface. Sliding tests reveal that the surface coverage of CTAC head groups determines the adhesion strength at the interface, but the adhesion is significantly lowered by humidity since water molecules disrupt the adsorption of CTAC.

10:20 AM

(ICG-SI-148-2019) Development of Inorganic-organic Hybrid Coating for Easy-to-clean Glass (Invited)

K. Tapasa*[1]; U. Pantulap[1]; K. Matcharee[1]; I. Youngthin[1]

1. Department of Science Service, Thailand

The aim of this project, therefore, to develop the hydrophobic glass surface by coated with the inorganic-organic hybrid film. The sol-gel process was used for the film synthesis. Tetraethyl orthosilicate (TEOS) was used as the inorganic part. From the comparison of several hydrophobic reagents (HR), which was the organic part, it is found that octyltriethoxysilane (OTES) was the best HR. The factor for the film synthesis namely, TEOS/OTES ratio, water/TEOS ratio (R), catalyst and annealing temperature were studied. It was found that the film composed of TEOS-OTES at the ratio of 80:20 volume, using R equals to 4 and annealed at 60°C resulted in the highest water droplet contact angle of 108°. Moreover, SiO_2 particles were to TEOS-OTES film to increase the hydrophobic properties. The results exhibited that the contact angle increased with increasing SiO_2 content but the transparency was decreased dramatically. The TEOS-OTES and TEOS-SiO_2-OTES had a very good chemical and weathering.

SII: Glass Physics

Session 3: Glass under Extreme Conditions III

Room: Clarendon (mezzanine)
Session Chairs: Jincheng Du, University of North Texas;
Shinji Kohara, Japan Synchrotron Radiation Research Institute

8:00 AM

(ICG-SII-203-2019) Ultrahigh-pressure form of SiO_2 glass with dense pyrite-type crystalline homology (Invited)

Y. Onodera*[1]; S. Kohara[2]; H. Inoue[3]; M. Murakami[4]

1. Kyoto University, Institute for Integrated Radiation and Nuclear Science, Japan
2. National Institute for Materials Science (NIMS), Research Center for Advanced Measurement and Characterization, Japan
3. The University of Tokyo, Institute of Industrial Science, Japan
4. ETH Zurich, Department of Earth Sciences, Switzerland

High-pressure synthesis of denser glass has been a longstanding interest in condensed-matter physics and materials science because of its potentially broad application. Nevertheless, understanding its nature under extreme pressures has yet to be clarified due to experimental and theoretical challenges. We found the formation of OSi_4 tetraclusters associated with that of SiO_7 polyhedra in SiO_2 glass under ultrahigh pressures to 200 gigapascal by a combination of high-pressure X-ray diffraction measurements and classical molecular dynamics (MD) simulations. Persistent homology analyses on the MD-generated atomistic configurations found increased packing fraction of atoms whose persistence diagram at ultrahigh pressures is similar to a pyrite-type crystalline phase, although the formation of tetraclusters is prohibited in the crystalline phase. This critical difference would be caused by the potential structural tolerance in the glass for distortion of oxygen clusters. Furthermore, an expanded electronic band gap calculated from DFT simulations demonstrates that chemical bonds survive at ultrahigh pressure.

8:30 AM

(ICG-SII-204-2019) Structure of amorphous oxides at mega-bar pressure: Insights from high-resolution NMR and inelastic X-ray scattering (Invited)

S. Lee*[1]

1. Seoul National University, Republic of Korea

When compressed above megabar pressures (100 Gigapasal), glasses may undergo structural transitions into more densely packed networks that differ from those at ambient pressure. Progress in inelastic X-ray scattering (IXS) and solid-state NMR provided insights into the pressure-induced bonding changes in oxide glasses; however, inherent lack of sensitivity in both element-specific experimental probes poses challenges for probing glass structures above 100 GPa. Here, we provide an overview of the recent experimental and theoretical progress and insights by IXS into electronic structures of key amorphous oxides under extreme compression beyond mega-bar pressure conditions, unveiling the systematic pressure-induced changes in band-gap, effect of densification on site-specific edge energy, and cation/anion coordination transformations up to ~125 GPa. The results confirm that the transition pressure of the formation of highly coordinated framework cations systematically increases with the decreasing atomic radius of the cations. High resolution solid-state NMR study of oxide glasses under compression up to 25 GPa revealed the previously unknown origin of anomalous pressure-dependence of multi-component oxide glasses.

9:00 AM

(ICG-SII-205-2019) Reactive simulation of shock propagation in sodium silicate glasses

P. Rathod[1]; R. Ravinder*[1]; R. Kumar[1]; N. Krishnan[1]

1. IIT Delhi, India

Glasses, during their service life, could be exposed shock compression leading to the structural failure. Despite the fundamental importance, effects of shock-wave propagation on silicate glasses remain poorly understood. Herein, using reactive molecular dynamics simulations we study the effect of shock-waves on the structure of sodium silicate glass. We investigate the role of chemical reactivity using two different potentials—the two-body Teter potential and reaxFF. We observe that the short-range and the medium-range orders of the glasses are significantly affected by the shock front. In particular, we observe that the bond-length monotonically decreases with increasing shock velocity for all the atomic pairs in the glass. Bond angles also exhibits increased broadening suggesting an increased disorder in the structure. Similarly, the ring distribution of the glass structure exhibits the presence of smaller and odd numbered rings suggesting the presence of homonuclear bonds. Further, we obtain Hugoniot curves for the system using the two different potentials. Overall, we show that reactive simulations can be a powerful tool to study the effect of extreme conditions on the structure and properties of silicate glasses.

9:20 AM

(ICG-SII-206-2019) Vibrational investigation of picosecond pulsed laser structured objects in silica glass

M. Bergler*[1]; K. Cvecek[2]; M. Schmidt[2]; D. de Ligny[1]

1. Friedrich-Alexander-University Erlangen-Nuremberg, Institute of Glass and Ceramics, Germany
2. Friedrich-Alexander-University Erlangen-Nuremberg, Institute of Photonic Technologies, Germany

Due to its low thermal expansion coefficient and thermal shock stability, pure silica glass is able to withstand extreme energy deposition conditions, which are generated in this study using a 10 ps ultra-short pulsed laser at diverse pulse energies and repetition rates. Further, the energy deposition per volume is controlled with the feeding speed of the sample. In this way, different temperature and pressure conditions inside the network are generated, resulting in a change of density and refractive index. This "memory" effect of the network is observed with a coupled Raman and Brillouin spectrometer (ARABICA) to identify structural changes. These rearrangements of the network are quantified using the main band position as well as the defect bands in the Raman spectrum. Thus, an estimation of the fictive temperature and the neutral pressure encountered are possible. By observation of the Brillouin shift of longitudinal acoustic modes, changes of the refractive index as well as elastic properties are studied. Additional pump-probe high-speed camera recordings will be provided, showing the modification process in detail with the evolution of the laser generated plasma as well as pressure waves running through the material.

Session 9: Modeling and Simulations (TC 06)

Room: Arlington (mezzanine)

Session Chair: Morten Smedskjaer, Aalborg University

8:00 AM

(ICG-SII-207-2019) Fracture Mechanics of Phase-Separated Glasses by Peridynamic Simulations

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1. University of California, Los Angeles, USA
2. Indian Institute of Technology Delhi, India

Silicate glasses exhibiting a controlled extent of phase separation could exhibit higher resistance to fracture while retaining their transparency. However, the effect of nanoscale phase separation on the fracture toughness of glasses remains poorly understood. Here, based on peridynamic simulations, we show that such nanoscale microstructure can significantly affect the toughness of silicate glasses. The effect of stiff and soft phases on the propagation of cracks is discussed.

8:20 AM

(ICG-SII-208-2019) Automated fractographic analysis of silicate glasses by computer vision

L. Ma*[1]; R. Dugnani[1]

1. UM-SJTU Joint Institute, Shanghai Jiao Tong University, Shanghai, China, China

Currently, the fracture strength of silicate glasses is estimated correlating fractographic features such as "mirror radii" to the fracture strength as described in the classic, 1972 work by L. Orr. Nonetheless, the literature reported that a 7.5% error in the estimated strength resulted from individuals' perception of the mirror radii. In this work, an unbiased computer vision method for estimating the strength of amorphous, brittle materials was developed. A baseline-set of fracture surfaces' profilometry scans consisting of eight, 2mm-thick, soda-lime glass plates fractured in bending (strength: 56-139MPa) was initially generated. Subsequently, multi-length scaled features (i.e., plate thickness, surface roughness, characteristic flaw size) were compared between the test samples and the baseline-set using hue-saturation histogram image analysis. The method coupled computer vision with the latest analytical model describing fracture-features' formation in silicate glasses and was tested on both annealed and chemically strengthened glasses of various composition and thicknesses. For the cases considered, the strength estimations were within 10% of the measured values. The method was especially attractive for samples with damaged origins as no knowledge of the mirror radius was required. A larger baseline-set and/or more sophisticated training was expected to substantially improve strength-estimations.

