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2019 Conference on Electronic Materials and Applications (EMA 2019)

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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Wednesday, January 23, 2019

Plenary Session I

Room: Orange A
Session Chair: Jon Ihlefeld, University of Virginia

8:40 AM

(EMA-PLEN- 001-2019) Electroceramic Thin Films for IR Plasmonic Applications

J. Maria*[1]

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

Transparent conductive oxides (TCOs) are an attractive materials platform for plasmonics and metamaterials in the near- and mid-infrared (MIR). This presentation will briefly review plasmonic oscillation modes, some interesting applications for plasmon polaritons, and the conductors and devices that have been recently explored. Among TCOs, the doped electroceramic cadmium oxide (CdO) exhibits exceptional electronic and plasmonic characteristics with tunable carrier concentration and high electron mobility, which enables low-loss plasmonic resonances. We have shown that through careful control of thin film growth and defect chemistry, doped CdO supports high quality plasmonic resonances across the entire MIR with tunable carrier concentrations spanning nearly than two orders of magnitude accompanied by maximum carrier mobilities over 500 cm^2/V●s. We will show that by controlling electron concentration, mobility, thickness, and film-substrate geometry, we can grow doped CdO films to target multiple plasmonic modes, including surface plasmon polaritons (SPP), epsilon-near-zero (ENZ) modes, and Brewster/Berreman modes. Additionally, by growing stacked doped/intrinsic/doped CdO layers we are able to access additional SPP dispersion branches below the lightline resulting from coupling between the doped layers.

S1: Characterization of Structure–Property Relationships in Functional Ceramics

Imaging and Analytical Techniques I

Room: Cypress B
Session Chairs: David McComb, The Ohio State University;
Arno Merkle, XRE

10:00 AM

(EMA-S1-001-2019) Supersonic Propagation of Atomic Motion by Phasons in Fresnoite (Invited)

M. E. Manley*[1]

1. Oak Ridge National Lab, Materials Science and Technology Division, USA

Our recent inelastic neutron scattering measurements reveal that waves of atomic motion move at surprisingly high speeds of up to 4.3 times the speed of sound in the form of phasons in the piezoelectric mineral fresnoite ($Ba_2TiSi_2O_8$). Phasons are quasiparticles that exist because of an incommensurate modulation (or 'wrinkles') in the flexible framework structure of fresnoite. They are associated with atomic rearrangements that change the phase of waves describing the incommensurate modulation. Phasons are usually overdamped and move diffusively, and are thus much slower than phonons (vibrations involving the translation of atoms). However, the phasons in fresnoite are found not to be overdamped owing to a characteristic rotation of the phasons away from the driving soft phonon, yielding the supersonic propagation. These supersonic phasons enhance thermal conductivity and channel lattice energy at speeds well beyond the limits of phonons. Eventually supersonic phasons might enable the development of high performance electronic or sensing devices.

10:30 AM

(EMA-S1-002-2019) Microscale electrical characterization and current path detection in ZnO varistor ceramics

B. Kaufmann*[1]

1. Montan University Leoben, Institut für Struktur- und Funktionskeramik, Austria

ZnO varistors are among the most relevant voltage dependent resistors in today's electronic industry. Their electrical behavior is strongly affected by the microstructure of the sintered ZnO, especially the grain boundaries. Some of their electrical properties can only be understood by investigating the fundamental microscopic processes that are responsible for their highly non-linear current-voltage characteristics. To cope with this issue, experimental methods on the microscale must be used. The first being presented here is the micro lock-in infrared thermography to detect very subtle heat differences in the micro scale range making it possible to identify preferential current paths through the ZnO ceramic. A complementary technique is the micro 4-point probe method where the tips of two very fine needles are placed at two different ZnO grains at a time. With this method the current-voltage characteristics between two grains, being not larger than a few microns, were measured. It was demonstrated that the current paths, generated in low voltage varistors, depend on polarity and that the grain-to-grain contacts can show asymmetric current-voltage characteristics as well as the grain-to-electrode contacts. Furthermore, it was found that these grain-to-electrode contacts behave like Schottky diodes, where the corresponding Schottky barriers are dependent on grain orientation.

10:45 AM

(EMA-S1-003-2019) Property-Thickness Dependencies for Dielectric and Dielectric/Piezoelectric Multilayer Thin Films

T. Moran*[1]; K. Suzuki[2]; J. Steffes[1]; S. Matonis[1]; T. Hosokura[2]; T. Okamoto[2]; K. Murayama[2]; N. Tanaka[2]; B. Huey[1]

1. University of Connecticut, Institute of Material Science, USA
2. MuRata Manufacturing Co., Ltd., Japan

The properties and performance of a range of functional ceramic devices depend on the 3-dimensional effects of microstructure, composition, strain gradients, multilayers, or simple geometry. Thickness dependencies are especially critical for realizing the ultimate limits of device engineering. Accordingly, stepped and graded thickness configurations of dielectric and piezoelectric thin films are investigated using Kelvin Probe Force Microscopy (KPFM) and Piezo Force Microscopy (PFM). Charge-discharge testing with KPFM is especially valuable for mapping the dielectric constant as a function of material and film thickness, while PFM reveals local ferroelectricity. Via $BaTiO_3$ specimens of distinct thicknesses, as well as a range of $BaTiO_3/SrTiO_3$ superlattices, functional properties for layers as thin as 7 nm are directly probed. Such studies provide valuable insight into strain and interface controlled phenomena, ultimately improving the engineered performance of micro- and nano- scale electronic devices such as multi-layer-chip-capacitors.

11:00 AM

(EMA-S1-004-2019) 3D modelling of ferroelectric composite using X-ray micro tomography images: Effective permittivity and tunability (Invited)

D. Bernard*[1]; C. Elissalde[1]; C. Estournes[2]; J. Lesseur[1]; E. Plougonven[1]; M. Maglione[1]

1. ICMCB-CNRS, France
2. CIRIMAT, LCMIE, France

Different approaches can be used to produce new ferroelectric materials with well-controlled properties (permittivity, Curie temperature, dielectric losses, tunability, ...). In our composite approach two powders are mixed to obtain by SPS a dense ceramic composite with dielectric inclusions distributed within a ferroelectric matrix. Optimisation of the process relies on diverse characterization and numerical methods. In this presentation measured permittivity and tunability values are compared to numerical values computed using X-ray Micro CT images as input. We first exposed the problem to solve at the microstructure scale. Then, it is shown that the model reproduces the permittivity anisotropy induced by the deformation of the dielectric inclusions due to SPS. For tunability we begin by introducing Johnson's law as constitutive law, then we derived the dimensionless form of the problem putting into evidence the main parameters. Fitting numerical results with experimental ones, it is shown that Johnson's law allows reproducing the experimental data with a very good precision, but it requires the introduction of an anisotropic non-linear coefficient. Consequences of this second anisotropy are discussed. Finally, the model is used to evaluate the effects on the dielectric properties of various changes in the internal morphology of the samples.

11:30 AM

(EMA-S1-005-2019) Characterizing defective 2-D oxides via operando X-ray total scattering: Links to pseudocapacitance

S. T. Misture*[1]; P. Metz[1]; R. Koch[1]; P. Gao[1]; M. Flint[1]; A. Ladonis[1]

1. Alfred University, MSE, USA

Manganese and vanadium oxide 2-D nanosheet assemblies have been studied in detail to define the effects of cation defects on charge storage and catalytic properties. We find a direct link between charged defects electrochemical pseudocapacitance. We focus our studies on 2-D nanosheets obtained by exfoliation, assembled into 3-D porous mesostructures. The use of X-ray pair distribution functions (PDFs), teamed with Raman scattering, has enabled reliable characterization and even operando studies of the materials. Complex fitting of models to the PDF data, supported by Bayesian statistical analyses to evaluate parameter uncertainties, is the centerpiece of the work. The in-situ and operando studies show that the defect content defines the capacitance and the extent of in-plane electrochemical strain, as well as controlling the cycling stability. We demonstrate that the defects modifying the surface features are critical in improving performance, but perhaps more importantly we have demonstrated a new method of quantifying the defects present in 2-D oxides.

11:45 AM

(EMA-S1-006-2019) Correlating structure and properties of amorphous functional ceramics using 4-dimensional scanning transmission electron microscopy (Invited)

J. Hwang*[1]; M. Abbasi[1]; R. Sakidja[2]; N. Oyler[4]; M. Paquette[3]; P. Rulis[3]

1. Ohio State University, MATERIALS SCIENCE AND ENGINEEING, USA
2. Missouri State University, Physics, Astronomy and Materials Science, USA
3. University of Missouri - Kansas City, Physics and Astronomy, USA
4. University of Missouri, Kansas City, Chemistry, USA

We present the novel characterization of the local structure in polymer derived amorphous ceramics for flexible dielectric applications using 4-dimensional scanning transmission electron microscopy (4D-STEM). Amorphous ceramics and oxides are widely used in functional devices, and their properties are often determined by the structural ordering at the nanoscale, commonly known as medium range ordering (MRO). Understanding MRO, however, is typically challenging because conventional characterization techniques are largely insensitive to such small and elusive ordering buried in the disordered matrix. Here we show the full-field electron nanodiffraction based on 4D-STEM to determine the local MRO in a series of amorphous hydrogenated ceramic films, including a-BC:H, a-SiBCN:H, and a-SiCO:H. 4D-STEM uses a new-generation pixelated STEM detector, which enables fast acquisition of diffraction patterns from each oversampled nanoscale volume of the sample. We perform the intensity fluctuation and angular correlation analyses on the 4D-STEM data to reveal the details of the MRO, including the type, size, distribution, and volume fraction of MRO, with unprecedented resolution and precision. The experimentally determined MRO information is then compared with their electrical and mechanical properties to establish new direct structure-property relationships.

Imaging and Analytical Techniques II

Room: Cypress B

Session Chairs: Julian Walker, Norwegian University of Science and Technoogy; Abhijit Pramanick, City University of Hong Kong

2:00 PM

(EMA-S1-007-2019) Revealing Switching Character in Ferroelectric Thin Films: Insights from Multidimensional Spectroscopy and Deep Learning (Invited)

L. W. Martin*[1]

1. University of California, Berkeley, Materials Science and Engineering, USA

Large susceptibilities in ferroelectrics depends on our ability to drive reconfiguration of the ferroic order parameter with externally-applied stimuli. Consequently, there is interest in understanding how ferroelectric order, at multiple length scales, responds under applied fields; and what this means for macroscopic properties. In recent years, in operando (e.g., piezoresponse force microscopy (PFM), transmission electron microscopy, etc.) capable of probing stimuli-driven changes in ferroelectric order at the appropriate length and time scales have become available. These approaches, however, have led to an orders-of-magnitude increase in the volume, variety, veracity, and velocity of the experimentally-generated data; rendering conventional analysis approaches untenable. Here, using multidimensional PFM spectroscopies we show how machine learning and deep learning bring physically-important phenomena concealed within "big" hyperspectral data into focus for interpretation. Specifically, we highlight how physically-guided featurization protocols in conjunction with machine learning and deep-learning neural networks can be applied to glean new insights regarding how nanoscale, 3D domain geometry can be exploited to enhance piezoelectric responses and electromechanical energy conversion.

2:30 PM

(EMA-S1-008-2019) Effect of lithium stoichiometry on acoustic phonon modes in $LiTaO_3$

J. Ivy*[1]; A. Pramanick[2]; G. L. Brennecka[1]

1. Colorado School of Mines, Metallurgical and Materials Engineering, USA
2. City University of Hong Kong, Materials Science and Engineering, Hong Kong

It is well known that ferroelectric properties of lithium tantalate ($LiTaO_3$) can vary drastically with relatively small deviations in stoichiometry. $LiTaO_3$ single crystals are typically grown at the congruent composition, meaning that these crystals are approximately 1.5 mol% lithium deficient and resulting in a coercive field approximately 200x greater than and a Curie temperature nearly 100 °C less than that of stoichiometric $LiTaO_3$. The large changes in these properties, commonly thought to be caused by intrinsic defect clusters arising from the lithium deficiency ($Ta_{Li}^{\bullet\bullet\bullet\bullet}+ 4V_{Li}'$), are likely correlated with decreased domain wall mobility and phonon transport. This study utilized inelastic neutron scattering to examine the effect of lithium stoichiometry on transverse and longitudinal acoustic phonon mode energies and highlights the differences found in the Σ_1 and Σ_2 bands. Initial results indicate that the phonon bands in the stoichiometric composition exist at lower energies and possess lower mode velocities than those of the congruent composition. These trends seem to suggest that the intrinsic defect clusters in $LiTaO_3$ do not mitigate phonon behavior, and by extension, domain wall behavior, as traditionally thought.

2:45 PM

(EMA-S1-009-2019) Raman spectroscopy of functional ceramics (Invited)

M. Deluca*[1]

1. Materials Center Leoben Forschung GmbH, Austria

Raman spectroscopy is a versatile non-destructive technique that recently attracted much interest for the study of structure-property relationships in functional ceramic materials, particularly for piezoelectric and dielectric applications. The method is based on the Raman effect, namely the inelastic scattering of light by optical phonons. Raman spectroscopy thus probes the vibrational energy of a crystal, which means that any changes in the lattice (such as those induced by phase transitions, deformation and defects) can leave a trace in the Raman spectrum. In this talk, the fundamentals of Raman spectroscopy will be laid down, and several examples of application on functional ceramics will be presented. We will focus in particular on the following case studies: (i) Quantification of domain texture distribution in PZT-based piezoactuators; (ii) ferroelectric-to-relaxor crossover in Ba-based solid solutions; (iii) residual stress analysis. Details on the capabilities/limitations of the technique and on practical aspects of Raman measurements will be given. It will be highlighted how Raman spectroscopy is complementary to other long- or short-range analytical methods, and how it can be advantageous to correlate the local structure of materials with the macroscopic properties, thus making it an attractive tool for material development.

3:15 PM

(EMA-S1-010-2019) Design of new Pb-free relaxors based on physicochemical effects of various atomic substitutions

A. Pramanick*[1]

1. City University of Hong Kong, Applied Physics and Materials Science, Hong Kong

Piezoelectric materials are of great importance in many modern technologies, including precision actuators, impact and load sensors, sonar, medical diagnostic imaging and energy harvesting. Large piezoelectric coefficients were previously obtained in Pb-based ferroelectric relaxors, which incorporate several physico-chemical attributes, including heterovalent substitutions, ferroelectrically active atomic displacements and stabilization of nanoscale domains below THz frequencies. However, due to negative environmental concerns surrounding the presence of Pb in electronic devices, design of new Pb-free alternatives have become necessary. Towards this end, a promising approach can be to investigate for similar structural characteristics as listed above in Pb-free ferroelectric solid-solutions. In this regard, I will present some recent insights about the effects of solid-solution additions in Pb-free relaxors on inducing co-operative multi-site atomic displacements and formation mechanisms of polar nanoregions, which were obtained from X-ray and neutron pair distribution function (PDF) analyses. Functional properties of new Pb-free relaxors designed using such local structural insights will also be presented.

4:00 PM

(EMA-S1-011-2019) Structure characterization of antiferroelectrics and relaxors (Invited)

X. Tan*[1]

1. Iowa State Univ, Mater. Sci. & Eng., USA

Antiferroelectric (AFE) perovskite oxides display nanoscale incommensurate modulations (IM) while relaxor (RE) ferroelectric (FE) oxides contain nanodomains. In this study, several techniques are employed to uncover the atomic and domain structures and their transitions under applied electric fields in representative compositions. In the AFE $Pb_{0.99}Nb_{0.02}[(Zr_{0.57}Sn_{0.43})_{0.94}Ti_{0.06}]_{0.98}O_3$ ceramic, the evolution of the space group and the IM during the AFE-to-FE transition was investigated with synchrotron X-ray diffraction. It was found that the transition takes place abruptly at 39 kV/cm with a volume expansion of 0.5 %. The space group changes from Bmm2 to R3c while the wavelength of the modulation remains unchanged before its disappearance at the transition. In $Pb_{0.99}Nb_{0.02}[(Zr_{0.57}Sn_{0.43})_{0.92}Ti_{0.08}]_{0.98}O_3$, the FE phase becomes metastable. Using the in-situ TEM technique, an unusual FE-to-AFE transition is directly observed. Furthermore, the Pb-cation displacements in these AFE ceramics are mapped out based on STEM-HAADF micrographs. Similarly, the FE phase in the $Pb_{0.92}La_{0.08}(Zr_{0.65}Sn_{0.35})O_3$ ceramic is metastable at room temperature and in-situ TEM experiments directly visualize an unlikely FE-to-RE phase transition under electric field. This transition is hidden in the polarization reversal process at coercive field, confirmed by changes in the domain morphology as well as in the electron diffraction pattern.

4:30 PM

(EMA-S1-012-2019) Reconstructing potential profile and band bending in functional heterojunctions: Examples of $SrTiO_3$/Ge(001) and $SrTiO_3$/Si(001) epitaxial films

P. Sushko*[1]; N. F. Quackenbush[2]; J. C. Woicik[2]; Z. Lim[3]; J. H. Ngai[3]; S. Chambers[1]

1. Pacific Northwest National Laboratory, Physical Sciences Division, Physical & Computational Sciences Directorate, USA
2. National Institute of Standards and Technology, Materials Measurement Science Division, Material Measurement Laboratory, USA
3. University of Texas-Arlington, Department of Physics, USA

Functional heterojunctions, in particular, junctions that trap quasi-two-dimensional electron or hole gas or facilitate separation of photo induced electron and hole charge carriers, underpin many of the recent advances in fundamental research and applied sciences. Functionality of such structures is determined by the profile of the electrostatic potential in the off-planar direction, which, in turn, determines the position of the band edges as a function of distance from the surface or interface. Quantitative characterization of these potential profiles remains challenging. To this end, transport measurements are often used to establish the concentration and mobility of carriers near the interface and, thus, determine the depletion depth using established relationships. Here we present an approach developed to reconstruct potential gradients in oxide/oxide and oxide/semiconductor heterojunctions. The method is based on fitting the hard x-ray photoelectron spectroscopy (HAXPES) spectra for relevant core levels while ensuring continuity of the potential function and its smoothness without assuming band-bending direction or an analytical form of the potential profile. We demonstrate this approach and physical insights it provides by reconstructing the potentials in prototype systems $SrTiO_3$/Ge(001) and $SrTiO_3$/Si(001).

4:45 PM

(EMA-S1-013-2019) Refining the local structure of functional materials using synchrotron X-ray and spallation neutron total scattering/pair distribution functions (Invited)

D. Keen*[1]

1. Rutherford Appleton Laboratory, ISIS Facility, United Kingdom

Local deviations from the average crystalline structure are increasingly of interest in crystallography because they are often key to understanding behaviour, such as the changes across phase boundaries in ferroelectrics. High-quality total scattering data provide an excellent experimental foundation for analysis of such systems, data which are now routinely available at X-ray synchrotron and spallation neutron facilities. This talk will describe the means of collecting these data, show how the data might be refined using RMCProfile, and present recent results that enable us to examine the role of local structure on physical properties.

S2: Advanced Electronic Materials: Processing Structures, Properties, and Applications

Advanced Electronic Materials: Processing

Room: Orange A

Session Chairs: Kui Yao, Institute of Materials Research and Engineering, A*STAR; Susan Trolier-McKinstry, Pennsylvania State University

10:00 AM

(EMA-S2-001-2019) Cold Sintering of PZT Ceramics (Invited)

D. Wang[1]; H. Guo[2]; C. Morandi[1]; C. Randall[1]; S. Trolier-McKinstry*[1]

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

This paper describes a cold sintering process for $Pb(Zr,Ti)O_3$ ceramics and the associated processing-property relations. $Pb(Zr,Ti)O_3$ has a very small, incongruent solubility that is a challenge during cold sintering. To circumvent this, a $Pb(NO_3)_2$ solution was used as the transient liquid phase. A bimodal PZT powder was densified to a relative density of 89% by cold sintering at 300 °C and 500 MPa. After the cold sintering step, the permittivity was 200, and the dielectric loss was 2.0%. A second heat-treatment involving a 3 h anneal at 900 °C, increased the relative density to 99%; the resulting relative dielectric permittivity was 1300 at room temperature and 100 kHz. The samples showed well-defined ferroelectric hysteresis loops, having a remanent polarization of 28 $\mu C/cm^2$. On poling, the piezoelectric coefficient d_{33} was ~200 pC/N. With a 700 °C 3 h second sintering, samples show a lower room temperature relative permittivity (950 at 100 kHz) but a 24 hr hold time at 700 °C produces ceramics where there is an improved relative dielectric constant (1050 at 100 kHz).

10:30 AM

(EMA-S2-002-2019) Densification and electrical properties of thermodynamically metastable SnO prepared by the cold sintering process

S. Bang*[1]; T. De Beauvoir[1]; C. Randall[1]

1. Pennsylvania State University, Materials Research Institute, USA

SnO is a promising functional p-type metal oxide but suffers from decomposition into SnO_2 and Sn at relatively low temperatures in ambient environments. By employing the cold sintering process (CSP), a process methodology to densify ceramics below 300 °C, SnO can be densified up to 89% of the theoretical density within a few minutes under uniaxial pressure of 350 MPa. The metastable phase is maintained at the sintering temperature of 70 – 265 °C. The particle size dependent thermal behavior shows that the smaller particles have a lower decomposition temperature of 200 °C. In the CSP, a transient liquid phase drives densification by particle re-arrangement concurrent with dissolution-precipitation process. Using acetic acid as the liquid medium increases the density by 4% and promotes anisotropic grain growth. Electrical conductivity and Seebeck coefficient of the cold sintered bulk pellet are measured as a function of temperature.

10:45 AM

(EMA-S2-003-2019) Quantifying Cold Sintering

R. Floyd*[1]; S. Lowum[2]; J. Maria[2]

1. North Carolina State University, USA
2. Pennsylvania State University, USA

Substantial densification can be promoted by mixing an oxide with a secondary phase – provided some finite solubility of the two – and uniaxially pressing and heating the die. We refer to this as Cold Sintering (CS) due to the relatively low temperature required for densification. CS has been successfully applied to a variety of binary and ternary ceramic compounds, including ZnO, WO_3, Li_2MoO_4, etc. These materials exhibit high relative densities, up to > 99%, and uniform microstructures with sharp grain boundaries. CS promotes a new method for densification of ceramic materials far below conventional sintering temperatures, allowing for control of grain sizes as well as stoichiometry in volatile complex oxides. In this presentation, we discuss the design of specialized equipment used for the CS process and the results that this equipment enables. Specifically, we introduce a custom press we refer to as the Sinterometer, which captures in-situ compaction of the sample. The resulting "sintegram" gives insight into densification events as a function of process variables (time, temperature, secondary phase, etc.). This equipment has led to experiments that call into question the role of the secondary phase and the necessity of water for densification. The goal of this work is to quantify the CS process and relate observed results with existing models to explain dominating mechanisms, and create a pathway to study the applicability of other materials.

11:00 AM

(EMA-S2-004-2019) Investigating Cold Sintering Mechanisms and Resulting Properties

S. Lowum*[1]; R. Floyd[2]; R. Bermejo[3]; J. Maria[1]

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3. Montanuniversitaet Leoben, Institut fuer Struktur- und Funktionskeramik, Austria

Cold Sintering (CS) entails densifying a ceramic through the use of a secondary transport phase, uniaxial pressure, and low temperatures below 300°C. This technique has resulted in relative densities approaching 100% for a variety of compositions, such as ZnO, NaCl, and Li_2MoO_4. CS temperatures are significantly reduced from solid state sintering temperatures, allowing for development of co-sintered polymer-ceramic composites as well as the potential to control stoichiometry and defect chemistry. To date, the CS process has most often been performed using a liquid transport phase with the dominant mechanism for densification suggested to be a dissolution-precipitation process. Prior work indicates that hydrothermal conditions drive dissolution and promote densification. In this presentation we examine additional mechanisms contributing to densification during CS, based on varying transport phase fractions and compositions, as well as the role and necessity of a liquid transport phase in CS. Additionally, mechanical properties of cold sintered and traditionally sintered materials will be compared. Characteristic strengths and Weibull moduli were obtained through Ball on Three Balls (B3B) testing. The goal of this research is to provide a fundamental understanding of the mechanisms behind cold sintering, broadening the application of the process to other materials and, subsequently, tailoring their properties.

11:15 AM

(EMA-S2-005-2019) Thermopower Determination using Pyrolytic Graphite and Aluminum Thermocouple

A. Hadi*[1]; B. Hill[2]

1. Montana Technological University, Materials Science and Engineering Department, USA
2. Montana Technological University, Electrical Engineering Department, USA

High temperature processes of metal casting require the use of specialized instruments for measurements. A thermocouple is one such instrument frequently used due to its many advantages of low cost, high accuracy and ease of access. With aluminum being one of the most widely used metals in the metallurgical and automobile industries, there is the need for a custom thermocouple for use in these sectors. In this research work, a custom thermocouple designed from pyrolytic graphite (PG) and aluminum is developed. The research effort is then concentrated on determining the

Seebeck coefficient of our instrument. A near-linear response was obtained for our instrument on a temperature-voltage graph. A thermopower/Seebeck coefficient of 15.8 μV/°C was obtained for the heating experiment while the cooling experiment produced a sensitivity of 14.0 μV/°C

11:30 AM

(EMA-S2-006-2019) Structure and properties of lead-free piezoelectric ceramic coatings derived from thermal spray process (Invited)

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1. Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), Singapore
2. National University of Singapore, Department of Mechanical Engineering, Singapore

For realizing intelligent structural monitoring and automatic control, implementation of a large number of distributed sensors and transducers are demanded. Despite the fact that individual discrete acoustic devices have proved their values for many applications, implementations of multiple acoustic transducers for effectively in-situ monitoring or control over a large structure are very limited. Producing high performance piezoelectric coatings directly on the structure offers a potential valuable technical solution. Here our recent investigation outcomes in the fabrication, structure and properties of lead-free piezoelectric ceramic coatings by thermal spray process will be presented, including potassium sodium niobate (KNN)-based and bismuth sodium titanate (BNT)-based perovskite systems. The mechanism of recrystallization from the melt and structural evolution in the thermal sprayed ceramics are analyzed, in contrast with solid state ceramic synthesis process. The environment-friendly compositions, scalable processing method and superior piezoelectric performance properties exhibit the great application value of the thermal sprayed lead-free piezoelectric ceramic coatings.

12:00 PM

(EMA-S2-007-2019) IR transparent ZnS ceramics sintered by VHP method using hydrothermally synthesized ZnS powders

B. Choi*[1]; S. Nahm[1]

1. Korea University, Advanced Materials Engineering, Republic of Korea

ZnS ceramics have been used for infrared optical devices because of their good photoelectrical and mechanical properties. Vacuum hot-pressing (VHP) has been used to produce the transparent ZnS ceramics. Microstructure and optical properties of ZnS ceramics produced by the VHP are considerably influenced by the purity and size of the ZnS nanopowders. Therefore, the ZnS nanopowders have been generally annealed under various conditions to remove defects and to control their particle sizes. In this work, ZnS nanopowders were synthesized using hydrothermal method at 220°C with various S/Zn ratios. The ZnS nanopowders with S/Zn ratio of 1.5 were used to synthesize the ZnS ceramics without annealing process. The ZnS ceramics were sintered at 1000°C by VHP using these ZnS powders. A 3.0 mm-thick ZnS ceramic showed the very high IR transmittance of 69% in the wavelength range of 6.0-12 μm, indicating that this ZnS ceramic can be used for optical devices in the infrared ranges. Detailed microstructural and optical properties of the ZnS ceramics synthesized using ZnS nanopowders without annealing will be discussed in this work.

12:15 PM

(EMA-S2-008-2019) Synthesis, Photoluminescence and Photocatalytic Characteristics of Nanocomposites of Reduced Graphene Oxide-Nanoparticles

A. Nemati*[1]; E. Nemati[2]

1. Sharif University of Technology, Tehran, Iran, Department of Materials Science & Engineering, Islamic Republic of Iran
2. Ecole de Technologie Superieure, Department of Mechanical Engineering, Canada

This study reports a brief review of synthesis, photoluminescence and photocatalytic characterization of Nanopartices-rGO nanocomposites: Titania –rGO(T-rGO), ZnO-rGO(Z-rGO) and Fe_3O_4-rGO(F-rGO) nanocomposites. They were synthesized, calcined at different temperatures, and their characteristics were evaluated by TEM/HRTEM, Raman, XPS, STA, XRD, SEM/FESEM, FTIR, DRS, DLS, and PL. The results revealed the formation of a few layers of rGO, with particle size of less than 50 nm. The electrical conductivity of T-rGO (with particle size of 20±2 nm) was increased from 4.6 (μS/cm) to 81.3 (μS/cm). The absorption spectra of this nanocomposite was shifted toward visible wavelengths and its band gap was reduced to 1.95 eV. PL results showed a peak shift from blue to green and yellow rang. It also showed a few numbers of PL peaks that were not related to presence of rGO. These sub-peaks depend on the kind of synthesis and creation of defects. The results indicated that rGO just changed the intensity of PL peaks, not the positions. The results on F-rGO nanocomposites (with crystallite size of 20 nm and particle size of 50 nm) showed photocatalytic degradation efficiency on MB. It was concluded that all of these nanocomposites can be an efficient multifunctional photoelectric for many applications such as the degradation of hazardous compounds.

Advanced Electronic Materials: Material Design

Room: Orange A
Session Chair: Ichiro Fujii, University of Yamanashi

2:00 PM

(EMA-S2-009-2019) Large electrically and optically induced strain in single crystals of methylammonium lead bromide and chloride hybrid perovskites (Invited)

L. M. Riemer[1]; B. Lim[2]; E. Horvath[3]; L. Forro[3]; D. Damjanovic*[1]

1. Swiss Federal Institute of Technology in Lausanne - EPFL, Group for Ferroelectrics and Functional Oxides, Switzerland
2. National University of Singapore, Singapore
3. Swiss Federal Institute of Technology in Lausanne - EPFL, Laboratory of Nanostructures and Novel Electronic Materials, Switzerland

Hybrid (organo-metal) methylammonium lead halide perosvkites ($MAPbX_3$; MA=$CH_3NH_3^+$, X=Br^-, Cl^- or I^-) are presently widely studied for their excellent photovoltaic energy conversion efficiency. Those materials also exhibit a number of other interesting optical and electronic properties. Ferroelectric- and piezoelectric-like respones have been reported for these materials. Many of those studies were carried out on thin films and piezoelectricity and ferroelectricity were reported only on a local scale using piezoforce microscopy or other local techniques. In this study, we use high quality, milimeter size single crystals of $CH_3NH_3PbBr_3$ and $CH_3NH_3PbCl_3$ and measure macroscopic strain on volumes up to 35 mm^3 induced by applying electric field up to 1kV/cm. We also mesure strain induced by ultraviolet light, with and without electric field. We observe large electrostrictive-, piezoelectric- and photostrictive-like strains at frequencies on the order of 10 mHz. The mechanisms of the electro-mechanical and photo-mechanical coupling will be discussed.

2:30 PM

(EMA-S2-010-2019) Water Printing of Ferroelectric Polarization (Invited)

J. Zhang*[1]

1. Beijing Normal University, China

Controlling chemical reactions and energy transformations at solid-liquid interface attract intense interests. Solid materials with charged surfaces like ferroelectrics, which generate an electric field across the solid-liquid interface, may provide a natural platform to control chemical reactions (physical properties) using physical fields (chemical stimuli). Here, we report that construction of chemical bonds at the surface of ferroelectric $BiFeO_3$ in aqueous solution leads to a reversible switching of its bulk polarization, which is usually achieved by electric field. Combining piezoresponse (electrostatic) force microscopy, X-ray photoelectron spectroscopy, scanning transmission electron microscopy, first-principles calculations and phase-field simulations, we discover that the reversible polarization switching is ascribed to the sufficient formation of polarization-selective chemical bonds at its surface. The deterministic control of the interfacial structures decreases the chemical energy across the interface, so that the bulk electrostatic energy can be effectively tuned by H^+/OH^- concentration. This water-induced ferroelectric switching allows us to construct large-scale type printing of polarization using green energy. Such a controllable chemical structure and energy inter-conversion across this interface opens up new opportunities for nanoscale sensing, high-efficient catalysis and data storage.

3:00 PM

(EMA-S2-011-2019) Search for the nitride perovskite LaWN3, from prediction to characterization

K. R. Talley*[1]; J. Mangum[1]; C. Perkins[2]; R. Woods-Robinson[2]; A. Mehta[3]; G. L. Brennecka[1]; A. Zakutayev[2]

1. Colorado School of Mines, Metallurgical Materials and Engineering, USA
2. Nationals Renewable Energy Labratory, USA
3. SLAC National Accelerator Laboratory, USA

Many metal oxide compounds exhibit the perovskite crystal structure and are used in a wide array of industrial applications. In contrast, there are currently no (confirmed/common) nitride perovskites. Likely reasons for this is the competition between nitrogen and oxygen, which makes the formation of pure nitride perovskites difficult and the synthesis of oxynitride perovskites more common in addition to the high valency needed from the cations to satisfy the nitrogen anions. In this work, thin films are synthesized and characterized for their chemical composition and crystal structure in search of the computationally predicted nitride perovskite, lanthanum tungsten nitride ($LaWN_3$). The properties have been predicted computationally as a moderate bandgap, large piezoelectric response, and possible ferroelectricity. Here, we produce experimental evidence of the perovskite structure in thin films of lanthanum tungsten nitride. A two-step synthesis method is established for producing crystalline thin films. Synchrotron-based diffraction experiments are used to determine the symmetry of the resulting perovskite. Auger electron spectroscopy depth profiling is used to examine anion and cation stoichiometries. The structure and chemistry are analyzed for octahedral tilting, bond valance sum, and tolerance factor, and are compared to the existing literature predictions.

3:15 PM

(EMA-S2-012-2019) Strain and polarization dynamics of relaxor-ferroelectrics from cryogenic to ambient temperatures

L. M. Riemer*[1]; I. Gaponenko[2]; D. Damjanovic[1]

1. Group for Ferroelectrics and Functional Oxides, Swiss Federal Institute, Switzerland
2. Department of Quantum Matter Physics, University of Geneva, Switzerland

Ultra-high piezoelectric properties of relaxor-ferroelectrics like $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ are widely ascribed to a polarization rotation mechanism in domain-engineered single crystals. This rotation mechanism, however, cannot explain the dielectric and piezoelectric anomalies in the cryogenic temperature regime that were recently discovered in several relaxor-ferroelectrics. These anomalies do not only raise questions about their mechanistic origin, but also about their significance for ultra-high piezoelectric properties of relaxor-ferroelectrics at ambient temperatures. In this work, we investigate electro-mechanical coupling in lead-based relaxor-ferroelectric single crystals along different crystallographic directions and at different length scales from cryogenic to ambient temperatures. On the macroscopic scale, amplitude and phase angle of the strain and polarization response in the sub-coercive regime are measured. In addition, switching experiments are conducted in a closed cycle refrigerator. Complementary microscopic measurements are performed in a cryogenic piezoresponse force microscope. We clearly observe different strain and polarization dynamics along different crystallographic directions. For a better understanding of electro-mechanical coupling, the results will be compared to measurements of barium titanate and lead-free relaxor-ferroelectric single crystals.