8:40 AM

(ICG-SII-209-2019) Predicting densities and elastic moduli of the SiO_2-based glasses by machine learning

Y. Hu*[1]; G. Zhao[2]; T. Del Rose[1]; Q. Zhao[3]; Q. Zu[3]; Y. Chen[3]; X. Sun[4]; M. De Jong[5]; L. Qi[1]

1. University of Michigan, Materials Science and Engineering, USA
2. Pennsylvania State University, Statistic, USA
3. Sinoma Science & Technology Co., Ltd., China
4. Continental Technology LLC, USA
5. University of California, Berkeley, USA

Chemical design of the SiO_2-based glasses with high elastic moduli and low weight is of great interest. Here we show that the density and elastic moduli of the SiO_2-based glass can be efficiently predicted by machine learning (ML) techniques across a complex compositional space, which includes 11 types of additive oxides besides SiO_2. Our machine learning approach relies on a training set generated by high-throughput molecular dynamic (MD) simulations, a set of elaborately constructed descriptors that bridges the empirical statistical modeling with the fundamental physics of interatomic bonding, and a statistical learning/predicting model developed by implementing least absolute shrinkage and selection operator with a gradient boost machine (GBM-LASSO). By just training with a dataset that only composed of binary and ternary glass samples, our model shows remarkable learning accuracy and outstanding extrapolation ability to predict the density and elastic moduli for k-nary (k can be much larger than 3) glasses that beyond the training set. Finally, as an example to illustrate the potential applications of our ML model, we perform a rapid screening over 82,251 compositions of a quinary glass system to construct a compositional-property database that allows for a fruitful overview on the glass density and elastic properties.

9:00 AM

(ICG-SII-210-2019) Enhanced Ductility in Silica Nanoglass by Room Temperature Consolidation

Y. Zhang*[1]; L. Huang[1]; Y. Shi[1]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA

The brittleness of oxide glass has dramatically restricted its practical applications as structural materials although it displays exceptional strength. Herein, we prepared silica nanoglass with enhanced ductility by consolidating amorphous nanospheres in molecular dynamics simulations. Low pressure (~2 GPa) is sufficient to achieve enhanced ductility (~40% failure strain) in silica nanoglass at room temperature, whereas more than 10 GPa is needed to compress bulk silica glass to achieve a similar effect. The significant reduction of the critical pressure to trigger the brittle to ductile transition can be attributed to both significant amount of flexible atoms near glass surface and the enormous shear stress generated during the consolidation process inside nanoglass. Remarkable ductility up to 100% can be achieved in silica nanoglass by using higher consolidation pressure to generate considerable amount of 5-fold Si atoms, which display higher propensity for shear deformation. Meanwhile, surprising work hardening effect was firstly observed in nanoglass, where yield strength is increased from 3 GPa to ~ 6 GPa due to the stress-assisted relaxation of 5-fold atoms to 4-fold atoms during deformation. We believe room temperature consolidation of nanoparticles may provide a universal method for synthesizing ductile oxide glasses to enable them as structural materials for a broad range of applications.

9:20 AM

(ICG-SII-211-2019) Irradiation induced brittle-to-ductile transition in α-quartz

A. Kumar[1]; R. Ravinder[1]; R. Kumar[1]; N. Krishnan*[1]

1. IIT Delhi, India

Crystalline and glassy forms of silica, namely α-quartz and glassy silica, are archetypical brittle materials. Upon irradiation, α-quartz undergoes significant disordering at the atomic level to form a structure comparable to that of glassy silica. While the effects of vitrification on the properties of silica are well-known, the effects on irradiation on the mechanical properties of α-quartz remains poorly understood. Herein, using molecular dynamics (MD) simulations, we analyze the fracture behavior of irradiated α-quartz. Interestingly, we observe that the α-quartz undergoes a room temperature brittle-to-ductile transition upon irradiation, which is consistent with previous experimental observations for silica glass. This enhanced ductility is evident from the brittleness index of 0.21 for irradiated quartz against the value of 0.94 for α-quartz. We demonstrate that the transition is due to the liquid-like structure of α-quartz which exhibits an energy landscape separated by low energy barriers leading to increased mobility and re-organization upon applied strain. This allows for a redistribution of the crack-tip stress by local self-organization, which eventually leads to crack blunting and a notable increase in ductility.

10:00 AM

(ICG-SII-212-2019) Crack branching in brittle glasses

J. Luo*[1]; B. Deng[1]; K. Vargheese[1]; A. Tandia[1]; J. C. Mauro[2]

1. Corning Incorporated, USA
2. Pennsylvania State University, Department of Materials Science and Engineering, USA

Brittle glasses can easily break into pieces through crack branching. However, the fundamental mechanism underlying this daily phenomenon is still controversial. In this study, using sub-micron scale atomic simulations with three independent force fields, we observe crack branching in brittle oxide glasses and reveal that crack branching in the most brittle glasses is triggered by multiple simultaneous cavitation events ahead of the crack tip. The critical speed at which crack branches is not a constant, but depends on the far field loading.

Session 9: Water and Aging Effects (TC 06)

Room: Arlington (mezzanine)
Session Chair: Morten Smedskjaer, Aalborg University

10:20 AM

(ICG-SII-213-2019) Micromechanical properties of hydrous oxide glasses (Invited)

J. Deubener*[1]; H. Behrens[2]; R. Müller[3]

1. Clausthal University of Technology, Institute of Non-Crystalline Materials, Germany
2. Leibniz University Hannover, Institute for Mineralogy, Germany
3. Bundesanstalt für Materialforschung und -prüfung (BAM), Germany

The paper reviews recent results on the impact of hydration on the micromechanical properties of various oxide glasses including silicate, borosilicate and borate compositions. Glasses with a total water content up to approx. 20 mol% using wet condition of melting under external pressure up to 6 kbar were studied. The effects on elastic constants, hardness, crack formation and propagation are discussed on the basis of changes in glass structure and sub-Tg relaxation induced by dissolved OH-groups and water molecules. On the other hand, selected mechanical tests were performed in different environments contrasting contributions of humidity with those of dissolved water species in the hydrous glasses.

10:50 AM

(ICG-SII-214-2019) Density, microhardness and elastic moduli of hydrous soda-lime silicate-glasses

P. Kiefer*[1]; J. Deubener[1]; R. Balzer[2]; H. Behrens[2]; T. Waurischk[3]; S. Reinsch[3]; R. Müller[3]

1. Clausthal University of Technology, Institute for Nonmetallic Materials, Germany
2. Leibniz University, Institute for Mineralogy, Germany
3. BAM Federal Institute for Materials Research and Testing, Materials Engineering, Germany

The effect of structural water on density, microhardness and elastic constants of soda-lime-silica glasses is studied. For that purpose hydrous glasses of up to 22 mol% total water were prepared in an internally heated pressure vessel at 500 MPa and tested at ambient pressure using buoyancy, ultrasonic echography and Vickers indentation. It is found that the Poisson's ratio and the water content are positively correlated, while density and the elastic moduli decrease with increasing water content. The dependencies are found to be non-linear reflecting the non-linear change in the concentrations of OH groups and H_2O molecules dissolved in the glass structure, which were quantified by IR spectroscopy and Karl-Fischer titration. Time-dependent hardness tests under dry nitrogen gas and in humid air are presented to contrast the effect of water speciation and humidity on microhardness.

11:10 AM

(ICG-SII-215-2019) Sub-critical crack growth in hydrous silicate glasses

T. Waurischk*[1]; R. Balzer[2]; P. Kiefer[3]; S. Reinsch[1]; R. Müller[1]; H. Behrens[2]; J. Deubener[3]

1. BAM Federal Institute for Materials Research and Testing, Germany
2. Leibniz University Hannover, Germany
3. Clausthal University of Technology, Germany

Ambient water influences sub-critical crack growth (SCCG) from microscopic surface flaws, leading to stress corrosion at the crack tip. The complex influence of humidity accelerating slow crack propagation (region I) is well studied only for dry commercial NCS glass (< 1000 ppm water). To shed light on this influence, the effect of water is mimicked by studying SCCG water-bearing glasses. For this purpose, water-bearing silicate glasses of 8 wt% total water were synthesized at 0.5 GPa and compared to dry glasses. SCCG was measured in double cantilever beam geometry.

For dry glasses, 3 trends in crack velocity vs. stress intensity, K_I, curve were found. The slope in region I increases in the order NCS < NBS < BaCS < NZnS < NAS glass. The velocity range of region II, reflecting the transition between corrosion affected and inert crack growth (region III), varies within one order of magnitude among these glasses. The K_I region of inert crack growth strongly scatters between 0.4 and 0.9 $MPam^{0.5}$. For hydrous glasses, it is found that water strongly decreases Tg, form a new sub-Tg internal friction peak caused by molecular water, and makes the glasses more prone to SCCG. The observed trends will be discussed in terms of the effects of Youngs Modulus on the strain energy release rate and energy dissipation related to mechanical glass relaxation phenomena.

11:30 AM

(ICG-SII-216-2019) Surface Stress Relaxation and Slow Crack Growth in Glasses

M. Tomozawa*[1]; E. Aaldenberg[1]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA

The entry of water in glass can promote slow crack growth, but it can also cause cracks to slow down at the fatigue limit as a result of surface stress relaxation. After extensive investigation by many researchers, the mechanism of the crack growth behavior has remained unclear. We propose that slow crack growth and surface stress relaxation share a common origin. Water entering through the surface of glass or at the crack tip causes local fluctuations in the composition. These fluctuations would decrease a local modulus of the glass, and the crack would preferentially grow through regions of lower modulus. At low stress intensities, where the fatigue limit takes place, sufficient time elapses for the water which entered ahead of the crack tip to relax the modulus before the crack is able to grow through these regions. Thus, the stress is relaxed and the crack driving force is reduced. Small quantities of water are able to produce a large dynamic mechanical relaxation strength as a result of the fluctuations.

11:50 AM

(ICG-SII-217-2019) Flaw size dependence of fatigue in silica

G. Scannell*[1]; S. Glaesemann[1]

1. Corning Incorporated, USA

When placed under stress, the mechanical strength of glass can decrease over time through the effects of sub-critical crack growth. This is increasingly relevant as glass is used in more applications where it is placed in a bent or curved shape and is continuously stressed. Having a higher fatigue resistance parameter, n, is important in determining what stresses the glass can be placed under. The fatigue resistance parameter, n, of silica glass is 40 for large flaws where the glass fails below 300 MPa, but quickly drops off to 20 for smaller flaws. To examine this flaw size dependence more closely, we measured this fatigue parameter in silica glass over a wide range of flaw sizes using dynamic fatigue testing on fibers and thin plates. For each flaw size, the dynamic fatigue parameter, n, was obtained using stressing rates that ranged seven orders of magnitude. The fatigue behavior of these surface flaws is compared to those from slow crack growth experiments in literature.

12:10 PM

(ICG-SII-218-2019) Fatigue of Mixed Alkali Glasses

J. S. Aaldenberg*[1]; P. J. Lezzi[1]; T. M. Gross[1]

1. Corning Incorporated, USA

Glasses fail when a crack is loaded at the fracture toughness. However, the strength of glass is well known to be time-dependent in an atmosphere containing water or water vapor due to subcritical crack growth. The crack growth behavior is dependent on both the glass composition and the environment. In this research the slow crack growth behavior of alkali-boro-alumino-silicate glass systems were investigated at ambient conditions where the alkali species was either Li^+, Na^+, or K^+. Furthermore, the relative molar concentrations of the alkali species were varied to investigate the mixed-alkali effects on slow crack growth fatigue behavior. Slow crack growth was measured using the double cantilever bean (DCB) crack growth technique.

Session 10: Acoustic Properties of Glass

Room: Hancock (mezzanine)

Session Chairs: Benoit Ruffle, Montpellier University; Anne Tanguy, INSA Lyon

8:00 AM

(ICG-SII-219-2019) Connection between the Boson peak and quasi-localized modes in amorphous solids (Invited)

A. Ikeda*[1]; M. Shimada[1]; H. Mizuno[1]; M. Wyart[2]

1. University of Tokyo, Graduate School of Arts and Sciences, Japan
2. EPFL, Institute of Physics, Switzerland

The low-temperature properties of amorphous solids are widely believed to be controlled by low-frequency quasi-localized modes. What governs their spatial structure and density is however debated. We study these questions numerically in very large systems as the jamming transition is approached and the pressure p vanishes. We find that these modes consist of an unstable core in which particles undergo the buckling motions and decrease the energy, and a stable far-field component which increases the energy and prevents the buckling of the core. The size of the core diverges as $p^{-1/4}$ and its characteristic volume as $p^{-1/2}$. These features are precisely those of the anomalous modes known to cause the Boson peak in the vibrational spectrum of weakly-coordinated materials. From this correspondence we deduce that the density of quasi-localized modes must go as $g_{loc}(\omega) \sim \omega^4/p^2$, in agreement with previous observations. Our analysis thus unravels the nature of quasi-localized modes and the connection between the Boson peak and the quasi-localized modes in a class of amorphous materials.

8:30 AM

(ICG-SII-220-2019) High-frequency acoustic modes in vitreous silica via ultrafast optical techniques (Invited)

M. Foret*[1]; A. Huynh[2]; E. Péronne[2]; J. Sheu[3]; T. Hung[4]; B. Perrin[2]; B. Ruffle[1]; R. Vacher[1]; C. Sun[4]

1. University of Montpellier, Physics, France
2. Sorbonne Universités, UPMC, Institut des Nanosciences de Paris, France
3. Department of Photonics and Advanced Optoelectronic Technology Center, National Cheng Kung University, Taiwan
4. Department of Electrical Engineering and Graduate Institute of Photonics and Optoelectronics, National Taiwan University, Taiwan

We use the advent of reliable ultrafast optical techniques to explore acoustic modes in glasses in the difficult but crucial frequency region between around 0.1 and 1~THz. Brillouin scattering of light allows to measure velocity and absorption of sound up to frequencies around 100~GHz and coherent inelastic x-ray scattering (IXS) is limited to frequencies larger than 1~THz. A rather universal property of glasses is that a large excess of modes exists, with a maximum density of states near 1~THz, forming the so-called boson peak. The acoustic modes are expected to be strongly affected as their frequency nears the boson peak. The onset of this effect, which is expected to be dominant in the 0.5 to 1~THz range, is observed here for the first time in v-SiO_2 as a function of temperature.

9:00 AM

(ICG-SII-221-2019) Inelastic light scattering on porous glasses: Estimation of structure sizes with Brillouin spectroscopy

M. Brehl*[1]; S. Sander[3]; A. Hajian[2]; U. Schmid[2]; H. Roggendorf[3]; D. de Ligny[1]

1. Friedrich-Alexander-University Erlangen-Nürnberg, Institute of Glass and Ceramics, Germany
2. TU Wien, Institute of Sensor and Actuator Systems, Austria
3. Martin-Luther-University Halle-Wittenberg, Section inorganic-nonmetallic materials (ceramics), Germany

Porous substrates with low permittivity and high electrical resistance could provide opportunity to develop new generation of high frequency devices. By taking advantage of spinodal decomposition occurring in borosilicate systems and selective etching of the boron-enriched phase, it could be possible to create porous glasses that can be use in such devices. Standard methods to estimate pore sizes like SEM image analysis or Mercury-Porosimetry are very time consuming. Spectroscopic methods could be very beneficial for pore characterization. During our studies, we observed that the Brillouin position, of wet chemical etched sodium borosilicate glasses, shifts to lower frequency and the peak width rises with increasing thermal treatment temperature. This effect is related to the evolution of the pore structure. By using samples with defined pore sizes, we will provide a calibration between pore size and the Brillouin signal. Furthermore, with simultaneously recorded Raman spectra we can determine if the etching process was complete or some residual phase remained in the glass. A further advantage of these methods is that they are non-destructive and spatially resolved. The combination of Brillouin- and Raman spectrometry provide a new easy characterization method.

9:20 AM

(ICG-SII-222-2019) The double-peak spectra of a fluoroborosilicate glass and its implication of the viscoelastic behavior

J. Wang*[1]; X. Wang[2]; R. Haihui[1]

1. The Hong Kong Polytechnic University, Department of Mechanical Enginerring, Hong Kong
2. City University of Hong Kong, Department of Mechanical Engineering, Hong Kong

Impulse excited technique (IET) is a widely used method to measure the elastic and damping properties of materials. It is generally expected that the Fourier spectrum of vibration of a beam specimen has one peak corresponding to the first flexural mode. However, the Fourier spectrum of glassy materials sometimes exhibits multiple peaks, which are very close to each other and cannot be ascribed to different vibration modes. In the present work, we demonstrate the double peaks in the sound spectra of a fluoroborosilicate glass (S-FSL5, OHARA Inc.) recorded at the temperatures above T_g. This glass also exhibits a positive temperature dependence of Young's modulus when the temperature is below T_g, indicating the complexity of its structural relaxation. To describe the double-peak spectrum, a differential viscoelastic model was first established, which can be well parameterized after fitting the spectra. Based on this model, we identify that the double-peak phenomenon is caused by the small oscillatory relaxation, which could be attributed to the fast "harmonic" modes associated with structural relaxation, known as the "β process". When the temperature is lower than T_g, the β relaxation still operates, leading to the dynamic local structural rearrangement and the abnormal temperature-dependence of Young's modulus.

10:00 AM

(ICG-SII-223-2019) From glasses to nanocomposites: The dramatic effect of elastic heterogeneities on acoustic phonons and thermal transport (Invited)

V. Giordano*[1]

1. ILM_CNRS, France

Nanocomposites, made of the intertwining at the nanoscale of materials with different elastic properties, are at the forefront of current research for energy harvesting applications, where thermal management represents a major challenge. Depending on the properties of the constituents, thermal conductivity can be greatly enhanced or drastically reduced, with almost no effect on other functional properties. The microscopic mechanisms behind such properties are however still ununderstood. State of the art Effective Medium Approaches cannot explain some simulation results, such as high energy phonons filtering, or enhanced phonon percolation. A microscopic investigation, directly looking to phonons, is needed for unveiling such mechanisms. Here we report our latest achievements in a fundamental understanding of acoustic and thermal transport properties in amorphous/nanocrystalline composites. By coupling macroscopic measurements, state of the art simulations and advanced synchrotron techniques, we are able to directly relate changes in thermal transport to phonon dynamics, and enlighten the mechanisms at play. We show then that the presence of elastic heterogeneities, as are introduced by the phase mixture at the nanoscale, induces glassy-specific features in acoustic phonon dynamics, effectively reducing the phase space of efficient propagative transport.