Advanced Electronic Materials: Property I

Room: Orange A
Session Chair: Soonil Lee, Changwon National University

4:00 PM

(EMA-S2-013-2019) Leveraging Momentum for Increased Tuning of Phonon-Polariton Metasurfaces

T. E. Beechem*[1]; C. Saltonsall[1]; J. Valentine[2]; T. Gilbert[2]; J. Matson[2]; F. Ugwu[2]; J. Caldwell[2]

1. Sandia National Laboratories, Optical Sciences, USA
2. Vanderbilt University, USA

Field-enhancement and sub-diffractional mode confinement drive the pursuit of metasurfaces and nanophotonics for applications ranging from sensing and imaging to home-health diagnostics. Multifunctional and tunable optical devices are also enabled by metasurfaces as small material property changes become amplified by the large optical fields they produce. While plasmons are typically utilized to these ends, phonon-polaritons are capable of sharper resonances. The "built-in" dipole of the phonon-polariton proceeds from polar-bonds, which create electric fields upon the atomic displacement created by vibration (i.e., phonons). Phonon-polaritons are therefore accessed via polar semiconductors—SiC, GaN, AlN, SiO_2, Al_2O_3, CdO, etc.—within their "Restrahlen-band" spanning the energies between the transverse- and longitudinal-optical (TO/LO) phonon modes. Here, we show that when polar-phonon modes interact with free charge, the dielectric function (i.e., optical properties) exhibits high dependence on momentum. From the perspective of phonon-polaritons, momentum dependence is of consequence as metasurfaces can impart substantial momentum beyond that of free-space light. Here, we examine the implications of this momentum dependence highlighting its potential as a "knob" enabling phonon-polariton based infrared filters exhibiting "push-button" spectral control with ultra-low loss.

4:15 PM

(EMA-S2-014-2019) High-performance Nanostructured Metal Oxide Gas Sensors using a Morphological Evolution

C. Kang*[1]; Y. Song[1]; S. Yi[1]; G. Kim[1]

1. Korea Institute of Science and Technology, Center for Electronic Materials, Republic of Korea

A variety of approaches have been used in attempts to improve the gas sensing performance through nanostructure, metal doping, and formation of heterostructure. Notably, these approaches are based on a highly porous nanostructure due to its high surface-to-volume ratio and nano-sized narrow necks. In here, we reported high-performance gas sensors using a morphological evolution to synthesize effective functional nanostructures. The morphological evolution of the nanostucture have great potential in not only gas sensitivity, but also selectivity by controlling preferred orientation, surface polarity, and surface curvature. Firslty, Rh-decorated WO_3 nanorods was successfully fabricated by glancing angle deposition (GLAD). Interestingly, morphogical evolution characterized by anomalous surface with numerous resgions of negatie curvature were observed upon decorating the bare WO_3 nanorods with metallic Rh. Also, a pointed pyramidal surface was observed by decorating metallic W on NiO nanoigloos surface. Underlying mechanisms of the morphological change were systematically investigated. Furthermore, effects of modulated surface properteis on interacitons with target gases are stepwisely demonstrated in detail.

4:30 PM

(EMA-S2-015-2019) Stability of Epitaxial Pseudocubic Group IV-V Semiconductors

D. L. Brown*[1]; S. R. Phillpot[1]; K. Jones[1]

1. University of Florida, Material Science and Engineering, USA

For the scaling of Moore's Law, new materials have to accommodate higher doping for lower contact resistance, and higher tensile strain for improved electron mobility. In recent years, highly doped Si:P and Si:As films have been studied for providing high dopant activation and source-drain stressors for FinFET devices. The tensile epitaxial strain is believed to be caused by vacancy stabilized Si_3P_4 and Si_3As_4 phases. In this study, the epitaxial stability of these vacancy stabilized Si_3P_4, Si_3As_4, Ge_3P_4, and Ge_3As_4 phases is studied from first-principles using electronic-structure calculations at the level of density functional theory. The strain study is implemented locking lattices to a Ge and Si substrates. These phases are metastable as "free" bulk, but the epitaxial strain calculations predict a stability of these phases compared to the precipitates. These phases are stable on a Si substrate, but unstable on a Ge substrate due to the increased tensile strain. The pseudocubic Ge_3P_4 phase is not found to be stable with epitaxial strain. This study corroborates the prediction of tensile strain for Si_3P_4 and Si_3As_4, and for compressive Ge_3As_4 on a Si substrate.

4:45 PM

(EMA-S2-016-2019) Electrically conductive AlN by incorporation of graphene nanoplatelets

D. Kenfaui[2]; S. Guillemet-Fritsch*[1]; P. Dufour[3]; C. Tenailleau[3]; M. Locatelli[2]; V. Bley[2]; L. Laudebat[2]; Z. Valdez-Nava[2]

1. CNRS CIRIMAT, Material Science, France
2. LAPLACE, Electrical Engineering, France
3. University de Toulouse, Material Science, France

Pure aluminium nitride (AlN) is a very attractive material for various applications, due to his high thermal conductivity, excellent mechanical properties and high electrical resistivity. Recently, several authors added low dimensional carbon based nanomaterial graphene to AlN to see the influence on the thermal and electrical properties. In the present work, we successfully obtained a new graphene AlN doped presenting improved properties. The structure, microstructure and physical properties of the obtained material are presented.

5:00 PM

(EMA-S2-017-2019) A comparison of photoelectric property of Titania, Ce-doped Titania and TiO_2-CeO_2 nanocomposite

A. Nemati*[1]; N. Ahmadi[2]; M. Bagherzade[2]

1. Sharif University of Technology, Tehran, Iran, Department of Materials Science & Engineering, Islamic Republic of Iran
2. IAU, Department of Materials Engineering, Islamic Republic of Iran

Photoelectric property of Titania, Ce-doped Titania (with different percentage of Ce) and TiO_2-CeO_2 nanocomposites with different Ce/Ti ratios was analyzed and compared. The nanoparticles and nanocomposites were calcined at different temperatures, and then were evaluated by STA, XRD, FESEM, FTIR, DRS and PL. Particles size was measured by DLS method. Finally, electrical conductivity of the samples was measured. More than99% anatase phase of titania was obtained at 400 C with crystallite size of 15.9 nm and average particle size of 43 nm. Its band gap was about 2.85 ev. In Ceria doped titania, the sample with Ce/Ti ratio of 75/0% and heat treated at 500 C resulted in more than %99.5 anatase phase. The crystallite size, average particle size and band gap were 27.1 nm of 25 nm, 2.46 ev respectively. In Ceria-Titania nanocomposites, the optimum sample was obtained with Ce/Ti ratio of %25 and heat treatment at 750 C. The average particle size was 32 nm. Its direct and indirect band gaps were about 2.63 and 1.98 ev, respectively. The results suggest that cerium doping into titania in optimal conditions postpone phase transformation from anatase to rutile, and inhibit from excessive growth of crystallite size of titania. They also shift absorption spectra toward visible wavelengths and increase the widths of absorption edge and the light absorption in the whole of visible range.

S3: Frontiers in Ferroic Oxides: Synthesis, Structure, Properties, and Applications

Magnetic, Magnetoelectric, and Multiferroic Phenomena

Room: Magnolia A

Session Chairs: John Heron, University of Michigan; Morgan Trassin, ETH Zurich

10:00 AM

(EMA-S3-001-2019) Connecting Anomalous Exchange Bias with Hidden Interface in Oxide Heterostructures

A. Chen*[1]

1. Los Alamos National Lab, USA

Advances in thin film synthesis enable unique opportunities to enhance and control the physical properties of interfaces by controlling the interactions in complex oxides. It is well known that interface layers provide opportunities to create or control functional properties of oxide heterostructures. However, the role of such an interfacial layer in controlling functionalities has not been fully explored. In this talk, the influence of buried interfaces in oxide heterostructures on their magnetic properties will be discussed. A shift of the magnetization hysteresis along the applied field axis was observed. We show the loop shift is an exchange bias (as opposed to the shift of a minor loop) and is present in single phase manganite thin films. Interestingly, the sign of exchange bias is controlled by the cooling field strength. When the cooling field is small, negative exchange bias is observed while positive exchange bias was observed for cooling fields exceeding a threshold. The origin of such an exchange coupling is related to the pinned interfacial layer, confirmed by polarized neutron reflectometry. Our results shed new light on using oxide interfaces to design functional devices.

10:15 AM

(EMA-S3-002-2019) Magnetic Properties of Ferroic Oxide Materials Integrated on Si (100) Substrates (Invited)

S. Singamaneni*[1]

1. The University of Texas at El Paso, Physics, USA

After the first integration of $SrTiO_3$ on silicon substrates by McKee and coauthors almost two decades ago, there have been a growing research interest in integrating ferroelectric, multiferroic and magnetic materials with semiconducting materials. Among all, Si (100) is a workhorse CMOS compatible substrate. This research activity is further fueled by recent push from the industry in realizing the nonvolatile low power computing applications for next generation memory and logic. This presentation discusses the major fundamental advances in the integration of multiferroic and magnetic materials onto ubiquitous silicon semiconductor platform. This approach allows the integration of multifunctional materials on a silicon chip, where sensing, manipulation and rapid response function are combined for next generation 'smart' devices. Of particular interest, this presentation focuses on the resulting magnetic properties such as magnetization, coercive force, exchange bias of several important thin film heterostructures including two-phase multiferroics such as $BiFeO_3$ (BFO)/$La_{0.7}Sr_{0.3}MnO_3$ (LSMO), $BaTiO_3$ (BTO)/LSMO, and heterostructures of two-ferromagnetic oxides such as LSMO/$SrRuO_3$ (SRO). The discussion will also include our first attempt in studying the electric-field induced magnetism in BFO/LSMO heterostructures deposited on silicon substrates using polarized neutron reflectivity measurements.

10:45 AM

(EMA-S3-003-2019) Ultralow energy electric field control of magnetism (Invited)

B. Prasad*[1]; Y. Huang[1]; S. Manipatruni[2]; T. Gosavi[2]; C. Lin[2]; D. Nikonov[2]; I. Young[2]; R. Ramesh[1]

1. University of California Berkeley, Materials Science and Engineering, USA
2. Intel Corp., Exploratory Integrated Circuits, Components Research, USA

Complex perovskite oxides exhibit a rich spectrum of functional properties, including magnetism, ferroelectricity, highly correlated electron behavior, superconductivity, etc., and hence provide the ideal playground for interdisciplinary scientific exploration with an eye toward real applications. Among the large number of materials systems, there exists a small set of materials that exhibit multiple order parameters; these are known as multiferroics, particularly, the coexistence of ferroelectricity and some form of ordered magnetism (typically antiferromagnetism). The electric-field manipulation of magnetism in mutltiferrroic based devices promises to reach atto-Joule (aJ) per bit operation in logic and memory devices. Among all multiferroic materials, $BiFeO_3$ (BFO) exhibits robust magnetoelectric coupling at room temperature. The canted antiferromagnetically aligned spins in BFO, give arise to the weak ferromagnetism due to the Dzyaloshinskii–Moriya(DM) interaction, causes strong exchange interaction with ultrathin ferromagnet, e.g. CoFe, which can be exploited to electrically control a spin valve device. Our current work is focused on ultralow energy electric field manipulation of magnetism as the backbone for the next generation of ultralow power electronics. In this talk, I will describe our progress to date on this exciting possibility. The talk will conclude with a summary of where the future research is going.

11:15 AM

(EMA-S3-004-2019) Strain-mediated Voltage Control of Magnetic Skyrmions: Phase-field Simulation and Analytical Model (Invited)

J. Hu*[1]

1. University of Wisconsin-Madison, Materials Science and Engineering, USA

Voltage control of chiral spin structures (e.g., chiral domain walls, skyrmions, vortices) represents one of the latest developments in the field of magnetoelectrics. It is not only fundamentally interesting but also may lead to new concepts of low-power magnetic and spintronic devices. In this talk, I will present our recent works on phase-field simulations of voltage-controlled magnetic skyrmion switching in hybrid ferromagnetic/heavy-metal/piezoelectric structures. It will be shown that a repeatable creation and deletion of magnetic skyrmions can be achieved purely by voltage-induced strains. The thermodynamic stability and switching dynamics of the skyrmion in a nanodisk with respect to biaxial in-plane strains will also be discussed. An analytical model that we developed to understand the dynamics of strain-mediated skyrmion switching will be presented.

Domains, Domain Walls, and Topological structures

Room: Magnolia A

Session Chairs: Morgan Trassin, ETH Zurich; John Heron, University of Michigan

2:00 PM

(EMA-S3-005-2019) Nanoscale Ferroelectric Domain Evolution in $BiFeO_3$

J. Steffes[1]; R. Cordier[1]; M. Martin[1]; T. Moran[1]; S. Matonis[1]; K. Atamanuk[1]; A. Chen[2]; Y. Huang[4]; B. Prasad[4]; R. Ramesh[3]; B. Huey*[1]

1. University of Connecticut, Materials Science & Engineering, USA
2. Los Alamos National Lab, USA
3. UC Berkeley, Materials Science and Engineering, USA
4. University of California Berkeley, Materials Science and Engineering, USA

Ferroelectric domain dynamics at the nanoscale are crucial to the optimization and energy consumption of a variety of switching devices, including some already commercially available as well as proposed systems for the future. This work emphasizes $BiFeO_3$ with various 2-dimensional and 3-dimensional strain states, polarization configurations, thickness, and Lanthanum doping. Principally by piezoforce microscopy, nucleation and growth phenomena are tracked and compared based on nanoscale-resolved movies of the evolving domain configurations while scanning with an applied bias that exceeds the coercive-field. Notably, although the local configuration of polarization orientations can frustrate complete ferroelectric switching, both multistep and complete 180° switching is observed for pure $BiFeO_3$ as well as La doped $BiFeO_3$.

2:15 PM

(EMA-S3-006-2019) Interconversion of domains and domain walls (Invited)

M. C. Weber*[1]; E. Hassanpour[1]; A. Bortis[1]; Y. Tokunaga[2]; Y. Taguchi[3]; Y. Tokura[3]; A. Cano[4]; T. Lottermoser[1]; M. Fiebig[1]

1. ETH Zurich, Department of Materials, Switzerland
2. University of Tokyo, Department of Advanced Materials Science, Japan
3. RIKEN Center for Emergent Matter Science CEMS, Japan
4. Institut NEEL, MCBT, France

One of the fingerprints of ferroics is the possibility to switch their order parameter under the application of an external field. This directly implies the formation and motion of domain walls that represent a modification of the ordered state between domains. This modification leads to exciting properties different from the bulk. In fact, domain walls may be regarded as novel states of a material. In view of these exciting domain-wall-induced effects, the original focus on the relation between bulk and fundamental properties of domain walls is easily neglected. Here, we will show experimentally that, under rather general circumstances, domains and domain walls are in fact two sides of a coin: They can continuously interconvert into each other across a first-order phase transition (PT) as has been theoretically proposed earlier. This establishes the dual character of domains and domain walls. We take (Dy,Tb)FeO_3 as our model compound and demonstrate how this duality of domains and domain walls promotes topological nucleation by tuning the system across its antiferromagnetic PT. This mechanism provides a rare opportunity towards deterministic nucleation in a first-order PT. Furthermore, it enables the engineering of higher-order domain-wall-like topological objects, such as one-dimensional skyrmions. We finally argue that the concept presented here occurs on a rather general basis going beyond the field of ferroic materials.

2:45 PM

(EMA-S3-007-2019) Topological structures as nanoscale functional elements (Invited)

J. Seidel*[1]

1. University of New South Wales, Australia

Topological structures in functional materials, such as domain walls and skyrmions, see increased attention due to properties that can be completely different from that of the parent bulk material. Such nanoscale materials features can for example provide interesting prospects for memory applications. I will discuss recent results on multiferroic phase boundaries and domain walls in $BiFeO_3$ and KNN-BNNO using SPM, TEM and theory, and discuss future prospects for applications in nanoelectronics and photonics.

3:15 PM

(EMA-S3-008-2019) Design of ferroelectric polarization states during epitaxial growth

N. Strkalj*[1]; G. De Luca[1]; S. Pal[1]; M. Campanini[2]; M. Rossell[2]; M. Fiebig[1]; M. Trassin[1]

1. ETH Zurich, Switzerland
2. EMPA, Switzerland

In ferroelectric thin films, the polarization state, i. e. the orientation and the domain architecture, defines the macroscopic ferroelectric properties such as the switching dynamics. Since most perovskite ferroelectric layers are grown below Tc in epitaxial systems, the polarization state is set already during the heterostructure design. To probe the polarization state during the thin film deposition, we use in situ optical second harmonic generation (ISHG), a non-invasive tool which enables monitoring the domain states even in buried layers. We directly observe the effect of epitaxial strain, interface termination, electrostatic environment and growth conditions on the polarization state. Taking $BaTiO_3$-$SrRuO_3$ capacitor-like heterostructure as a model system, we monitor in real time the impact of the evolving electrostatic environment on the domain state simultaneously with the growth. Furthermore, we shed light on the formation of complex domain architectures in ferroelectric superlattices. We address the depolarizing field and the parameters involved in the emergence of polar flux closure and vortices in $PbTiO_3$-$SrTiO_3$ superlattices. Our work paves the way towards tailoring heterostructures with arbitrary sequences of polarization states and complex ferroelectric domains.

Ferroelectric films and ceramics: Domain States, Switching, and Applications

Room: Magnolia A
Session Chairs: Morgan Trassin, ETH Zurich; Jinxing Zhang, Beijing Normal University

4:00 PM

(EMA-S3-009-2019) Direct Imaging of Polarization Gradients by Atomic Resolution Differential-Phase Contrast STEM (Invited)

M. Campanini*[1]; M. Rossell[1]; J. Nordlander[2]; M. Trassin[2]; C. Yang[3]; R. Ramesh[4]; M. Fiebig[2]; R. Erni[1]

1. Empa, Swiss Federal Laboratories for Materials Science and Technology, Electron Microscopy Center, Switzerland
2. ETH Zurich, Department of Materials, Switzerland
3. Korea Advanced Institute of Science and Engineering (KAIST), Department of Physics, Republic of Korea
4. Lawrence Berkeley National Laboratory, Materials Sciences Division, USA

In the last years, differential-phase contrast (DPC) technique in scanning transmission electron microscopy (STEM) has attracted a great attention for allowing phase-contrast imaging at the very high spatial resolution typical of probe-corrected transmission electron microscopes. With respect to conventional phase-contrast TEM techniques, which allow for reconstructing the phase of the electron beam, in DPC-STEM the local electric-fields in the specimen plane induce a displacement of the center of mass of the transmitted electron beam that can be detected by means of a segmented detector. In this way, the electric-field can be directly retrieved in both its amplitude and phase by measuring the differential signals between pairs of opposite quadrants. In this contribution, we will show the latest advances on the characterization of ferroelectric domain structures in multiferroic oxides by differential-phase contrast STEM and compare the results to indirect methods. In particular, we prove that atomic resolution DPC-STEM is capable of detecting local atomic electric-field fluctuations in ferroelectric materials, thanks to its sensitivity to charge redistribution. The sensitivity of DPC-STEM to atomic-scale electric fields will be demonstrated by some selected examples.

4:30 PM

(EMA-S3-010-2019) Functionalized ferroic coatings on metallic medical implants

P. Vilarinho*[1]; S. Zlotnik[1]; M. Maltez da Costa[1]; M. Fernandes[1]

1. University of Aveiro, Department of Materials and Ceramics, Portugal

Biomedical metals have excellent mechanical properties and commonly used as orthopedic implants. However their poor bioactivity leads to problematic successful osseointegration. If implant itself is able to deliver particular chemical and physical functions stimulating faster tissue regeneration and avoiding scarring, some of these limitations will be overcome. This implies a major transformation of the biomedical metal. Here we present an interdisciplinar alternative strategy, based on the exploitation of functionalized (via electrical charging or UV-light irradiation) ferroelectric $LiTaO_3$ (LTO) as a coating of 316L stainless steel biomedical substrates to stimulate biological responses. In vitro bioactivity studies of LTO coated 316L-SST were conducted and apatite formation on the surface of LTO coatings was analyzed. The effect of the functionalization of LTO coatings (electric charging and photo-functionalization) on the protein adsorption process was also tested. Functionalized LTO coatings (electric field or UV-light) on 316L-SST favor the formation of polar groups (carboxyl and carbonyl) on the surface of LTO coatings leading to the increase of: i) surface wettability and energy, ii) rate of calcium phosphate formation, and iii) adsorption of BSA proteins. Relevant, functionalization type affects protein conformation. Our results are a good example of ferroics integration for new medical devices applications

4:45 PM

(EMA-S3-011-2019) Grain-grain interaction effect on ferroelastic switching in polycrystalline ferroelectric thin films

K. Yazawa*[1]; J. Blendell[1]

1. Purdue University, School of Materials Engineering, USA

There are many factors that can enhance the strain response of ferroelectric polycrystalline materials. Ferroelastic switching can induce much larger strains than piezoelectric strains. Grain boundary misorientation has been shown to affect the local switching behavior. The relationship between switching behavior and the grain boundary misorientation angle was analyzed to understand the effect of the local environment on the switching. Ferroelastic switching in polycrystalline ferroelectric films under an electric field was identified using 3D piezoelectric force microscopy (PFM). The misorientation of neighboring grains was obtained by electron backscattering diffraction (EBSD). From the grain orientation analysis, it was observed that the neighboring grain orientation plays an important role in determining switching behavior. One possible mechanism of the neighboring grain orientation effect is the elastic stresses due to the inhomogeneous piezoelectric response across grain boundaries depending upon the misorientation. The stress distribution at the grain boundary due to an applied electric field was calculated using finite element analysis. The results validate the neighboring grain effect on the ferroelastic switching.

5:00 PM

(EMA-S3-012-2019) Enhanced Energy Storage in Sn-doped BZT-BCT Thin Films

R. Yuan*[1]; D. Xue[2]; T. Lookman[1]; A. Chen[1]

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2. Xi'an Jiaotong University, China

Bulk $Ba(Zr_{0.2}Ti_{0.8})O_3$-x$(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-BCT) ceramics have attracted tremendous interests in the last decade because of its superior piezoelectric effect. Some efforts have been made but still far from sufficient and impressive owing to the difficulty associated with the growth of high-quality thin films of such complex compounds. Compared to their bulk counterparts, thin films process much higher electric break down field that makes them excellent candidates for energy storage applications. We found out that Sn doped BCT-BZT thin films show outstanding energy storage performance than that in most of the Pb-based and undoped BCT-BZT thin films, owing to the slim polarization versus field curves and the high break down electric field. To explore the origin of relaxor ferroelectric behavior, (scanning) transmission electron microscopy have been used to characterize the microstructure of these films. Moreover, ferroelectric domain evolutions were presented from the view of phase field simulation which gleans some understanding for the physical origin of enhanced energy storage performance.

5:15 PM

(EMA-S3-013-2019) Ferroelectric $Na_{0.52}K_{0.44}Li_{0.04}Nb_{0.84}Ta_{0.10}Sb_{0.06}O_3$ ceramic: Giant piezoelectric response with intrinsic polarization and resistive leakage analyses

A. Hussain*[1]; B. Kumar[1]

1. University of Delhi, Department of Physics and Astrophysics, India

Environment friendly lead free $Na_{0.52}K_{0.44}Li_{0.04}Nb_{0.84}Ta_{0.10}Sb_{0.06}O_3$ (NKLNTS) ceramic was synthesized by solid state reaction method in search of a potential candidate to replace lead based ceramics such as $PbZrO_3$-$PbTiO_3$ (PZT), $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) etc., for various electronics devices applications. The giant piezoelectric response (direct piezoelectric charge coefficient: d_{33} ~ 700 pC/N and converse piezoelectric charge coefficient: d_{33}^* ~ 750 pm/V) was obtained for the synthesized ceramic which indicated its potential for use in transducers and actuators. High values of Curie temperature (T_c~305 °C) and pyroelectric coefficient (p ~ 1870 $\mu Cm^{-2}\,°C^{-1}$) suggested the utility of NKLNTS ceramic in high temperature ferroelectric devices and pyroelectric detector applications. NKLNTS ceramic showed fatigue free behavior over 10^7 switching cycles. Remanent hysteresis task was performed to determine the true-remanent (or intrinsic) polarization which showed that a major portion (83.10 %) of the remanent polarization (P_r) is switchable in the sample which makes NKLNTS ceramic a suitable material for memory switching devices applications. Time-Dependent Compensated (TDC) hysteresis task which revealed resistive leakage free nature of the ceramic.

S4: Complex Oxide Thin Film Materials Discovery: From Synthesis to Strain/Interface Engineered Emergent Properties

Controlled Synthesis I

Room: Orange B

Session Chairs: Elizabeth Paisley, Sandia National Laboratories; Megan Holtz, Cornell University

10:00 AM

(EMA-S4-001-2019) Pushing the frontiers of complex oxide thin film growth (Pioneer talk) (Invited)

R. Engel-Herbert*[1]

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

Complex oxides with perovskite structure that contain a transition metal element is a particularly interesting material class for electronic application. Owed to the rich functionality arising from the coupling of spin, orbital, charge and lattice degree of freedom, competing ground states with dramatically different electronic, optical and magnetic properties exist. Harnessing these properties in applications by identifying economically viable growth strategies, while ensuring good stoichiometric control to not degrade the performance of the films is one of the holy grails in the synthesis of complex oxides. In this talk I will review and discuss a thin film growth strategy dubbed hybrid molecular beam epitaxy that combines the advantages of chemical vapor deposition and conventional solid source molecular beam epitaxy in an ideal way. While first growth studies to co-supply elements in a metalorganic as well as in their elemental form have been reported in the early 1990s, the method has gained a lot of attention since, triggered by the demonstration of ultraclean $SrTiO_3$ and $SrVO_3$ thin films. The ability to grow epitaxially integrate complex oxides on Si in a scalable way and the large compositional space that has not been exploited yet projects a bright future for hybrid molecular epitaxy.

10:30 AM

(EMA-S4-002-2019) Utilizing self-regulated growth windows in vanadate thin films

J. Lapano[1]; M. Brahlek[2]; J. Roth[1]; T. Kuznetsova[1]; R. Engel-Herbert*[1]

1. The Pennsylvania State University, Materials Science and Engineering, USA
2. Oak Ridge National Lab, USA

Perovskite oxides with vanadium occupying the B-site dramatically change their properties depending on the valence state of the transition metal element. If vanadium is in the 4+ state (d^1 configuration), like in the case of $SrVO_3$ and $CaVO_3$, it is metallic exhibiting a high electrical conductivity and good optical transparency, making it a suitable transparent conductor material. If vanadium assumes the lower oxidation state 3+ (d^2 configuration), such as $LaVO_3$ or YVO_3, it is semiconducting, assuming a Mott insulator state, exhibiting a complex interplay of spin and orbital order at low temperature. In this talk we present structural and physical properties of vanadate thin films in different valence states grown by hybrid MBE. Emphasis is placed on the ability to access a self-regulated growth window irrespective by the type of element occupying the A-site in the perovskite structure. Epitaxial strain has been found to have a dramatic effect on the structural and magnetic properties of rare earth vanadate films, giving rise to different order and phase arrangement occurring at different length scales. The intimate interplay of octahedral rotation and epitaxial strain gives rise to such an order, will be discussed in light of the structural constraints imposed by the substrate.

10:45 AM

(EMA-S4-003-2019) Novel Functionalities in Atomically Controlled Oxide Heterostructures by Pulsed Laser Deposition (Pioneer talk) (Invited)

G. Rijnders*[1]

1. University of Twente, MESA+ Institute, Netherlands

In recent years, it has been shown that novel functionalities can be achieved in oxide heterostructures in which the interfaces are atomically controlled, in terms of atomic stacking as well as in terms of the local symmetry. In this contribution, I will highlight the recent developments in atomic controlled growth of epitaxial oxides by pulsed laser deposition, with a focus on heterostructures showing manipulated magnetic and electronic properties. Emergent phenomena in oxide heterostructures such as interface charge transfer, two dimensional electron gas and ferromagnetism between two non-magnetic materials, are induced by the dedicated coupling between spin, orbital, charge and lattice degrees of freedom. Developing strategies to engineer these intimate couplings in oxide heterostructures is crucial to achieve new phenomena and to pave the path towards novel functionalities with atomic scale dimensions. Strong oxygen octahedral coupling has recently been demonstrated, which transfers the octahedral rotation from one oxide into the other at the interface region. As a result, we possess control of the lateral magnetic and electronic anisotropies by atomic scale design of the oxygen octahedral rotation. I will furthermore highlight some recent new insights in the "physics" of pulsed laser deposition, focusing on the influence of oxygen pressure on the deposited species during growth.

11:15 AM

(EMA-S4-004-2019) Charge transfer at the $LaCoO_3$-$LaTiO_3$ interface

J. Geessinck*[1]; G. Koster[1]; G. Rijnders[1]

1. University of Twente, Faculty of Science and Technology, Netherlands

Thin films of perovskite oxides have shown interesting properties and can be relatively easily combined, making them suitable building blocks for novel electronics. However, when perovskite thin films are combined, interface effects can strongly affect the overall properties. We have studied the charge transfer at the interface between LaTiO3 and LaCoO3, and found that interfacial charge transfer is a promising way to electrically dope materials without disrupting the structure. Ultra-thin layers of LaCoO3 and LaTiO3 were grown on LaAlO3-buffered SrTiO3 and LaAlO3 substrates by Pulsed Laser Deposition. Subsequently, X-ray Absorption Spectroscopy and photoemission techniques have been used to determine the valence of the transition metal ions. Scanning Transmission Electron Microscopy in combination with Electron Energy Loss Spectroscopy (STEM-EELS) was used to find the spatial distribution of transition metal valence. In LaCoO3, the expected Co3+ valence was observed. However, when LaCoO3 was sandwiched between LaTiO3, a strong Co2+ signal was visible, up to a 100% Co2+ signature for a 2 unit cell thick LaCoO3 layer. Systematically changing the LaCoO3 thickness and monitoring the Co3+ to Co2+ ratio, allowed to quantify the charge transfer to about 1.5 electron per unit cell interface. In this contribution, the atomically controlled growth of the complex oxide heterostructure will be hightlighted as well as the resulting properties.

11:30 AM

(EMA-S4-005-2019) Ab initio thermodynamics of complex surface oxides under controlled growth conditions (Pioneer talk) (Invited)

A. Soon*[1]

1. Yonsei University, Materials Science and Engineering, Republic of Korea

Acquiring an accurate atomistic understanding of the interactions between the molecular gas phase and a surface plays an important and fundamental role in elucidating atomic-scale mechanisms in many important surface and interface processes. In an oxygen-rich atmosphere, pristine metal surfaces are directly exposed to an oxidative environment and the oxides will start to form. For this oxidation process, the initial adsorption of oxygen on metal surfaces often gives rise to stable chemisorbed overlayers before proceeding to the formation of complex oxidic structures on the surface. These embryonic oxidic overlayers (commonly termed as "surface oxides") may possess distinct structural and electronic properties to their corresponding bulk metals and bulk oxides. If such surface oxide films could be thermodynamically stable under technologically relevant conditions, new and novel functionalities could then be exploited. Using the O/Cu and O/Cu/Au systems as examples, the key steps of metal/alloy oxidation are investigated using first-principles density-functional theory coupled with atomistic thermodynamics, and the surface phase diagrams for physically accessible (p,T)-space from ultra-high vacuum to technically relevant conditions are constructed. This provides a first-principles approach to examine and probe gas phase environment-dependent properties of the oxygen-metal system.

12:00 PM

(EMA-S4-006-2019) Expiscating the accurate atomic structure of complex surface oxides on Cu(111): A first-principles investigation

Y. Lee*[1]; T. Lee[1]; A. Soon[1]

1. Yonsei University, Materials Science & Engineering, Republic of Korea

Metal oxides thin films on metal substrates are useful in a wide range of electronic applications e.g. gas sensing, transparent electrode, and hole-transport layer in photovoltaic cells. In particular, the oxidation of Cu(111) has been studied extensively in literature -- from oxygen chemisorption on Cu(111) to the formation of complex surface oxides. Many of these reconstructed O/Cu(111) surface structures have been proposed theoretically and experimentally, including the so-called p4, "29", and "44" structures on Cu(111) resembling the (111) surface of Cu_2O. Here, we face mainly two challenges: (1) A detailed atomic structure of these complex surface oxides is still far from complete, and especially so for the "44" surface oxide (2) To provide a more accurate description of the scanning tunneling microscopy (STM) image, we have attempted to go beyond the Tersoff-Hamann (TH) approximation and included the (functionalized) metal tips explicitly in our STM calculations. Via first-principles density-functional theory (DFT) calculations, we construct various complex oxide models of O/Cu(111) –– namely, the "29" and "44" surface oxides to determine their thermodynamic stability under growth conditions. Using the revised Chen's derivative rules, we demonstrate how our simulated STM images account for key features that could be easily missed via the simple TH approach.

12:15 PM

(EMA-S4-007-2019) Epitaxial (Li,La)TiO_3 thin films by means of Pulsed Laser Deposition

E. Farghadany*[1]; n. Bagués Salguero[2]; R. E. Williams[2]; D. W. McComb[2]; A. Sehirlioglu[1]

1. Case Western Reserve University, Materials Science and Engineering, USA
2. Center for Electron Microscopy and Analysis (CEMAS), USA

(Li,La)TiO_3 (LLTO) is a solid-state electrolyte material with high ionic conductivity for Li. In bulk, grain boundaries are a huge barrier for Li conductivity. In addition, the extended diffusion path for Li in 3-D due to ordered domains along <001>, rather than the preferred 2-D path between electrodes limits its use. In this work, single crystal thin film LLTO has been deposited by Pulsed Laser Deposition (PLD). Single crystal epitaxial thin film eliminates grain boundaries, and creates a flatter diffusion path for Li ions. The deposition process is monitored with in-situ Reflection High Energy Electron Diffraction to determine the number of atomic layers grown and verify the crystallinity of the film. Processing windows in temperature, deposition atmosphere, laser fluence and pulse frequency were determined. Chemical composition of the film was measured by Inductively Coupled Plasma Mass Spectroscopy to check the composition transfer in the PLD chamber. The crystal structure of the film and the epitaxy were investigated by X-ray diffraction techniques such as Reciprocal Lattice Mapping. The local structure was studied using high resolution Transmission Electron Microscopy and relaxation mechanisms were investigated. Even though up to date the relaxation mechanism in the film is not fully understood, microscopy showed the success in epitaxial growth with a sharp interface with minimal intermixing.

Controlled Synthesis II

Room: Orange B
Session Chairs: Roman Engel-Herbert, The Pennsylvania State University; Uwe Schroeder, Namlab gGmbH

2:00 PM

(EMA-S4-008-2019) Ferroelectric Barium Titanate and Barium Strontium Titanate Thin Films (Invited)

E. L. Lin[1]; B. I. Edmondson[1]; J. G. Ekerdt*[1]

1. University of Texas at Austin, Chemical Engineering, USA

Barium titanate (BTO) films and $La_xSr_{1-x}TiO_3$ ($x \leq 0.15$) perovskite heterostructures are grown on strontium titanate (STO)-buffered Si(001) using atomic layer deposition at 225 °C. X-ray diffraction confirms compressive strain in BTO films for films as thick as 66 nm with the c-axis oriented out-of-plane. Post-deposition annealing above 650 °C leads to in-plane c-axis orientation. Piezoresponse force microscopy (PFM) verified the ferroelectric (FE) switching. Electrical and electro-optic measurements confirm BTO film FE behavior at the μm-scale. The $La_xSr_{1-x}TiO_3$ ($x \leq 0.15$) perovskite heterostructures sandwiched between Si(001) and BTO permits examination of a quantum metal between Si and a FE film. These heterostructures are strained to Si(001) and are c-axis out-of-plane. PFM demonstrates the BTO FE behavior on the La-doped STO. Sheet resistance and capacitance-voltage measurements establish the conductivity of the La-doped STO layer. Optical second-harmonic generation in reflection characterized variations in the second-order nonlinear optical susceptibility of 10 to 50 nm thick $Ba_{1-x}Sr_xTiO_3$ (BSTO) alloy films grown epitaxially on $SrTiO_3$(001) as Sr molar ratio x changed from 0 to 1. The results suggest composition and strain control can optimize ferroelectric and electro-optic properties of BSTO films grown on STO buffer layers.

2:30 PM

(EMA-S4-009-2019) Interfacial Oxygen Defect Engineering in Binary Oxide Heterostructures

Q. Lu*[1]; D. Lee[2]; C. Sohn[1]; L. Sun[3]; G. Hu[4]; P. Ganesh[4]; B. Yildiz[3]; H. Lee[1]

1. Oak Ridge National Laboratory, Materials Science and Technology Division, USA
2. University of South Carolina, Department of Mechanical Engineering, USA
3. Massachusetts Institute of Technology, Department of Nuclear Science and Engineering, USA
4. Oak Ridge National Lab, Center for Nanophase Materials and Sciences, USA

Oxygen defects are essential building blocks for designing functional oxides with remarkable properties, ranging from electrical and ionic conductivity to magnetism and ferroelectricity. Oxygen stoichiometry can profoundly alter crystal and electronic structures and enables emergent phenomena unattainable with other tuning parameters. In this work, we studied the formation and control of oxygen vacancies by interfacing two dissimilar oxides. Two material systems are examined to study interface enabled novel functionalities. First, we discovered formation of high density oxygen vacancies at interfaces between CeO_2 and Y_2O_3. The chemical and structural dissimilarities between CeO_2 and Y_2O_3 induced enrichment of oxygen vacancies at (111) interfaces. The high concentration of oxygen vacancies and Ce^{3+} at interfaces is appealing for applications in solid oxide electrochemical cells. The vacancy enrichment can be further tuned by using bixbyite oxides with different lattice parameters, which impose strains on CeO_2. Secondly, control of metal-insulator transition (MIT) in VO_2 by interfacing with TiO_2 is studied. It is found that a TiO_2 capping layer on an epitaxial VO_2 thin film suppresses the MIT in VO_2. We combined X-ray photoelectron spectroscopy and transport measurements with first principles calculations to show that oxygen vacancy migration from TiO_2 to VO_2 is responsible for the suppression of MIT.

2:45 PM

(EMA-S4-010-2019) Defect chemistry in $SrFeO_{3-\delta}$

Y. Du*[1]

1. PNNL, USA

The creation, clustering, and ordering of oxygen vacancies (VOs) in perovskite-structured oxides (ABO3, B being a transition metal) give rise to a special class of materials, such as Brownmillerite (BM) structured SrCoO2.5, SrFeO2.5 (BM-SFO), and rhombohedral structured SrCrO2.8 (R-SCrO). In this work, epitaxial thin films of SrFeO3-d were grown on various lattice matched substrates by molecular beam epitaxy and plused laser deposition to examine the effect of growth and processing condtions on their structural and physical properties. We show that by varying synthesis and processing conditions, the orientation of OVCs can be selectively controlled. Optical ellipsometry, in-plane transport, 18O isotope exchange, and scanning transmission electron microscopy studies reveal that these configurations offer distinct different physical and oxygen transport properties. A topotactic phase transition from BM-SFO (R-SCrO) to perovskite SrFeO3 (SrCrO3) can be promoted, delayed, or prohibited based on the interfacial strain conditions, highlighting the importance of interface engineering in designing robust and efficient ion conducting materials.

3:00 PM

(EMA-S4-011-2019) Topotactic synthesis and properties of epitaxial $SrMnO_{3-\delta}F_\gamma$ oxyfluoride films

J. Wang*[1]; Y. Shin[2]; E. Arenholz[3]; J. Rondinelli[2]; S. May[1]

1. Drexel University, Materials Science and Engineering, USA
2. Northwestern University, Department of Materials Science and Engineering, USA
3. Lawrence Berkeley National Laboratory, Advanced Light Source, USA

Controlling the carrier concentration through doping is of fundamental importance in engineering the properties of complex oxides.

In ABO_3 perovskites, F^- substitution on the anion site provides a way to tailor the B-site valence, the ionicity of B-O bond, and the lattice volume. Here, we present the synthesis of epitaxial perovskite oxyfluoride $SrMnO_{3-\delta}F_\gamma$(SMOF) films via topotactic fluorination of as-grown $SrMnO_{2.5}$(SMO) films. We synthesized the SMOF films with three fluoropolymers of different F:H ratios: PVDF($C_2H_2F_2$), PTFE(C_2F_4), and PVF(C_2H_3F), along with polyethylene(C_2H_4) as a control process. X-ray photoemission spectroscopy and X-ray diffraction show that the F concentration, its spatial uniformity, and the crystalline quality of the SMOF films depends strongly on the fluoropolymer and the reaction temperature. Density functional theory and X-ray absorption spectroscopy reveal that F^- incorporation occurs largely through a F^-/O^{2-} substitution mechanism that reduces the nominal Mn valence toward mixed $Mn^{2+/3+}$ from the Mn^{3+} state found in the as-grown films. The electrical resistivity increases with increasing F concentration while the optical absorption decreases, results that illustrate how the F doping can be used to alter thin film properties. Work at Drexel was supported by the National Science Foundation (NSF Grant No. CMMI-1562223).

3:15 PM

(EMA-S4-012-2019) A facile path for electron transport in NbO_2

G. Kim[2]; Y. Zhang[2]; T. Min[1]; H. Suh[4]; J. Jang[4]; H. Kong[1]; J. Lee[1]; J. Lee[1]; T. Jeon[5]; I. Lee[6]; J. Cho[7]; H. Ohta[3]; H. Jeen*[1]

1. Pusan National University, Department of Physics, Republic of Korea
2. Hokkaido University, Graduate School of Information Science and Technology, Japan
3. Hokkaido University, Research Institute for Electronic Science, Japan
4. Korea Basic Science Institute, Republic of Korea
5. Pohang Accelerator Laboratory, Republic of Korea
6. Pusan National University, Department of Naval Architecture and Ocean Engineering, Republic of Korea
7. Pusan National University, Department of Physics Education, Republic of Korea

Complex transition metal oxides often show anisotropic physical properties due to their ainisotropic structures. Well-known examples are ferroelectric polarization in layered titanates, anisotropic oxygen reduction reactions and diffusion in brownmillerites, and quasi-one dimensional transport behavior in niobates. Here, we showed such anisotropic properties from structurally simple binary oxides. Among many oxides, we chose NbO_2 as a model system because it has distorted rutile structure at the lower temperature via Peierls intability. By stabilization of different orientations by r. f. magnetron sputtering, we could explore electronic properties of each crystallographic directions. We observed facile transport route, which has not been found, with exceptionally low carrier effective mass. These results can clearly explained by density functional theory. The results indicate the importance of orientation control in oxide electronics

Advanced Characterization of Oxide Heterostructures

Room: Orange B

Session Chairs: Scott Chambers, Pacific Northwest National Laboratory; Peter Meisenheimer, University of Michigan

4:00 PM

(EMA-S4-013-2019) Non-equilibrium Manipulation of Phases in Complex Oxide Heterostructures (Invited)

J. Freeland*[1]

1. Argonne National Laboratory, USA

Oxide heterostructures offer new opportunities to control the phases of strongly correlated electrons and to seek out phases that do not exist in the bulk counterparts. Through the utilization of strain, confinement, interfacial charge transfer, and putting distinct phases in close proximity, one can create new boundary conditions in the search for new quantum many-body phenomena. In this talk, I will highlight scientific opportunities in understanding non-equilibrium phases of complex oxides, where the key challenge is understanding how to efficiently drive between these different phases and the non-equilibrium energy landscape. By using complex oxides heterostructures, we can not only tune the energy landscape in order to counterpoise degrees of freedom to generate novel phases, but also use them to understand existing states. This work centers on driving these states away from equilibrium and probing how they evolve with ultrafast X-ray and optical probes. I will present examples involving disentangling order parameters in Nickelates and optical creation of hidden polar phases in Titanate superlattices. The work at Argonne is supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357 and materials and ultrafast experiments are supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC-0012375.

4:30 PM

(EMA-S4-014-2019) Probing structure-property relationships in complex oxides using X-ray diffraction imaging and scanning probe microscopies

Q. Li*[1]; H. Wen[1]

1. Argonne National Laboratory, Advanced Photon Source, USA

Understanding the structure and property relationships of complex oxide materials at microscopic scales is important to the exploitation of their functionalities. Scanning probe/near-field optical microscopy (SPM/SNOM) can probe a multitude of localized physical properties; however, they rarely provide direct information about underlying structures, causing difficulties in identifying localized structure and dynamics information. Here at the Advanced Photon Source (APS), we have developed a multimodal platform integrating SPM/SNOM with X-ray diffraction microscopy. Using this new platform, we have recently demonstrated correlative imaging of the crystal structure of materials and their electronic responses, with in-situ local manipulation of material states using tip electric bias and force stimuli. In this talk, I will briefly review the instrument development, present a few case studies and discuss broader applications for complex oxide materials. In particular, we have systematically explored the structural basis of mechanical switching phenomena in ferroelectric thin films. Through the observations and modeling of local Huang diffusing scattering, an oxygen vacancy defect-coupled polarization switching mechanism has been revealed for the first time.

4:45 PM

(EMA-S4-015-2019) Probing electronic and Magnetic Interactions at Complex Oxide Interfaces (Invited)

D. P. Kumah*[1]

1. North Carolina State University, Physics, USA

Transition metal oxides (TMOs) exhibit a wide range of electronic and magnetic phases which are intimately linked to their atomic-scale structural properties. Understanding and tuning these phases is crucial for the development of the next generation of devices for energy storage and conversion and information processing. The ability to fabricate monolayers of TMOs using molecular beam epitaxy allows for the manipulation of these phases at crystalline hetero-epitaxial interfaces. High-resolution imaging of the atomic-scale structure of the interface between monolayers of colossal magnetoresistive $LaSrMnO_3$ and antiferromagnetic $LaCrO_3$ films is achieved using a combination of synchrotron X-ray diffraction imaging and X-ray phase retrieval techniques. A correlation is established between the structural interactions at the LSMO/LCO interface and magnetic and electronic ordering. These results have important implications for the rational design of novel electronic and magnetic materials.

5:15 PM

(EMA-S4-016-2019) Competing spin-orbital entanglement in ferroelastic heterostructures

E. Guo*[1]

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

The ferroelastic nonmagnetic $LaCoO_3$ (LCO) has attracted increasing attention due to its active spin state transition by the strain-induced octahedral perturbation. The delicate interplay between the crystal field splitting and exchange interaction controls the electron redistribution between orbitals, manipulating the multiferroic functionalities of LCO films. In this talk, I will firstly discuss the observation of a one-dimensional ferroelastic domain in LCO thin films. The unidirectional structural modulation is achieved by selective choice of the substrates possessing broken symmetry. We observe the distinct anisotropy in both orbital configuration and electronic state, leading to an unexpected in-plane magnetic anisotropy. A second example illustrates the quantitatively measure of atomic density and magnetization distribution in LCO films by polarized neutron reflectometry (PNR). We find that the LCO layers near the heterointerfaces exhibit a reduced magnetization but an enhanced atomic density, whereas the film bulk region shows an opposite trend. We attribute these nonuniformities to a symmetry mismatch induced local structural distortion owing to the ferroelastic nature of LCO. This assertion is tested by systematic application of hydrostatic pressure through PNR experiments. The magnetization can be directly controlled at a rate of -20.4% per GPa.

S7: Superconducting and Magnetic Materials: From Basic Science to Applications

Superconducting and Magnetic Materials I

Room: Citrus A

Session Chair: Gang Wang, Institute of Physics, Chinese Academy of Sciences

10:00 AM

(EMA-S7-001-2019) Quasi-one-dimensional topological insulators and superconductors: Bi_4X_4 (X=I,Br) (Invited)

F. Zhang*[1]

1. University of Texas at Dallas, Department of Physics, USA

We are all witnessing or participating the grand discovery of various topological states of matter. In this talk, I will introduce a family of newly discovered quasi-one-dimensional topological materials Bi_4X_4 (X=I,Br) and discuss their fascinating properties from both fundamental and application perspectives. (i) The alpha and beta phases of Bi_4I_4 are trivial and topological insulators, respectively, with a structure transition observed at room temperature. A small strain can tune the topological transitions and the number of surface states of the beta phase. (ii) Recently, the alpha phase of Bi_4Br_4 has been predicted as a prototypical higher-order topological insulator, i.e., an exotic state with conducting hinges but insulating bulk and surfaces. (iii) While Bi_4I_4 has been made superconducting under pressure, both intrinsic and extrinsic topological superconductivity hosting Dirac/Weyl and Majorana quasiparticles can be achieved by metal intercalation and proximity effect, respectively. Evidently, the Bi_4X_4 family provides an unprecedented platform for electronics and spintronics, based on the room-temperature-switchable and strain-tunable surface states, the novel hinge modes, the emergent Dirac/Weyl nodes, and the desired Majorana anyons.

10:30 AM

(EMA-S7-002-2019) Nematicity and superconductivity: New methods and new materials to study the effects of nematic quantum criticality (Invited)

I. Fisher*[1]

1. Stanford University, Applied Physics, USA

Electronic nematic order in crystalline solids corresponds to a spontaneously broken discrete rotational symmetry driven by interactions between low-energy electronic degrees of freedom. The empirical observation that nematic order occurs in, or near to, superconducting phases in Fe-based materials and possibly also cuprates motivates a series of fundamental questions about the possible role(s) that nematicity might play in such systems, in particular proximate to a nematic quantum critical point. In this talk I will describe new methods to continuously tune the critical temperature of such systems. In particular, I will emphasize that orthogonal antisymmetric strain is an important, and thus far largely neglected, tuning parameter for nematic order. The method, including a description of how to perform an appropriate decomposition in to different symmetry channels, is demonstrated for underdoped compositions of representative Fe-based superconductors. I will also discuss results from applying similar methods to materials that exhibit ferroquadrupole order, a specific realization of nematic order, which can be tuned to a quantum phase transition.

11:00 AM

(EMA-S7-003-2019) Discovery of a novel spin-triplet superconductor in a uranium based compound (Invited)

S. Ran*[1]; C. Eckberg[2]; T. Metz[2]; S. Saha[2]; I. Liu[2]; J. Paglione[2]; N. Butch[1]

1. NIST, Center for Neutron Research, USA
2. University of Maryland, Center for Nanophysics and Advanced Materials, Department of Physics, USA

We discovered a novel spin-triplet superconductor with the highest T_c among all the other candidates. The normal state is paramagnetic and shows no indication of magnetic ordering. The bulk superconductivity is observed at 1.6 K in resistivity, AC magnetization and specific heat measurements. The H_{c2} value largely exceeds paramagnetic limit in all three directions, and also exceeds orbital limit along b-axis. The large positive curvature and unusual shape of H_{c2} curve reminisces those of a ferromagnetic superconductor UCoGe. In addition, the specific heat data show a large residue density of state in the superconducting state, almost half of the normal state value. All of these results strongly indicate that the superconductivity in this uranium compound is carried by spin-triplet pairs. The strong field dependence of the superconducting coupling strength suggests that the pairing mechanism arises from ferromagnetic spin fluctuations.

11:30 AM

(EMA-S7-004-2019) The melilite-type room temperature ferromagnetic semiconductor candidate (Invited)

H. Yang[1]; B. Gong[1]; K. Liu*[1]; Z. Lu[1]

1. Renmin University of China, Department of Physics, China

The seeking of room temperature ferromagnetic semiconductors has been a long-term goal of scientists and engineers. Here, we predict a new class of high temperature ferromagnetic semiconductors based on the melilite-type oxysulfide Sr2MnGe2S6O by using the spin-polarized first-principles calculations. Due to the moderate distances between the Mn ions, the weak antiferromagnetic order in the parent compound Sr2MnGe2S6O can be easily suppressed by charge doping with either p-type or n-type carriers, giving rise to the expected ferromagnetic order. At a doping concentration of 25%, both the K-doped and La-doped compounds can achieve a Curie temperature (Tc) above 300 K. Our study provides an effective approach for exploring new types of high temperature ferromagnetic semiconductors, which have potential applications in electronic and spintronic devices.

12:00 PM

(EMA-S7-005-2019) Magnetic Skyrmion Nanodomains in Centrosymmetric Magnets (Invited)

W. Wang*[1]

1. Institute of Physics, China

Magnetic skyrmion nanodomains are presently attracting immense research interest on the global level as they are arguably the smallest spin textures in nature and thus are anticipated to overcome the storage limit challenge for conventional material, promising to be the next-generation of high density spintronic devices. Current-driven skyrmion motion such as rotation and translation using low current density has been realized in skyrmion lattice crystals. Alarmingly, such a current-driven motion occurs at temperatures far below room temperature and suffers a narrow manipulation temperature window. Here, we introduce centrosymmetric MnNiGa and Fe3Sn2 compound showing the individual kyrmion magnetic nanodomains at and above room temperature. We found that the electric-current can substantially reduce the threshold magnetic field to form the skyrmions in MnNiGa, and the single chain of individual skyrmions can subject to a recorded-high temperature of 630K in Fe3Sn2 nanosheets. More importantly, we further demonstrate unusually large and anisotropic magnetic tenability in Fe3Sn2 and points to an underlying correlated magnetic topologic ground state. This easy and efficient tuning options together with fascinating topological features with the uniform chirality makes this material excellent candidate for technical application as information carriers in the next generation ultra-dense magnetic spintronic devices.

Superconducting and Magnetic Materials II

Room: Citrus A

Session Chair: Timothy Haugan, U.S. Air Force Research Laboratory

2:00 PM

(EMA-S7-006-2019) Orbital Origin of Extremely Anisotropic Superconducting Gap in Nematic Phase of FeSe Superconductor (Invited)

X. Zhou*[1]

1. National Lab for Superconductivity, Institute of Physics, China

The iron-based superconductors are characterized by multiple-orbital physics where all the five Fe 3d orbitals get involved. The multiple-orbital nature gives rise to various novel phenomena like orbital-selective Mott transition, nematicity and orbital fluctuation that provide a new route for realizing superconductivity. In this talk, we report direct observation of highly anisotropic Fermi surface and extremely anisotropic superconducting gap in the nematic state of FeSe superconductor by high resolution laser-based angle-resolved photoemission measurements. We find that the low energy excitations of the entire hole pocket at the Brillouin zone center are dominated by the single d_{xz} orbital. The superconducting gap exhibits an anti-correlation relation with the d_{xz} spectral weight near the Fermi level, i.e., the gap size minimum (maximum) corresponds to the maximum (minimum) of the dxz spectral weight along the Fermi surface. These observations provide new insights in understanding the orbital origin of the extremely anisotropic superconducting gap in FeSe superconductor and the relation between nematicity and superconductivity in the iron-based superconductors.

2:30 PM

(EMA-S7-007-2019) Synthesis and study of novel superconducting materials (Invited)

B. Lv*[1]

1. The University of Texas at Dallas, Department of Physics, USA

In this presentation, I will discuss our research efforts to develop new and better superconductor materials in the past few years. I shall first focus on several new superconducting materials discovered by our research groups, and then extend to other superconductors and new interesting materials currently studied in our group. The system we will present are: 1) site-selective superconductivity in the transition metal-doped Zr_5Ge_3 compound; 2) superconductivity in the organic co-intercalated two dimensional $SnSe_2$ system; 3) “claimed” dopant-independent superconductivity in the doped black phosphorus; 4) new ternary superconducting materials $SrPt_{10}P_4$. Other materials, such as quasi-one-dimensional $K_2Mo_3As_3$ and $Rb_2Mo_3As_3$ compounds, and several new layered compounds, will be discussed and presented if time permits.

3:00 PM

(EMA-S7-008-2019) Structural Domains and Intrinsic Pinning in Ni-substituted $Ba(Fe_{1-x}Ni_x)_2As_2$

M. Susner*[1]; S. Chong[2]; T. J. Haugan[3]

1. Air Force Research Laboratory, USA
2. Victoria University of Wellington, New Zealand
3. U.S. Air Force Research Laboratory, AFRL/RQQM, USA

Fe-based superconductors have been a subject of much research based on 1) their modest to relatively high T_cs and very high B_{c2}s and 2) their interesting physics in which superconductivity is associated with magnetic/structural phase transitions. Previous reports on Co-doped $BaFe_2As_2$ single crystals have noted that high intrinsic pinning, and thus enhanced J_c, is present in samples with twin boundaries in the antiferromagnetic orthorhombic phase present in underdoped samples that coexists with superconductivity at these compositions (i.e. near a quantum critical point). In this work we examine a similar phenomenon in single crystals we grew of the $Ba(Fe_{1-x}Ni_x)_2As_2$ system where we use resistive, calorimetric, magnetic, and diffraction measurements to map quantum criticality in this material. We analyze J_c in terms of dopant concentration, temperature, and pressure to determine the effects of the domain boundaries on the intrinsic pinning in these single crystal specimens. These analyses reveal that superconducting $Ba(Fe_{1-x}Ni_x)_2As_2$ contains a high intrinsic J_c that is enhanced by the presence of magnetic domain boundaries. We acknowledge funding from the Air Force Research Laboratory under an Air Force Office of Scientific Research grant (LRIR No. 18RQCOR100) and a grant from the National Research Council.

3:15 PM

(EMA-S7-009-2019) Phase diagram of Rb-intercalated $NbSe_2$ synthesized by solid-state reaction

X. Fan[1]; H. Chen[1]; S. Jin[1]; G. Wang*[1]; X. Chen[1]

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

2H-$NbSe_2$, a typical layered transition metal dichalcogenide (TMD), has attracted tremendous research interest for its substantially higher superconducting transition temperature (T_c = 7.2 K) than those for the majority of TMDs (2-4 K) and hosting of charge density wave (CDW). The van der Waals (vdW) bonding between $NbSe_2$ layers makes it a good platform for tuning of the crystal structure, superconducting gap, and CDW by metal intercalation. Here we report the investigation of crystal structures, magnetic, and electrical properties of Rb-intercalated 2H-$NbSe_2$ prepared by solid-state reaction. With Rb intercalation, T_c of Rb_xNbSe_2 decreases from 7.2 K for x = 0 to 4.2 K for x = 0.025. For higher Rb intercalation level, the crystal structure of Rb_xNbSe_2 is found to develop from 2H (Phase I) for $0 \le x \le 0.025$, via 6R (Phase II) with space group R-3m, finally to 2H (Phase IV) with space group $P6_3/mmc$ for $0.375 \le x \le 0.5$. By annealing at relatively low temperature, Phase II transforms to Phase III (rare 6H) with space group $P6_3/mmc$. It is noticeable that 6R and 6H phases both are firstly obtained in metal-intercalated 2H-$NbSe_2$ compounds. A phase diagram of Rb_xNbSe_2 ($0 \le x \le 0.5$) is established accordingly.

Superconducting and Magnetic Materials III

Room: Citrus A
Session Chair: Ian Fisher, Stanford University

4:00 PM

(EMA-S7-010-2019) Single crystals and films of (Li,Fe)OHFeSe superconductors: Electronic phase separation and exotic charge transport (Invited)

X. Dong*[1]

1. Institute of Physics, CAS, China

By developing the novel methods of hydrothermal ion-exchange and MAHEG, we succeeded in synthesizing a series of high-quality single crystals and thin films of (Li, Fe)OHFeSe, respectively. We observed an evident drop in the magnetization at T_{afm} ~125 K, in the powder and single crystal samples (T_c < ~38 K). This indicates the coexistence of an antiferromagnetic (AFM) state with the superconducting state. Such coexistence can be explained by electronic phase separation (EPS), similar to that in cuprates and iron arsenides. A microscopic EPS was proposed for samples showing no magnetic drop at ~125 K. However, this static EPS reaches vanishing point in high-T_c (~42 K) samples, as suggested by the occurrence of 2d AFM spin fluctuations below nearly the same temperature as T_{afm}. A complete phase diagram for (Li, Fe)OHFeSe was thus established. In the film samples, we found that both the electron and hole carriers contribute to the charge transport. Moreover, the values of electron and hole mobility, which become rather high and distinct from each other in high-T_c samples, tend to diverge prior to the superconducting transition.

4:30 PM

(EMA-S7-011-2019) Frustrated ordering instabilities and superconductivity in quasi-one-dimensional $K_2Cr_3As_3$ (Invited)

K. M. Taddei*[1]; G. Xing[4]; j. Sun[4]; Y. Fu[4]; Y. Li[4]; Q. Zheng[2]; A. Sefat[3]; D. J. Singh[4]; C. de la Cruz[1]

1. Oak Ridge National Laboratory, Neutron Scattering Division, USA
2. Oak Ridge National Lab, Materials Science and Technology Divison, USA
3. Oak Ridge National Laboratory, USA
4. University of Missouri, Columbia, Physics and Astronomy, USA

Quasi-one-dimensional $A_2Cr_3As_3$ (with A = K, Cs, Rb) is an intriguing new family of unconventional superconductors which exhibit many similar features to the cuprate and iron-based superconductor families – but are expected to have enhanced electron correlations due to further reduced dimensionality. Yet in contrast to these systems, no charge, orbital or magnetic ordering has been observed which could provide the electronic correlations presumed necessary for an unconventional superconducting pairing mechanism - an absence which defies predictions of first principles models. Here, we revisit the density functional theory work using our experimentally determined structure to study possible instabilities in $K_2Cr_3As_3$. Using the resulting predictions as guidance we use neutron scattering techniques to probe for possible experimental signals. Our results reveal several instabilities in this system despite the absence of long-range order - suggesting an important similarity to the wider family of unconventional superconductors.

S9: Ion–Conducting Ceramics

Lithium Ion Batteries

Room: Citrus B
Session Chairs: Yingge Du, PNNL; Erik Spoerke, Sandia National Laboratories

10:00 AM

(EMA-S9-001-2019) Using in-situ and operando methods to characterize phase changes in charged lithium nickel cobalt aluminum oxide cathode materials (Invited)

E. A. Stach*[1]; S. Hwang[2]; K. Karki[3]; S. Kim[4]; W. Chang[4]; G. Zhuo[5]; M. Whittingham[5]; Q. Yang[6]

1. University of Pennsylvania, Department of Materials Science and Engineering, USA
2. Brookhaven National Laboratory, Center for Functional Nanomaterials, USA
3. Hummingbird Scientific, USA
4. Korea Institute of Science and Technology, Republic of Korea
5. Binghamton University, USA
6. Brookhaven National Laboratory, USA

Lithium nickel cobalt aluminum oxide cathode materials ($LixNi_{0.8}Co_{0.15}Al_{0.05}O_3$ – "NCA") are seeing increasing use in demanding energy storage applications due to their high energy storage capacity. However, these materials can experience undesirable thermal runaway, leading to catastrophic failures. I will review our work investigating the atomic scale changes that occur in NCA during thermal excursions. These studies will mostly focus on the use of in-situ transmission electron microscopy (TEM) but will include information gleaned from complementary probes such as in-situ x-ray diffraction and x-ray absorption. We have used these approaches to understand how thermal excursions can lead to bulk oxygen loss from the structure, how this oxygen loss is correlated with the movement of the transition metal ions, and how these movements lead to a series of structural changes from the spinel structure to the 'disordered spinel' structure to the rock-salt structure on the surface of the particles. Environmental TEM also allows us to explore how to tune the surface activity, leading to the suppression of both oxygen loss and initiation of the phase transitions.

10:30 AM

(EMA-S9-002-2019) Lithium ion diffusion during the growth induced the new materials discovery

L. Wang*[1]; Z. Yang[1]; M. Bowden[2]; S. Chambers[1]; Y. Du[1]

1. Pacific Northwest National Laboratory, Physical and Computational Sciences Directorate, USA
2. Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, USA

$LiCoO_2$ is the most commonly used cathode material for rechargeable Li-ion batteries. The layered structure of $LiCoO_2$ is well suitable for the rapid deintercalation and intercalation of lithium. On the other hand, tungsten oxides and their compounds have a high potential for application in electrochemical devices. The empty centers in WO_3 allow the facile and reversible intercalation/removal of small ions, such as Li+, Na+. Here, we report a reliable and reproducible way of obtaining Li_2WO_4 thin films by depositing WO_3 on the top of $LiCoO_2$ covered $SrTiO_3$ substrates by pulsed laser deposition. We think that chemical delithiation occurs in the $LiCoO_2$ layer due to Li out diffusion, meanwhile Li_2WO_4 forms due to the lithiation behavior when continuously depositing WO_3. Our XRD and TEM results confirmed the discovery of the Li_2WO_4 epitaxial thin films and its crystal orientation is along (004) direction for films grown on (001)-oriented $SrTiO_3$ substrates. Our TEM observation also find that the Li_2WO_4 structure is highly unstable under high energy electron beam irradiation. By changing the orientation of the substrates or controlling the laser frequency, the surface topography

of the Li_2WO_4 epitaxial thin films can display huge difference. This unique approach may significantly increase the rate at which novel electronic, magnetic, and optical materials are discovered.

10:45 AM

(EMA-S9-003-2019) Defect generation in TiO_2 nanotube anodes via heat treatment in various atmospheres for lithium-ion batteries

A. I. Savva[1]; K. A. Smith[1]; M. Lawson[1]; C. D. Jones*[1]; S. R. Croft[1]; A. E. Weltner[1]; P. J. Simmonds[1]; L. Li[1]; H. Xiong[1]

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

Ordered TiO_2 nanotubes were grown on a Ti substrate via electrochemical anodization and subsequently annealed at 450 °C for 4 hours under various atmospheres to create different point defects. Oxygen-deficient environments such as Ar and N_2 were used to develop oxygen vacancies, while a water vapor (WV) atmosphere was used to generate titanium vacancies. Computational models by density functional theory predicted that the presence of oxygen vacancies would cause electronic conductivity to increase, while the presence of Ti vacancies could lead to decreased conductivity. The predictions were confirmed by two-point electrical conductivity measurements and Mott–Schottky analysis. Raman spectroscopy was also conducted to confirm the presence of defects. The annealed samples were then evaluated as anodes in lithium-ion batteries. The oxygen-deficient samples had an improvement in capacity by 10% and 25% for Ar- and N2-treated samples, respectively, while the WV-treated sample displayed a capacity increase of 24% compared to the stoichiometric control sample (annealed in O_2). Electrochemical impedance spectroscopy studies revealed that the WV-treated sample's increased capacity was a consequence of its higher Li diffusivity.

11:00 AM

(EMA-S9-004-2019) Atomic-to-mesoscale mechanism of ion conductivity in nanostructured metal oxide and carbon materials (Invited)

M. Sushko*[1]

1. Pacific Northwest National Laboratory, USA

Nanostructuring is a powerful method for enhancing the performance of electrode materials. However, designing such materials requires an in-depth understanding of the structure - ion transport relationship spanning multiple length scales. This challenge is addressed theoretically using a novel hierarchical hybrid multiscale simulation technique. The model uses a multiphysics approach, in which instead of formal consecutive upscaling novel types of collective long-range interactions along with short-range effects of the finer scale models are introduced. The fine scale models take advantage of high accuracy quantum mechanical simulations of elementary charge transport. The collective long-range electrostatic and excluded volume interactions are introduced on the mesoscale (10-500 nm) via classical Density Functional Theory coupled with the Poisson-Nernst-Planck formalism for dynamic effects. The applications of the approach to designing nanocomposite metal oxide/graphene hybrid electrode materials for Li-ion batteries and hard carbon electrode materials for Na-ion storage will be discussed.

11:30 AM

(EMA-S9-005-2019) Cold Sintering Process for Development of All-Solid-State Li Batteries

J. Seo*[1]; E. Gomez[2]; T. Mallouk[3]; C. Randall[1]

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

All-solid-state Li batteries can offer several advantages such as high safety, high energy density and a long cycle stability. Many types of solid electrolytes with high conductivity have been developed to replace liquid electrolytes. However, fabrication process of the all-solid-state battery such as sintering of the solid electrolytes at high temeprature is still one of the challenges to practical applications. Therefore, it is required not only to increase the conductivity of solid electrolytes but also to develop fabrication process for dense structured electrodes/electrolytes and good interfaces between them. Recently, a low temperature sintering process, named "cold sintering process", has developed for sintering of ceramics and ceramic-based composites. This process has been considered as a promising densification process not only to save energy but also to avoid any material losses and side reactions during the sintering process. Using CSP, highly densified structures can be obtained through a mediate dissolution-precipitation process in transient aqueous conditions at low temperature. The cold sintering process can be employed to fabricate highly densified electrodes and electrolyte layers for all solid-state batteries at low temperature. In this presentation, it will be introduced how to apply the cold sintering process for the fabrication of all solid-state Li batteries.

11:45 AM

(EMA-S9-006-2019) $Li_4Ti_5O_{12}$–$Li_{0.45}La_{0.52}TiO_3$–Ni all-solid-state lithium-ion battery anode composites

W. Huddleston*[1]; F. Dynys[2]; A. Sehirlioglu[1]

1. Case Western Reserve University, Department of Materials Science and Engineering, USA
2. NASA Glenn Research Center, USA

Strain free $Li_4Ti_5O_{12}$ (LTO) anodes were investigated for inherently safe all-solid-state lithium-ion batteries. Design of active materials for structural applications enables multifunctional energy storage systems that provide systems-level weight savings in next generation green aerospace concepts. In order to improve the electrical and ionic conductivity for high power applications, processing-property-performance relationships need to be developed for sintered composites with metallic nickel current collector and $Li_{0.45}La_{0.52}TiO_3$ (LLTO) electrolyte. Percolation behavior of LTO-Ni, introduced as NiO, was determined as a function of Ni vol% and porosity. Densification characteristics of LTO-LLTO two-phase composites were determined as a function of LLTO volume fraction and sintering temperature. In conjunction, these studies informed the processing of three phase composites by high temperature sintering and intermediate temperature hot pressing that reach full densification, tune particle size ratios for percolation, and recover from high temperature phase transformations. Sintering at 1100°C and annealing below 900°C in 5%H_2-Ar was necessary to fully densify and recover the spinel structure, but Ni coarsening was observed. Microstructural effects on electrochemical performance were surveyed for improving conductivity, capacity, and rate capability.

12:00 PM

(EMA-S9-007-2019) Defects/Disorder-Mediated Fast Ion Conduction in Ceramics (Invited)

Y. Hu*[1]

1. Florida State University, Chemistry & Biochemistry, USA

Defects and disorder play important roles in ion-conducting ceramics. This study examines the nature of defects and disorder and their effects on ion transport in several high-performance lithium (Li) and sodium (Na) ion conductors including $Na_{3-d}PS_{4-a}X_a$(X =Cl, Br, and I), $xLi_3PS_4/yLiI$, and Argyrodites. Experimental investigations combine both long- and short-range structure tools to determine the characteristics of defects. Tracer-exchange NMR is used to map out ion transport pathways and identify functional structural features that facilitate ion conduction. Computational efforts are employed to study how defects/disorder alter ion conduction mechanisms and enhance ionic conductivities. The gained insights have been invaluable for designing new ion conductors with achieved ionic conductivities up to 13 mS/cm at room temperature.