10:30 AM

(ICG-SII-224-2019) Propagation and Diffusion of excitation in amorphous/nanocrystalline composites

P. Desmarchelier*[1]; V. Giordano[4]; Y. Beltukov[2]; K. Termendzidis[3]; A. Tanguy[1]

1. INSA Lyon, LaMCoS, France
2. Ioffe Physical Technical Institute, Department of Solid State Physics, Russian Federation
3. CETHIL - INSA Lyon, France
4. University Lyon1, France

We used molecular dynamics simulations to study the propagation of acoustic excitations in an amorphous/nano-crystalline silicon nano-composite. Thanks to the analysis of the propagation of coherent and randomly polarized monochromatic excitations, we studied the impact of inclusions on the heat conduction. In nano-composites the interfaces between the phases are expected to play an important role on the transmission of phonons and on their contribution to thermal transfer. This role is awaited to be enhanced by the impedance mismatch between the phases. On one hand, it was found that a higher rigidity contrast promotes the pinning of kinetic energy between inclusions, confirming the effect of the mismatch on the attenuation of propagons (low frequency excitations). On the other hand, the diffusivity of the different configurations seems marginally impacted by the inclusions and is very close to that of a purely amorphous material. The consequence is, as detailed in, that the thermal conductivity is not simply dependent on the acoustic mismatch between the matrix and inclusions, but results from the more complex relative weight of propagative and diffusive transfer of damped acoustic excitations.

10:50 AM

(ICG-SII-225-2019) Mechanical elastic hysteresis in silicate glasses

T. Deschamps*[1]; M. Christine[1]; B. Champagnon[1]; E. Barthel[2]

1. Institut Lumière Matière, France
2. ESPCI, France

We used in situ vibrational spectroscopy to characterize the mechanical behaviour of soda-lime silicate glass under high-pressure at different length scales. Starting from a non-densified glass, the elastoplastic behaviour is similar to pure silica one: full reversibility

under the elastic limit, and appearance of a residual deformation for larger stresses. However, a remarkable elastic hysteretic behaviour is observed (both by means of Raman and Brillouin spectroscopies) during load/unload pressure cycles experienced from a densified silicate glass. Such mechanical behaviour reveals fundamental differences between partially depolymerised and fully polymerised SiO_2 network. By means of time relaxation experiments, we demonstrate that this closed hysteretic loop is due to mechanical instabilities rather than viscoelastic phenomenon. Probing the evolution of Q^n speciation using Raman scattering measurements, this hysteresis is interpreted at the structural scale by a gradual polymerisation of the network under pressure, a reversible but pressure-delayed phenomenon during unloading.

11:10 AM

(ICG-SII-226-2019) Anharmonic damping, sound attenuation and density of vibrational states in silica and silicate glasses

G. Baldi*[1]

1. University of Trento, Department of Physics, Italy

I will review the results of a series of experiments performed by means of inelastic X-ray scattering on silica and sodium silicate glasses. A first observation is the striking similarity between the spectrum of the glass and that of the corresponding polycrystal, suggesting that the glass vibrations closely resemble those of the polycrystal, with excitations related to the acoustic and optic modes of the crystal. I will then describe a second important finding, namely the unusually large temperature dependence of the sound attenuation of a sodium silicate glass at terahertz frequency, an unprecedentedly observed phenomenon. The anharmonicity can be ascribed to the interaction between the propagating acoustic wave and the bath of thermal vibrations. Finally, I will present a preliminary analysis of the density of vibrational states (DOS) of silica, recently obtained by means of inelastic X-ray scattering with nuclear resonance analysis with an energy resolution of 150 meV. The high resolution has allowed us to probe the low frequency part of the DOS, which is connected to the sound propagation and damping at frequencies between 100 GHz and 1 THz, a range which is difficult to probe with other techniques.

11:30 AM

(ICG-SII-227-2019) Acoustic Energy Dissipation in Glasses with Harmonic Interactions

A. Tanguy*[1]; D. Rodney[2]; Y. Beltukov[3]; T. Damart[2]

1. INSA Lyon, LaMCoS, France
2. Université Lyon 1, France
3. Ioffe Institute, Russian Federation

In amorphous samples, acoustic waves scattering takes place at all scales. We show numerical results with evidence of simple scattering at long wave-lengths, multiple scattering at smaller wavelengths, and mixed regime in between, near the Boson Peak's frequency. When the amorphous solid is submitted to a permanent oscillatory deformation, it gives rise to an out-of-phase stress response identified as a frequency dependent Internal Friction. Internal Friction is a way to dissipate energy. We show that the Internal friction at high frequencies, results directly from the high sensitivity of the stress in the specific eigenmodes of the amorphous sample. We then discuss its possible measurement with the help of the Dynamical Structure Factor.

SIV: Emerging Applications of Glass

Session 6: Glass and Glass Ceramics for Packaging and Sealing

Room: Cambridge (4th floor)
Session Chairs: Amber Tremper, Corning Incorporated; Eiken So, Schott AG

8:00 AM

(ICG-SIV-189-2019) Glasses for packaging in electronic applications (Invited)

M. Letz*[1]

1. Schott AG, R&D, Germany

Packaging of electronic components sees increasing interest. This trend has main drivers in (i) higher integration and therefore miniaturization, in (ii) higher frequencies and larger data rates and therefore increased requirements in manufacturing accuracy and in (iii) high power applications where increasing thermal loads need to be handled. Glasses are a class of materials which cover an enormous range of material properties and are in discussion for numerous packaging solutions. The stiffness of glasses allows high manufacturing accuracy. Dielectric constants can be tuned in the range from $3.8 < \varepsilon' < 21$. Low dielectric constants are needed at high frequencies and/or high data rates, where parasitic capacitances need to be miniaturized, signal speed has to be high and limits of manufacturing accuracy are reached. High dielectric constant materials allow at lower frequencies to reduce the size of e.g. resonators or antenna structures. The thermal expansion is adjustable in a range from $0 < CTE < 12$ ppm/K. Several glasses can be produced as sheets with dimensions around 600mm x 600mm and a thickness range from 0,02mm to 3mm. Structuring technologies are available which allow economic production of $> 10^5$ holes per glass sheet together with cut-outs of complicated shape. We show a series of examples where structured glasses are used for packaging of electronic components.

8:30 AM

(ICG-SIV-190-2019) Photosensitive Glass Ceramics for RF Electronic Packages (Invited)

J. H. Flemming*[1]

1. 3D Glass Solutions, Office of CTO, USA

Glassy materials offer a number of advantages over traditional packaging materials, such as laminates and ceramics, including: (1) better material properties, (2) decreased surface roughness to mitigate current crowding, (3) the ability to create small precise features with greater densities, and (4) the opportunity to integrate passive devices such as High-Q inductors into device packages. Several glass manufacturing techniques are available on the market today for the formation of through glass vias (TGVs) for I/Os and interconnects, including laser ablation, electrostatic discharge, ultrasonic milling, and wet chemical etching. While each of these approaches have unique advantages, wet chemical etching offers a number of benefits. These include: (1) process simplicity, (2) low tool capital cost, (3) batch manufacturing for lower production costs, and (4) the decreased formation of micro-fractures between structures from high thermal and mechanical stress manufacturing processes. The presented work describes a Photosensitive Glass Ceramic (PSG) material that enables the production of highly anisotropic 3D structures in glass using photolithographic patterning, baking, and wet chemical etching. We will present our work on (1) microscopic 3D glass structuring, (2) manufacturing approach, (3) manufacturing repeatability, (4) product reliability and lifetime testing, and (5) electronic testing of PSGs devices.

9:00 AM

(ICG-SIV-191-2019) Microstructure of Sealing Glass-ceramic with Linear Thermal Strain

S. Dai*[1]; M. Rodriguez[1]; P. Lu[1]

1. Sandia National Laboratories, Materials Science Center, USA

High expansion crystallizable lithium-alumina-silicate glass-ceramics were used to form matched seals to stainless steels. However, the thermal strain of these sealing glass-ceramics is highly nonlinear owing to the a-b inversion in the dominant Cristobalite phase. New glass-ceramics with near-linear thermal strain have been developed by sequentially crystallizing both high expansion Quartz and Cristobalite from the same parent glass. To study the microstructure base of improved thermal strain rate from multiple crystallization, SEM and AFM characterization were conducted on the HF etched glass-ceramics to reveal the morphology of crystalline and glassy phases. XRD quantitative data showed preferential removal of certain crystalline and glass phases during HF etching. A high resolution TEM analysis with selected area electron diffraction (SAED) identified both Cristobalite and Quartz crystals in the glass-ceramics and provided a hint on crystallization mechanisms of these two silica polymorphs. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525

9:20 AM

(ICG-SIV-192-2019) Mechanical properties of glass-ceramic sealants of the system SrO-MgO-B_2O_3-SiO_2

V. M. Justo[1]; T. R. Ferreira[1]; L. S. Gallo[2]; L. S. Just[3]; S. Rodriguez-López[4]; M. Pascual[4]; F. C. Serbena*[1]

1. State University of Ponta Grossa, Brazil
2. Federal University of Lavras, Brazil
3. State University of Ponta Grossa, Brazil
4. Institute of Ceramics and Glass, CSIC, Spain

The search for new sources of energy has favored extensive research on solid oxide fuel cells. The most common materials to be used as sealants are glass-ceramics due to their good electrical insulation and mechanical properties and the possibility of changing the composition to improve some of these properties. However, cracks can appear during thermal cycles, which may cause leaks leading to a drop of stack performance. In this work, glass-ceramics of the system SiO_2-SrO-MgO-B_2O_3 with addition of 15% ZrO_2 fibers (10B(Sr)+15ZrO_2) and another with 5% Al (10B(Sr)+5Al) were investigated and compared with glass-ceramics without these additions (10B(Sr)). The glass-ceramics were heat treated at 750°C for 24h, 100h and 800h. Biaxial strength (σ), fracture toughness (K_{IC}), adhesion (G) and self-healing properties were tested. σ did not vary with heat treatment time for the 10B(Sr) samples, but increased for 10B(Sr)+15ZrO_2 and decreased for 10B(Sr)+5Al when tested at room temperature. The same results were observed when tested at 750°C. K_{IC} were similar for all compositions when heat treated for 24h and the 10B(Sr) samples presented the higher toughness after 800h of heat treatment. G measured at room temperature were higher for 10B(Sr) followed by 10B(Sr)+15ZrO_2 and 10B(Sr)+5Al. The self-healing properties of both 10B(Sr)+15ZrO_2 and 10B(Sr)+5Al samples were superior to 10B(Sr).