Cation Conducting Ceramics for Energy Storage

Room: Citrus B
Session Chairs: Hui Xiong, Boise State University; Yan-Yan Hu, Florida State University

2:00 PM

(EMA-S9-008-2019) Ion conducting quantum materials (Invited)

S. Ramanathan*[1]

1. Purdue University, MSE, USA

Ceramic ion conductors are traditionally based on wide gap insulators, famous examples include zirconia and ceria. Point defects are created by alio-valent doping to enhance ion conduction, such as Y doping in ZrO2 to create oxygen vacancies selectively. Most efforts to enhance ion conduction suffer from inherent problem of chemical or structural instability under low oxygen potentials and severely limits innovation in the materials space. We present a new approach that starts from electron conducting oxides which transition into a strongly correlated insulating phase by ion-electron doping. Perovskites such as rare-earth nickelates are narrow gap semiconductors or metallic at room temperature and electron doping by hydrogen or other small ions induces a large transport gap rendering them insulating while functioning as excellent ion conductors. This approach enables fundamental re-think of ion conductor design and opens up a vast space of materials design utilizing strong Coulomb repulsion in partially-filled orbitals. We will discuss the physics of the charge doping process, ion conduction mechanisms and illustrate representative examples in solid state fuel cells, lithium-ion shuttles and neuromorphic hardware.

2:30 PM

(EMA-S9-009-2019) Rethinking Solid State Sodium Ion Conductors for Low Temperature Batteries

E. Spoerke*[1]; A. Peretti[1]; S. Percival[1]; J. A. Bock[1]; H. J. Brown-Shaklee[1]; L. Small[1]

1. Sandia National Laboratories, USA

New, zero-crossover solid state separators with high ionic conductivity are key to advancing emerging low temperature (<100C) Na-based batteries. Formed as traditional sheets or tubes, conventional Na-conducting ceramic separators, such as NaSICON ($Na_3Zr_2PSi_2O_{12}$) or β”-Al_2O_3, typically require elevated temperatures (150-300C) to achieve optimal ionic conductivity. Lowering battery operational temperature presents new challenges to such ion-conducting separators. Here, we describe our efforts to tailor the composition and structure of solid state separators for use in low temperature Na-based batteries. Toward improved NaSICON-based separators, we explore traditional cationic doping, as well as the processing and properties of hybrid architectures and composite materials that promise novel separator performance. We address not only requirements of ionic conductivity in these materials, but also challenges of mechanical behavior, thermal stability, and chemical compatibility. These early materials offer great promise toward enabling a new class of robust and reliable energy storage technologies. 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.

2:45 PM

(EMA-S9-010-2019) Low temperature processing of sodium ion battery electrodes and electrolytes via the Cold Sintering Process

Z. M. Grady*[1]; T. De Beauvoir[1]; A. Ndayishimiye[1]; J. Seo[1]; C. Randall[1]

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

Safety and raw material sourcing concerns have prompted research into alternatives to the ubiquitous lithium-ion batteries (LIB’s), such as sodium-ion based batteries (SIB’s). Promising results in recent work on SIB electrodes and electrolytes has demonstrated the feasibility of large scale adoption of SIB’s in certain applications, like grid-based energy storage. The family of sodium-iron-sulfate hydrates, for example, have produced voltages as high as 3.8V for over 20 cycles and gravimetric capacities ca. 80 mAh*g^{-1} at a rate of 0.1C. However, many of these promising Na^+ conducting materials suffer from undesirable phase transformation or gaseous decomposition at the elevated temperatures required for conventional sintering techniques. This has motivated the application of newly developed alternative sintering techniques to the densification of these materials. Taking advantage of the low temperatures characterizing the Cold Sintering Process, we will present SIB materials which have been densified at ultra-low temperatures (<300°C), including the aforementioned Fe-redox centered sodium sulfates. We will report on the processing, microstructure, and properties of these cold sintered polyanionic Na^+ conducting cathodes, in addition to other cold sintered SIB components such as Na^+ conducting electrolytes.

3:00 PM

(EMA-S9-011-2019) Computing the Anisotropic Chemical Strain in Non-Stoichiometric Oxides for Solid Oxide Fuel Cell and Li-ion Battery Applications (Invited)

Y. Qi*[1]

1. Michigan State University, Department of Chemical Engineering and Materials Science, USA

Accurate characterization of chemical strain is required to study a broad range of chemical-mechanical coupling phenomena. By combining density functional theory (DFT) and elastic dipole tensor theory, the chemical strain tensor induced by dilute point defects is predicted. First, we demonstrate that, even in cubic $CeO_{2-\delta}$, both the short-range deformation surrounding an oxygen vacancy and the long-range chemical strain are anisotropic. The origin of this anisotropy is the charge disproportionation between the four cerium atoms surrounding each oxygen vacancy when a neutral oxygen vacancy is formed. Under an external bias, such as an applied electric field, the chemical strain can be oriented to show the anisotropic effect. This successfully explained the giant electrostriction effect reported in $CeO_{2-\delta}$. Next, we show strains induced by coupled vacancies in Li_2MnO_3, which represents the Li-excess intercalation compounds that need to be “activated” to deliver the high capacity. The chemical strain of the energetically favorable vacancy dumbbell structure is smaller than the sum of the chemical strain of one V_o and two V_{Li}s. The chemical expansion coefficient averaged for the polycrystalline samples and the experimentally measured stress change provided a novel method to in situ track the irreversible chemical changes in Li-excess cathode materials.

4:00 PM

(EMA-S9-012-2019) Magnesium and mobility: An investigation of defects and Mg mobility in spinel oxides

S. Lapidus*[1]; R. Bayliss[2]; B. Key[3]; J. Cabana[2]

1. Argonne National Lab, X-Ray Science Division, USA
2. University of Illinois, Chicago, USA
3. Argonne National Lab, USA

Mg oxide cathodes can theoretically surpass the energy density of current Li-ion technology. A possible explanation for the absence of functional Mg batteries is poor Mg^{2+} mobility within oxides, which limits intercalation reactions at the cathode. Currently, the understanding of magnesium cation mobility is lacking. Detailed structural characterization and the elucidation of defect models is critical to the understanding of structure/property relationships. Powder diffraction is a direct bulk probe of the crystalline structure and defects thereof. Herein, a detailed structural study, utilizing both x-rays and neutrons, of Mg mobility within a family of spinel oxides was performed. These results provide insight into structural features and defects that determine the mobility of Mg^{2+} cations in these compounds. These results were then coupled with Mg NMR and computation to probe the correlation between defects, local structure and Mg mobility.

4:15 PM

(EMA-S9-013-2019) Morphological and Chemical Changes Associated with the Precipitation of Cobalt Oxide Nanosheets Using Various Cations

K. Pachuta*[1]; E. Pentzer[2]; M. Berger[3]; A. Wu[3]; A. Sehirlioglu[1]

1. Case Western Reserve University, Materials Science and Engineering, USA
2. Case Western Reserve University, Chemistry, USA
3. Mines Paris Tech, France

This research aims to understand the chemical and structural changes that occur from various processing treatments during the chemical exfoliation of lithium cobalt oxide into atomically thin nanosheets. Starting from a layered bulk structure, lithium cobalt oxide can undergo chemical exfoliation through a two-step method: treatment with a protic acid, then treatment with tetramethylammonium hydroxide which intercalates the layered structure and yields exfoliated nanosheets. Due to harmful solvents used in the exfoliation process, post-processing (salt precipitation and re-dispersion) of the nanosheet solutions are needed for their use in most applications. Precipitation of cobalt oxide nanosheets was proven from various cations (Li^+, Na^+, K^+, Cs^+, Ca^{2+}, Al^{3+}, etc.). Analysis of selected precipitated nanosheets microstructure, composition, morphology, crystallographic structure, and valance was accomplished using Scanning Electron Microscopy, Inductively Coupled Plasma-Optical Emission Spectroscopy, Transmission Electron Microscopy, and Electron Energy Loss Spectroscopy and is reported. Changes in morphology and cobalt valance (2.7 - 3.1) were observed for precipitated nanosheets and are related to the cation size of the salt used.

4:30 PM

(EMA-S9-014-2019) High-quality tungsten oxide epitaxial film and its neuromorphic application (Invited)

C. Ge*[1]

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

Owing to the outstanding electrochromic, catalytic and gas-sensing properties, tungsten oxides (WO_3) have attracted intense research interest and emerged as one of the key materials in many multifunctional devices. In this work, we fabricated WO_3 epitaxial films on different perovskite oxide substrates $LaAlO_3$, LSAT, and $SrTiO_3$ by using pulsed laser deposition. We found a new type of line defect by employing high-resolution scanning transmission electron microscopy (STEM). This strain-engineered line defect appearing in STEM images corresponds to a pseudo-perovskite cell rotated by 45 degrees. As predicted from DFT+U calculations, doping holes would form a conduction channel along the line defect under the 5% compressive strain. Moreover, we prepared an electrolyte-gated transistor using WO_3 with a unique tunnel structure, which can emulate the ionic modulation process of biological synapses. Our transistor successfully realizes the synaptic functions of both short-term and long-term plasticity. The energy consumption of several pJ per stimulation is much lower than that of an artificial synapse based on conventional CMOS circuits (~900 pJ per stimulation). These results provide a new recipe for designing synaptic electrolyte-gated transistors through the electrostatic and electrochemical effects.

5:00 PM

(EMA-S9-015-2019) Development of Solid Oxide Reversible Fuel Cells for energy storage systems applications

J. Ahn*[1]; Y. Choi[1]; S. Woo[2]; S. Kim[2]; T. Kim[2]

1. Research Institute of Industrial Science and Technology, Republic of Korea
2. Korea Institute of Energy Research, Republic of Korea

The research institute of industrial science and technology (RIST) has been developing solid oxide fuel cells (SOFCs) since 2007. Most research topics so far were focused onto use and processings of conventional ceramic materials for SOFCs as stationary or distributed generation applications. With some achievements on fuel cell researches, recently we have enlarged our research area to reversible fuel cells, which enable us to operate fuel cell and electrolysis mode with one device. At this moment, SOFC based electrolysis cells (SOECs) cannot mass-produce hydrogen due to some technological issues. Main obstacle to mass production of hydrogen is difficulty in manufacturing large power SOECs with good stability. For this reason, solid oxide revisable fuel cells (SORFCs) for ESS applications are promising. The power rating for SORFC stacks is relatively small. SORFC based ESS use hydrogen as energy carrier. Recently we have manufactured 1.2kW SORFCs and demonstrated good stability on both fuel cell and electrolysis modes. Also, the stack was FC-EC cycled more than 70 times under several operation modes. The basic stack design concepts will be discussed in the presentation. The ceramic processings for manufacturing the cells and quality-control systems will be discussed.

5:15 PM

(EMA-S9-016-2019) 3D nm-thick membrane for ultrafast selective mass transportation

S. Liang[1]; T. Wang[2]; Z. Qi[1]; M. Biener[1]; M. Worsley[1]; T. Braun[1]; Y. Wang[1]; J. Biener[1]; T. Baumann[1]; S. Kim[2]; J. Ye*[1]

1. Lawrence Livermore National Laboratory, USA
2. University of Illinois at Chicago, USA

High permeance, high selectivity, and multi-functional membranes that can mimic nature's designs have tremendous industrial and bio-medical applications. Conventional membrane structures often show pronounced trade-offs among permeance, selectivity, mechanics, and multi-functionality. Here, we report a brand-new concept of 3D assembled nanometer-thick membrane that can overcome the shortcomings of conventional 2D-like membranes. The 3D membrane composes two interwoven channels that are separated by a continuous nm-thick amorphous ceramic layer. The dramatically increased surface area and nm-thick diffusion distance allow ultrafast water and gas molecular transport. The conformal amorphous separating layer although with only nanometer thickness still shows very high rejection rates towards specific ions and molecules. The 3D connected architecture renders self-supportive mechanical properties that eliminate the need of additional supporting media. Furthermore, the template approach allows facile surface modifications that generate firstly reported 3D Janus membranes, which enables multifunctional applications such as directional mass transport, and energy storage. This study just reveals a tip of the iceberg in designing 3D complex membrane systems. Future structural and material optimizations could transform the development of artificial membranes.

S12: Thermal Transport in Functional Materials and Devices

Nano-HX: Fundamentals & Applications I

Room: Cypress C
Session Chairs: Brian Donovan, United States Naval Academy; Brian Foley, Georgia Institute of Technology

10:00 AM

(EMA-S12-001-2019) Phonon thermal transport: Reconciling predictions with reality (Invited)

L. Lindsay*[1]

1. Oak Ridge National Laboratory, Materials Science and Technology Division, USA

The management of heat and the understanding of heat transfer are ubiquitous challenges in numerous sciences and technologies, from models of Earth's thermal history to managing local hot spots in microelectronics. Computational materials physics is now playing an increasingly important role in developing fundamental insights into the lattice thermal conductivity of solids, a fundamentally important parameter that determines the utility of a material for energy-related applications including thermoelectricity, nuclear power generation, heat dissipation and manipulation, and thermal analogs to electronic components (e.g., thermal diodes and switches). Here I will discuss a predictive method for modeling lattice dynamical properties and thermal conductivity of materials: Peierls-Boltzmann transport / density functional theory / Green's function calculations. Focus will be given to application of these methods toward interactions with experimental research, as a predictive tool and toward guiding understanding of measured properties. In particular, I will highlight work related to ultrahigh thermal conductivity of BAs, and recent theoretical/experimental efforts examining vibrational properties of BN and GaN related to novel functionalities and measurements. L.L. acknowledges support from the Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division.

10:30 AM

(EMA-S12-002-2019) High thermal conductivity in the cubic BAs crystals

S. Li[1]; Q. Zheng[2]; Y. Lv[2]; X. Liu[1]; C. Li[3]; X. Wang[1]; P. Y. Huang[2]; D. A. Broido[3]; D. G. Cahill[2]; B. Lv*[1]

1. University of Texas at Dallas, Department of Physics, USA
2. University of Illinois at Urbana-Champaign, Department of Materials Science & Engineering and Materials Research Laboratory, USA
3. Boston College, Department of Physics, USA

In this presentation, we shall discuss our experimental efforts on the high thermal conductivity in the zinc blende cubic BAs crystals. This material, is predicted to have ultra-high thermal conductivity due to two unique characteristics: 1) a large frequency gap between acoustic and optic phonons, and 2) the bunching of the acoustic phonon dispersions. The high quality crystal growth of this material remains a challenge due to incongruent melting of BAs, low solubility of B in the common metal fluxes, and the careful control of the defect concentration during the crystal growth. Herein, we reported our experimental efforts to grow single domain, defect-free, mm-sized BAs crystals, evidenced by both single crystal diffraction and scanning transmission electron microscopy (STEM) studies. More importantly, ultrahigh thermal conductivities, ~1000W/m/K for BAs, have been achieved through time-domain thermoreflectance (TDTR) measurement. The measured thermal conductivity value is compared to the theoretical values based on three+four phonon (3ph+4ph) scattering process. The high thermal conductivity in the cubic BP and ^{11}BP crystal will also be discussed.

10:45 AM

(EMA-S12-003-2019) Electrical and Thermal Analysis of Vertical GaN-on-GaN PN Diodes

L. Yates*[1]; S. Usami[2]; G. Pavlidis[1]; K. Nagamatsu[2]; Y. Honda[2]; H. Amano[2]; S. Graham[1]

1. Georgia Institute of Technology, Mechanical Engineering, USA
2. Nagoya University, Japan

In this study, we fabricated two sets of vertical GaN-on-GaN PN diodes and performed extensive electrical and thermal characterization to evaluate the performance of the diodes. The diodes consisted of a 420 μm n-GaN substrate on which MOCVD was used to grow 15 μm n^- GaN, 500 nm p-GaN, and 30 nm p^+-GaN. One set of devices was subjected to passivation with a polyimide film, while the other set was left non-passivated. Electroluminescence (EL) was performed on both sets of devices and it was found that non-passivated devices demonstrated increased EL intensity at the mesa edges due to surface recombination, and subsequently showed IV characteristics that outperformed the passivated devices in terms of power handling capabilities at high forward voltages. A high-power operating set point for a diode causes an increase in temperature, which leads to reliability issues inherent in the cyclic operation of a power device. The diode thermal properties were investigated with time domain thermoreflectance (TDTR). The thermal conductivity of the GaN PN diode was measured as a function of thermal penetration depth. Thermoreflectance imaging was used to observe variations in heating profiles across devices of different diameters when operated at the same power densities, and to observe the temperature rise and fall of the diodes.

11:00 AM

(EMA-S12-004-2019) Thermal boundary conductance across heteroepitaxial ZnO/GaN interfaces: Experimental assessment of the phonon gas model

J. Gaskins*[1]; G. N. Kotsonis[6]; A. Giri[5]; E. Sachet[3]; C. T. Shelton[4]; S. Ju[7]; A. Rohskopf[8]; Y. Wang[9]; T. Bai[9]; Z. Liu[10]; Z. Cheng[2]; B. M. Foley[6]; S. Graham[2]; T. Luo[10]; A. Henry[8]; M. Gorsky[9]; J. Shiomi[7]; J. Maria[6]; P. E. Hopkins[1]

1. University of Virginia, Mechanical and Aerospace Engineering, USA
2. Georgia Institute of Technology, Mechanical Engineering, USA
3. North Carolina State University, MSE, USA
4. North Carolina State University, USA
5. University of Virginia, USA
6. Pennsylvania State University, USA
7. The University of Tokyo, Japan
8. Massachusetts Institute of Technology, USA
9. University of California, Los Angeles, USA
10. University of Notre Dame, USA

We present experimental measurements of the thermal boundary conductance (TBC) from 77 – 500 K across isolated heteroepitaxially grown ZnO films on GaN substrates. This data provides an assessment of the underlying assumptions driving phonon gas based models, such as the diffuse mismatch model (DMM), and atomistic Green's function (AGF) formalisms used to predict TBC. Our measurements, when compared to previous experimental data, suggest that TBC can be influenced by long wavelength, zone center modes in a material on one side of the interface as opposed to the "vibrational mismatch" concept assumed in the DMM; this disagreement is pronounced at high temperatures. At room temperature, we measure the ZnO/GaN TBC as 490[+150, −110] MW m^{-2} K^{-1}. The disagreement among the DMM and AGF, and the experimental data at these elevated temperatures, suggests a non-negligible contribution from other types of modes that are not accounted for in the fundamental assumptions of these harmonic based formalisms, which may rely on anharmonicity. Given the high quality of these ZnO/GaN interfaces, these results provide an invaluable, critical, and quantitative assessment of the accuracy of assumptions in the current state of the art computational approaches used to predict phonon TBC across interfaces.

11:15 AM

(EMA-S12-005-2019) Interfacial defect vibrations enhance thermal transport in amorphous multilayers with ultrahigh thermal boundary conductance

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1. University of Virginia, USA
2. University of Virginia, Mechanical and Aerospace Engineering, USA
3. Intel Corporation, USA
4. Massachusetts Institute of Technology, Mechanical Engineering, USA

The role of interfacial nonidealities and disorder on thermal transport across interfaces is traditionally assumed to add resistance to heat transfer, decreasing the thermal boundary conductance (TBC). However, recent computational works have suggested that interfacial defects can enhance this thermal boundary conductance through the emergence of unique vibrational modes intrinsic to the material interface and defect atoms, a finding that contradicts traditional theory and conventional understanding. By manipulating the local heat flux of atomic vibrations that comprise these interfacial modes, in principle, the TBC can be increased. In this work, we provide experimental evidence that interfacial defects can enhance the TBC across interfaces through the emergence of unique high frequency vibrational modes that arise from atomic mass defects at the interface with relatively small masses. We demonstrate ultrahigh TBC at amorphous SiOC:H/SiC:H interfaces, approaching 1 GW m^{-2} K^{-1} and are further increased through the introduction of nitrogen defects. The fact that disordered interfaces can exhibit such high conductances, which can be further increased with additional defects, offers a unique direction to manipulate heat transfer across materials with high densities of interfaces by controlling and enhancing interfacial thermal transport.

11:30 AM

(EMA-S12-006-2019) The Importance of Optical Like Phonons in Disordered Solids

H. Seyf*[1]; A. Henry[2]

1. Georgia Institute of Technology, George W. Woodruff School of Mechanical Engineering, USA
2. Massachusetts Institute of Technology, Department of Mechanical Engineering, USA

Current understanding of phonons is based on the phonon gas model (PGM), which is best rationalized for crystalline materials. However, most of the phonons/modes in disordered materials have a different character and thus may contribute to heat conduction in a fundamentally different way than is described by PGM. For the modes in crystals, which have sinusoidal character, one can separate the modes into two primary categories, namely acoustic and optical modes. However, for the modes in disordered materials, such designations may no longer rigorously apply. Nonetheless, the phase quotient (PQ) is a quantity that can be used to evaluate whether a mode more so shares a distinguishing property of acoustic vibrations manifested as a positive PQ, or a distinguishing property of an optical vibrations manifested as negative PQ. In thinking about this characteristic, there is essentially no intuition regarding the role of positive vs. negative PQ vibrational modes in disordered solids. Given this gap in understanding, herein we studied the respective contributions to thermal conductivity for several disordered solids as a function of PQ. The analysis sheds light on the importance of optical like/negative PQ modes in structurally/compositionally disordered solids, whereas in crystalline materials, the contributions of optical modes are usually small.

Nano-HX: Fundamentals & Applications II

Room: Cypress C
Session Chairs: Brian Foley, Georgia Institute of Technology; Brian Donovan, United States Naval Academy

2:15 PM

(EMA-S12-007-2019) Probing Hot Electron Relaxation in Transparent Conducting Oxides

B. F. Donovan*[1]; R. Warzoha[1]; A. Giri[2]; R. Basu[1]

1. United States Naval Academy, USA
2. University of Virginia, Mech Engineering, USA

Transparent conducting oxides (TCOs) are critical to a variety of applications including solar energy and optical displays. Ideal functionality of these materials involves long term reliability under fluctuating thermal loads. In order to optimize the use of TCOs, it is important to understand the mechanisms involved with interaction between mobile, excited electrons and the atomic nuclei in these complex oxides. In this study, we demonstrate a method for conducting this measurement of electron-phonon coupling using Time Domain Thermoreflectance, a technique that is well known for conducting these measurements on noble metals, but has not been used to characterize semi-transparent materials or oxides as of yet. This measurement opens a new tool for understanding conducting oxides in general and will help to advance the functionality of this critically important subset of ceramic materials.

2:30 PM

(EMA-S12-008-2019) Electrical, Thermal and Contact Properties of VO_2Thin Films during Metal-Insulator Transition

Z. Cheng*[1]; Z. Zhu[2]; B. M. Foley[1]; S. T. White[2]; R. F. Haglund[2]; S. Graham[1]

1. Georgia Institute of Technology, Department of Mechanical Engineering, USA
2. Vanderbilt University, USA

The metal-insulator transition (MIT) in $VO_2$is attracting increasing attention for its potential applications in neuromorphic computing (memristors), optical and electronic devices, and thermal switches. The electrical conductivity changes by several orders of magnitude at MIT while the variation in thermal conductivity remains controversial. Moreover, the variation of metal-VO_2contact resistance across MIT remains unknown even though it plays a significant role in threshold switching in memristor devices. In this work, we study the electrical and thermal properties of rf-sputtered VO_2thin films with transfer-length method (TLM) and time-domain thermoreflectance (TDTR). Our results show that the electrical conductivity of VO_2increases more than three orders of magnitude after switching to the metallic state, while the thermal conductivity of VO_2does not change with temperature during the MIT (about 70 °C) due to the relatively small electronic contribution to thermal conductivity. Furthermore, similar electrical switching and hysteresis are observed for electrical resistivity of $VO_2$and Al-VO_2electrical contact resistance, indicating that electrode-VO_2contact resistance switching is an important factor that contributes to the electrical switching in memristor devices.

2:45 PM

(EMA-S12-009-2019) Thermal properties of thin Nb_2O_5 determined by thermoreflectance method

L. Mitterhuber*[1]; E. Kraker[1]; K. Fladischer[1]; S. Defregger[1]

1. Materials Center Leoben Forschungs GmbH, Microelectronics, Austria

Niobium pentoxide (Nb_2O_5) films can be found in optical filter, electrochromic device, sensors, transparent conductive oxides, capacitors and microelectronic devices. Therefore, lots of investigations were done in terms of Nb_2O_5's optical and structural properties. However, rarely investigations about their thermal properties can be found in literature, even though they are an important parameter for their device's reliability. In devices, Nb_2O_5-films are used with thicknesses down to the range of nanometers. Regarding this length scale, the material's thermal conductivities could deviate from their bulk values and the thermal boundary resistance becomes influential in the heat dissipation. In this study, Nb_2O_5 films were thermally investigated with the time domain thermal reflectance (TDTR) method. The method is applicable to determine the thermal diffusivity of these films. The investigations enabled to determine the thermal properties, relying on the structure (crystalline or amorphous), thickness of films, temperature dependency as well as their boundary resistance.

3:00 PM

(EMA-S12-010-2019) Thermal Conductivity Mapping of High Entropy Carbides and Diborides

J. L. Braun*[1]; C. M. Rost[1]; J. Gild[2]; T. Harrington[2]; D. Olson[1]; J. Luo[2]; K. Vecchio[2]; P. E. Hopkins[1]

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2. University of California, San Diego, Materials Science and Engineering, USA

In the search for ultra-high temperature ceramics, high entropy ceramics, consisting of 5 or more components, have emerged as a new class of materials with unique properties. While early development of UHTCs were focused on SiC and Si3N4, currently there is a strong interest in transition metal diborides such as hafnium diboride (HfB2) and zirconium diboride (ZrB2) as well as carbides such as hafnium carbide (HfC) and tantalum carbide (TaC) and alloys thereof. While physical properties, in particular thermal

conductivity, of these constituent diborides and carbides have been well studied, high entropy variations of these ceramics allow for vastly different properties. In this work, we measure the thermal conductivity of a high entropy diboride (HfZrTaNbTi)B10 and high entropy carbide (HfNbTaTiZr)C5. Using time-domain thermoreflectance, we map the thermal conductivity of bulk samples, which have ~30 micron grains. Comparison of the thermal conductivity map to SEM and EBSD images reveals the role of grain boundary scattering of phonons and electrons on reducing the overall thermal conductivities of these samples.

3:15 PM

(EMA-S12-011-2019) Rethinking phonons in random alloys

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1. Georgia Institute of Technology, George W. Woodruff School of Mechanical Engineering, USA
2. Massachusetts Institute of Technology, Department of Mechanical Engineering, USA

Current understanding of phonons treats them as plane waves/quasi-particles of atomic vibration that propagate and scatter. The problem is that conceptually, when any level of disorder is introduced, whether compositional or structural, the character of vibrational modes in solids changes, yet nearly all theoretical treatments continue to assume phonons are still waves. For example, the phonon contributions to alloy thermal conductivity (TC) rely on this assumption and are most often computed from the virtual crystal approximation (VCA). Good agreement is obtained in some cases, but there are many instances where it fails—both quantitatively and qualitatively. Here, we show that the conventional theory and understanding of phonons requires revision, because the critical assumption that all phonons/normal modes resemble plane waves with well-defined velocities is no longer valid when disorder is introduced. Here we show, surprisingly, that the character of phonons changes dramatically within the first few percent of impurity concentration, beyond which phonons more closely resemble the modes found in amorphous materials. We then utilize a different theory that can treat modes with any character and experimentally confirm its new insights.

Tunable Thermal Properties

Room: Cypress C
Session Chairs: Brian Foley, Georgia Institute of Technology; Brian Donovan, United States Naval Academy

4:00 PM

(EMA-S12-012-2019) Tunable thermal conductivity of π-conjugated two-dimensional polymers

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2. Virginia Tech, USA

Two-dimensional (2D) polymers are organic analogues of graphene. Compared to graphene, 2D polymers offer a higher degree of tunability in regards to structure, topology, and physical properties. The thermal transport properties of 2D polymers play a crucial role in their applications, yet remain largely unexplored. Using the equilibrium molecular dynamics method, we study the in-plane thermal conductivity of dubbed porous graphene that is comprised of π-conjugated phenyl rings. In contrast to the conventional notion that π-conjugation leads to high thermal conductivity, we demonstrate, for the first time, that π-conjugated 2D polymers can have either high or low thermal conductivity depending on their porosity and structural orientation. The underlying mechanisms that govern thermal conductivity were illustrated through phonon dispersion. The ability to achieve two orders of magnitude variance in thermal conductivity by altering porosity opens up exciting opportunities to tune the thermal transport properties of 2D polymers for a diverse array of applications.

4:15 PM

(EMA-S12-013-2019) Thermal transport and variable thermal conductivity of antiferroelectric lead zirconate (PZO) through the paraelectric phase transition

J. Tomko*[1]; J. Gaskins[2]; D. Olson[2]; T. Grant[1]; J. Ihlefeld[1]; P. E. Hopkins[2]

1. University of Virginia, Materials Science and Engineering, USA
2. University of Virginia, Mechanical and Aerospace Engineering, USA

This work investigates the temperature-dependent thermal conductivity and phonon scattering mechanisms in both thin films and bulk lead zirconate (PbZrO3) through the Curie temperature. Due to the array of technological applications of antiferroelectrics, finding use as energy-storage capacitors and displacement transducers, both of which can be subjected to inherently increased operating temperatures, this research serves to provide an understanding of the physical mechanisms driving thermal transport in antiferroelectrics as well as their varying thermal properties at temperatures exceeding the Curie point. Using time-domain thermoreflectance (TDTR) and hot disc to measure the thermal conductivity of these PZO thin films and bulk systems, respectively, we find the thermal conductivity of antiferroelectric orthorhombic-phase PZO exhibits a glass-like trend with increasing thermal conductivity as a function of temperature. Further, we show a large increase in thermal conductivity following the phase transition to a cubic, paraelectric crystal structure. To investigate the potential contributions of mode softening and domain wall scattering to the observed changes in thermal conductivity, we perform time-domain Brillouin scattering measurements across the same temperature range.

S13: From Basic Science to Agile Design of Functional Materials: Aligned Computational and Experimental Approaches and Materials Informatics

Materials by Design: Computational/Experimental Emerging Strategies

Room: Magnolia B/C
Session Chair: Mina Yoon, Oak Ridge National Laboratory

10:00 AM

(EMA-S13-001-2019) Predicting the surface phase diagram of Ag(111) using ab initio grand canonical Monte Carlo (Invited)

R. B. Wexler[1]; T. Qiu[1]; A. M. Rappe*[1]

1. University of Pennsylvania, Chemistry, USA

The structure of a surface can dramatically affect its properties. For example, reconstructions can occur that change band alignments relative to vacuum and/or the catalytic activity of a surface. Currently, ab initio thermodynamics is the method of choice for determining the most stable surface of a material. However, the selection of surfaces to study is done manually and this induces bias that can prevent one from finding global minima in the surface energy. Here, we present the implementation of ab initio grand canonical Monte Carlo (GCMC) to automatically predict surface phase diagrams and apply it to the Ag(111) system, which took 40+ years to solve. Using this method, we obtain an Ag_7O_{10} oxide overlayer, which is consistent with the most stable reconstruction found in experiment and computationally. Additionally, we extracted structure-stability trends from our simulation data using machine learning and found that surface coordination and bond angles are important descriptors for stability. Finally, we analyzed the stochastic evolution of the surface and discovered a possible mechanism for the formation of the Ag_7O_{10} overlayer. Ab initio GCMC therefore offers a rich set of possibilities for studying interfacial systems such as heterogeneous catalysts.

10:30 AM

(EMA-S13-002-2019) Quasi-two-dimensional magnetism and unusual intermediate spin state in Cobaltite involving isolated CoO_4 tetrahedra (Invited)

Q. Zhang*[1]; G. Cao[1]; F. Ye[2]; H. Cao[2]; S. Chi[2]; M. Matsuda[2]; W. Shelton[1]; S. Nagler[2]; D. Tennant[2]; W. Plummer[1]; R. Shelton[1]; J. Zhang[1]

1. Louisiana State University, Physics and Astronomy, USA
2. ORNL, USA

Quasi-two-dimensional (2D) magnetism exists in bulk magnetic materials when the dominant magnetic interactions are intra-planar, which is commonly ascribed to intrinsically layered crystalline structures diminishing the inter-planar coupling through spacing effects. Here, we demonstrate that the material Ba_2CoO_4 exhibits quasi 2D magnetism by combining neutron scattering and linear spin waves theory studies, although the system lacks a 2D layered stacking structure and displays comparable nearest-neighbor Co-Co distances. Instead, the reduced quasi 2D magnetism as revealed from the anisotropic spin wave dispersions and magnetic exchange constants is interpreted in terms of a frustrated network of super-superexchange pathways where the overlap of the O 2p-orbital tails provides the long-range exchange mechanism. Intriguingly, the ordered moment, relatively large spin gap and spin-lattice coupling indicate an unusual and very rare intermediate spin state of Co^{4+} as the ground state in Ba_2CoO_4. Our study may reshape the fundamental understanding on the quasi-2D magnetism and provide a significant insight on the interplay between coordinate polyhedron, spin exchange interaction, and spin states in Cobaltites.

11:00 AM

(EMA-S13-003-2019) First principles investigation of metal-to-insulator transitions in rare earth nickelates induced by chemical doping

P. Yoo[1]; P. Liao*[1]

1. Purdue University, USA

Recent experiments demonstrated that the electrical conductivity of $SmNiO_3$ decreases by ~8 orders of magnitude when it is chemically modified by hydrogen atoms. This metal-to-insulator transitions (MIT) driven by chemical doping open up opportunities for developing solid-state field effect devices, solid electrolytes for solid oxide fuel cells, and active broad spectrum photonic devices. We applied first principles calculations to study geometric, electronic and optical properties of perovskites during chemical doping induced MIT. We showed that the DFT+U method with the PBEsol functional and $U_{eff} = 2$ eV produced results in good agreement with experiments for both insulating and metallic phases of $SmNiO_3$. We further examined changes in geometry and electronic structures for hydrogen doping in a series of rare earth nickelates. These current findings provide physical insights for future experimental investigation to develop efficient metal-insulator switching devices.

11:15 AM

(EMA-S13-004-2019) Potential Ferroelectric Binary Oxides--Hafnia and Beyond (Invited)

R. Batra*[1]; H. Tran[1]; B. S. Johnson[2]; G. Rossetti[3]; J. L. Jones[2]; R. Ramprasad[3]

1. Georgia Institute of Technology, Materials Science and Engineering, USA
2. North Carolina State University, Materials Science and Engineering, USA
3. University of Connecticut, USA

In the past couple of years, there have been extensive empirical and theoretical efforts to elucidate the surprising phenomenon of ferroelectricity recently discovered in hafnia (HfO_2) thin films (<30 nm). While the origin of this unexpected ferroelectric (FE) behavior is associated with the formation of the metastable orthorhombic ($Pca2_1$) phase owing to unusual thermodynamic or processing conditions [2,4], the most critical lesson to be learned from the example of hafnia is that even binary oxides can be FE if low-lying metastable (or stable) polar phases are present. Thus, in this contribution, we extend the findings from the case of hafnia to discover new FE binary oxides, as opposed to the traditionally explored class of perovskite-structured oxides, using computations. We employed a combination of structural search methods, first principles computations and group-theoretical considerations to find at least six simple oxides as potential ferroelectric candidates. Among them, a previously unexplored candidate, CaO_2, was successfully synthesized in the polar $Pna2_1$ phase, in accordance with our theoretical predictions. Furthermore, the high occurrence (~40 %) of low-energy polar phases among the oxides considered in this work strongly advocates the possibility of discovery or engineering ferroelectricity in many more simple oxides beyond hafnia.

11:45 AM

(EMA-S13-005-2019) Theory, design and experiments on transparent microwave absorbers for window application

R. Deng*[1]; K. Zhang[1]; T. Zhang[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Window-use Microwave Absorbers (WMA) with high optical transparency are significant in both civil and military fields. In this work, proceeding from transmission line theory, two equivalent circuit models are established and quantitatively analyzed for two kinds of WMA metamaterials. Based on the theoretical discussions, a practical design method, which can effectively guide the rapid designs of WMA with adjustable single-band, dual-band or broadband absorptions, is proposed. As example, a novel flexible broadband WMA is designed to work in 6~18 GHz. Origin of dissipation, loss features, contributions of each part and metamaterial behaviors of the absorber are analyzed thoroughly to reveal the absorption mechanisms. Evidenced by experimental measurements, the large-scale WMA can achieve 90% absorption in a wide band, which is in great agreement with simulated results. In addition, the WMA can also maintain high absorption regardless of incident angles. Even through it is curved, the flexible WMA can still operate well, which indicates a promising future for applications in nonplanar situations. Evaluated in imitating usage scenario, efficiency of dye-sensitized solar cell (DSSC) decreases only a little after having the WMA put on because of its high optical transparency. The WMA has advanced comprehensive performances. The equivalent circuit model is also proved of high reliability.

12:00 PM

(EMA-S13-006-2019) Modelling of the highly non-linear electrical behavior of ZnO varistor ceramics

B. Kaufmann*[1]

1. Montan University Leoben, Institut für Struktur- und Funktionskeramik, Austria

ZnO varistors are the leading overvoltage protection elements in today's electronic industry. Their highly non-linear current-voltage characteristics, very fast response times, good reliability and attractive cost of production are unique in this field. Yet, there are challenges and questions to be addressed. Especially, the urge to create even smaller, more versatile and reliable parts that fit industry's demands brings manufacturers to the limits of their capabilities. Nearly all modern varistors are made from sintered, doped ZnO, where the individual grains are conductive, but the grain boundaries behave like double Schottky barriers leading to highly non-linear current-voltage characteristics. In order to describe and predict the behavior of a modern low voltage varistor, models are necessary that take into account the microstructural features of the material. In this work two different models were developed, based on computer simulations and experimental data. The first one uses resistor networks built on simulated 3D liquid phase sintered microstructures. The second one is a strong simplification of the first one using parallel connected current paths. Both models use experimental data from grain-to-grain and grain-to-electrode contact measurements and were able to reproduce the current-voltage characteristics of different types of ZnO varistors.

Novel Phenomena: Interface/Multi-scale/Low-D

Room: Magnolia B/C
Session Chair: Peilin Liao, Purdue University

2:00 PM

(EMA-S13-007-2019) Understanding the Carrier Mobility in Two-Dimensional Semiconductors (Invited)

Y. Liu*[1]

1. The University of Texas at Austin, USA

Two-dimensional (2D) semiconductors have attracted great interest for next-generation electronics and optoelectronics. However, they typically have a low mobility of electrons/holes, compared with Si/III-V semiconductors. Here we will discuss our recent theoretical understandings of the mobility-limiting factors in 2D semiconductors, and strategies of increasing the mobility. These results are based on the calculation of electron-phonon coupling matrix using density functional perturbation theory and the Wannier interpolation, as well as the Boltzmann transport theory.

2:30 PM

(EMA-S13-008-2019) Transport Properties of Low-Dimensional Electronic Materials

L. Li*[1]

1. Boisie State University, USA

Transition metal dichalcogenides TMDs are of interest due to their applications as intrinsic p-n junctions and tunneling field-effect transistors. Laterally adjoining TMD materials enable the formation of atomically thin heterostructures. To design effective semiconductor devices, understanding the scattering mechanism at the heterojunction is critical. We used first-principles approaches, Boltzmann transport theory, and atomistic Green's function to screen their transport properties, depending on the heterojunctions and interfacial strains. We firstly focused on MoS_2-WSe_2 and MoS_2-WS_2 heterostructures and found that tensile forces could minimize the band gaps and switch the band alignments between direct and indirect. Using our newly developed atomistic Green's functional-based code, we examined interfacial thermal transport processes and estimated phonon transmission coefficients and thermal boundary conductance. We found that high-frequency phonons were scattered by the heterojunctions. Acoustic phonons also showed the critical angles for transmission due to relatively heavy transition metal elements. We then extended the screning studies to 600 TMD heterostructures and used a data-driven approach to determine the controlling factors for structural design.

2:45 PM

(EMA-S13-009-2019) Ab Initio Data Analytics Approaches to Catalyst Design (Invited)

S. V. Levchenko*[1]

1. Skolkovo Institute of Science and Technology, Center for Electrochemical Energy Storage, Russian Federation

We present a first-principles data analytics approach for a high-throughput study of CO_2 activation on complex oxide semiconductor surfaces. The approach combines an exceptional subgroup discovery (SGD) data-mining method with the sure independence screening plus sparsifying operator (SISSO) compressed-sensing approach. The SGD+SISSO scheme is used to find a set of complex descriptive parameters (descriptors) for a fast and reliable evaluation of CO_2 activation indicators, including adsorption energy, OCO angle, and C-O bond elongation. The subgroup definitions and the descriptors contain only features of clean surfaces, including site-specific features. This allows for the evaluation of the adsorbed CO_2 properties on all unique adsorption sites simultaneously, without the need to perform much more computationally expensive atomic relaxations of the adsorbed CO_2 molecule at each site. From the analysis of the descriptors we have found a direct dependence of CO_2 chemisorption stability on the electric field above the surface. We show that active O sites can be split in two groups: with predominantly ionic and covalent bonding to surface cations. The activation at the sites from the different groups have different mechanisms. We demonstrate that the combined SGD+SISSO approach significantly improves the accuracy of the found descriptors compared to SISSO alone, and predict a set of new promising materials for CO_2 activation.

3:15 PM

(EMA-S13-010-2019) Predicting Synthesizable Functional Edge Reconstructions in 2D Monolayers

G. Hu*[1]; X. Sang[1]; R. Unocic[1]; P. Ganesh[1]

1. Oak Ridge National Lab, USA

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have attracted tremendous interest due to their exceptional electronic and optical properties. More interestingly, it has been found that edges of 2D TMDCs are responsible for their promising catalytic activity, while the basal plane is chemically inert. In addition to the conventional armchair and zigzag edges, more complex edge reconstructions have recently been realized by various experiments. Therefore, it is highly desirable to computationally predict the family of stable edges so as to screen their functional properties. Here we report development of such a computational approach and demonstrate it on the 2D TMDC family of systems such as MoS_2 & $MoSe_2$. Starting from configuration ensemble generations, we screen for stable edges using cheaper force-fields or surrogate (Neural-Network-based) models, which are then further refined using DFT-level of theory. We predict many stable edges that are superior for hydrogen evolution reaction (HER). Our study thus provides a comprehensive yet tractable computational approach for predicting synthesizable functional edges in 2D monolayers.

3:30 PM

(EMA-S13-011-2019) Symmetry-Based Identification of 2D Materials for Piezoelectric Applications

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For two-dimensional (2D) materials, symmetry has been a topic that has limited potential applications. Often the symmetry of 2D materials is classified using wallpaper groups, but these neglect the finite extent of the majority of real monolayer materials. As a result, they are insufficient for classification and property selection. In this work, we utilize the space group for materials of reduced dimensionality and begin by summarizing how 2D space groups relate to common 3D space groups. We show that 3D space group identification tools will not cause a monolayer to be identified as over- or under-symmetric, and discuss the impact of a 2D material's symmetry on piezoelectricity. We then identify which 2D prototype structures in the MaterialsWeb.org database can have piezoelectric behavior and calculate the tensor for materials with these prototype structures using density functional theory. Finally, we discuss the implications of 2D symmetry on other materials properties.

Poster Session

Room: Orange C/D

5:30 PM

(EMA-P001-2019) Mechanisms of Enhanced Thermal Stability of Polarization in Lead-Free $(Bi_{1/2}Na_{1/2})_{0.94}Ba_{0.06}TiO_3$/ZnO Ceramic Composites

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2. Nanjing University, China
3. Ames Laboratory, USA

$(Bi_{1/2}Na_{1/2})_{0.94}Ba_{0.06}TiO_3$ (BNBT6) undergoes a depolarization at the T_d about 100 ºC, above which the micron-sized ferroelectric domains and the associated piezoelectric behavior vanish. Recently, T_d was found to be shifted up to 250 °C in BNBT6 when forming composite with ZnO particles (BNBT6/0.3ZnO). But the mechanism underlying such a significantly enhanced thermal stability of polarization is still unclear. In the present study, a variety of advanced transmission electron microscopy techniques, including in-situ heating, annular bright-field, geometric phase analysis, energy-dispersive spectrum and electron energy-loss spectroscopy, are employed to clarify the ZnO's influences upon the thermal depolarization process in BNBT6. It was revealed that some ZnO particles become Zn_2TiO_4 after sintering via reaction with BNBT6. The incorporation of Zn into the BNBT6 lattice close to the interface facilitates the formation of micron-sized ferroelectric domains in BNBT6 at room temperature. The remaining ZnO particles provide the "pinning force", which originates from its spontaneous polarization, to the micron-sized domains and prevents them from disruption into nanometer-sized domains as temperature increases. As a consequence, T_d of BNBT6/0.3ZnO is not simply delayed, but becomes diffused and spreads over a wide temperature window of from T_d to T_m.

(EMA-P002-2019) Sequence of polarization switching events in polycrystalline perovskite ferroelectrics

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The fundamental properties of ferroelectrics are intimately related to the reversibility of the polarization vector with external fields. However, theoretical and experimental reports are inconsistent regarding the sequence of individual events that take place during the polarization reversal process. To address this issue, we simultaneously measured macroscopic polarization and strain dynamics of a model polycrystalline ferroelectric $Pb(Zr,Ti)O_3$ over a broad time range using high voltage pulses. Supplementary in situ time resolved diffraction measurements enabled a deeper insight into the mechanical stresses, which arise due to the coupling of the grains in the polycrystalline matrix. Landau free energy calculations were utilized to identify the driving forces for individual switching events. Based on this synergetic approach, the sequence of individual switching events could be revealed: initial non-180° domain wall movement triggers the main switching phase due to an interplay between local electric and mechanical fields. In the main switching phase >60% of the polarization reversal occurs by 180° or synchronized strain-free non-180° switching events. This is followed by creep-like non-180° domain wall movement, whereby the polarization vector is parallel to the applied electric field.

(EMA-P003-2019) Effect of off-stoichiometry, structural heterogeneity and piezoelectricity on lead-free $Na_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$ system

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1. Indian Institute of Science, Materials Engineering, India

$Na_{0.5}Bi_{0.5}TiO_3$ (NBT) -based piezoceramics are now being considered as suitable alternative to lead based ones. As compared to the other lead-free piezoelectrics NBT and its family are more disordered on the nanometer scale. This influences the crystal structure and properties. We have analysed the role of structural heterogeneity on the piezoelectric response of the MPB (x=0.06) and a pre-MPB composition (x=0.03) of (1-x)$Na_{0.5}Bi_{0.5}TiO_3$-(x)$BaTiO_3$. We tune the off stoichiometry on the A-site to vary the structural heterogeneity, which is characterized in terms of a "cubic-like phase". We correlate the trend in the piezoelectric property with global structure of the system in its poled state. We found that an optimal off-stoichiometry leads to the maximum piezoelectric response for both the compositions (x=0.03 and 0.06). From structural analysis it was concluded that this occurs because the system retains an optimum amount of structural heterogeneity after poling. By the help of dielectric dispersion, we are able to establish a relationship between the piezoelectric response and the amount of the change in the polar-structural disorder induced by the poling field. Our study confirms that structural heterogeneity plays an important role in enhancing piezoelectric response in lead free ferroelectric ceramics.

(EMA-P004-2019) Investigation into the role of grain-to-grain interaction in determining the coupling between lattice-strain and non-180° domain switching in rhombohedral perovskite piezoceramics

N. Kumar*[1]; R. Ranjan[1]

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While it is recognized that the important contributing factors towards large electromechanical response of morphotropic phase boundary piezoceramics are ferroelectric-ferroelastic domain switching, lattice strain, and phase transformation, the discussion regarding the nature of coupling/interaction between these contributing mechanisms is still evolving. Here, we use a special experimental/analysis approach involving x-ray diffraction in-situ with electric field on randomly oriented piezoelectric grains in their unclamped and clamped states, to examine the coupling in the rhombohedral phase of two different alloy systems $Pb(Zr_xTi_{1-x})O_3$ and (1-x)$PbTiO_3$-(x)$BiScO_3$. We found that for a similar domain switching fraction the (200) lattice strain in the clamped grains is nearly double the corresponding value in the free grains suggesting that the coupling between domain switching and lattice strain is intrinsic to the individual ferroelectric grains of the piezoceramic, and is amplified by the grain-to-grain interaction in dense piezoceramics

(EMA-P005-2019) Probing the poling-induced change in the degree of structural disorder in of $BaTiO_3$-based piezoceramics with Eu^{+3} photoluminescence

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Morphotropic phase boundary is the most important consideration for the rationale design of piezoelectric alloys with large piezoelectricity. An important question which has not received sufficient attention is: how the poling field, a mandatory processing parameter in piezoceramics, affects the degree of the overall structural heterogeneity of the MPB compositions. Here, we address this issue using rare-earth photoluminescence (PL) as a probe by exploiting the sensitivity of the hypersensitive Stark bands towards structural disorder. As a model study, we use Eu^{+3} PL to investigate the lead-free piezoelectric system $Ba(Ti_{1-x}Sn_x)O_3$ in the vicinity of its composition induced tetragonal (P4mm)-orthorhombic (Amm2) phase boundary. We succeeded in identifying the characteristic Stark lines corresponding to the tetragonal (P4mm) and orthorhombic (Amm2) ferroelectric phases, and found that poling leads to a considerable increase in the intensity of the $^5D_0$ à $^7F_2$ hypersensitive Eu^{+3} Stark band, shifting the color of emission towards dark red. Our study suggests that the poling-field induced extensive movement of interfaces (domain walls and interphase boundaries) on the local length scale increases the degree of structural disorder in the system, which can contribute to the piezoelectricity enhancement of the piezoceramic body.

(EMA-P006-2019) Electrocaloric effects in $BaTiO_3$- based single crystals and ceramics

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The electrocaloric (EC) effect is considered as one option to replace liquid coolants by the use of a solid state cooling media. Ferroelectric systems offer fairly large heats at ferroic transitions that can potentially yield a decent cooling technology. In this contribution we display $BaTiO_3$-based relaxor compositions and their EC properties. Single crystals exhibit strongly anisotropic effects and a negative EC effect in certain crystal orientations. In pure ferroelectrics large caloric effects are only observed near a phase transition. Doping is a good tool to extend the range of operating temperature away from this transition temperature. Relaxors, e.g $Ba(Ti_{1-x}Sn_x)O_3$ and $Ba(Ti_{1-x}Zr_x)O_3$, offer a fairly large electrocaloric effect across a much extended temperature range. We compare direct adiabatic and isothermal measurements with the indirect method.

(EMA-P007-2019) Advances in Neutron 3-D Reciprocal Space Mapping for in-situ and Texture studies

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Time-resolved diffraction has become a vital tool for probing dynamic responses to an applied stimulus. Such experiments typicaly rely on hardware histogramming of diffraction data measured using stroboscopic methods to achieve the needed timining. In contrast; coupling measured event-based data, which time-stamps diffraction data with 100 ns accuracy, with metadata about the applied stimuli enables researchers to define how data are processed using a software solution. Data measured using the TOPAZ time-of-flight Laue neutron diffractometer probes large volumes of reciprocal space with <1°angular resolution. This high-resolution is ideally suited to identify sublet lattice rotations during applications of electric fields. Furthermore, applying high-resolution reciprocal space to probe the intensity distribution of polycrystalline materials provides a unique opportunity to study changes in the distribution crystal orientations in response to an external stimulus (e.g., electric field, temperature, stress …). Full volumes of diffraction space, that probes the intensity distribution sphere, can be rapidly sampled without overlap or averaging in as few as one to four sample settings, dependent on symmetry. We demonstrate this approach by observing ferroelectric/ferroelastic domain wall motion during electric field cycling of $BaTiO_3$.

(EMA-P008-2019) Maleic acid-doped triglycine sulphate single crystal for high performance of opto-electronics devices

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Single crystals of pure triglycine sulfate (TGS) and maleic acid doped triglycine sulfate (MA-TGS) were grown by adopting a slow evaporation technique. Incorporation of maleic acid in the TGS crystals was confirmed qualitatively by powder X-ray diffraction. UV-Vis-NIR spectroscopy and dielectric study revealed increase in optical band gap from 6.20 eV to 6.52 eV and Curie temperature from 49 to 51 °C due to MA doping. The value of piezoelectric charge coefficient, d_{22} was observed to enhance from 56 pm/V for pure TGS single crystal to 72 pm/V for MA-TGS single crystal. An increase in the value of remanent polarization was observed for doped TGS crystal. Also, the value of true-remanent polarization was determined for doped TGS crystal using Remanent Hysteresis Task. Mechanical stability of grown crystals was examined using a nanoindentation technique which revealed that MA-TGS crystal have a greater capability to withstand deformation caused by applying various loads. Comparative optical, mechanical, dielectric, piezoelectric, ferroelectric and pyroelectric studies provide useful scientific information of an important class of TGS crystals and suggest MA-TGS crystal as a better alternative than pure TGS crystal for various opto-electronics and ferroelectric devices applications.

(EMA-P009-2019) Ferroelectric HfO_2 thin films with abundant dopants

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Recently, thin films of HfO_2-based solid solution systems receive great attention as novel ferroelectric materials with non-perovskite-type crystal structure. The ferroelectric HfO_2 phase with orthorhombic crystal symmetry is formed by ion doping using rare metal species such as Y and La, although these ion species are generally valuable and environmentally disadvantage. Here, we tried to produce the ferroelectricity of HfO_2 by utilizing abundant dopants for reducing process costs and environmental burdens. Doped HfO_2 thin films were fabricated on (111)Pt/TiO_2/(100) Si substrates by simple technique, chemical solution deposition (CSD). The film samples with thicknesses of ~ 40 nm were crystallized by heat treatment up to 800 °C (RTA) in N_2. In this work, we confirmed ferroelectricity in HfO_2 with various abundant dopants. For example, Ca -doped HfO_2 films included orthorhombic HfO_2 phase (ferroelectric) as well as monoclinic and cubic HfO_2 phases (non-ferroelectric phases), whereas pure HfO_2 films consisted of non-ferroelectric HfO_2 phase. Well-saturated P-E curve concerning ferroelectricity was obtained with maximum remnant polarization of approximately 7 $\mu C/cm^2$ for the film with chemical composition of $Ca_{0.08}Hf_{0.92}O_2$. These results suggest that abundant dopants can produce the ferroelectricity of HfO_2. Experimental results of other dopant species well be presented on the conference.

(EMA-P010-2019) Preferential crystal growth of $BaTiO_3$ thick film using nanosheet templates interface layer

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$BaTiO_3$ (BT) is one of promising candidate for lead free dielectric, ferroelectric and piezoelectric devices because of its lower toxicity and environmental loads. Dielectric and ferroelectric properties of BT can be enhanced by aligning their polar axis by controlling the crystal orientation. In this study, in order to fabricate oriented BT films on versatile substrate, we propose the $Ca_2Nb_3O_{10}$ nanosheet (ns-CN) templates which possess pseudo-perovskite-type crystal structure and favorable lattice matching with BT crystal. Ns-CN templates prepared from layered compounds of $KCa_2Nb_3O_{10}$ by ion-exchanging followed by chemical exfoliation were supported on platinized Si wafer by dip coating process. Then, the oriented BT films were fabricated on ns-CN/Pt/Si substrates using chemical solution deposition technique. XRD analyses indicated that the degree of BT $(100)_c$ crystal orientation was enhanced from 23% for the film without ns-CN layer to 61% for the film with ns-CN layer. Orientation-controlled BT films were grown up to 1 μm on ns-CN/Pt/Si substrate successfully. Lower dielectric constant (ε_r = ~267) was observed for the film on ns-CN/Pt/Si, compared with that of fabricated on Pt/Si (ε_r = ~529). We assumed from the measurement result of lattice parameters that the cubic BT film with relatively lower dielectric constant (not c-axis-oriented tetragonal BT film) was grown on ns-CN/Pt/Si.

(EMA-P011-2019) Structure and electrical properties of $SrTiO_3/BiFeO_3$ thin films for energy storage applications

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Because of high power density, ultrafast charging/discharging speed, long lifetime and wide operating temperature, dielectric capacitors have attracted much attention recently for energy storage applications. However, its energy density is low. To improve energy storage density, sandwich-structured $SrTiO_3/BiFeO_3/SrTiO_3$ (STO/BFO/STO) thin films were designed since paraelectric STO shows high breakdown strength and ferroelectric BFO displays high polarization. The thin films were prepared using a sol-gel method, structure and electrical properties were analyzed. It shows that the heterostructure thin films demonstrate good frequency stability of dielectric properties at 300~1MHz and excellent temperature stability of dielectric constant (25°C-200°C, $\Delta C/C_{25^{o}C} \leq \pm 6.0\%$). Compared with pure STO thin films, the electrical breakdown strength and energy storage performance of STO/BFO/STO thin films enhance obviously. Meanwhile, STO/BFO bilayered films were prepared and studied for comparison with STO/BFO/STO thin films. It was observed that the energy storage density of the latter is much higher than that of the former, which is attributed to that the latter has more STO/BFO interface and hinders the electrical tree in the dielectrics. The results confirm that sandwich-structure and interface modulation are effective and feasible ways to improve the energy storage properties for applications.

(EMA-P012-2019) Investigation of Domain Reorientation and Phase Transitions due to Inhomogeneous Stresses in Potassium Sodium Niobate-based Piezoelectrics

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Lead-free, potassium sodium niobate (KNN)-based materials have been widely investigated for the development of eco-friendly piezoelectric devices, such as high-strain multilayer ceramic actuators (MLCAs). It is known that when a voltage is applied to a MLCA, a large amount of inhomogeneous stresses develop at the interdigitated electrode edges and dead zones. A monolithic piezoceramic with a 50% top/bottom electrode ratio is used as a partial electrode model to help understand the stress and electric field states in a MLCA due to the existence of a dead zone. Finite element modeling (FEM) predicts the stress concentration near the partial electrode edge is almost 1000 times higher than between the electrodes in the KNN-based partial electrode model. In situ high-energy X-ray diffraction (XRD) with an ultra-small beam size was performed at the Advanced Photon Source (APS) to sequentially scan a region near the electrode edge in the KNN-based partial electrode model under applied electric fields. The room temperature results show that an orthorhombic phase (Amm2), which is normally observed below 15ºC, is non-uniformly induced from the tetragonal phase (P4mm) near the electrode edge. However, this field-induced phase transition does not occur in other regions of the sample; only domain reorientation is observed between the electrodes.

(EMA-P013-2019) Heat Transfer and Package Design for Integrated Thermoelectric and Piezoelectric Energy Conversion

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A standalone, self-powered traffic sensing module has been designed and demonstrated. The module operates while in situ--embedded in road asphalt. A piezoelectric (PZT) device is used to simultaneously measure traffic weights and generate power. Multiple thermoelectric generators (TEGs) are used to supplement the power produced by the PZT sensor. This paper reports computational and experimental design of the module with a focus on heat transfer and TEG optimization. The module was designed to maintain thermal contact between the TEGs and high and low thermal reservoirs at the surface of the road and below, respectively. At the same time, the module permits the vertical strain cycles applied by traffic. A heatsink structure was designed and validated which accommodates these design constraints.

(EMA-P014-2019) A Study on the effect of a-FeOOH@SiO_2 structure on the chromaticity

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A hollow metal micro/nanomaterial with a porous structure is one of the most attractive structures for catalysts. Silica is used in shell materials to minimize oxidation and aggregation of materials. Porous silicas have attracted considerable attention because of their distinguished performance in adsorption technology, catalysis and, medical applications. We tried to investigate the effect of the density of the silica coating layer on the color of the pigment. In this study, we SiO_2-coated on α-FeOOH nanorod and we used an etchant to arbitrarily change the structure of a silica layer. We used a basic catalyst to control the structure (pore, density) of the silica layer. The change of shape was observed by TEM analysis and we selected the appropriate reaction time and compared the chromaticity according to the silica layer structure. In particular, it was confirmed that yolk-shell structure of α-FeOOH pigments had a median chromaticity value.

(EMA-P015-2019) A Study on the Improvement of Dispersion of TiO_2 by Surface Modification and Silica Coating

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Rutile-type TiO_2 is a white pigment with a high refractive index and has attracted attention in the fields of architecture, paint, cosmetics. Recently, the production method has been changed by the chlorine method rather than the sulfuric acid method in order to improve the characteristics of the pigment such as coloration. In this study, we tried to improve the physical properties by increasing the dispersibility of TiO_2 through surface treatment and silica coating. Prior to silica coating, TiO_2 particles were surface treated by adjusting the ammonia concentration. Then, a core-shell type silica coating layer was formed using tetraethly orthosilicate (TEOS) for the surface-treated TiO_2 for various each concentration. The silica coated TiO_2 was compared by zeta potential analysis. In addition, we tried to control the dispersibility without using surface treatment by using silica coating material as sodium silicate. Details of the morphology and dispersibility of suface-treatment and silica-coated TiO_2 samples were characterized by TEM (transmission electron microscopy) and zeta potential.

(EMA-P016-2019) Functionalization of grain boundaries using cold sintering

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Cold sintering provides a low temperature method of densifying many ceramic oxides. By utilizing this method, grain boundaries can be functionalized by the inclusion of other materials such as polymers, carbon nanofibers, metal organic frameworks, buckyballs, or 2D materials. This creates new methods to tailor the electronic properties of densified ceramics, starting at the smallest level. By including specific materials, the electronic or ionic conductivities, boundary layers and dielectric properties can be modified. These composites have shown remarkable properties in many electronic devices including batteries, gas sensors and varistors.

(EMA-P017-2019) Property and Structure Analysis of Novel 2D Group-III Oxides Predicted by Evolutionary Algorithm

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The discovery of new, 2D materials has been a rising interest in the scientific community as they offer unique and tunable properties to adapt to various applications. We apply a genetic algorithm coupled with density functional theory (DFT) to search for low-energy 2D structures in the family of group-III A2O3 oxides and explore their electronic properties. For B2O3 we discover a completely planar 2D structure that exhibits a low formation energy of 20 meV/atom. For the for the Al and Ga 2D oxides, we find the same 2D crystal structure ground, with formation energies of 103 and 109 meV/atom, respectively. 2D In2O3 forms a hexagonal lattice with a formation energy of about 212 meV/atom. We characterize the electronic structure using semi-local (PBE) and more accurate hybrid (HSE06) functionals. The HSE06 calculations show that B2O3 and Al2O3 are insulators with bandgaps of 7.2 and 6.4 eV, whereas Ga2O3 and In2O3 are semiconductors with bandgaps of 3.9 and 3.5 eV. The bandgap of In2O3 is in the visible range, which opens the opportunity for its use in optoelectronic devices. We show that Ga2O3 and In2O3 are stable in aqueous environments, indicating their potential for applications as gate dielectrics and protective coatings.

(EMA-P018-2019) The synthetized diamonds micro structures consolidation and fractal relation to thermal-electro conductivity

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Most diamonds are good thermal conductors, but electrical insulators, investigation of thermal and electro conductivity can be used for distinguishing it from other materials and identifying impurities in a genuine diamond. Synthetized diamonds show different properties. The knowledge of basic properties of the materials allows better using of their applications in different scientific and other areas. By experimental procedures, it is observed interesting phenomena, that if electrical conductivity is increasing, the thermal conductivity has reciprocal behavioral. Considering that grain size is very small in deposited films of synthetized diamonds, there are a lot of grain boundaries on entire volume of film. This leads to very complex electronic transport properties which are different to commonly used lattice-based band approximations. Electronic properties can be improved by involving impurities. Analysis of this phenomena is subject of this paper.

(EMA-P019-2019) Spontaneous relaxor to ferroelectric transition in $(Bi_{1/2}Na_{1/2})TiO_3$-$BaTiO_3$ piezoceramics and role of point defects

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Using temperature-dependent X-ray diffraction, Raman spectroscopy and dielectric measurement, the $(0.88Bi_{1/2}Na_{1/2})TiO_3$-$0.12BaTiO_3$ (BNT-12BT) solid solution is shown to exhibit a spontaneous ferroelectric to relaxor (FE-R) transition at 200 °C during heating, a behavior similar to BKT ($(Bi_{1/2}K_{1/2})TiO_3$) or PST ($Pb(Sc_{1/2}Ta_{1/2})O_3$). The microscopic mechanisms responsible for stabilization of ferroelectric phase on adding BT to relaxor BNT have been discussed. Further, point defects were intentionally introduced using nonstoichiometry. It is found that on addition of excess bismuth in BNT-12BT, the concentration of oxygen vacancies reduces, which is accompanied by a reduction in FE-R transition temperature (149.1 °C). On the other hand, a bismuth deficiency resulted in a higher oxygen vacancy concentration and FE-R temperature (225.7 °C). Finally, electric field-temperature (E-T) phase diagrams have been constructed, which summarise the evolution of polar nanoregions (PNRs) with temperature and electric field, and demonstrate the role of oxygen vacancies.

(EMA-P020-2019) Optical and electrical properties of MPS/PANI:Er

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Macroporous silicon (MPS) doped with different fractions of PANI and Erbium (Er) was manufactured for applications in photonic devices. The MPS structures were fabricated via anodic corrosion on substrates of crystalline P-type silicon submerged an electrolytic solution composed of HF diluted in DMF (1:9) in volume. Then, the deposition process of the PANI film doped with different Er fractions was carried out. The measurements of current and electrochemical impedance were made at different points, heterostructural and longitudinal, of the sample confirming that the polymer layer is not homogeneous. The optical measurements confirmed the presence of the Er in the layers of MPS. With this, results showed that the sample presents optical, electrical and structural properties for application in photonic devices. Acknowledgements: The authors thank to Capes, Cnpq and Fapemig for financial support.

(EMA-P021-2019) DC and AC lifetimes of multilayer ceramic capacitors under highly accelerated aging conditions

H. J. Brown-Shaklee*[2]; J. A. Bock[2]; L. Garten[3]; R. H. Wilke[1]; C. Fitzgerald[2]

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2. Sandia National Laboratories, Electronic, Optical, and Nano Materials, USA
3. U.S. Naval Research Laboratory, USA

Wide band gap semiconductor switches are enabling solid state transformer technologies for grid scale power regulation. These high-power switching devices rely on circuit designs that create emerging challenges in thermal management and passive component lifetimes. Low inductance capacitors required for this application may be required to operate at temperatures above 250°C which presents concerns about accelerated aging. We compared DC reliability to square bi-polar switched aging behavior. We demonstrate that X7R capacitor time to failure at ~10x rated voltage (70kV/cm) and 250°C is improved under bipolar switching. Capacitors exhibited longer life as the frequency increased from between 0.1Hz and 10Hz suggesting that oxygen vacancy pile up at the cathode is frustrated by the bipolar switching. Thus, time to failure is likely related to the oxygen diffusion distance to a trapping site, oxygen diffusion coefficient in the dielectric and time spent at a given polarity. This work is supported by the Department of Energy Office of Electricity Delivery and Energy Reliability (OE). 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.

(EMA-P022-2019) Leakage Current Measurements of X7R MLCC Capacitors Under Gamma Radiation

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A key design challenge for radiation environments is increased leakage currents under penetrating ionizing radiation such as hard x-rays or gamma rays. The gamma-irradiation facility at Sandia Labs was used for irradiation of samples using gamma rays from Co^{60} with does rates up to ~400 rad/s. DC leakage measurements show an increase in conductivity under radiation as expected. Low-field ohmic conduction is supersceeded with space-charge limited currents near the rated voltage and above. At much higher electric fields a shottkey-barrier like field dependencie is found. Under 300rad/s conditions the barrier height associated with the Schottky barrier was measured via temperature-dependent leakage currents to be only 0.37eV, lower than the 0.6eV measured under ambient conditions. Other work associated with modeling of leakage currents using impedance spectroscopy as a function of radiation dose rate will also be presented. This work was supported by the Laboratory Directed Research and Development (LDRD) Program at Sandia National Laboratories. Sandia National Laboratories is a multimission 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-NA-0003525.

(EMA-P023-2019) Large Magnetoelectric Coupling in (Bfco-Pzt) Multiferroic Composites

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Magneto-electric materials with exchange interaction due to reorganization of crystallographic domain and structural phase transition are interesting due to application in spin based electronics. Bismuth Iron Oxide ($BiFeO_3$) exhibits ferroelectricity (Tc~1103 K) and anti-ferromagnetism (TN~643 K) at room temperature which makes it the potential candidate in the field of information technology and optoelectronic devices. Recently, an enormous deal of experiment has revealed BFO and the multiferroic properties in BFO. To get such an enhancement of the multiferroic properties, driven by compositional tuning, a mixture of BFO doped with Co and PZT was studied in equivalent molar concentration to investigate their multifunctional properties in details. Magnetoelectric and magnetic measurements were performed and associated to structural characterizations using X-ray diffraction, Raman diffusion and scanning electron microscopy. A large improvement of the magnetoelectric coupling was observed in composite samples compared to BFCO alone. The study of this magnetoelectric coupling showed that the coefficient decreases from composite to solid solution. In accordance with this result, the magnetic measurements of the samples showed a similar behaviour. The evolution of saturation magnetization in these mixtures decreased from BFCO-PZT composite to solid solution.

(EMA-P025-2019) Multiferroic Bi_2WO_6-based Two-Phase Nanocomposites

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Multiferroics have gained significant attention in the past few decades. However, due to the scarcity of single-phase multiferroics at room temperature in both natural forms and synthesized materials, an effective approach has been developed via two-phase nanocomposites in thin film form. In this study, bismuth tungstate (Bi_2WO_6) (BWO) has been selected as the base material for the design of the two-phase nanocomposites, because of its unique layered structure and ferroelectric property. To introduce ferromagnetic component into BWO, two methods have been explored. The first method incorporates Mn cations into the BWO matrix (BWMO) by pulsed laser deposition (PLD) method. The second method couples $CoFe_2O_4$ (CFO) as secondary phase with BWO to form a vertically aligned nanocomposite (VAN) system. Both systems exhibit robust ferromagnetic and ferroelectric response at room temperature and demonstrate their promise for room temperature multiferroics for future spintronics and memory applications.