10:00 AM

(ICG-SIV-193-2019) Compliant Glass Composite Sealants for SOFC Stacks (Invited)

J. Hsu*[1]; C. Kim[2]; R. Brow[1]; J. Szabo[2]; A. Zervos[2]

1. Missouri S&T, USA
2. MO-SCI Corporation, USA

In an earlier collaboration, researchers at MO-SCI Corp. and Missouri S&T developed an alkali-free barium borosilicate viscous sealing glass, designated G102, which possesses the requisite viscosity, electrical resistivity, and thermal and chemical stability under operating conditions for SOFC hermetic seals. A disadvantage of G102 is that its coefficient of thermal expansion, CTE = 7.3 ppm/°C, is lower than SOFC component materials. Thus, the major objective of the present work was to design composite sealing materials with greater values of CTE (10-12 ppm/°C), and that retain the other desirable traits of G102. The composites were made by adding various oxide and metallic filler materials, with greater CTE values, to glasses like G102. The CTE and sealing-range viscosity of the composite materials were evaluated as a function of filler contents and temperature up to 900°C. The thermochemical reactions that occur at the composite seal/SOFC material interfaces and between the glass matrix and the additive material particles were characterized using SEM and XRD. The electrochemical performance and leak testing in an SOFC cell configuration were also conducted at temperature up to 900°C. This work was supported by the US Department of Energy SBIR program (DE-FOA-0001975).

10:30 AM

(ICG-SIV-194-2019) Novel Feedthroughs for High Temperature Applications (Invited)

C. Mix[1]; I. Mitra*[1]; H. Hartl[1]

1. SCHOTT AG, Germany, Germany

Feedthroughs under high temperature conditions face the challenge to maintain the requirements of mechanical stability in combination with electrical resistance. In some cases, e.g. the application of sensors, the devices additionally need to be protected against highly corrosive environment. As a leading supplier of gas-tight feedthroughs and components, SCHOTT AG developed a novel glass-ceramic sealing technology to offer feedthroughs now withstanding the demands of harsh environments: A new technology was especially designed for high operating temperatures of 1000°C and above. SCHOTT sensor feedthroughs for automotive applications proved to withstand the corrosive attack of exhaust gas. In this presentation, the principles and basic tradeoffs of glass-ceramic-to-metal sealing technology will be explained: Thereby, the advantages of glass used for hermetic sealing are combined with the enhanced thermo-mechanical properties provided by ceramic phases. The later are formed in a controlled manner subsequently.

11:00 AM

(ICG-SIV-195-2019) Glass coating for transparent spinel $MgAl_2O_4$ ceramics

J. Hormadaly*[1]

1. Ben-Gurion University of the Negev, Chemistry, Israel

Optical properties of glass coating for spinel (MgAl2O4) transparent ceramics are described. The glass coating is transparent and enhances the transmission of spinel, transmission of glass coated unpolished spinel is higher than that of polished spinel. Applications of the glass coating to bond spinel to spinel and as a surface coating to reduce cost of polishing spinel are discussed.

Session 8: Advanced Glassy Waste Forms

Room: Whittier (4th floor)
Session Chairs: Michael Ojovan, The University of Sheffield; Donna Guillen, Idaho National Laboratory

8:00 AM

(ICG-SIV-196-2019) Glass Bead As Material of Choice for Immobilization of High Level Radioactive Nuclear Waste

S. Mandal*[1]; S. Sen[2]; A. Roy Chowdhury[1]; S. Ghorui[1]; S. Barik[1]; R. Sen[3]

1. CSIR-Central Glass and Ceramic Research Institute, Specialty Glass Technology Division, India
2. CSIR-Central Glass & Ceramic Research Institute, Material Characterizations and Instrumentation Division, India
3. CSIR-Central Glass & Ceramic Research Institute, Glass Division, India

Management of radioactive wastes is one of the important issues that needs to be resolved keeping in view the huge demand of nuclear power programme. Amongst many other classes of materials, glass has

emerged as the ideal material of choice for immobilization of high level radio-active liquid waste (HLW) due to its unique random network. The glass bead in the five component borosilicate glass matrix has been indigenously developed in the form of spherical shaped bead of desired sizes with stringent physical, chemical and mechanical properties. Several new borosilicate glass compositions varying sodium and iron content has also been developed. Further, glasses were prepared using seven component glass beads named as centroid composition (C–0) and derived composition (C-2). In general, resistivity is decreased after loading waste oxide of simulated HLW due to increase of modifier content. The resistivity of five component product glass has come down to 1.6 ohm.cm from 6.1 ohm.cm as compared to glass beads while in case of C-0 and C-2, it has been reduced from 7.2 ohm. cm and 22.5 ohm.cm to 2.6 to 3.4 ohm.cm, respectively. This presentation therefore will focus on the indigenous development of glass beads meeting desired properties based on five and seven component borosilicate glass systems suitable for immobilization of high level radioactive nuclear waste in an efficient way.

8:20 AM

(ICG-SIV-197-2019) Asbestos containing materials and their vitrification process (Invited)

C. Leonelli*[1]; A. F. Gualtieri[2]; D. Malferrari[2]; M. LIgabue[2]; M. Vaccari[2]; S. Marchetti Dori[2]; G. Lusvardi[2]

1. University of Modena and Reggio Emilia, Department of Engineering "Enzo Ferrari", Italy
2. University of Modena and Reggio Emilia, Department of Chemical and Geological Sciences, Italy

The management of hazardous waste is an issue of great concern worldwide which is even more complicated in the case of asbestos containing materials (ACM) whose environmental exposure may cause malignant mesothelioma. The thermal transformation processes of ACM appear to be one an ideal solution to the problem as the hazardous waste is transformed into a secondary raw material (end of waste) that can be recycled in different industrial applications. In Italy, the asbestos problem is an emergency because a rough esteem of the amount of ACM points to 40 million tons still present in the life environment, causing exposure of the population. To find a proper and conclusive solution for the disposal of this hazardous waste, recently the Italian Ministry of the Environment has funded a project aimed at the high temperature thermal transformation of this waste into a secondary raw material. This solution is an alternative to the landfill disposal, reducing the environmental impact and feeding the Circular Economy in the field of traditional ceramics. With this premise, the project presents a process for the vitrification of inert secondary raw derived from thermally treated ACMs to accomplish the complete phase transformation of the hazardous waste into an material to be recycled as "ceramic frit". These frits are used for the production of ceramic slabs with high technological performance.

8:50 AM

(ICG-SIV-198-2019) TEM with in-situ ion irradiation studies of nuclear waste packages and gel-layers

A. Mir*[1]

1. University of Huddersfield, Electron Microscopy and Materials Analysis, United Kingdom

Glasses and glass-ceramic composites are potential candidates for nuclear waste confinement and disposal. To demonstrate and ensure their long-term durability and safety, studies are necessary to understand their evolution under self-irradiation damage and helium accumulation. Furthermore, the impact of He accumulation and radiation damage on radioisotope leaching and the effect of radiation damage on the so-called "gel-layers" - formed as a result of leaching are pivotal in obtaining a reliable picture of waste package evolution under geological conditions. Over the past few years we have undertaken detailed ion irradiation and gas implantation studies using TEM with in-situ irradiation to address some of these issues. This work will present these results to highlight the role of grain-boundaries, interfaces, temperature and composition on radiation damage and nucleation of gas bubbles. More recently we have also undertaken TEM studies of gel-layers to evaluate their porous structure and the impact of radiation damage on the porosity of the gel layers. These results with potential future studies will also be highlight and discussed.

9:10 AM

(ICG-SIV-199-2019) Effects of gamma and alpha irradiation on iron-free and iron-containing high-level nuclear waste base glasses

P. Rautiyal*[1]; P. K. Kulriya[3]; R. Edge[2]; L. Leay[2]; A. H. Jones[1]; P. A. Bingham[1]

1. Sheffield Hallam University, Materials and Engineering Research Institute, United Kingdom
2. University of Manchester, Dalton Cumbrian Facility, United Kingdom
3. Inter University Accelerator Center, India

Performance assessment of the resistance of high-level radioactive waste (HLW) glasses to radiation damage is of crucial importance to ensure safe and economic disposal over geological disposal periods. Two international base glasses, namely UK MW lithium-sodium borosilicate and Indian sodium-barium borosilicate, which are being used as glass matrices for HLW immobilisation by the UK and India respectively, were studied. The same base glasses containing iron in different molar concentrations were also studied. Glasses were prepared using a melt-quench method and annealed below Tg (glass transition temperature). These glasses were irradiated to a dose of ~5 MGy gamma using a ^{60}Co radioactive source and with 600 KeV alpha radiation with four different doses in an ion-accelerator. Here we present results from structural characterization using Raman spectroscopy, X-ray diffraction (XRD), electron paramagnetic resonance (EPR), Mössbauer and UV-Vis-IR optical spectroscopies to investigate the effects of irradiation. EPR and UV-Vis-IR results indicated the presence of different radiation-induced defect centers in the different glasses after irradiation. Self-healing or defect hopping, enabled by Fe through controlled redox mechanisms, is believed to occur, supporting the view that iron is beneficial for remediation of irradiation damage in HLW glasses.