(EMA-P026-2019) Thin film modeling of colossal permittivity materials

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A colossal permittivity ($\varepsilon_r > 10000$) and low dielectric loss ($\tan\delta < 0.05$) with small frequency dependence was reported using In/Nb co-doping technique in rutile-TiO_2. [1] This mechanism is still investigated using bulk ceramics and single crystal, however definite model is still not coming yet. Surface Barrier Layer Capacitor (SBLC) effect is one of considerable origin of low leakage current in this materials. In this study, SBLC structure is modeled by epitaxial thin films. TiO_2 /5%(In+Nb):TiO_2 /TiO_2 thin films as SBLC model were prepared on bottom electrode coated (100)TiO_2 single crystal substrate by pulsed laser deposition. Crystal structure, surface morphology and dielectric property was investigated by RHEED, X-ray diffraction, atomic force microscopy and LCR meter. Relative permittivity and tanδ of Pure TiO_2 and 5%(In+Nb):TiO_2 thin films were < 200 and < 0.1, and > 1000 and > 1, respectively. In the case of 1/8/1 layered film in thickness ratio, relative permittivity and tanδ were > 700 and < 0.3, respectively. Dielectric properties of co-doped thin film were almost similar as that of bulk material. This result indicates that SBLC model is the origin of low leakage current. We will discuss about SBLC effect using different thickness ratio's samples.

(EMA-P027-2019) ZnO Varistors: A Thin Film Study

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Varistor ceramics are technologically important due to nonlinear electrical characteristics enabling them to be used for switches or surge protection. The prototypical varistor is the ZnO-Bi2O3 system, which forms an electrostatic barrier at grain boundaries due to Bi2O3 segregation. While this system is used extensively, there is not yet a complete understanding of the mechanisms by which dopant locations and defect chemistries determine the barrier height as bulk studies are difficult due to the detection limits of conventional techniques. To better understand this system, we use thin film prototypes to simulate grain boundaries and better understand dopant diffusion characteristics and defect chemistries. We then correlate these to changes in electrical behavior to better understand the mechanisms controlling the barrier. For this study, we have investigated as deposited and -annealed thin film ZnO-Bi2O3 stacks, simulating the diffusion, defect chemistries, and electrical properties of bulk ceramic varistors. We have also used conventional ZnO dopants of Co and Mn to modulate the electrostatic barrier height within ZnO heterostructures. 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.

(EMA-P028-2019) Visualization of Domain Structure and Switching Property of Defect Engineered Nickel Ferrite for the Next Generation Non-volatile Memory Devices

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Multiferroic materials where two or more ferroic order parameters are coupled inside the material system, has attracted much attention due to its potential applications such as next generation nonvolatile memory devices, sensor and actuator with additional degree of freedom. However, there is fundamental problem in the ferroelectric characterization of multiferroic material because of its high leakage current. Herein, using piezoresponse force microscopy which can minimize the effect of leakage current, we analyzed the ferroelectric properties and domain structures of defect engineered nickel ferrite to understand the multiferroic properties and related domain structure as well as its switching behavior at the nanoscale. First, in order to understand the switching characteristics of oxygen deficient nickel ferrite, we measured and analyzed the hysteresis loops using switching spectroscopy PFM (SS-PFM). Second, we investigated the domain structures using angle-resolved PFM (AR-PRM) to derive the sample's complex polarization state. We envision that our results will help us to understand the origin of multiferroicity in terms of the domain structure and contribute to the development of future nonvolatile memory devices.

(EMA-P029-2019) Nanoscale Computational Studies of Ferroelectric Mesa Structures

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Here we present the results of a synergistic investigation involving piezo force microscopy (PFM) measurements and nanoscale computational modeling, to study electroactive properties of sub-micron sized ferroelectric mesa structures. Our computational approach involves finite element method based simulations utilizing phenomenological Landau-Ginzburg-Devonshire theory, implemented in the open-source software package Ferret. We employ this approach to study (a) the local piezoelectric response in all 3 dimensions through the thickness of the mesas, and (b) dynamic switching of the ferroelectric polarization throughout the mesa structures. Our computational method predicts not just an enhancement of the piezoelectric d_{33} coefficient at the strain-relieved edges of PMN-PT mesa structures, but also a corresponding radial piezoactuation from their centerline, both in excellent agreement with PFM experiments. For PZT mesa structures, our modeling approach reveals specific pathways for the domain wall motion within the mesa shape under applied electric field. Combined with the results of the PFM experiments, a better understanding of the ferroelectric switching dynamics in such structures is attained.

(EMA-P030-2019) Structure-property relationships in lacunar spinels from band theory

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Transition metal oxides (TMOs) exhibiting metal-insulator transitions are ideal candidates to achieve highly efficient computing. Among these TMOs we are particularly interested in the lacunar spinel family AM_4X_8, where A site can be Al, Ga or Ge, M site could be transition metals, e.g. V, Nb, Ta, Mo and the X site is either S or Se. Indeed, some members of this family exhibit a dramatic change in electric resistivity of three to four orders of magnitude under electric pulse at low temperature, which could lead to a new class of non-volatile resistive random access memory. We systemetically studied the structure-property relationship within the lacunar spinel family using density functional theory simulations. We find that semi-local GGA functionals outperform LDA functionals in predicting reasonable lattice constants and electronic structures. In addtion, the metallic and insulating phases of these materials can be tuned through changes to lattice structure, electronic correlation, and relativist spin-orbit interactions. The d-orbitals of the transition metals form molecular orbital-like bands that have narrow bandwidth; for this reason, orbital ordering is strongly correlated with the local transition-metal cluster distortion. Our findings will assist the design of new materials exhibiting metal-insulator transitions for highly tunable electronic materials platforms.

(EMA-P031-2019) Beamline 11-BM at the Advanced Photon Source: Synchrotron Powder Diffraction Simplified

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Synchrotrons have revolutionized powder diffraction. They enable the rapid collection of high quality powder diffraction patterns with tremendous resolution and superb signal to noise. In addition, the high penetration and exceptional data sensitivity possible at high-energy light sources, like the Advanced Photon Source (APS), allow exploration of trace containment levels, insitu sample environments and crystallographic site occupancies which previously demanded neutron sources. Despite all these advantages, relatively few scientists today consider using a synchrotron for their powder diffraction studies. To address this, the high resolution synchrotron powder diffractometer beamline 11-BM at the APS offers rapid and easy mail-in access for routine structural analyses with truly world-class quality data. This instrument offers world-class resolution and sensitivity and is a free service for non-proprietary users. The instrument can collect a superb pattern suitable for Rietveld analysis in less than an hour, is equipped with a robotic arm for automated sample changes, and features variable temperature sample environments. Users of the mail-in program typically receive their high-resolution data within two weeks of sample receipt. The diffractometer is also available for on-site experiments requiring more specialized measurements.

(EMA-P032-2019) Variations in the electronic structure during chemical exfoliation of $LiCoO_2$ into CoO_2

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$LiCoO_2$ (LCO) is a widely utilized cathode material for commercial Li-ion batteries, and its bulk properties have been extensively studied. LCO is a layered oxide material and can be exfoliated into two-dimensional nano-sheets through a two-step chemical exfoliation: (i) protonation and (ii) intercalation with bulky molecules. Presented in this poster are the changes in the electronic structure determined by X-ray Photoelectron Spectroscopy (XPS). Core peaks (Co 2p, Co 3p, Co 3s, O 1s, C 1s) and valence spectra have been analyzed throughout the chemical exfoliation treatment process as a function of varying processing parameters. In addition to the reactant powders during each exfoliation step, the supernatants have also been characterized to determine the mass and charge balance for the whole system. A low-spin state is determined for Co and although the Co t_{2g} orbitals are considered non-bonding in first approximations, it is likely that the oxygen experiences the decrease in electron occupancy via an increase in covalency between O 2p and Co e_g. It is found that cobalt, as well as oxygen, undergo a partial oxidation process during the exfoliation of bulk $LiCoO_2$ into CoO_2-nanosheets.

(EMA-P033-2019) Structural and Magnetic studies in S = 1/2 trigonal lattice $Ba_3CuV_2O_9$

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Frustrated magnetic materials are of current interest as their arrangement of crystal structure does not allow magnetic ordering down to lowest temperatures. Here, we report structural, magnetic and electrical properties of $Ba_3CuV_2O_9$ which crystallizes in trigonal structure (R-32). In this material, magnetic Cu^{+2} (S = 1/2) forms a layer which is separated by layer of nonmagnetic V^{+5} ($3d^0$). Therefore, magnetic exchange interaction is only mediated through Cu-O layer. Our magnetic measurements data show this material exhibits no signature of magnetic ordering down to around 2 K. Moreover, we do not find any bifurcation between the magnetization data measured under zero-field-cooled and field-cooled protocol.

Similarly, no hysteresis is observed in field dependent magnetization data at low temperature. We, however, observed a high value of Curie temperature and magnetic moment at low temperature. This material exhibits a highly insulating state where the charge transport mechanism follows a power-law behavior. The experimental observations suggest that this material could be a possible candidate of spin-liquid state with S = 1/2 spin state. *This work has been done during summer project at School of Physical Sciences, Jawaharlal Nehru University, New Delhi – 110067.

(EMA-P034-2019) Utilizing Polarization Extension in (1-x) $NaNbO_3$-(x)$BaZrO_3$ Perovskites to Discover a Novel Relaxor Ferroelectric Material

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Lead Zirconate Titanate (PZT) is the industry standard for piezoelectric materials due to its low cost and large piezoelectric response at the morphotropic phase boundary (MPB), but the continued use and disposal of lead containing compounds has led to the desire to replace lead containing materials with lead-free alternatives. The increased response at the MPB is due to the mechanism of polarization rotation where the polarization vector can freely rotate increasing the number of available polarization states. This method though needs three separate polar phases to work and even with decades of research into finding an alternative PZT is still largely unmatched, and as such we are attempting to utilize a different mechanism, polarization extension, to synthesize new groups of piezoelectric materials. Polarization extension in contrast to rotation changes one of the starting polar materials to a nonpolar one. This drastically increases the number of starting materials available and allows for a multitude of new possibilities. For this project, Sodium Niobate and Barium Zirconate are the end members and the goals are to completely characterize the structure and property relationships in this new pairing. Thus far, results show a novel relaxor ferroelectric material and further experiments could potentially provide a viable lead-free replacement material.

(EMA-P035-2019) Li-Substituted Layered-Spinel Cathode Material for Sodium-Ion Batteries

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The O3-type layered $Na(Ni_xFe_yMn_z)O_2$ (0 < x, y, z< 1) cathode materials have attracted great interest in sodium-ion batteries due to the abundance and cost of raw materials and their high specific capacities. However, the cycling stability and rate capability at high voltages remains an issue. In this work, we successfully synthesized a Li-substituted layered-tunneled (O3-spinel) intergrowth cathode (LS-NFM) to address the aforementioned issues. The remarkable structural compatibility and connectivity of the two phases were confirmed by X-ray diffraction (XRD), selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM). LS-NFM reached a larger discharge capacity, capacity retention and enhanced rate capability in comparison to the un-doped control layered cathode (NFM). The effective Na^+ diffusivity of the LS-NFM electrode measured by galvanostatic intermittent titration technique (GITT) significantly increased compared to the control cathode. The results from ex situ hard/soft X-ray adsorption spectroscopy (XAS) suggest that the capacity of LS-NFM cathode mainly resulted from the Ni^{2+}/Ni^{4+} redox couple, and partially from the Fe^{3+}/Fe^{4+} redox couple. The voltage profile of the LS-NFM cathode exhibited a reversible plateau above 4.0V, indicating great stability at high voltages, and structural stabilization by the spinel phase.

(EMA-P036-2019) Synergistic effect of microstructure engineering and mechanical decladding on long term cycling of lithium lanthanum titanate (LLTO) based solid

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Perovskite $Li_{3x}La_{2/3-x}TiO_3$ has received much attention as a promising solution for the sever safety problem of solvent-electrolytes based conventional Li ion battery. However, the inherently poor grain boundary conductivity and poor cycling performance still remains challenge to address. Here, aiming to improve the grain boundary and total conductivity, $Li_{3x}La_{2/3-x}TiO_3$ was coupled with Lithium lanthanum zirconate. The obtained ceramic pellets demonstrates recordable grain boundary and total conductivity of 3.41×10^{-4} and 3.03×10^{-4} S/cm, respectively. The improvement is ascribed to the synergistic effect of microstructure engineering on grain boundary and superstructure in grains. To further decrease the grain boundary resistivity, the composited pellets with micron-scale grain is mechanically crushed into nano powder. The fragile LLTZO demonstrates typical transgranular fracture behavior and the interior lattice planes are sufficiently exposed. A cell of LFP|Li metal is adopted to demonstrate the enhanced performance of LLTZO. The solid state battery renders an excellent specific capacity above 101.2 $mAhg^{-1}$ after 300 cycles at a rate of 0.5C. The manufacturing of solid battery based on an all-coating approach provides a promising approach to achieve practical application.

(EMA-P037-2019) Preparation and electrical conductivity of Lithium Zinc Silicate as oxide-based solid electrolyte material

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$Li_{2+X}Zn_{1-X}GeO_4$ (X=0.25,0.5) is one of the solid solution group (LISICON) of the high-temperature phase g-Li_3PO_4 type having lithium ion conductivity. In our laboratory, we are focusing on lithium zinc silicate for having a composition in which Ge is replaced with Si, in preparation of $Li_{2+2X}Zn_{0.5}M_XSi_{1-X}O_4$ to which other element M (Co, Cr..etc.) is added and evaluate its electrical characteristics. In this experiment, $Li_{2+2X}Zn_{1-X}SiO_4$ (X= 4.0~6.0) was prepared and a sintered $Li_3Zn_{0.5-Y}Co_YSiO_4$ (Y=0.02~0.10) added with Co as another element was prepared, and the electrical characteristics of each sintered body were evaluated. A sintered body of $Li_{2+2X}Zn_{1-X}SiO_4$ (X= 4.0~6.0) was prepared from Li_2CO_3, ZnO and SiO_2 by a solid phase reaction at 950 ° C. for 6 hours. In the case of adding Co, each raw material composition of $Li_3Zn_{0.5-Y}Co_YSiO_4$ (Y=0.02~0.10) was prepared using a reagent of Co_3O_4, each sintered body was prepared from the same firing conditions as above It was. Each sintered body that prepared was subjected to XRD measurement to identify the generated phase, and then the fracture surface of the sintered body was observed by SEM. The electrical characteristics of each sintered body were evaluated from an Arrhenius plot diagram prepared at a measurement temperature of 50~300 ° C.

(EMA-P038-2019) Electrical properties in Tysonite-based solid electrolyte

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It is known that in ceramics solid electrolytes the grain boundariy resistance limits the ion movement and determine ionic conductivity. However, it is difficult to specify the origin of grain boundary resistance. In this study, we focused on the Tysonite-type fluoride ion conductor in which the influence of the grain boundary resistance on the total resistance largely varies depending on fabrication conditions. Fluorine has the highest electronegativity and forms a chemically stable structure because it bonds strong ionic bonds with metal ions. In addition, since the fluoride ion (F^-) is the smallest a mobile anion, high ionic conductivity is expected in the fluoride at low temperature range such as room temperature. We focused on rare earth fluorides such as LaF_3 and CeF_3, and investigated the grain boundary ionic conduction characteristics. As a result, grain boundary resistance was greatly reduced by slightly replacement by Sr, and the ratio of the grain boundary resistance to the intragranular resistance at 50 °C could be greatly reduced. It was suggested that the large grain boundary potential of CeF_3 gradually reduced by Sr doping.

(EMA-P039-2019) Redox stability of Sc-substituted $La_{0.6}Sr_{0.4}Fe0_{3-d}$ interconnector for solid oxide cells

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Under various synthetic conditions, $La_{0.6}Sr_{0.4}Fe_{1-x}Sc_xO_{3-d}$ was synthesized for the purpose of introducing a redox stable and electrically conductive SOC ceramic interconnector. The crystalline phases of LSFSc are stable when the solution pH is low (pH=2), and the calcination temperature is sufficiently high (T=1200°C). From the XPS analysis it is accepted that incorporation of Sc in the LSF lattice further stabilizes its structural stability under reducing conditions. When the Sc concentration exceeds 10 mol%, phase stability of $La_{0.6}Sr_{0.4}Fe_{1-x}Sc_xO_{3-d}$ was obtained. The electrical conductivity of $La_{0.8}Sr_{0.2}FeO_{3-d}$ is remarkably low at both oxidation and reduction atmospheres due to the high area specific resistance. However, the ASR of $La_{0.6}Sr_{0.4}FeO_{3-d}$ is less than half of $La_{0.8}Sr_{0.2}FeO_{3-d}$ when exposed to air at one side and is exposed to H_2 on the opposite side. $La_{0.6}Sr_{0.4}FeO_{3-d}$ shows big augment due to the decomposition at reduction atmosphere. Moreover, the instability against high relative humidity (RH) is the main downside of $La_{0.6}Sr_{0.4}FeO_{3-d}$. For these reasons, it is difficult to employ $La_{0.6}Sr_{0.4}FeO_{3-d}$ as an interconnector material. Among the proposed materials, $La_{0.6}Sr_{0.4}Fe_{0.9}Sc_{0.1}O_{3-d}$ exhibited the most desirable performances at the various gas conditions for 1000 h.

(EMA-P040-2019) Alkaline Earth Substituted Bismuth Pyrostannate ($Bi_{2-x}M_xSn_2O_{7-x/2}$); M= Mg, Ca, Sr, Ba

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Pyrochlore structured materials are commonly studied for ionic conduction due to their similarities to the fluorite structure. The pyrochlore structure can be thought of as a defect-fluorite structure with cation ordering and anion vacancies. Improved ionic conduction in pyrochlores can be achieved by inducing cation disorder. Bismuth containing pyrochlores are commonly researched because of the stereochemically active lone pair on bismuth. Polymorphic bismuth pyrostannate ($Bi_2Sn_2O_7$) has three pyrochlore related structures: the room temperature α-phase, the β-phase which manifests between 390 K and 900 K, and the γ-phase which exists above 900 K. The distorted pyrochlore $Bi_2Sn_2O_7$ exhibits many important properties including oxide-ion conduction, dielectric properties, and photocatalysis. A variety of new pyrochlore materials ($Bi_{2-x}M_xSn_2O_{7-x/2}$) have been synthesized by substituting alkaline earth cations (M= Mg, Ca, Sr, Ba) for bismuth in the distorted pyrochlore lattice of $Bi_2Sn_2O_7$. The substitution of divalent cations into the pyrochlore structure introduces oxygen vacancies which opens pathways for improving oxide ion conduction in the crystal lattice.

(EMA-P041-2019) Exploratory Data Analysis of Exfoliated Cobalt Oxide Nanosheet Solutions

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This research aims to understand the UV-Vis absorption of cobalt oxide nanosheets as it pertains to various processing treatments. Starting from a layered bulk structure, lithium cobalt oxide can undergo chemical exfoliation through a two-step method: treatment with a protic acid, then treatment with tetramethylammonium hydroxide which intercalates the layered structure and yields exfoliated cobalt oxide nanosheets. Using UV-Vis spectroscopy, information about the electronic transitions of the exfoliated nanosheet solutions was collected. By utilizing exploratory data analysis techniques such as principal components analysis, spline fitting, machine learning, and pairwise plots observed changes peak width, position, intensity and ratio were examined. From this analysis, it was determined that two patterns occur within the data set regardless of certain processing treatments. By relating the observed patterns with known properties, we have constructed simple structure-property relationships related to defect concentration and electron mobility. Furthermore, the oxidation state, defect concentration, thickness, lateral width, and surface charge of exfoliated nanosheets were examined as potential reasons for changes in absorbance spectra as these may relate to the material's electronic and thermal conductivity, band gap, and redox chemistry.

(EMA-P042-2019) Protonic Ceramic Electrochemical Devices by Integrated 3D Printing and Laser Processing

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Low-temperature (250-600°C) protonic ceramic electrochemical devices (PCED) such as fuel cells, electrolysis cells, hydrogen/water permeable membranes, and electrochemical gas sensors have attracted increasing attention recently. The fabrication of PCEDs with high volumetric power densities, especially, protonic ceramic fuel cells and multichannel catalytic membrane reactors, needs significant efforts. In this work, the technique of integrated 3D printing and laser processing based on digitally layer-by-layer processing and rapid laser consolidation and machining was developed to fabricate PCEDs efficiently, which includes a 3D high-precision motion stage by integrating 3D micro-extrusion, CO_2 laser drying, and picosecond laser micro-machining. After the preparation of high-quality printable pastes, we fabricated versatile protonic ceramic parts including tube membrane reactor substrates, cylinders, rings, and cones. Furthermore, the complicated geometry fabrication (e.g., lobed tubes with the larger surface area) with a smooth surface was fulfilled by picosecond machining. The smooth substrate fabricated by the combination of 3D printing and laser processing has been demonstrated to be suitable for thin film deposition by dip coating, which makes it possible to prepare PCEDs.

(EMA-P043-2019) Densification and Grain Growth in the $Mg_xZn_xNi_xCu_xCo_xO$ (x=0.2) Entropy Stabilized Oxide System

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Entropy has been shown to stabilize equimolar amounts of MgO, ZnO, CuO, CoO, ZnO, and NiO into a homogenous, cubic, rock-salt phase with the metal ions randomly distributed within the cation sublattice. With the configurational entropy dominating the thermodynamics of the system and the limited binary solubility between the various oxides, is important to study the kinetics of this unusual material system. While the single rock-salt phase can be reliably formed with five components when heated to temperatures above 870 °C, fabrication of a dense bulk sample is necessary for extensive characterization of material properties that would otherwise be dominated by porosity. Sintering studies utilizing dilatometry and electron microscopy have allowed for the determination of a thermal profile that yields samples that approach full density (~97%). After successfully creating these fully dense samples, grain growth studies were conducted to gain insight into mobility and diffusion mechanisms of the system which allows for tunable grain sizes. With dense samples and an improved understanding of the kinetics, more reliable characterization of electrical and thermal properties is possible, revealing the impact of the disorder within the system.

(EMA-P044-2019) Thermal Conductivity Investigations of Cubic Strontium Niobate, $SrNbO_3$.

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Strontium niobate, $Sr_xNb_xO_y$ is typically a layered structured perovskite-based oxide that displays glass-like thermal conductivities, despite high crystallinity. This work investigates thermal transport in the non-layered, cubic phase of strontium niobate, $SrNbO_3$, prepared under low oxygen partial pressure conditions. By using the optical pump-probe technique, time-domain thermoreflectance (TDTR), thermal conductivity of thin film $SrNbO_3$ was measured as a function of temperature from 78 to 500K and was determined to be .94 W/mK at room temperature. The results of this study are compared to previous work exploring the glass-like thermal conductivity of the layered phase of strontium niobate, $Sr_2Nb_2O_7$, which was reported to be 0.6 W/mK. This study provides new insight into the role of weakly bound layers in complex oxides on thermal transport.

(EMA-P045-2019) The influence of titanium adhesion layer oxygen stoichiometry on thermal boundary conductance at gold contacts

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We experimentally demonstrate the role of oxygen stoichiometry on the thermal boundary conductance across Au/TiOx/substrate interfaces. We evaporate two different sets of Au/TiOx/substrate samples under both high vacuum and ultrahigh vacuum conditions to vary the oxygen composition in the TiOx layer from $0 \leq x \leq 2.85$. We measure the thermal boundary conductance across the Au/TiOx/substrate interfaces with time-domain thermoreflectance and characterize the interfacial chemistry with x-ray photoemission spectroscopy. Under high vacuum conditions, we speculate that the environment provides a sufficient flux of oxidizing species to the sample surface such that one is essentially co-depositing Ti and these oxidizing species. We show that slower deposition rates correspond to a higher oxygen content in the TiOx layer, which results in a lower thermal boundary conductance across the Au/TiOx/substrate interfacial region. Under the ultrahigh vacuum evaporation conditions, pure metallic Ti is deposited on the substrate surface. In the case of quartz substrates, the metallic Ti reacts with the substrate and getters oxygen leading to a TiOx layer. Our results suggest that thin Ti layers with relatively low oxygen compositions are best suited to maximize the thermal boundary conductance.

(EMA-P046-2019) Molybdenum nitride as a zero dimensional electride

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Electrides exhibit high electrical conductivity derived from spatially localized electrons, which act as anionic species. Although they are found in diverse chemistries, here we assess whether the previously reported superconducting ceramic, Mo2N, belongs to this class of materials. We use electronic structure calculations to show that β-Mo_2N is zero dimensional electride with high electrical conductivity derived from both strong N 2p – Mo 4d orbital hybridization and strong metal-metal bonding. The latter is due to the spatially extended Mo orbitals. In addition, the nitride exhibits an anti-anatase structure, which can be described as an ordered nitrogen vacancy structure of distorted and defective derivative of the NaCl structure, permitting weakly bound anionic electrons to be trapped in cages. Because β-Mo_2N can undergo a structural phase transition to the γ phase with fewer vacant sites, we describe routes to control the electride character across the β-to-γ transition. Last, we point out that most electrides are not superconductors, making Mo_2N one of the few exceptions to this observation. To this end, we also explore the role of electron-phonon coupling in supporting the superconductivity state. Last, we propose relevant experiments to verify the assignment of Mo_2N as a zero dimensional electrides.

(EMA-P047-2019) Computational Discovery of One-Dimensional Semiconductors and Magnets

J. C. Lu*[1]; J. T. Paul[1]; S. Shah[1]; R. G. Hennig[1]

1. University of Florida, Materials Science and Engineering, USA

In this work, we use the topological scaling algorithm (Phys. Rev. Lett. 118, 106101 (2017)), which determines the dimensionality of structural motifs of crystal structures, to discover novel one-dimensional (1D) materials. We search the MaterialsProject database to identify candidate materials and then perform density functional calculations on a subset of 263 of the most promising ones. To estimate their metastability, we determine the formation energies of these 1D materials normalized both by atom and by linear dimension. We compare the results to those of single chain tellurium, since individual sheets of Tellurium have already been synthesized experimentally. We characterize the electronic and magnetic properties of the 1D chains by calculating their electronic structure with the meta-GGA SCAN functional. We found that 50 of them have magnetic moments that exceed 1 Bohr magneton, and several are semiconductors. We complete this work by comparing the electronic and magnetic behavior of several of the 1D materials to their 3D counterparts to determine how dimensionality impacts these properties.

(EMA-P048-2019) Electronic structure of the Ruddlesden-Popper analogs of methylammonium lead iodide

B. Phan*[1]; R. G. Hennig[1]; S. R. Xie[1]; S. R. Phillpot[1]; P. Li[1]

1. University of Florida, material science and engineering, USA

Ruddlesden-Popper phases have been a topic of much fascination, and harbor potential for growth in many disciplines. Ruddlesden-Popper phases are layered relatives of the perovskite structure consisting of layered perovskite slabs separated by layers of cations. Inorganic Ruddlesden-Popper phases have widely different properties from their analogous cubic perovskite phases. We explore the stability and electronic structure of Ruddlesden-Popper phases for the hybrid organic-inorganic lead iodide perovskite, An+1BnX3n+1, with A=CH3NH3, B=Pb, X=I. We determine thermodynamic stability, band gap, and effective mass of the Ruddlesden-Popper phases using density functional theory and show the trends in properties with increasing number of octahedral layers, n, between the cation layers. We find that these properties are affected by the choice of functional (PBE, SCAN, and HSE06) as well as the inclusion of van der Waals corrections and spin-orbit coupling.

Thursday, January 24, 2019

S1: Characterization of Structure–Property Relationships in Functional Ceramics

Imaging and Analytical Techniques III

Room: Cypress B
Session Chairs: Hugh Simons, Technical University of Denmark; Scott Misture, Alfred University

10:00 AM

(EMA-S1-014-2019) Atomic-Scale Mechanisms for Interfacial Damage Resistance in Ion-Irradiated $La_2Ti_2O_7$ / $SrTiO_3$ Thin Film Heterostructures

S. R. Spurgeon*[1]; M. Sassi[2]; T. Kaspar[2]; V. Shutthanandan[3]

1. Pacific Northwest National Laboratory, Energy and Environment Directorate, USA
2. Pacific Northwest National Lab, Physical and Computational Sciences Directorate, USA
3. Pacific Northwest National Lab, Environmental Molecular Sciences Laboratory, USA

The emergent functional properties of oxide interfaces have enabled a wide variety of electronics, sensors, and storage devices. However, as these devices are deployed in high-radiation environments, such as spacecraft and nuclear cores, they degrade through complex and poorly understood pathways. In contrast to typical metals, far less work has focused on the ion-irradiation damage evolution of oxide interfaces and heterostructures. Here we examine the damage resistance of $La_2Ti_2O_7$ / $SrTiO_3$ (110) heterojunctions using a combination of advanced analytical scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), and ab initio theory calculations. We observe that the interface is markedly more damage resistant to 1 MeV Zr^+ ion bombardment in contrast to the bulk of the film or substrate. We discuss possible atomistic damage mechanisms and identify unique features of the interface that can mitigate the damage process. Our study illustrates how new atomic-scale characterization methods can be uniquely applied to probe the radiation dynamics of functional oxide interfaces.

10:15 AM

(EMA-S1-015-2019) Microstructure Tailoring of Oxide Thermoelectrics to Increase the Figure of Merit (ZT) Value

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1. Jozef Stefan Institute, Nanostructured Materials, Slovenia
2. Sabanci University, FENS MatSE and NanoEng, Turkey

Figure of merit (ZT) of oxide-based thermoelectric (TE) materials can be improved by incorporating planar faults into their microstructure thus reducing thermal conductivity due to enhanced phonon scattering. Such microstructure tailoring resulting in higher ZT values was demonstrated in TE materials with the perovskite and the wurtzite crystal structures, namely in CaO/SrO-doped $Sr(Ti_{0.8}Nb_{0.2})O_3$ (STN) and In_2O_3/Al_2O_3-doped ZnO. The microstructure analysis of the STN samples revealed that the addition of CaO/SrO into the STN resulted in the formation of Ruddlesden-Popper-type (RP) planar faults with a rock salt-type structure. These RP faults formed either random 3D networks consisting of individual RP faults running along {001} STN crystallographic planes or more or less ordered polytypoidic sequences with a general formula $(Sr,Ca)O{\cdot}n(Sr(Ti,Nb)O_3)$. In In_2O_3-doped ZnO ceramics pure indium monolayers were readily observed by the HAADF STEM. These basal inversion domain boundaries (IDB's) run parallel to the {0001} ZnO lattice planes and separate domains with different orientation. Measurements of thermoelectric properties confirmed that in-growth planar faults reduced thermal conductivity in both investigated materials systems and that by such nanostructured modifications of the material it is possible to improve the ZT values in oxide-based thermoelectric materials.

10:30 AM

(EMA-S1-016-2019) $Y_2BiFe_5O_{12}$: The Saga Continues

N. Herrera-Pineda*[2]; M. García-Guaderrama[3]; G. Herrera-Perez[5]; M. E. Fuentes-Montero[1]; J. Napoles-Duarte[1]; J. P. Palomares-Baez[1]; C. M. Ornleas-Gutierrez[4]; E. M. Guerrero-Lestarjette[4]

1. UACH, Computacional Chemistry, Mexico
2. UACH, Mexico
3. U de G, Mexico
4. NanoTech, Mexico
5. CONACyT, Mexico

The Bi-YIG (Yttrium Bismuth Iron Garnet), has been reported with a dielectric, magnetic, magneto-optical and ferroelectric properties. The properties are committed to the method and synthesis conditions, size particle, morphology, and its crystalline structure. It is necessary that the experimental results agree with the crystallographic space group and, in turn, corresponds to the properties. Structural and morphological characterization by transmission electron microscopy (TEM) of Bi-YIG has been studied, to explain the dielectric, ferroelectric and the possibility of a magneto-electrical coupling. The synthesis of the samples was carried out by the sol-gel combustion route at 1000, 975 and 950 ° C. The refinement of X-ray diffraction patterns by the Rietveld method using the Fullprof software version 2017 suggest a garnet structure with a single cubic phase and Ia-3d space group for Bi-YiG. The bright field (BF), high annular dark-field and high-resolution (HR) TEM images were collected in a scanning mode in a JEM-2200FS operated at 200kV. The dispersive energy spectra were obtained at five different points and used to perform a semi-quantitative analysis. The BF images were analyzed to determine the particle size and the particle shape morphology. HR-TEM images were used to determine the d-spacing. The selected area electron diffraction (SAED) were indexed, and our results corroborated the interpretation performed by the XRD characterization.

10:45 AM

(EMA-S1-017-2019) Exploring the potential of metal-organic framework hybrid ferroelectric perovskites for energy harvesting applications

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1. Norwegian University of Science and Technoogy, Materials Science and Engineering, Norway

Metal-organic framework (MOF) hybrid perovskites are currently being developed as cost effective, efficient photovoltaic materials. However, recent research has produced MOF ferroelectrics with polarizations of 5 $\mu C/cm^2$ and piezoelectric coefficients of up to 180 pC/N. The piezoelectric response suggests that these materials may be of interest for piezoelectric applications such as energy harvesting. The current state of the art in flexible cantilever piezoelectric energy harvesting is dominated by oxide thin films supported by flexible passive elastic layers in the form of thin metal foils and polymer substrates. These devices often require complex processing methods to overcome oxide and substrate temperature incompatibility issues. By comparison some MOF hybrid perovskites, exhibit a plastic crystal phase, in which the materials are cubic, readily malleable and can be formed in to thin and thick films by hot pressing powders at temperatures above usually <120C). Here we focus on tetramethylammonium bromotrichloroferrite (III) with a reported piezoelectric coefficient of 110 pC/N and dielectric constant of 100 and explore its potential use for flexible cantilever energy harvesting devices. We report on the mechanical, and electrical properties, and processing methodology and flexibility.

11:00 AM

(EMA-S1-018-2019) Electromechanical and structural characterization of piezoceramics under high-power drive (Invited)

M. Slabki[1]; J. Daniels[2]; J. Koruza*[1]

1. TU Darmstadt, Germany
2. University of New South Wales, Australia

Piezoceramics are widely used in high-power devices, whereby the piezoelectric element is driven in the vicinity of its resonance frequency by a comparatively-high AC electric field. Characterization of material's electromechanical and structural properties at high-power conditions is challenging due to high currents, high frequencies, and overheating. This talk will present a methodology for the study of structure-property relationships in hard piezoceramics at resonance conditions. The piezoelectric coefficients under high-power drive are first determined using the pulse drive method with burst excitation. In a second stage, the sample is excited at the resonance frequency, while synchrotron diffraction is used to measure the resulting structural changes in situ. This method enabled to establish the correlation between the decrease of the mechanical quality factor at high vibration velocities and domain wall motion. Moreover, contributions of domain wall motion to the overall macroscopic strain response at resonance conditions were evaluated for a hard-type $Pb(Zr,Ti)O_3$. The vibration-velocity- and temperature-dependent properties of this classical piezoelectric, hardened by acceptor doping, will be compared to the behavior of emerging lead-free piezoceramics with alternative hardening concepts.