Session 8: Glass-ceramic Waste Forms

Room: Whittier (4th floor)
Session Chair: Elise Regnier, CEA

10:00 AM

(ICG-SIV-200-2019) Effect of Thermal History on the Microstructural Development of a Complex Borosilicate Glass-Ceramic for High-Level Nuclear Waste Vitrification

P. Porter*[1]; N. Roberts[1]; R. Brow[1]

1. Missouri University of Science & Technology, Materials Science and Engineering, USA

Microstructural development of a complex borosilicate glass-ceramic developed at Pacific Northwest National Laboratory has been investigated using a combination of constant cooling and isothermal experiments. Constant cooling experiments were performed using several techniques with quench rates varying from the Canister-Centerline-Cooling profile (~0.008°C/s) to roller quenching at over 300°C/s. Isothermal experiments were performed using a tin bath technique to rapidly quench and hold sample melts from 1300°C to temperatures between 600 and 1100°C for up to 1 hour. Analysis of phase compositions and morphologies provided insight into the solidification behavior of the material, and a mechanistic description of microstructural development and crystallization pathways across treatment conditions has been produced.

Time-Temperature-Transformation and Constant-Cooling-Transformation diagrams have been constructed for the major crystalline phases, Powellite and Oxyapatite, and show crystallization rates for both phases are maximized at 1000°C. Powellite crystallizes from Mo-rich droplets that separate from the borosilicate matrix, and Oxyapatite crystals then form in the modified glass, sometimes nucleated by insoluble Ru-rich particles present in the waste form. This work was supported by the US Department of Energy, contract NEUP 15-8112

10:20 AM

(ICG-SIV-201-2019) Durability assessment of spent ion exchange materials converted into glass-ceramics via thermal treatment methods

L. J. Gardner*[1]; S. Walling[1]; L. Harnett[1]; S. Sun[1]; C. Mann[1]; C. L. Corkhill[1]; N. C. Hyatt[1]

1. The University of Sheffield, Materials Science and Engineering, United Kingdom

Thermal treatment using Hot Isostatic Pressing (HIP) and Reactive Spark Plasma Sintering (RSPS) technologies were utilised to showcase conceptual wasteforms for spent ion exchange materials generated at nuclear facilities such as, Sellafield, UK and Fukushima, Japan. These materials require conditioning into passively safe wasteforms to reduce the associated risks of easily dispersible granular particles and hydrogen production via radiolysis of entrained water. Cs-exchanged chabazite (waste simulant) was converted into glass ceramics, the closed-system nature of HIP and RSPS resulted in no detectable cesium loss, which could be advantageous over traditional vitrification routes. Characterisation by XRD and SEM/EDX revealed the presence of heterogeneous phase assemblages with K-feldspar as the main crystalline phase dispersed within a glassy matrix. Wasteform durability assessments performed using ASTM C1284-14 methodology resulted in residual dissolution rates (day 0 to 28) of 10^{-3} g m^{-2} d^{-1} [Si] at 90 °C, suggesting that these wasteforms could be suitable for long-term storage and disposal concepts. Overall, this study successfully demonstrated the thermal treatment of spent ion exchange materials into robust glass-ceramic wasteforms with potential for volume reduction and minimal voidage/porosity through the utilisation of HIP or RSPS technologies.

10:40 AM

(ICG-SIV-202-2019) Hot isostatic pressing and durability testing of alkali tin silicate glass as a wasteform for the immobilisation of plutonium

A. R. Mason*[1]; M. C. Stennett[1]; N. C. Hyatt[1]

1. University of Sheffield, United Kingdom

UK stocks of separated civil plutonium, resulting from nuclear fuel reprocessing, have exceeded 140 tons. This material may require immobilisation in a proliferation resistant wasteform, should it prove uneconomic to recycle in MOX fuel. We have investigated and optimised alkali tin silicate (ATS) glass compositions for the immobilisation of this stockpile using CeO_2 as a PuO_2 surrogate. A two-fold increase in Ce solubility was achieved by in-situ reduction of CeO_2 to Ce_2O_3 through the addition of zero valent iron, which also assisted in reducing the processing temperature. As well as improving waste loading, Fe additions have been shown to significantly reduce the mass loss of glass formers and alkali elements in PCT-B durability tests. Hot isostatic pressing has also been investigated as an alternative thermal treatment process for this material, enabling batch-wise processing of ATS glasses, which is advantageous from fissile material accountancy and criticality considerations. This work demonstrates the feasibility of hot isostatic pressing as an alternative and simple approach to conditioning the plutonium stockpile which is potentially compatible with the full envelope of plutonium feedstock requiring immobilisation.

11:00 AM

(ICG-SIV-203-2019) Understanding iron redox chemistry in sodium aluminoborosilicate glasses as a function of P_2O_5 and its impact on their crystallization behavior

Y. Zhang*[1]; A. Goel[1]; S. Kamali[2]

1. Rutgers University, Material science and engineering, USA
2. University of Tennessee Space Institute, Mössbauer Laboratory, USA

P_2O_5 is a component of Hanford HLW, though in small concentrations except for bismuth and phosphorus rich waste streams. Although present in small concentrations, P_2O_5 can have significant impact on the structure, crystallization and chemical durability of the glassy waste forms due to its ability to form bonds with both aluminum and boron, as well as to compete with iron for oxygen in the glass structure. Despite its considerable impact on the properties of HLW glass, the role of P2O5 in HLW glasses has been poorly studied. Therefore, the present study is focused on understanding the impact of P2O5 on the redox chemistry of iron in model HLW glasses designed in the primary crystallization field of nepheline. Accordingly, a series of glasses in the system Na_2O–Al_2O_3–B_2O_3–P_2O_5–Fe_2O_3–SiO_2 has been investigated for the redox chemistry of iron and its impact on their crystallization behavior and chemical durability. The results will be discussed in the presentation.

Session 11: Fiber Glass Science and Technology (TC 28)

Room: Stuart (4th floor)
Session Chairs: Yuanzheng Yue, Aalborg University;
Hong Li, Nippon Electric Glass

8:05 AM

(ICG-SIV-204-2019) Development of reinforcment fibres with high Youngs moduli (Invited)

A. Prange[1]; C. Roos*[1]; K. Philipps[1]

1. RWTH Aachen University, Glass and Ceramic Composites, Germany

In times of energy transition on the one hand and the greatest possible mobility on the other hand, reinforcement fibre manufacturers as suppliers for automotive and wind industry must come up to the highest expectations, especially due to the fierce competition with the producers of carbon fibres, a quite expensive product with properties advantageous in weight and stiffness but similar strength compared to glass fibres. Thus a number of process and product related parameters has to be improved; e.g. to enable a stable fibre drawing process, a specific viscosity-temperature relation has to be established, the final product has to fulfill different demands regarding the field of application with a strong focus on mechanical properties essential for reinforcement. Such a theoretical glass development step is combined with an experimental characterization of the different glasses. For this purpose, the following standard equipment is available: XRD, XRF, ICP-OES, high-T viscometer and hot stage microscope. Elastic moduli of bulk glasses are measured by impulse excitation technique. Beside this, the attenuation ability of a glass composition can be tested in single filament devices depicting the industrial process on the lab scale. Tensile testing of pristine fibres can also be carried out.

8:35 AM

(ICG-SIV-205-2019) What are the key parameters for assessing the quality of glass fibers?

Y. Yue*[1]

1. Aalborg University, Denmark

The physical characteristics of glass fibers are more complicated than those of bulk glasses, since fibers are generated under extreme forming conditions such as larger deformation force and much fast quenching. Consequently, fibers possess different microstructure, higher potential energy and entropy and a significantly larger surface area, in contrast to their bulk counterpart. Owing to rather small

diameters of glass fibers, accurate characterizations of the physical properties are particularly challenging, and time consuming. Therefore it would be highly beneficial, if the glass fiber community could find and agree on two or three representative parameters that can be used to assess the fiber quality (note: not functionality). Such parameters should be easily measured and connected to other parameters. In this talk, I suggest two or three key parameters to be used as possible criteria for assessing fiber quality, with focus on both continuous fibers for reinforcement and wool fibers for insulation. One parameter is related to the surface characteristics, while the other is connected to the bulk properties. I discuss why these parameters are chosen, and I use a couple of examples to illustrate how to determining them.

8:55 AM

(ICG-SIV-206-2019) Development of low-loss lead-germanate glass for mid-infrared fiber optics: Optimization of the glass preparation

P. Wang*[1]; H. Ebendorff-Heidepriem[2]; J. Bei[2]

1. Xi'an Institute of Optics and Precision Mechanics, CAS, China
2. University of Adelaide, Institute of Photonics and Advanced Sensing, Australia

Reducing the absorption loss of hydroxyl (OH) groups and metallic Pb species induced scattering loss in mid-infrared range for lead-germanate glass fibers is essential to pave the way for their applications as low-loss mid-infrared fiber optics. We report the understanding factors that affect to which extent dehydration and metallic Pb formation during the lead-germanate glass fabrication procedures, combining a dry O_2-rich atmosphere containing ultra-dry N_2 together with the use of chloride dehydration agent and nitrate oxidation agent compound, to ensure both low OH absorption and absence of reduced metallic Pb scattering sources in the dehydrated glasses. These fabrication procedures have overcome previous limitations on preparation of similar kinds of heavy metal oxide (HMO) glasses only in a pure O_2 atmosphere and prevented deterioration of the glass thermal stability. This work can provide guidance for developing other low-loss mid-infrared glasses/fibers containing multivalent heavy metal ions such as Pb, Bi, Te, Sb, etc.