11:30 AM

(EMA-S1-019-2019) Strain Engineering Thermal Conductivity in Oxide Perovskites (Invited)

A. Sarantopoulos[3]; E. Langenberg[3]; D. Saha[1]; W. Ong[4]; D. Schlom[2]; F. Rivadulla[3]; J. A. Malen*[1]

1. Carnegie Mellon University, USA
2. Cornell University, Department of Materials Science and Engineering, USA
3. Universidad de Santiago de Compostela, Spain
4. Zhejiang University, China

Strain engineering thin films of $SrTiO_3$ and $PbTiO_3$ is known to control their lattice structure. We show that this has profound effects on their thermal conductivity. Thin films of (100) $SrTiO_3$ were grown in compression on LSAT substrates and tension on $DyScO_3$ substrates and their thermal conductivities were measured by frequency domain thermoreflectance (FDTR). At room temperature $SrTiO_3$ on LSAT exhibited a thermal conductivity of 6 W/m-K, while $SrTiO_3$ on $DyScO_3$ exhibited a thermal conductivity of 2.5 W/m-K. We hypothesize that this discrepancy results from the $SrTiO_3$ on LSAT films being in the paraelectric phase, while the $SrTiO_3$ on $DyScO_3$ films being in the transition region between the paraelectric and ferroelectric phases. Unlike the paraelectric phase, the ferroelectric phase exhibits domain boundaries that have been shown to scatter phonons and reduce thermal conductivity. Upon cooling the thermal conductivity of the $SrTiO_3$ on $DyScO_3$ films continues to decrease before levelling off at 0.8 W/m-K at 225 K, where the transition to the ferroelectric phase is complete. Similarly, (100) $PbTiO_3$ was grown on $SrTiO_3$ to create single domain films, and on $DyScO_3$, $TbScO_3$, $GdScO_3$, and $SmScO_3$ substrates to create thin films with ferroelectric domains of varied size. In these films the room temperature thermal conductivity measured by FDTR correlates closely with the domain sizes measured by piezoresponsive force microscopy.

S2: Advanced Electronic Materials: Processing Structures, Properties, and Applications

Advanced Electronic Materials: Property II

Room: Orange A

Session Chairs: Barbara Malic, Jozef Stefan Institute; Brahim Dkhil, Université Paris-Saclay

10:00 AM

(EMA-S2-018-2019) $Pb(Mg_{1/3}Nb_{2/3})O_3$-based multilayer elements: Processing, electrocaloric effect and fatigue properties (Invited)

L. Fulanovic[1]; A. Bradesko[1]; S. Drnovsek[1]; V. Bobnar[2]; B. Malic*[1]

1. Jozef Stefan Institute, Electronic Ceramics Department, Slovenia
2. Jozef Stefan Institute, Condensed Matter Physics, Slovenia

A contribution to increasing needs of society for electricity, heating, or cooling have become a global priority may be implementation of nonlinear dielectrics in cooling by exploiting the electrocaloric effect (ECE). Materials exhibiting a large ECE over a temperature range of a few 10 K close to room temperature include lead-based relaxors, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) or PMN-rich (1-x)PMN-x$PbTiO_3$ (PMN–100xPT) solid solutions. PMN-10PT is one of the most suitable and thus studied materials for cooling applications due to a high EC temperature change in a wide temperature interval, close to room temperature. Multilayer elements (MLE) have recently been shown to sustain higher electric fields than bulk ceramics which can be also related to the lower thickness of individual layers, and they also need lower applied voltages, which is suitable for applications. In the contribution we report on a comprehensive EC study of PMN and PMN-10PT MLEs for potential use in cooling devices. By using MLEs instead of bulk ceramics the required voltages for reaching high electric fields are significantly reduced, while the EC temperature changes of respective materials remain comparable to their bulk counterparts. In terms of practical use, the EC stability of MLEs upon electric field cycling is found to be almost fatigue-less for 10^6 unipolar cycles.

10:30 AM

(EMA-S2-019-2019) Antiferroelectric Materials as Dielectric Coolants

B. Rozic[1]; B. Asbani[2]; H. Uršič[3]; M. El Marssi[2]; R. Pirc[1]; J. Koruza[4]; B. Malic[3]; Z. Kutnjak*[1]

1. Jozef Stefan Institute, Slovenia
2. University of Picardie Jules Verne, France
3. Jozef Stefan Institute, Electronic Ceramics Department, Slovenia
4. Technische Universitaet Darmstadt, Germany

The electrocaloric (EC) effect has recently attracted significant interest for developing new heat-management devices that have the potential to replace the existing technologies. In this contribution the theoretical investigations of the large EC effect near antiferroelectric phase transition in ceramic materials will be presented. These results will be compared with directly measured EC effect in antiferroelectric n/95/5 PLZT and PBZ ceramics. Here, it is demonstrated that both negative and positive EC response can be arbitrarily invoked in antiferroelectric materials by properly controlling the electric field and temperature, demonstrating that these materials otherwise suitable for large electric energy storage are also good dielectric coolants.

10:45 AM

(EMA-S2-020-2019) Microstructural evolution in antiferroelectric ceramics under monotonic and cyclic electric fields

Z. Fan*[1]; X. Tan[1]

1. Iowa State University, USA

The most prominent feature of an antiferroelectric (AFE) ceramic is its reversible phase transition to a ferroelectric (FE) phase under applied electric fields. In some peculiar compositions at certain narrow temperature ranges, the induced FE phase is metastable and a reverse electric field can trigger an unlikely FE-to-AFE transition. The microscopic mechanisms underlying these phase transitions still lack of understanding. Also, electric fatigue becomes relevant in consideration of device applications of these AFE ceramics. However, research on both issues has been so far almost limited to assessing the macroscopic behavior. In the present work, we employed in situ TEM to reveal the microstructure mechanisms in $PbZrO_3$-based antiferroelectric ceramics under DC and AC electric fields. In particular, our experiments were focused on grains with coexisting AFE/FE phases. Under a moderate field, a novel type of AFE↔FE phase transition was directly observed at the AFE/FE interface. During electric cycling, on the other hand, the directional movement of the AFE/FE interface occurs, indicating the stabilization of the AFE/FE phases.

11:00 AM

(EMA-S2-021-2019) Doped $Ba_{0.06}Na_{0.47}Bi_{0.47}TiO_3$ lead-free ceramics for high temperature electronics

V. Mussi Toschi*[1]; C. Bogicevic[1]; H. Laville[2]; P. Janolin[1]

1. CentraleSupélec, Université Paris Saclay, Laboratoire Structures, Propriétés et Modélisation des Solides UMR CNRS, France
2. Exxelia Technologies, France

The design of materials that can work at temperatures as high as 350°C is a great issue nowadays, due to the fast growth of high-temperature applications. The multi-layer ceramic capacitors (MLCC) are traditionally produced with $BaTiO_3$-based materials, which cannot be used at high temperatures. Some lead-based materials have satisfactory performances; however, new regulations restrict their use. Therefore, the development of new lead-free materials to meet expectations of electronics at high temperature is imperative. Ceramics based on $Ba_{0.06}Na_{0.47}Bi_{0.47}TiO_3$ are among the best candidates, since they combine high performance and easy manufacturing. This solid solution close to the morphotropic phase boundary results in high and stable permittivity, low dynamic and static losses within a large temperature range. The addition of dopants like Co_3O_4 or MnO_2, used to decrease losses, make it suitable for the industry. The synthesis of BNBT was optimized and a study of structure and properties was performed. The compatibility of the ceramics the MLCC were also tested. Dielectric measurements were associated to structural characterizations using XRD and SEM. A focus was put on the hysteresis properties after a few heating and cooling cycles, since there was a change in structure, dielectric and ferroelectric properties. This allowed the characterization of the stability and the reliability of the ceramic.

11:15 AM

(EMA-S2-022-2019) Investigation on Terahertz time-domain spectroscopy in mixed rare earth orthoferrite

A. Wu*[1]

1. Shanghai Institute of Ceramics, CAS, China

Terahertz time-domain spectroscopy (THz-TDS) was used to study the ferromagnetic mode and antiferromagnetic mode of mixed rare earth orthoferrites $Sm_{0.5}Tb_{0.5}FeO_3$ and $Sm_{0.4}Er_{0.6}FeO_3$ which excited by THz pulse. The resonant amplitude and frequency of antiferromagnetic mode were significantly changed in the spin reorientation transition temperature range, which demonstrates that the antiferromagnetic mode can be directly and non-thermally excited. The room temperature terahertz time-domain spectroscopies of $Sm_{0.4}Er_{0.6}FeO_3$ demonstrate that the antiferromagnetic mode and ferromagnetic mode can be excited when the magnetic field of THz pulse were parallel and vertical to magnetic vector of rare earth orthoferrites, respectively. Our measurement demonstrates that the terahertz time-domain spectroscopy is a sensitive mean to explore the spin reorientation transition in rare earth orthoferrite

11:30 AM

(EMA-S2-023-2019) Ferroelectrics as a toolbox for refrigeration (Invited)

B. Dkhil*[1]

1. CentraleSupélec-Univ. Paris-Saclay, France

The search for alternative solid-state refrigeration materials to hazardous gases in conventional and cryogenic cooling devices is a very active field of condensed matter. Here, we explored various aspects of ferroelectrics to reveal their potentialities as solid state coolers such as the ferroeletric phase transitions, the multiphase points composition, the stress-sensitivity through elasto-caloric responses, the inverse electrocaloric effect in antiferroelectrics, the asymmetric effect arising from non-ergodic state, the use of dual-stimuli by taking advantage of multicaloric effects as well as the use of defects. B.D. acknowledge Fonds National de la Recherche (FNR) du Luxembourg through the InterMobility project 16/1159210 "MULTICALOR"

12:00 PM

(EMA-S2-024-2019) Phase Equilibria and Relaxor Ferroelectric Behavior in (1-x)$[Bi_{1/2}(Na_{0.5}K_{0.5})_{1/2}TiO_3]$-x$PbZrO_3$ System

S. K. Gupta*[1]; B. Gibbons[1]; D. Cann[1]

1. Oregon State University, Mechanical, Industrial, and Manufacturing Engineering, USA

The perovskite solid solution (1-x)$[Bi_{1/2}(Na_{0.5}K_{0.5})_{1/2}TiO_3]$-x$PbZrO_3$ ceramics ($0 \le x \le 0.20$) were investigated to examine the phase equilibria, ferroelectric and piezoelectric properties. The composition corresponding to x=0 exhibits tetragonal symmetry with classical ferroelectric behavior. In this system, crossover from classical ferroelectric behavior to relaxor behavior is encountered with the addition of $PbZrO_3$ (x = 0.10). This is indicated by a constriction in the polarization-electric field (EF) hysteresis loops along with a broad, frequency dependent maxima in the relative permittivity versus temperature data. With further increase in x (> 0.10), typical ferroelectric characteristics are again observed. The combined results demonstrate that there exists a narrow ferroelectric (FE)-relaxor (R) boundary near x=0.10 where both, FE and R phases coexist along with an enhancement in the piezoelectric properties including d^*_{33} (317 pm/V). This transition in dielectric properties is consistent with changes in the observed phase equilibria for the current material system, where the symmetry transitions from tetragonal for x=0, to pseudo-cubic for the relaxor behavior, to orthorhombic for the re-entrant ferroelectric phase. The composition-induced transition FE-to-R-to-FE in the (1-x)$[Bi_{1/2}(Na_{0.5}K_{0.5})_{1/2}TiO_3]$-x$PbZrO_3$ system is of great scientific and technological interest.

12:15 PM

(EMA-S2-025-2019) The slope approach to enhance magnetoelectric coupling in 0-3 composite ceramics

M. Naveed-Ul-Haq[1]; V. Shvartsman[1]; H. Trivedi[1]; S. Salamon[2]; S. Webers[2]; H. Wende[2]; U. Hagemann[3]; M. Labusch[4]; J. Schröder[4]; D. C. Lupascu*[1]

1. University of Duisburg-Essen, Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), Germany
2. University of Duisburg-Essen, Faculty of Physics and Center for Nanointegration Duisburg-Essen, Germany
3. University of Duisburg-Essen, Interdisciplinary Center for Analytics on the Nanoscale (ICAN) and Center for Nanointegration Duisburg-Essen (CENIDE), Germany
4. University of Duisburg-Essen, Institute of Mechanics, Department of Civil Engineering, Germany

It is well established that the highest magnetoelectric coupling can be achieved for systems that use a mechanical resonator at or near resonance typically realized as 2-2-layered devices of a magnetostrictive phase and a piezoelectric material. Statically, the coupling must, nevertheless, not be so high, because amplitude enhancement at high mechanical quality factor can be enormous. We show that statically also 0-3 composites show considerable coupling. It is in particular advantageous to seek for a material combination that uses not necessarily large absolute magnetostriction and electrostrictive strain, but rather places the system at external fields, where the largest changes of each arise. A very significant improvement of magnetoelectric coupling was achieved when combining $NiFe_2O_4$ with a relaxor ferroelectric system based on $(Ba,Ca)(Zr,Ti)O_3$.

Advanced Electronic Materials: Lead free I

Room: Orange A
Session Chair: Jacob Jones, North Carolina State University

2:00 PM

(EMA-S2-026-2019) $(K,Na)NbO_3$-based Lead-free Piezoceramics : Simultaneous Enhancement of Piezoelectricity and Temperature Stability (Invited)

J. Li*[1]; Q. Liu[1]; Y. Zhang[1]; K. Wang[1]; X. Zhang[1]; L. Li[1]

1. Tsinghua University, School of Materials Science and Engineering, China

Extensive studies have been concentrated on $(K,Na)NbO_3$ (KNN) based lead-free piezoceramics. A series of our studies have been focused on a simultaneous enhancement of piezoelectricity and temperature stability, which has been realized by incorporating perovskite compounds with Zr ion at B-site. The piezoelectric coefficient d_{33} rose to ~450 pC/N, which can be maintained within 10% change in a wide temperature range from room temperature to 80 °C. The piezoelectric strain also reached 0.13% with a small variation (<10%) from room temperature to 130 °C. The converse piezoelectric coefficient d_{33}^* can be enhanced to a high level >600 pm/V by further compositional modification. The intrinsic and extrinsic contributions to the piezoelectric effect were analyzed by using a modified Rayleigh law as well as systematic analyzes on crystalline structure and electrical properties. It is revealed that incorporating perovskite compounds with Zr ions with multiple A-site ions lead to diffused phase transition that is responsible for the enhanced stability. The nanostructure observation also indicated the importance of introducing nanoscopic local structural heterogeneity in lead-free ceramics for simultaneous enhancement of piezoelectricity and temperature stability.

2:30 PM

(EMA-S2-027-2019) Lead-free hard-type relaxor $(Na_{1/2}Bi_{1/2})TiO_3$-$BaTiO_3$ composites for high power piezoelectric applications

L. Kodumudi Venkataraman*[1]; M. Slabki[1]; J. Koruza[1]; J. Rödel[1]

1. Technical University Darmstadt, Germany

Thermal depolarization, wherein the macroscopic piezoelectricity vanishes, is one of the major limitations of $(Na_{1/2}Bi_{1/2})TiO_3$-$BaTiO_3$ based compositions in high power applications. This work demonstrates enhanced thermal depolarization temperature (~190 °C) in the composites with a relaxor $(1-x)(Na_{1/2}Bi_{1/2})TiO_3$-$xBaTiO_3$ matrix phase and ZnO inclusions. The results are presented for different matrix NBT-xBT compositions exhibiting different crystal symmetry. The enhanced thermal stability is established from the temperature-dependence of the permittivity, piezoelectric constant and electromechanical hysteresis. Apart from improved thermal stability, the composites also exhibit hardening of the electromechanical properties as established by the increased mechanical quality factor, Q_m, and reduced ferroelastic hysteresis. The temperature-dependent Q_m and high power characteristics are contrasted to that of a commercially used lead-zirconate-titanate.

2:45 PM

(EMA-S2-028-2019) The influence of K_2O non-stoichiometry on the electrical properties of $(K,Na)_{1/2}Bi_{1/2}TiO_3$ ceramics

L. Li*[1]; M. Li[2]; D. C. Sinclair[1]

1. University of Sheffield, Materials Science & Engineering, United Kingdom
2. University of Nottingham, Department of Mechanical, Materials and Manufacturing Engineering, United Kingdom

The solid solution $(K_xNa_{0.5-x})Bi_{0.5}TiO_3$ (KNBT) between $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) and $K_{1/2}Bi_{1/2}TiO_3$ (KBT) has been extensively researched as a candidate lead-free piezoelectric material because of its relatively high Curie temperature (T_C) and good piezoelectric properties, especially near the morphotropic phase boundary (MPB) at x ~ 0.10 (20 mol% KBT). Here we report low levels of excess K_2O in the starting compositions can significantly change the conduction mechanism and electrical properties of KNBT. Impedance Spectroscopy measurements reveal significantly higher bulk conductivity (σ_b) values for $y \geq 0.10$ samples (activation energy, Ea, ≤ 0.95 eV) compared to the corresponding x-series samples which possess band-gap type electronic conduction (Ea ~ 1.26 to 1.85 eV). The largest difference in electrical properties occurs close to the MPB composition where the difference (at 300 °C) can be 4 orders of magnitude. This demonstrates the electrical properties of KNBT to be sensitive to low levels of A-site nonstoichiometry which can lead to undesirable high dielectric loss and leakage currents at elevated temperatures.

3:00 PM

(EMA-S2-029-2019) Electrical properties of crystalline $(Na_{1-x}K_x)NbO_3$ thin film grown at low temperature using two-dimensional $Sr_2Nb_3O_{10}$ nanosheet seed layer

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A monolayer $Sr_2Nb_3O_{10}$ (SNO) nanosheet was deposited on a $Pt/Ti/SiO_2/Si$ substrate using the Langmuir-Blodgett method. This monolayer SNO nanosheet with a (001) surface termination was used as a seed layer to reduce the growth temperature of the crystalline $(Na_{1-x}K_x)NbO_3$ (NKN) film. The crystalline NKN film was preferentially grown along the [001] direction at 350°C. The ferroelectric and piezoelectric properties of this NKN film were influenced by the post-annealing atmosphere due to the variations in the amounts of oxygen vacancies in the NKN film. The crystalline NKN film annealed at 300°C under 50 Torr O_2 atmosphere showed promising ferroelectric and piezoelectric properties; ε_r of 280 and tan δ of 1.7% at 100 kHz, P_s of 31.3 $\mu C/cm^2$, P_r of 17.1 $\mu C/cm^2$, E_c of 133 kV/cm, and d_{33} of 175 pm/V. This NKN film showed the lowest leakage current, which can be explained by the Schottky emission mechanism. The Schottky barrier heights of the Pt/NKN and NKN/SNO/Pt interfaces were calculated to be 1.08eV and 0.45eV, respectively. The results of this work suggest a new method to grow crystalline thin films at low temperatures by using metal oxide nanosheets as the seed layer.

3:15 PM

(EMA-S2-030-2019) $AgNbO_3$-based Lead-free Antiferroelectrics for Energy Storage Applications

J. Gao*[1]; L. Zhao[2]; Y. Zhang[1]; Q. Liu[1]; S. Zhang[3]; J. Li[1]

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2. Hebei University, China
3. University of Wollongong, Australia

Antiferroelectric materials with double hysteresis loops are favorable for energy storage due to their large polarization and small remanent polarization. Despite the good energy storage performance achieved in lead-based antiferroelectric ceramics, the growing environmental concerns stimulate the research about lead-free alternatives. Recent studies have been focused on $AgNbO_3$, which has been confirmed to be antiferroelectric. In this work, pure AgNbO$_3$ ceramics were fabricated using conventional solid-state method. The antiferroelectric phase stability of AgNbO$_3$ ceramics was investigated and the antiferroelectric-ferroelectric phase transition with both electric field and temperature dependence was discussed in detail. Through further modification with Ta$_2$O$_5$ and WO$_3$, it was found that besides tolerance factor, other factors including the polarizability of the cations may play a decisive role in determining the phase stability of AgNbO$_3$-based ceramics. A- and B-site doping would cause local structure variation and consequently affect the dielectric property of AgNbO$_3$ ceramics. As a result of enhanced antiferroelectric phase stability, a high energy density of 4.4 J/cm^3 was achieved in doped AgNbO$_3$ ceramics. These findings may provide the paradigm to tailor properties of the AgNbO$_3$-based materials through structure manipulation and pave a way for further development of lead-free energy storage materials.

Advanced Electronic Materials: Lead free II

Room: Orange A
Session Chair: Jing-Feng Li, Tsinghua University

4:00 PM

(EMA-S2-031-2019) Robust Dielectric/Ferroelectric Response in 2D Perovskite Nanosheets (Invited)

B. Li*[1]; M. Osada[2]; T. Sasaki[2]

1. Wuhan University of Technology, Center for Smart Materials and Devices, China
2. National Institute for Materials Science, WPI-MANA, Japan

Atomic-scale control of intriguing physical properties in ultrathin perovskites is an important challenge for exploring new physics and device functionality at atomic dimension. Here, we demonstrate atomic-scale engineering of dielectric responses using two-dimensional (2D) homologous perovskite nanosheets (Ca$_2$Na$_{m-3}$Nb$_m$O$_{3m+1}$; m = 3–6), which are synthesized by delaminating Dion-Jacobson layered perovskites via soft-chemical exfoliation. In this homologous 2D material, the thickness of perovskite layers can be incrementally controlled by changing m, and such atomic layer engineering enhances the high-k dielectric response and local ferroelectric instability. The end member (m = 6) attains a high dielectric constant of 470, which is the highest among all known dielectrics in the ultrathin region (< 10 nm). The stable high-k dielectric response and highly insulating nature ($J < 10^{-7}$ A cm^{-2}) remained substantially unchanged in a wide temperature range of -50 to 600 ºC. These results suggest that 2D perovskite nanosheets could act as a building block to construct high-k ferroelectrics and multiferroics for use in ultra-scaled high-density capacitors and post-graphene technology.

4:30 PM

(EMA-S2-032-2019) Fabrication of <110>-oriented 0.85(Bi$_{0.5}$Na$_{0.5}$)TiO$_3$-0.15BaTiO$_3$ ceramics by a reactive templated grain growth method and thier electric properties (Invited)

I. Fujii*[1]; K. Kawachi[1]; S. Ueno[1]; S. Wada[1]

1. University of Yamanashi, Japan

<110>-oriented ceramics with the composition of 0.85(Bi$_{0.5}$Na$_{0.5}$)TiO$_3$-0.15BaTiO$_3$ with a high Curie temperature of ~250 ºC were successfully fabricated by reactive templated grain growth of layered hydrogen titanate platelets with (Bi$_{0.5}$Ti$_{0.5}$)TiO$_3$ and BaCO$_3$ matrix powders. A large degree of <110> orientation F_{110}= 84% was achieved by decreasing green sheet thickness and application of pressure on a compact during sintering. Consequently, improved remanent polarization was observed in the ceramics compared with randomly oriented ceramics, owing to easier polarization switching. A piezoelectric constant d_{33} of 103 pC/N and an electromechanical coupling factor k_{33} of 0.44 were obtained for the <110>-oriented ceramics.

5:00 PM

(EMA-S2-033-2019) Fatigue Mechanisms of Lead Free (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-BaTiO$_3$ Piezoceramic System

X. Shi*[1]; N. Kumar[1]; M. Hoffman[1]

1. University of New South Wales, School of Materials Science & Engineering, Australia

The (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-BaTiO$_3$-(K$_{1/2}$Na$_{1/2}$)NbO$_3$ (BNT-BT-KNN) relaxor ferroelectrics exhibit attractive piezoelectric properties, accompanied by a phase transformation from relaxor to ferroelectric phase with external electric field. The electric field-temperature (E-T) phase diagrams were constructed using polarization hysteresis measurements and used to design electrical fatigue measurements to gain greater insight into fatigue mechanisms. Fatigue measurements were performed under different conditions on three representative compositions (94BNT-6BT, 88BNT-12BT, 91BNT-6BT-3KNN). Non-stoichiometry was also introduced in these samples to study the influence of point defects on fatigue. It was observed that during initial electrical cycles at high fields, domain wall pinning by point defects dominate fatigue, where piezoelectric properties could be fully restored on annealing. On further cycling, electrode damage and "dead layer" formation were observed, leading to permanent damage. Further, samples with less oxygen vacancies showed "fatigue-free" behavior due to reduced domain wall pinning. Similarly, ergodic relaxors with unstable domain structures, exhibited less severe fatigue behavior.

5:15 PM

(EMA-S2-034-2019) Lead-free Bi$_{0.5}$Na$_{0.5}$TiO$_3$-BaTiO$_3$ epitaxial films: Thickness-dependent phase transition and piezoelectricity

Z. Zhou*[1]; J. Li[1]

1. Tsinghua University, School of Material Science and engineering, China

Solid-solution (1-x%)Bi$_{0.5}$Na$_{0.5}$TiO$_3$–x%BaTiO$_3$(BNT-BT$_x$) is one of the most promising candidates for lead-free piezoelectrics. The morphotropic phase boundary at x=6, where the piezoelectricity reaches a maximum, separates a rhombohedral phase (x<6) and tetragonal phase (x>6). In this work, we investigated the phase structures and piezoelectricity of the BNT-BT$_x$(x=2,6,11,15) epitaxial thin films with different thickness on Nb:SrTiO$_3$ substrates to achieve an enhanced piezoelectricity at the phase boundary through stress control. As x increases, the lattice parameter of BNT-BT$_x$ increased and exceeded that of SrTiO$_3$. Thus the residual stress subject to substrate changed from tensile to compressive stress, resulting in different thickness-dependent phase transitions from composition to composition. For BNT-BT$_2$, increasing thickness led to a phase transition from monoclinic to rhombohedral phase and the piezoelectricity reached the maximum at ~200nm. For BNT-BT$_6$, the stress relaxed and the piezoelectricity boosted when thickness was over ~200 nm. For BNT-BT$_{11}$, since its lattice parameter was too close to the SrTiO$_3$, no significant thickness-dependent change in phase and piezoelectricity was observed. While for BNT-BT$_{15}$, all films kept a tetragonal phase. A decrease in c/a ratio with increasing thickness due to the stress relaxing resulted in a gradually enhanced piezoelectricity.

S4: Complex Oxide Thin Film Materials Discovery: From Synthesis to Strain/Interface Engineered Emergent Properties

Functionality: Ferroic I

Room: Orange B
Session Chairs: Er-Jia Guo, Beijing National Laboratory for Condensed Matter Physics; Qiyang Lu, Oak Ridge National Laboratory

10:00 AM

(EMA-S4-017-2019) Root causes of ferroelectricity in doped HfO_2 (Pioneer talk) (Invited)

U. Schroeder*[1]; T. Mittmann[1]; T. Schenk[2]; A. Kersch[4]; J. LeBeau[3]; E. D. Grimley[3]; J. L. Jones[3]; T. Mikolajick[1]

1. Namlab gGmbH, Ferroelectrics, Germany
2. Luxembourg Institute of Science and Technology, Luxembourg
3. North Carolina State University, Materials Science & Engineering, USA
4. Hochschule München, Germany

Ferroelectric behavior of thin, doped hafnium oxide films caused by a non-centrosymmetric orthorhombic phase was reported recently. Continuous research was ongoing to understand the root cause of this so far unknown phase. Accordingly, the ferroelectric properties and crystal structure of doped HfO_2 thin films were investigated for material parameters, processing conditions and at different temperatures. Piezo-response force microscopy (PFM) in conjunction with transmission electron microscopy (TEM) measurements revealed a domain size in the order of single grains with a grain diameter of ~20-30 nm in lateral and the physical film thickness in horizontal direction. Some of these grains showed an orientational relationship mainly to the bottom electrode. A qualitative model describing the influence of basic parameters like stress, dopant and oxygen vacancy concentration, surface and interface energy of grains, on the crystal structure of HfO_2 was proposed. Ab initio simulations confirmed the influence of various factors on the phase stability. In addition, the influence of these parameters on the field cycling behavior was examined. This revealed the wake-up effect in doped HfO_2 to be dominated by a combination of interface-induced effects and field induced phase transitions.

10:30 AM

(EMA-S4-018-2019) Field cycling improvement of HfO_2 based ferroelectric capacitors using IrO_2 electrodes

T. Mittmann*[1]; M. H. Park[2]; L. Pintilie[3]; T. Mikolajick[4]; U. Schroeder[1]

1. namlab, Germany
2. Pusan National Unoversity, School of Material Science and Engineering, Republic of Korea
3. National Institute of Materials Physics, Romania
4. TU Dresden, Chair of Nanoelectronic Materials, Germany

Perovskite ferroelectric memories provide nanosecond swichting and non-volatile retention. However, due to their poor compatibility to CMOS technology and limited scalability, memory array sizes are limited. The discovery of ferroelectric properties in doped hafnium oxide thin films eliminates these problems. Hafnium oxide based ferroelectric capacitors (FeCap) and ferroelectric field effect transistors are promising devices for emerging memory applications. But these devices still struggle with problems like wake up effect and early breakdown during field cycling. The typically used TiN/HfO_2/TiN FeCap stack offers good ferroelectric properties, but the formation of an interface at the electrodes affects these properties negatively. In perovskite ferroelectric memories reliability issues could be solved e.g. by using oxide electrodes. In this study the advantages and disadvantages of IrO_2 electrodes for hafnium oxide FeCaps will be investigated. According structures were prepared and characterized electrically and structurally (TEM, SEM, XRD) with regard to their ferroelectric properties. Here IrO_2 electrodes and oxygen anneals could improve the field cycling endurance at even higher remanent polarization.

10:45 AM

(EMA-S4-019-2019) Time Dependence of Pyroelectric Response in Ferroelectric $Hf_{0.58}Zr_{0.42}O_2$ Films

S. W. Smith*[1]; M. Henry[1]; M. Rodriguez[1]; J. Ihlefeld[2]

1. Sandia National Laboratories, USA
2. University of Virginia, Department of Materials Science and Engineering, USA

HfO_2 based ferroelectrics are a promising family of ferroelectrics stable as thin films. The ferroelectric response in HfO_2 thin films is associated with a metastable orthorhombic phase, typically seen in films < 30 nm thick, stabilized by doping, electrode material, deposition conditions and annealing. Thin HfO_2 based ferroelectrics are attractive for use in memory, energy harvesting, and sensing applications, however the polarization response of the thinnest of these films, <~5 nm, has been reported to be unstable over time. In this work we show that the pyroelectric response of 5 nm $Hf_{0.58}Zr_{0.42}O_2$ with TaN electrodes decreases logarithmically after biasing, decreasing from an initial value of -58 $\mu Cm^{-2}K^{-1}$ to ~-40 $\mu Cm^{-2}K^{-1}$ in the first 24 hours. While films 10 nm and thicker have a pyroelectric response that is constant on the same timescale. 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.

11:00 AM

(EMA-S4-020-2019) Polarization and permittivity dependence on electrode stress for ferroelectric $Hf_{0.58}Zr_{0.42}O_2$ films

S. S. Fields*[1]; S. W. Smith[2]; M. Henry[2]; S. L. Wolfley[2]; M. Rodriguez[2]; P. S. Davids[2]; J. Ihlefeld[1]

1. University of Virginia, Department Materials Science and Engineering, USA
2. Sandia National Laboratories, USA

We report on the electrode film stress dependence of remanent polarization (P_r), wake-up cycling behavior, phase assemblage, and permittivity (ε_r) in 20 nm thick $Hf_{0.58}Zr_{0.42}O_2$ (HZO) films. Atomic layer deposited 20 nm HZO films were prepared between TaN top and bottom electrodes. TaN films were rf magnetron sputtered with controlled stress states varied (-1455 to 234 MPa) by altering background pressure such that the bottom (top) electrode was near-neutral and the top (bottom) varied across the stress range. P_r values were found to increase with wake-up cycling and correlate with stress magnitude in both the top and bottom varied capacitor series. The most extreme stress states demonstrated P_r values 1.2 and 0.6 $\mu C/cm^2$ larger than the neutral stress state, respectively. Qualitative phase assemblages, as assessed by grazing incidence x-ray diffraction, reveal stress dependent trends. Films with the largest magnitudes of stress possessed the lowest concentration of monoclinic phase and highest concentration of tetragonal/orthorhombic phases. Low field permittivity measurements indicated the highest stress samples possessed the largest ε_r values, consistent with high volume fractions of ferroelectric phases. Our results demonstrate that large tensile and compressive electrode stress values can aid in stabilizing the ferroelectric phase of HZO.

Functionality: Ferroic II

Room: Orange B

Session Chairs: Mikel Holcomb, West Virginia University; Mimoun El Marssi, Université de Picardie Jules Verne

11:15 AM

(EMA-S4-021-2019) Interfaces in oxide quantum heterostructures (Pioneer talk) (Invited)

H. Lee*[1]

1. Oak Ridge National Lab, USA

The controlled synthesis of quantum oxide heterostructures provides tremendous opportunities in producing materials with remarkable physical properties and functionalities. We have successfully synthesized superlattices and heterostructures composed of 3d and 5d transition metal oxides (TMOs) by pulsed laser epitaxy. These material systems are an ideal test bed to take the advantage of the strong correlation in 3d TMOs and the spin orbit coupling in heavy-element 5d TMOs. To manipulate the Dzyaloshinskii-Moriya interaction in 3d-5d heterostructures, we engineered the interfaces between 3d and 5d TMOs, in such way to break the inversion symmetry. We will present our observations on exotic quantum phenomena, including charge transfer induced interfacial magnetism and topologically non-trivial spin textures, that are not present in the constituent materials. We will also present work on the creation and strain control of oxygen vacancies in various oxides, including $LaNiO_3$, VO_2/TiO_2, and CeO_2/Y_2O_3 heterostructures. This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division and through the Computational Materials Sciences Program.

11:45 AM

(EMA-S4-022-2019) Nanoscale Ferroelectric Switching Dynamics and Through-Thickness Mapping of $CoFe_2O_4$ and $BiFeO_3$ Vertically Aligned Nanocomposites

M. Martin*[1]; R. Cordier[1]; J. Steffes[1]; A. Chen[2]; B. Huey[1]

1. University of Connecticut, USA
2. Los Alamos National Lab, USA

Vertically Aligned Nanocomposite (VAN) thin films of magnetic $CoFe_2O_4$ and ferroelectric $BiFeO_3$ are promising because the distinct phases are laterally patternable, lateral epitaxy can be maintained, and therefore they allow tunable magnetoelectric coupling. To better understand their multiferroic properties, CFO/BFO VAN's are investigated with piezoforce microscopy. In particular, we map ferroelectric switching as a function of bias and time. Piezoelectricity through the thickness of the VAN's is also now uniquely available. These investigations visually and statistically reveal the influence of the strained CFO/BFO vertical interfaces, both on BFO polarization as well as domain nucleation and growth dynamics.

12:00 PM

(EMA-S4-023-2019) Effect of doping on the pyroelectric properties of sputtered PZT films

A. Berenov*[1]; L. Allers[3]; B. Moffat[2]; J. Phair[2]; P. K. Petrov[1]; R. Whatmore[1]

1. Imperial College London, Materials, United Kingdom
2. Pyreos Limited, United Kingdom
3. Korvus Technology Ltd, United Kingdom

Ceramic thin films of lead zirconate titanate (PbZrxTi1-xO3 - PZT) are extensively used in numerous applications such as piezoelectric MEMS, temperature, motion detection; energy harvesting and electrocaloric cooling. PZT films are attractive for the pyroelectric applications as they exhibit large pyroelectric coefficient, small dielectric constant and low dielectric losses. In this work the effect of doping on pyroelectric performance of PZT films is evaluated. Series of Nb and Mn doped PZT (up to 10 at.%) films were grown by co-deposition from a single ceramic PZT target and metallic targets by RF and DC magnetron sources, respectively. The effect of the deposition conditions such as substrate temperature (500 – 650 °C), gas atmosphere and sputtered material fluxes, on the film chemical composition, phase formation and film epitaxy were established. The formation if detrimental pyrochlore phase was inhibited by the pre-deposition of intermetallic seed layer. The dielectric/ferroelectric/pyroelectric properties of doped PZT films were studied as a function of doping and temperature and related to the defect model of aliovalently doped perovskites. Acknowledgements This work was supported by Innovate UK under Project "Advanced manufacturable sputtering of high performance pyroelectric thin films (HiPer-Spy)", Ref No: 103525.