9:15 AM

(ICG-SIV-207-2019) Glass Fibre Strength: How testing can impact the apparent properties of glass filaments

T. Becker*[1]; A. Lüking[1]; T. G. Gries[1]

1. Institut fuer Textiltechnik of the RWTH Aachen University, Germany

The tensile strength of glass fibres is one of the key properties discussed in both industry and academic literature. Various different values for the strength of E-Glass are regularly quoted without any regards to how these were determined. Glass fibre manufacturers regularly quote fibre strengths which leave some room for interpretation. Often little clarity is provided regarding the testing processes, and the wide range of recorded strengths is an indication for the different testing methods. This phenomenon is not limited to the glass fibre industry, but can be identified in all other reinforcement fibre industries, for example the carbon fibre industry. This study investigates various different factors which impact the measurement results of single filament tensile tests. Furthermore, commercially available glass fibres were tested and the results compared to the manufacturers specifications. While different glass compositions, sizings, and process parameters can have a great impact on the actual fibre strength, the testing methods should be considered as a further key factor when examining the strength of glass fibres.

9:55 AM

(ICG-SIV-208-2019) Design of the high performance fiberglass compositions (Invited)

Q. Zu*[1]; S. Huang[1]; Q. Zhao[1]

1. Nanjing Fiberglass Research & Design Institute, China

High performance fiberglass compositions were studied by different design methods. For irradiation resistant glass fibers, the ingredients of fiberglass should select the elements with lower neutron absorption cross section, and also need to consider increasing the polymerization of glass network structure. Many experiments had been taken for proper manufactory process with different compositions. S class high strength glass fiber has higher melting temperature and easy to crystallize. SiO2-A12O3-MgO system glass formula was modified by the statistical learning method based on the database, in order to improve mechanical performance as well as the manufacture process. For fiberglass design, it is also necessary to set up models to predict some characteristic temperatures such as glass melting, fiber forming and liquid temperature. Molecular dynamics simulation and first principles study have been studied to predict base physical characteristics of glass, while the performance prediction for complex glass composition systems require the collection of the methods above.

10:25 AM

(ICG-SIV-209-2019) New Low-Temperature and High Strength/Modulus Fiber Glass: Properties, Crystallization, and Network Structures

H. Li*[1]; S. Vennam[1]; T. Charpentier[2]; N. Ollier[3]

1. Nippon Electric Glass, Fiber Glass Science & Technology, USA
2. NIMBE, CEA, CNRS, Université Paris-Saclay, France
3. Ecole Polytechnique, Laboratoire des Solides Irradies, CEA, France

A newly developed fiber glass, RE_2O_3 (RE = Sc,Y, La)-MgO-CaO-Al_2O_3-SiO_2, has presented a great potential for high performance FRP composite applications focusing on high strength and high Young's modulus (US9,278,883B2, 2016). The new glass fiber can be made at significantly lower temperatures using E-Glass fiber technology to produce high performance fibers like S-Glass fiber that can be only made at greater than 1500°C by using a small paramelter platform. This presentation discusses rare earth effects on fiber mechanical properties, high temperature viscosity, liquidus temperature, and crystalline phases. Speciation reactions of aluminate and silicate groups of the network, by using ^{27}Al and ^{29}Si MAS NMR and Raman spectroscopic methods, are highlighted. Rare earth oxides were shown to have a dual functionality, i.e., decreasing melt viscosity like a network modifier depolymerizing glass network at higher temperatures for glass melting and fiber drawing, but increasing viscosity at lower temperatures due to strengthening the glass network. Liquidus temperature is sensitive to the type of RE ions, which increases with Sc^{3+} , but decreases with La^{3+}. Y^{3+} resembles Sc^{3+} only at a higher concentration. The replacement of CaO by RE_2O_3 increases AlO_5 at the expense of AlO_4 based on ^{27}Al MQMAS NMR study. Raman study suggests that RE_2O_3 depolymerizes the silicate network.

10:45 AM

(ICG-SIV-210-2019) Effect of Boron Oxide on Acid Corrosion Kinetics of E-Glass Fibers

J. Xie*[1]; J. Zhang[1]; J. Han[1]; J. Wang[1]; C. Liu[1]; X. Zhao[1]; J. Du[2]

1. Wuhan University of Technology, China
2. University of North Texas, USA

Glass fiber is widely used due to its good corrosion resistance, high mechanical strength, good insulation, heat resistance and other excellent performance. In this paper, mechanisms of boron-free E-CR Glass fibers (MgO-CaO-Al_2O_3-SiO_2 system) corrosion behavior under acid environment, both with and without binder (or

sizing), were investigated and compared with those of boron-containing E-Glass fibers. Sample weight loss, elemental release of glass constituents, and fiber surface composition as a function of time (up to 144 h) were measured. The results show that the weight loss of fibers with organic binder coating is lower than the bare fibers, suggesting the organic layer generates a diffusion barrier that slows down the rate of ion exchange between the fiber and the solution. Scanning electron microscopy (SEM) was used to characterize fiber surface morphology, and the results show that the boron-containing E-glass fibers developed a thicker surface layer than the boron free E-CR Glass fiber surfaces. Raman spectroscopy study of E-CR Glass fibers before and after 144 h leaching suggests that little change on the fiber surface network structures.

11:05 AM

(ICG-SIV-211-2019) Practical Recycling Alternatives for Glass LFT Mchining Residue

K. N. Hardin*[1]

1. Nippon Electric Glass, Applications Development, USA

Long fiber thermoplastics (LFT) have propelled the growth of thermoplastics as they are accepted as a suitable alternative to conventional fiber reinforced thermoplastics and even metals for numerous applications. Commonly, end of life LFT products are granulated and compounded with a virgin parent thermoplastic to be reprocessed into pellets. Forgoing the size reduction and compounding steps would be more economical, particularly in a high volume manufacturing setting. The objective of this study was to repurpose waste stream material produced from a high volume production LFT component. 10 wt. % of 50 wt. % glass fiber/nylon-6,6 (GF/PA66) LFT machining residue was used in place of size reduced material and simply blended and extrusion compression molded with virgin 50 wt. % GF/PA66 LFT. The resulting recycled composite was characterized mechanically and compared to 100 wt. % virgin LFT composites. Fiber length analysis was performed and Moldex3D simulation was conducted to validate fiber alignment theories. The current study shows virgin material can be combined with small quantities of production scrap with varying fiber lengths to obtain components with comparable mechanical properties to the virgin LFT composites. This creates a sustainable and economic avenue for post-production scrap that is generally landfilled.

11:25 AM

(ICG-SIV-212-2019) Dissolution of stone wool materials coated with organic binder in a synthetic lung fluid

D. Okhrimenko*[1]; S. H. Barly[1]; M. Solvang[1]; Y. Yue[2]; S. L. Stipp[3]

1. Rockwool International, Denmark
2. Aalborg University, Department of Chemistry and Bioscience, Denmark
3. Technical University of Denmark, Department of Physics, Denmark

Stone wool, composed of man-made vitreous fibers (MMVF) and organic binder, is widely used in many construction applications, such as materials for heat insulation and protection against spread of fire. One of the important requirements for stone wool products is safety to the humans during production, installation and use, in cases where fibers can be inhaled. In this work, we investigated the dissolution behavior of stone wool fibers coated with different amounts (0 to 6 wt. %) of organic binder (phenol-urea-formaldehyde), using the typical industrial coating procedure. The amount of coating that was deposited was monitored with thermogravimetry and dissolution was studied in a synthetic lung fluid (modified Gamble's solution) both in batch and under continuous flow conditions at 37 C. Scanning electron microscopy showed homogeneous dissolution of uncoated fibers, whereas fibers with organic coating preferentially dissolved at the uncoated points, resulting in surface cavity formation. However, the results of ICP-OES analysis of the reacted solutions and X-ray photoelectron spectroscopy of fiber surfaces showed that dissolution in the synthetic lung fluid was close to being congruent for all investigated materials and that the organic binder presence does not decrease the dissolution rate of the stone wool materials.

11:45 AM

(ICG-SIV-213-2019) Preparation and Properties of Fluoride Fibers

Y. Jiang*[1]; L. Zhang[1]; Y. Ju[1]

1. Shanghai Institute of Optics and Fine Mechanics.CAS, Chinese Academy of Sciences, China

The flexible multi-directional fluoride fiber is considered to be the best high power medium-infrared laser material due to its extremely low loss, high damage threshold and excellent mid-infrared performance. However, fabrication of high quality fluoride fiber has always been a technical difficulty due to the limitations of preparation techniques. In this study, the infrared fluoride fibers with loss of 0.10dB/m were successfully fabricated by improving raw material purification, glass melting, prefabricated rod preparation and fiber drawing. Related performance is systematically studied.

SVII: Arun K. Varshneya Festschrift

Arun K. Varshneya Festschrift VI

Room: Georgian (mezzanine)
Session Chair: John Mauro, Pennsylvania State University

8:00 AM

(ICG-SVII-047-2019) Structural control of the coloration of alkali borate glasses by transition-elements

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1. Sorbonne Université, Institute of Mineralogy (IMPMC), France
2. SOLEIL Synchrotron, France

The presence of transition elements in alkali borate glasses is at the origin of one of the most noticeable chemical dependence of the color of oxide glasses. We will discuss the chemical dependence of optical absorption data of borate glasses containing Cr, Co, Ni, Cu and U. The variation of coordination numbers, crystal-field splitting, site distribution or site geometry depends on the existence of either only one or several sites occupied by the transition element. These spectroscopic properties will be discussed at the light of recent findings on the medium-range organization in borate glasses, in particular on the role played by $^{[3]}$B in the geometry of borate superunits. Alkali concentration in borate glasses causes an important modification in the speciation of transition elements, with major changes observed when $^{[3]}$B is present, i.e. at alkali concentration lower than 20 mole%. The local rigidity induced by planar $^{[3]}$B triangles also explains the formation of ordered element clusters, already demonstrated by EXAFS and XANES in low-alkali borate glasses containing Ni, Co or Zn. Finally, the significance of $^{[5]}$Ni and $^{[5]}$Co will be discussed at the light of similar speciations observed in crystalline borates.

8:20 AM

(ICG-SVII-048-2019) Conventional and electric-field assisted ion-exchange of innovative float glass

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1. University of Trento, Italy

An innovative float glass from Nippon Sheet Glass has been subjected to conventional and electric-field assisted ion-exchange process. Pure KNO_3 salt and KNO_3/KCl mixtures were used at temperatures ranging from 350°C to 450°C. Electric-field assisted processes were carried out by using a specifically realized equipment which allowed to change the polarity and the applied voltage and to measured instantly the flowing current. Ion-exchange parameters such as surface K/Na exchange rate, potassium

penetration, interdiffusion coefficient, residual stress and case depth were measured and correlated with the processing conditions. The results revealed a higher propensity of the considered glass to be chemically strengthened and a tremendous beneficial effect of the applied electric field in terms of processing time and temperature.

8:40 AM

(ICG-SVII-049-2019) Materials Science Lessons from Chemically Strengthened Glass (Invited)

M. Dejneka*[1]

1. Corning Incorporated, USA

Chemically strengthened glasses were crucial to the success of smartphones because of their scratch performance, optical quality, and retained strength after damage. Strengthened glasses have since found their way into tablets, windshields, and portable electronic device backs for wireless charging. This talk will cover the technological advances made to ion exchanged glasses to improve their strength, scratch resistance and aesthetics. We will then show how seemingly mundane secondary properties can make the difference between an invention and a billion dollar success and how important controlling materials interactions can be when putting a glass into mass production.

9:00 AM

(ICG-SVII-050-2019) Evolution of Mobile Consumer Electronics Device Cover Glass: 10+ Years and Counting

K. Eckart (Barefoot)*[1]; S. Donthu[1]

1. Corning Incorporated, USA

When companies were first researching cover materials for touch screen, non-flip phone devices, there was much to think about when choosing the material between plastic, sapphire and glass. Each one of these materials has been or continue to be used for this application. However, glass is by far the most preferred material of choice for several reasons. Since the birth of this industry about a decade ago, more than 20 different glass compositions have been introduced by different glass manufacturers for this application. This rapid innovation of glass compositions has enabled the design space of smartphones to expand and has underpinned the popularity of glass as a material of choice for this application. This talk will give an overview on the evolution of cover material over the last decade and highlight the attributes of different materials to demonstrate why glass continues to be the dominant material for this application. The talk will also highlight the evolving trends from smartphone manufacturers and end-user's perspective, and show why glass is the best material to meet the needs of the industry.

9:20 AM

(ICG-SVII-051-2019) Cover screens for personal electronic devices, Part 2 (Invited)

P. Bihuniak*[1]; A. K. Varshneya[2]

1. Hidden Point Consulting, LLC, USA
2. Saxon Glass Technologies, USA

Since Apple introduced the iPhone in 2007, the market has been growing explosively. In 2017, annual sales topped 1.5 billion units generating close to $500 B in revenue. In less than a decade, these complex devices have become an indispensible companion for just about everyone. It's estimated that the average U.S. user spends almost three hours per day on their phone. It shouldn't come as a surprise that dropping a phone is a common occurrence. Unfortunately, the glass cover screens all too frequently break. It's been reported that 50% of consumers have experienced a cracked screen. In a previous discussion, the authors compared chemically strengthened glass with sapphire crystal, an alternative that promised to better survive inevitable consumer clumsiness. While sapphire has intrinsic hardness and scratch resistant advantages, continuous thin glass manufacturing processes followed by ion exchange tempering are considerably less expensive than the batch fusion processes used to manufacture sapphire. Further, sapphire production was a commercial failure. Chemically strengthened glass remains the only significant smart screen transparency. In this review, we will examine ongoing efforts to improve ion exchanged glass performance along with alternative potential materials such as transparent ceramics, ceramic composites and glass-ceramics, which have glass fabrication economics along with ceramic fracture toughness.

10:00 AM

(ICG-SVII-052-2019) Effect of electric field on indentation deformation of glass

S. Panyata[1]; H. Moawad[1]; H. Jain*[1]

1. Lehigh University, Institute for Functional Materials and Devices, USA

Electric field induced softening (EFIS) is a recently discovered phenomenon. It shows that the furnace temperature T_{ft}, at which a typical alkali silicate glass softens, is significantly reduced when subjected to moderate electric fields. For example, when a sodium disilicate glass bar (5 mm x 5mm x 10mm) is heated at 10 °C/min under 10 MPa compressive load, the value of T_{ft} at which glass begins to deform decreases from 550 °C to <400 °C upon application of 200 V across its length. This novel effect is expected to yield considerable energy saving in operations like surface structuring of glass. To advance such applications we have explored specifically the effect of electric field on the indentation deformation of glass under initial load of 430 MPa. The compressive force is applied by an especially designed conical indenter made of tungsten, which also serves as anode while heated in a furnace at constant rate. Significant differences are observed between deformation under uniform load in EFIS vs. non-uniform load in indentation experiments. Corresponding mechanisms of deformation under electric field are discussed.

10:20 AM

(ICG-SVII-053-2019) Plastic Deformation Mechanisms in Silicate Glasses

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1. Cornell University, Materias Science and Engineering, USA
2. Corning Incorporated, USA

Residual indentations and scratches in silicate glass surfaces indicate the ability of these materials to deform plastically to surprisingly large extents, even at room temperature. Plastic deformation under contact with a sharp object can relax stresses that would otherwise lead to fracture. Thus, understanding this plasticity is important to creating durable glass devices. Unfortunately, very little is known about the mechanisms of plastic deformation in silicate glasses. In this talk, a holistic materials science approach to structure and properties of glass typified by Arun Varshneya is used to describe plastic deformation in silicate glasses. A brief overview of the atomic level processes that must occur and how these mechanisms contribute to shear and densification will be given. A taxonomy of mechanisms and recent results including hardness measurements and structural characterization using Raman spectroscopy and MD simulations are used to demonstrate how specific mechanisms account for both shear and densification.

10:40 AM

(ICG-SVII-054-2019) A Bond Exchange Approach to Glass Viscosity

D. R. Swiler*[1]

1. Owens Illinois, R&D, USA

A model for glass viscosity based upon bond exchange and topological constraint is proposed. The model is considers the probability of bonds being broken in the glass network combined with the ability of the broken bond to reform at a different site in the glass

structure, and differentiates between the contributions of primary covalent and secondary ionic bonding to the immobilization of the structure. The resultant equation has the form 1/viscosity = $M(T-T_0)$ $\exp(-E/(T-T_0))$ where T_0 represents the temperature below which changes in secondary bonding strongly contributes to the viscosity response. Fit for this equation vs VFT will be provided for SLS glasses. This model can also be used to improve understanding of the effects of glass network structure and surface bonding on viscosity.

11:00 AM

(ICG-SVII-055-2019) Role of Zr in alteration gels of simplified Nuclear glasses

L. Galoisy*[1]; G. Calas[1]; P. Jollivet[2]; S. Gin[2]; F. Angeli[2]

1. Sorbonne Université, Institute of Mineralogy (IMPMC), France
2. CEA, France

Vitrification of high - level radioactive waste in borosilicate glasses has received great attention in several countries since decades. Glass leaching by water in geological repository is an important phenomenon that needs to be understand to better constrain the long-term evolution of the glasses used to store these wastes. Structural features of the evolution of representative simplified nuclear glasses under forcing conditions will be presented. During the alteration by water, an amorphous gel is formed at the surface of the glass. The durability of the gel and its properties depend on the structural role played by different elements. New generations of spent fuels require higher content of Zr^{4+} in glasses. In this study, the modifications of the Zr^{4+} environment in the gel has been investigated as a function of increasing ZrO_2 content from 1 to 8 mol% in simplified 5-oxide glass compositions at various pH using Zr L-2,L-3-edge and K-edge XANES and by Zr K-edge EXAFS. In glasses and alteration gels, Zr may adopt three coordination numbers: $^{[6]}$Z, $^{[7]}$Zr or $^{[8]}$Zr. The structural evolution of the gel around Zr^{4+} in two distinct layers illustrates the molecular-scale alteration of the glass when in contact with water.

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