12:15 PM

(EMA-S4-024-2019) Smearing of antiferroelectric phase transition and emergence of new structures in $PbZrO_3$ epitaxial thin films

R. Burkovsky*[1]

1. Peter the Great St. Petersburg Polytechnic University, Physical Electronics, Russian Federation

Antiferroelectric (AFE) perovskites find applications in sensors, energy storage devices and prospective types of non-volatile memory. We report on the study of temperature-induced phase transitions in epitaxial thin films of a prototypical antiferroelectric $PbZrO_3$ using X-ray and dielectric characterization techniques. The $PbZrO_3/SrRuO_3/SrTiO_3$ heterostructures with PbZrO3 thickness range from 25 to 1000 nanometers were synthesized at UC Berkeley and characterized at ID03 beamline of ESRF using grazing-incidence diffraction and diffuse X-ray scattering. This allowed for the first time to study temperature dependences of finite-wavevector order parameters (AFE, incommensurate, antiferrodistortive) and relevant critical dynamics in these objects. We have identified the effect of smearing of AFE transition on decreasing the thickness of the film, tentatively similar to the extensively studied phenomenon of smearing of ferroelectric transitions. The AFE smearing requires a different type of explanation, because the AFE order parameter does not couple directly to the interface-induced homogeneous electric field, which is typically responsible for ferroelectric smearing. We explore alternative scenarios, including the competition with the intermediate high-temperature ferroelectric phase and influence of nanoscale inhomogeneity due to large substrate/film lattice mismatch.

Controlled Synthesis III

Room: Orange B

Session Chairs: Guus Rijnders, University of Twente; Paul Rogge, Drexel University

2:00 PM

(EMA-S4-025-2019) Single-crystal high entropy perovskite oxide epitaxial films

Y. Sharma*[2]; B. Musico[1]; X. Gao[2]; C. Hua[2]; H. Lee[2]; V. Keppens[1]; T. Ward[2]

1. University of Tennessee, Department of Material Science and Engineering, USA
2. Oak Ridge National Lab, USA

Recently, entropy-stabilized oxides with rock-salt, perovskite, and spinel structures have been synthesized and promised to open many new functional opportunities. However, these synthesis efforts have been limited to bulk ceramics. Here, we demonstrate the ability to grow ABO_3-type high entropy perovskite oxide (HEPO) thin films with 5 cations residing on the B-site sublattice as phase pure single crystals. Pulsed laser epitaxy is used to grow the configurationally disordered HEPO perovskite, $Ba(Zr_{0.2}Sn_{0.2}Ti_{0.2}Hf_{0.2}Nb_{0.2})O_3$, epitaxially on $SrTiO_3$ and MgO substrates. X-ray diffraction and scanning transmission electron microscopy demonstrate that the films are single phase with excellent crystallinity and atomically abrupt interfaces. Atomically resolved electron-energy-loss spectroscopy mapping shows a uniform and random distribution of all B-site cations. The ability to stabilize perovskites with this level of configurational disorder offers new possibilities for designing materials from a much broader combinatorial cation pallet while providing a fresh avenue for fundamental studies in strongly correlated quantum materials. We will close by discussing how the capability to select designer combinations of B-site stoichiometries offers new potentials to tailoring materials' properties and speculate on the possibilities of discovering previously unobserved disorder-driven physical responses.

2:15 PM

(EMA-S4-026-2019) Spectroscopic Characterization of Epitaxial $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$ Thin Films

G. N. Kotsonis*[1]; C. M. Rost[3]; B. Wang[2]; J. Maria[1]

1. Pennsylvania State University, Materials Science and Engineering, USA
2. Pennsylvania State University, Electrical Engineering, USA
3. University of Virginia, Mechanical and Aerospace Engineering, USA

Single-phase, epitaxial thin films of the composition $Mg_{0.2}Ni_{0.2}Co_{0.2}Cu_{0.2}Zn_{0.2}O$ were grown using pulsed-laser deposition and characterized optically using variable angle spectroscopic ellipsometry. A pronounced structural transformation occurs as a function of substrate temperature accompanied by a ~17% change in the dielectric permittivity at near-infrared frequencies. The direct band gap of all films lies in the visible region, shifting by a total of 0.5 eV across the substrate temperature range investigated. The large dielectric tunability implies a fundamental change in the electronic structure of $Mg_{0.2}Ni_{0.2}Co_{0.2}Cu_{0.2}Zn_{0.2}O$ films as a function of deposition temperature.

2:30 PM

(EMA-S4-027-2019) Defect and disorder driven dielectric properties of entropy-stabilized oxides

S. Chae*[1]; Z. Wang[2]; J. Schwartz[1]; L. Williams[1]; S. Novakov[1]; P. B. Meisenheimer[1]; D. Schlom[2]; R. Hovden[1]; E. Kioupakis[1]; J. Heron[1]

1. University of Michigan, Materials Science and Engineering, USA
2. Cornell University, USA

Entropy-stabilized oxides (ESO) are a solid solution of five or more binary oxides in a single lattice, stabilized by the large configurational entropy from cationic disorder. Due to their tunable chemical heterogeneity and intrinsic disorder, ESO are expected to demonstrate novel functional behavior. Point defects in oxides, however, can have a strong influence on functional properties, yet an understanding of point defects in ESO is unknown. Here we present on a theoretical and experimental investigation of point defects and disorder in (MgCoNiCuZn)O-based ESO using density functional theory (DFT) and dielectric measurements. We theoretically predicted that the thermodynamic stability of vacancies in ESO strongly depends on their nearest-neighbor configuration, indicating that the types and concentrations of defects can be tuned by the composition of cations, particularly Cu. Our calculated dielectric constant varies depending on vacancy and cation composition. To experimentally characterize these materials, we have integrated single crystalline entropy-stabilized oxide thin films into vertical capacitor devices by using $MgO/SrTiO_3$ buffered conductive Si substrates and performed dielectric testing over a wide range of frequencies. We varied the composition of the films and observed the effect of local lattice distortion that arises from the composition of Cu on the dielectric behavior of ESO.

2:45 PM

(EMA-S4-028-2019) Lateral anionic heterostructures in oxide films via lithographically-defined topochemical reactions

B. M. Lefler*[1]; S. May[1]

1. Drexel University, Materials Science and Engineering, USA

Heterostructured materials are of interest for anisotropic media and photonic and optoelectronic applications. Epitaxial film deposition techniques allow for precise control of vertically-layered superlattices to elicit complex phenomena. However, there are limited routes to synthesize laterally heterostructured materials. Here, we present a thin film technique offering post-growth anionic patterning of single crystal films with the geometric control of lithography while maintaining the crystalline integrity of the films. Metal-dielectric lateral heterostructures derived from $SrFeO_{3-\delta}$, including patterns of $SrFeO_{2.5}/SrFeO_3$ and $SrFeO_{2.5}/SrFeO_2F$, are prepared through post-growth topotactic reactions with periodic feature sizes of 4-200 μm. X-ray diffraction and optical ellipsometry confirm the coexistence of phases which retain their pure-phase properties, while a 3-order of magnitude electronic anisotropy is achieved in resistance measurements parallel and perpendicular to the striped superstructure at room temperature. Transience of the superstructures is also achieved through thermal reduction. This broadly applicable approach opens the door to engineering tunable anisotropic electronic, optical, ionic, and thermal properties in oxide heterostructures with the geometric specificity afforded by lithography and the chemical flexibility enabled by topochemical reactions.

3:00 PM

(EMA-S4-029-2019) Growth of epitaxial oxide thin films on Graphene

B. Zou*[1]; C. Walker[1]; K. Wang[1]; V. Tileli[1]; O. Shaforost[1]; N. Harrison[2]; N. Klein[1]; N. Alford[1]; P. K. Petrov[1]

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

Graphene has attracted great interests because of its outstanding electronic, optical and physical properties. For developing industry-attractive graphene based devices, high quality oxide thin films are required on the surface of graphene. The development of technology for fabrication of oxide on graphene structures is essential for the realization of those graphene based devices. Therefore, it is necessary to develop a method for deposition of atomically uniform oxide layers without damaging the underlying graphene and without creating high interface defect density between the graphene and oxide materials. Here we show a mechanism, supported by first principles simulation and structural characterisation results, for the growth of oxide thin films on graphene. We describe the growth of epitaxial SrTiO3 (STO) thin films on a graphene and show that local defects in the graphene layer (e.g. grain boundaries) act as bridge-pillar spots that enable the epitaxial growth of STO thin films on the surface of the graphene layer. This study, and in particular the suggestion of a mechanism for epitaxial growth of oxides on graphene, offers new directions to exploit the development of oxide/graphene multilayer structures and devices.

3:15 PM

(EMA-S4-030-2019) $BiFeO_3$ film growth conditions: Effects on strain, interface and functional properties

P. Vilarinho*[1]; M. Tomczyk[1]; A. Tkach[1]; I. M. Reaney[2]

1. University of Aveiro, Department of Materials and Ceramics, Portugal
2. University of Sheffield, Materials Science and Engineering, United Kingdom

Interface engineering is a smart way to design properties and overcome size reduction effects in complex oxide thin-films. Rich in properties and functionality $BiFeO_3$ (BFO) is a relevant lead-free single-phase multiferroic. Monophasic BFO is extremely difficult to prepare due to the thermodynamics and kinetics of $Bi_2O_3–Fe_2O_3$ system. Compositional instability, often resulting in variation in functional properties, is a major obstacle to full practical utilization.

Moreover electrical response of ferroelectric capacitors is not only affected by ferroelectric films intrinsic nature but also by the interface with the conducting layer underneath. In this work strain, microstructures, and interface controlled performance is addressed in BFO films grown by chemical solution deposition on a range of conducting layers. ADF imaging, STEM, HRTEM, EDX and grazing incident XRD were used to analyze structure, microstructure, phase formation and strain induced defects of BFO thin-films on Pt/TiO_2/SiO_2/(100)Si, $LaNiO_3$(LNO)/Pt/TiO_2/SiO_2/(100)Si and IrO_2/TiO_2/SiO_2/(100)Si. Ferroelectric hysteresis, current loops, leakage current measurements were used to characterize the electrical functionality. Interface -based reduced coercivity and leakage currents of BFO films are presented and discussed. BFO/LNO interfaces enhance crystallinity and orientation reflected in optimization of BFO films functional properties

Functionality at Oxide/Metal Interface

Room: Orange B

Session Chairs: Yogesh Sharma, Oak Ridge National Laboratory; George Kotsonis, The Pennsylvania State University

4:00 PM

(EMA-S4-031-2019) Layer-resolved Determination of Built-in Potentials at the n-$SrTiO_{3-d}$/p-Ge(001) and n-$SrNb_{1-x}Ti_xO_{3-d}$/i-Si(001) Heterojunctions

S. Chambers*[5]; P. Sushko[5]; Y. Du[1]; S. R. Spurgeon[2]; M. Bowden[4]; N. F. Quackenbush[3]; J. C. Woicik[3]; J. H. Ngai[6]; Z. Lim[6]; M. Chrysler[6]; Z. Zhu[4]; J. LeBeau[7]; A. Penn[7]; T. Lee[8]; J. M. Ablett[9]

1. Pacific Northwest National Laboratory, Physical Sciences Division, USA
2. Pacific Northwest National Laboratory, Energy and Environment Directorate, USA
3. National Institute of Standards and Technology, Materials Measurement Science Division, USA
4. Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, USA
5. Pacific Northwest National Laboratory, Physical and Computational Sciences Directorate, USA
6. University of Texas at Arlington, Department of Physics, USA
7. North Carolina State University, Materials Science & Engineering, USA
8. Diamond Light Source, United Kingdom
9. Soliel Light Source, France

Crystalline oxides on Group IV semiconductors have been of interest in the past primarily for their potential utility as high-k gate dielectrics. In this context, insulating oxides have been the focus, and band alignments with large offsets at both the valence and conduction band edges have been sought in order to minimize gate leakage. However, the ease with which $SrTiO_3$ can be n-doped with V_O, La_{Sr}, or Nb_{Ti} creates new possibilities for novel interface physics and device concepts. We have been investigating both perpendicular and lateral transport in heterojunctions consisting of n-$SrTiO_3$ (STO) on p-Ge and solid solutions of n-$SrNb_xTi_{1-x}O_3$ (SNTO) on intrinsic Si, and seeking to directly measure band edge profiles that drive the observed transport properties. To this end, we have employed hard x-ray photoemission spectroscopy (HAXPES) and have developed a new method of data reduction whereby the depth dependences of the valence band maxima and conduction band minima in both the oxide and the Group IV semiconductor can be extracted from core-level spectra. In this talk, I will present results for these investigations which have revealed completely unexpected interface physics, yet generate potential profiles that explain the observed transport data quite satisfactorily.

4:15 PM

(EMA-S4-032-2019) Interfacial structures and built-in field at the n-$SrTiO_3$(001)/p-Ge(001) heterojunctions

P. Sushko*[1]; Y. Du[1]; S. R. Spurgeon[2]; M. Bowden[3]; J. M. Ablett[4]; T. Lee[5]; N. F. Quackenbush[6]; J. C. Woicik[6]; S. Chambers[1]

1. Pacific Northwest National Laboratory, Physical Sciences Division, Physical & Computational Sciences Directorate, USA
2. Pacific Northwest National Laboratory, Energy and Environment Directorate, USA
3. Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, USA
4. L'Orme des Merisiers, Synchrotron SOLEIL, France
5. Diamond Light Source, United Kingdom
6. National Institute of Standards and Technology, Materials Measurement Science Division, Material Measurement Laboratory, USA

The properties of structurally and compositionally well-defined epitaxial oxide/semiconductor heterojunctions are of considerable interest for both fundamental and applied research. Due to the sizeable lattice mismatch between SrTiO3 (STO) and Ge, STO epitaxial films on Ge may exhibit ferroelectric distortions. Our ab initio calculations reveal that the STO/Ge interface has two most stable structures: in one case the interfacial layer is formed by 0.5 ML of Sr and, in the other, by a TiO plane. In both cases, the interface is stabilized by the transfer of two electrons per interface Ge atom into the substrate and by the formation of Ge-Sr and Ge-Ti bonds. Epitaxial STO films deposited on Ge using molecular beam epitaxy, and characterized using transmission electron microscopy, exhibit both of these structures as well as anti-phase boundaries (APBs) separating corresponding regions of the film. Yet, no indication of these two distinctly different structural motifs resulting in different valence band offsets were found. Ab initio modeling shows that the calculated valence band offsets associated with these structures are the same and in quantitative agreement with experiment if STO films are assumed to contain oxygen vacancies. We discuss how composition control at the growth stage can be used to control relative fractions of these interfacial motifs and the density of APBs.

4:30 PM

(EMA-S4-033-2019) Strontium titanate ($SrTiO_3$): A complex oxide substrate for thin films and heterostructures with emergent properties (Pioneer talk) (Invited)

A. Hebard*[1]; H. Jin[1]; X. Zhu[1]

1. University of Florida, Physics, USA

We discuss here two manifestations of unexpected emergent behavior when strontium titanate ($SrTiO_3$) is used as a substrate for the preparation of thin films or thin-film heterostructures. In the first example, 60 nm-thick thin films of insulating ferromagnetic stoichiometric $BiMnO_3$ are grown with an (001) orientation using pulsed laser deposition. The films grow with an islanded morphology that gives rise to extrinsic relaxor ferroelectricity, which is not present in centrosymmetric bulk perovskite $BiMnO_3$. In addition to this unexpectedly robust extrinsic ferroelectricity, we also observe a strong magnetoelectric coupling that is especially pronounced in the region where the ferromagnetic and ferroelectric transitions simultaneously occur. SrTiO3 (STO) can also be made semiconducting and even metallic using high temperature anneals to create oxygen vacancies. We have found that metals or exfoliated flakes of van der Waals crystals when contacted to semiconducting oxygen-vacancy-doped STO can form high quality Schottky barriers. Noise and temperature-dependent capacitance measurements are used to identify the energy states of the defects associated with oxygen vacancies and utilize this information to tune growth parameters with the goal of engineering novel electronic and optoelectronic applications.

5:00 PM

(EMA-S4-034-2019) Characterization of defects in metal/$SrTiO_{3-\delta}$ Schottky-like junctions

H. Jin*[1]; X. Zhu[1]; A. Hebard[1]

1. University of Florida, Physics, USA

Heterojunctions based on $SrTiO_3$ (STO) serve as an important platform for both exploring emergent phenomena and developing novel devices. Lying near the STO interface, the defects that are mainly associated with oxygen vacancies could either determine or alter the junction properties. Accordingly, knowledge of the ubiquitous defects are critical for the fabrication and further understanding of STO related junctions. Here we present a comparative study of Schottky-like junctions formed at the interface of gold (Au) and oxygen-deficient STO prepared by various thermal reduction processes. Using temperature-dependent capacitance measurements and low frequency noise spectroscopy, we find that higher annealing temperatures in general increase the concentration of free carriers and the defects that predominantly reside near 0.5 eV below the STO conduction band minimum. Those deep level defects are probably due to the formation of oxygen vacancy complexes. We also find that a shorter annealing duration induces more vacancies and associated inhomogeneity, which is evidenced by the larger reverse bias leakage current and forward bias noise intensity.

5:15 PM

(EMA-S4-035-2019) First-principles analysis of interface capacitance in metal/dielectric/metal capacitors

D. Hirai*[1]; A. Honda[1]

1. Murata Manufacturing Co., Ltd., Japan

Due to the strong demand for small-sized multi-layer ceramic capacitor (MLCC) with high capacitance, extensive efforts to thin the dielectric layers have continuously been made. However, the degradation of capacitance was observed in epitaxially grown thin-film capacitors, and this is often explained by the formation of low capacitance layer across the interface, so-called the dead layer. To realize further miniaturization of MLCC with high capacitance, the origin of the dead layer must be clarified. Various theoretical analyses showed that the depolarizing field caused by the imperfect screening of metallic electrodes influences the dead layer. Although the dielectric itself is also expected to affect the depolarizing field, only a few studies have been reported. In this work, we examined the dielectric profile across the interface of the following metal/dielectric/metal structures: Pt/$SrTiO_3$/Pt, Pt/$BaZrO_3$/Pt, and Pt/MgO/Pt, by using density functional theory combined with the orbital-separation approach. As a result, we demonstrated the formation of dead layers in Pt/$SrTiO_3$/Pt and Pt/$BaZrO_3$/Pt, where the dielectric constants of $SrTiO_3$ and $BaZrO_3$ are 505 and 55, respectively. Our result suggests that even dielectrics having dielectric constant less than 100 cannot avoid the dead layer effect by thinning dielectric layer.

S5: Mesoscale Phenomena in Ferroic Nanostructures: Beyond the Thin–Film Paradigm

Mesoscale Phenomena in Ferroic Nanostructures: Beyond the Thin–Film Paradigm I

Room: Citrus B
Session Chairs: Edward Gorzkowski, Naval Research Lab; Eric Patterson, US Naval Research Lab

2:00 PM

(EMA-S5-001-2019) Strain works as "nanorobot" to synthesize novel multiferroics (Invited)

H. Lee*[1]; C. Sohn[1]

1. Oak Ridge National Lab, USA

Ferroelectricity is one of the most desired ingredients to develop functional materials. Narrow gap photovoltaics, multiferroics, and polar metals are notable examples of promising functionalities based on ferroelectrics. Here, we propose a new strategy of realizing and controlling such functional properties by using site-specific alloying and strain engineering on composite ferroelectrics. The layered ferroelectric $Bi_4Ti_3O_{12}$ is alloyed with ABO_3 (A= La, Bi) oxide perovskites [$LaBO_3$ (B = transition metal) and $BiFeO_3$]. By taking advantage of the robust ferroelectricity and the large unit cell size of $Bi_4Ti_3O_{12}$, we demonstrate that the incorporation of various perovskites in $Bi_4Ti_3O_{12}$ can make the material complementarily multifunctional. We will show examples of the reduced optical band gap, induced long-range magnetism, and modified ferroelectric properties. Furthermore, we also show that strain can be used as a nano-scale assembly tool, i.e., "nanorobot," by which one can position a transition metal at a specific position within the $Bi_4Ti_3O_{12}$ unit cell, yielding novel multiferroics. Our approach provides an excellent example of the synthesis-science driven approaches for developing novel materials with remarkable properties. This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

2:30 PM

(EMA-S5-002-2019) Ferroelectric polarization switching induced interfacial magnetic phase competitions at LSMO/PZT heterostructures

B. Paudel*[1]; I. Vasiliev[1]; M. Hammouri[2]; E. Fohtung[1]; A. Chen[3]

1. New Mexico State University, Physics, USA
2. California State University at Los Angeles, Physics, USA
3. Center for Integrated Nanotechnologies, Los Alamos National Laboratory, USA

Electric field induced magnetism manipulation in heterostructures of anti/ferromagnetic and ferroelectric layers has attracted attention in recent years due to their applications in spintronics, tunnel junctions and memory devices. With combined polarized neutron reflectometry (PNR) and density functional theory (DFT) calculations, we studied magnetoelectric coupling at the interface of $PbZr_{0.2}Ti_{0.8}O_3$ /$La_{0.67}Sr_{0.33}MnO_3$ heterostructure grown on STO (001) substrate by switching polarization direction of the PZT layer. The PNR results show that LSMO at the PZT/LSMO interface exhibit antiferromagnetic (AFM) couplings when the polarization points away from the interface. However, the interface remains ferromagnetic (FM) when the polarization points towards the interface. Along with such changes in interfacial magnetic ordering, polarization alters the global magnetization of the LSMO. LSMO magnetic moments drop significantly at the interface for negative polarization and remain intact for positive polarization, which strongly supports the PNR results. All the strain states show phases mixing of AFM with FM at interface for negative polarization, which agrees with magnetic phase evolution for tetragonal distortions. As these magnetic phases also result due to accumulation or depletion of holes in LSMO, such interfacial couplings could be both strain and charge modulated.

2:45 PM

(EMA-S5-003-2019) Nanoscale investigation of room temperature ferromagnetism in Li-doped Bismuth ferrite

Y. Sharma*[1]; R. Agarwal[2]; L. Collins[3]; A. Ievlev[3]; I. Ivanov[3]; V. R. Cooper[4]; S. Kalinin[3]; S. Hong[5]; T. Ward[5]

1. Oak Ridge National Laboratory, Materials Science & Technology Division, USA
2. Drexel University, Materials Science and Engineering, USA
3. Oak Ridge National Lab, USA
4. Oak Ridge National Laboratory, Materials Science and Technology Division, USA
5. KAIST, Materials Science, Republic of Korea

Recently, lithium (Li) doped bismuth ferrite ($BiFeO_3$) has been reported to show room temperature ferromagnetism, promising for spintronic and magnetoelectric multiferroic applications. However, the physical origin of such behavior remains unclear. Here, we present a detailed study on physical and chemical properties of $Li_xBi_{1-x}FeO_3$ (x = 0–0.05) bulk ceramics to explore the reason of ferromagnetism due to Li-doping. Using a combined approach with scanning probe microscopy (SPM), time-of-flight secondary ion mass spectroscopy, and mirco-Raman imaging techniques, we observe the formation of nanoscale clusters of spinel-lithium ferrite ($LiFe_5O_8$) as a secondary phase within the parent $BiFeO_3$. The spinel-phase forms inevitably during the synthesis process and is solely responsible for the room temperature ferromagnetic behavior. Furthermore, these clusters grow bigger, from nano to micro-scale size, with increasing Li-doping concentration which significantly enhances the bulk magnetization, as confirmed by magnetometry measurements. We will close by discussing how the Li-doping approach could be useful to design new multifunctional composites and ferroic nanostructures with tunable properties.

3:00 PM

(EMA-S5-004-2019) From local to macroscale effects of defects on ferroelectric polarisation and domain walls (Invited)

P. Paruch*[1]

1. University of Geneva, Physics, Switzerland

In ferroelectric thin films, the intrinsic configuration, growth, shape, and stability of domains with different polarisation depend crucially on the presence of defects. Using PFM, structural and compositional analysis we explore these effects. We demonstrate how defect engineering can be used via controlled growth temperature in $PbTiO_3$ thin films to control polarisation orientation. Assigning the observed effects to gradients of Pb-O divacancy defect dipoles, we show that the resulting internal electric fields modelled in a Ginzburg-Landau-Devonshire approach agree well with the experimental results obtained by the independent real space and reciprocal space techniques. In PZT thin films with different defect densities, we observe strikingly different nucleation-dominated vs. domain-wall-motion dominated switching. Tracking these over long-duration measurements, we map with single pixel fidelity the individual domain nucleation, motion and merging events which contribute to the macroscale polarisation switching, and extract their avalanche statistics.

4:00 PM

(EMA-S5-005-2019) The Role of Tubular Scaffold Network in Self-Assembled Vertically Aligned Nanocomposite Films

H. Han*[1]; T. Lookman[2]; A. Chen[1]

1. Los Alamos National Lab, USA
2. Los Alamos National Lab, Theoretical Division, USA

The perovskite complex oxides have received much interest due to the potential for numerous applications (solid-oxide fuel cells, information storage, and magnetic field sensors etc.). Here we studied lanthanum strontium manganese oxide ($La_{0.7}Sr_{0.3}MnO_3$, LSMO) which shows colossal magnetoresistivity (CMR). The magnetization can be controlled by electrostatic doping due to the correlation between electronic properties, magnetic interaction, and carrier density. Nevertheless, epitaxial strain is an alternative approach to manipulate charge and orbital degrees of freedom in complex oxide. Two-phase vertically aligned nanocomposites (VAN) have been studied to induce the strain by high density vertical phase boundaries. Although nanoscaffold network in nanocomposite plays the critical role for manipulating functionalities such as magnetism, magnetic anisotropy, and electron transport, there is still room for improvement. Here, we demonstrated that vertical lattice strain in the LSMO film matrix can be controlled by both film growth and subsequent selective etching. With partially removing the MgO pillars, the intermediate strain induced by tubular MgO significantly enhances the magnetic properties. Chemically etching in VANs provides an interesting approach to tune functionalities in oxides.

4:15 PM

(EMA-S5-006-2019) Size Controlled Functionalities in Ferroic Nanocomposites (Invited)

A. Chen*[1]; Z. Wang[2]; J. MacManus-Driscoll[3]; R. Prasankumar[1]; L. Chen[4]; J. Li[5]; T. Lookman[1]; H. Wang[6]; Q. Jia[7]

1. Los Alamos National Lab, USA
2. International Iberian Nanotechnology Laboratory, Portugal
3. University of Cambridge, Dept. of Materials Science, United Kingdom
4. The Pennsylvania State University, Materials Science and Engineering, USA
5. University of Washington, Seattle, USA
6. Purdue University, School of Materials Engineeringn, USA
7. University at Buffalo, Materials Design and Innovation, USA

To tune the functional properties of nanostructured materials such as nanoparticles and nanowires, one of the approaches is to manipulate the dimensionality of these materials. Recently, vertically aligned heteroepitaxial nanocomposites have been explored to improve the functionalities of ferroic materials where the ferromagnetism, ferroelectricity, and/or multiferroicity are the interests. In the vertically aligned nanocompistes, strain and functionalities are strongly related to the feature size of the nanopillars. In this presentation, we will first discuss the synthesis and characterization of different types of ferroic nanocomposite thin films from a perspective of strain, defect and interface. In the second part of this presentation, we will focus on how the feature size of the nanopillars can be used to tune the functional properties such as magnetism, magnetotransport in $La_{0.7}Sr_{0.3}MnO_3$:MgO and magnetoelectric coupling in $BaTiO_3$:$CoFe_2O_4$. Via a combination of controlled synthesis, advanced probing, and theoretical modeling, we are able to reveal the key role of the pillar feature size on functionalities in epitaxial ferroic nanocomposite films.

4:45 PM

(EMA-S5-007-2019) Mesoscale-level computational studies of size, shape and anisotropy effects in particulate ferroelectric-dielectric composites

D. Zhu[1]; J. Mangeri[2]; K. Pitike[1]; R. Wang[3]; P. Alpay[1]; O. Heinonen[4]; S. Nakhmanson*[1]

1. University of Connecticut, Materials Science and Engineering, USA
2. Institute of Physics, Czech Academy of Sciences, Czechia
3. Wuhan University, School of Civil Engineering, China
4. Argonne National Laboratory, USA

Ferroelectric-dielectric composite systems display a wide range of phenomena that are attractive for future technological applications, such as superparaelectricity, enhanced dielectric tunability and energy storage density, multi-state ferroelectric switching, and reduced conductivity and loss. In particulate dispersed phases, precise control of the inter-particle spacing and arrangement, particle concentration, shape morphology and surface crystallography and, as well as selection of materials for both phases, can produce structures with preprogrammed behavior and novel functionalities. Here we utilize an open-source highly scalable real-space finite-element-method based code Ferret, which is being developed by this collaboration, to study both equilibrium and field-induced properties of ferroelectric-dielectric composites. We evaluate the influence of particle size, shape and anisotropy on the material functional response and consider the cases of both noninteracting and interacting particles. The developed insights provide new routes for the design of composite metamaterials whose dielectric properties can be controlled and tuned by selecting the morphology and mutual arrangement of their ferroelectric components.

5:00 PM

(EMA-S5-008-2019) Thin film magnetoelectric resonators for magnetic field sensing (Invited)

M. Staruch*[1]; S. Bennett[1]; J. Baldwin[1]; B. Matis[1]; K. Bussmann[1]; P. Finkel[1]

1. U.S. Naval Research Laboratory, USA

Magnetoelectric (ME) devices consisting of magnetostrictive and piezoelectric materials have been of increasing interest for novel magnetic field sensors, as the direct magnetic field to electric field conversion significantly reduces power consumption to < 1 mW. Here we evaluate the resonance shift of a free-standing ME, doubly clamped micro-beam resonator for sensitive, low-power magnetic field sensing. The microfabricated resonating beam is comprised of a heterostructure of magnetostrictive FeCo and piezoelectric AlN. The magnetoelastic layer produces a shift in resonance when the device is placed in a magnetic field, which can be tracked using the piezoelectric voltage or change in inductance in the piezoelectric material. These are also compared with resonators of just the magnetostrictive phase that are driven with an external piezoelectric stack actuator. The introduction of shape anisotropy can significantly impact the magnetic properties. Using a magneto-optic indicator film technique, we are able to separately evaluate the magnetic switching behavior of the beams as well as the anchor pads. This highlights the extent to which the fabrication of magnetic micro-devices with complex patterns at different length scales will strongly affect the local magnetization and complicate analysis of bulk measurements. The effects of this on the frequency shift and magnetic field sensitivity will be presented.

S6: Complex Oxide and Chalcogenide Semiconductors: Research and Applications

Oxide Semiconductors

Room: Magnolia A
Session Chairs: Ryan Comes, Auburn University; Koustav Ganguly, University of Minnesota

10:00 AM

(EMA-S6-001-2019) Modifying the conductivity of strontium titanate by light exposure (Invited)

V. Poole[1]; J. Huso[1]; M. McCluskey*[1]

1. Washington State Unversity, USA

Strontium titanate ($SrTiO_3$) is a complex oxide with interesting physical properties. Bulk single crystals that are thermally treated exhibit persistent photoconductivity (PPC). Upon exposure to sub-band-gap photons > 2.9 eV, the electrical resistance decreases by three orders of magnitude. After the light is turned off, the heightened conductivity persists “forever” at room temperature. We attributed large PPC in $SrTiO_3$ to hydrogen impurities that absorb light and become liberated from substitutional sites in the lattice, leaving behind empty oxygen vacancies. Because oxygen vacancies in $SrTiO_3$ are shallow double donors, they contribute electrons to the conduction band. There is a significant barrier for hydrogen to return to the substitutional site, leading to metastability at room temperature. The observation of PPC in $SrTiO_3$ crystals is unique because it is large, very persistent, and occurs at room temperature. This opens up possibilities for data storage, reconfigurable electronics, and surface modification. The ability to define conductive regions on an insulating substrate without using a mask has the potential to reduce cost and enable one to reuse the same substrate for several runs. Recent experiments on $SrTiO_3$ thin films, and potential applications of this novel effect, will be discussed.

10:30 AM

(EMA-S6-002-2019) Surface Studies of $SrTiO_3$ Films Grown by Hybrid MBE

S. Thapa*[1]; M. Blanchet[1]; W. Bowers[1]; E. Roeder[2]; S. Chikara[1]; R. B. Comes[1]

1. Auburn University, Dept. of Physics, USA
2. University of Washington- Bothel, Physics, USA

Hybrid oxide molecular beam epitaxy (hMBE), where transition metal cations are delivered using a metal-organic precursor, has emerged as the state-of-the-art approach to the synthesis of electronic-grade complex oxide films. However, numerous questions remain regarding the mechanism of the growth process and the surface properties of the resulting films. To examine these properties, thin film $SrTiO_3$ (STO) was prepared by hMBE using a titanium tetraisopropoxide (TTIP) precursor for Ti delivery and an elemental Sr source on STO and $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}$ substrates with varying Sr:Ti flux ratios to examine the conditions for the reported stoichiometric growth window. The grown samples are transferred to an appended x-ray photoelectron spectroscopy (XPS) system to the MBE under UHV. XPS analysis enabled studies of the surface elemental composition in the STO samples. Ion scattering spectroscopy (ISS) measurements were also performed to correlate the XPS data with the surface termination. To compare the surface sensitive results with previously reported bulk measurements, samples were also examined using Rutherford back scattering (RBS) and x-ray diffraction (XRD) to compare with literature. These studies help to explain the mechanisms of hMBE growth and the resulting surface structure of films grown within the MBE growth window. Such results open new opportunities for the study of interfacial structures synthesized via hMBE.

10:45 AM

(EMA-S6-003-2019) Strain-Engineered Stannate Heterostructures with High Mobility (Invited)

A. Prakash[2]; B. Jalan*[1]

1. University of Minnesota, Chemical Engineering and Materials Science, USA
2. University of Minnesota, USA

Doped-$BaSnO_3$ and $SrSnO_3$ are promising materials for transparent conductors and high-power electronic applications owing to wide bandgap (~3 – 4.5 eV), high conductivity with reasonably high room temperature electron mobility, and excellent thermal stability. Materials issues limiting these functionalities include the presence of large density of threading dislocations in films including the control over cation stoichiometry. Related to this issue, strain engineering has not yet been possible in stannate films. In this talk, I will review these challenges and will present our group's effort to address these challenges using a new radical-based hybrid MBE technique. I will present a comprehensive growth, and electronic transport study of La-doped $BaSnO_3$ and $SrSnO_3$ yielding a record-high conductivity through defect management. Using a systematic MBE study, I will present the role of compressive and tensile strain on structure and transport in doped $SrSnO_3$ films. Important role of defects such as dislocations, and non-stoichiometry on electronic transport in addition to discussing different scattering mechanisms that limit the room temperature electron mobility will be discussed. Work supported by the NSF, and AFOSR YIP Program.

11:15 AM

(EMA-S6-004-2019) Mobility Optimization in High-Pressure Oxygen Sputter-Deposited Epitaxial $Ba_{1-x}La_xSnO_3$ Thin Films

K. Ganguly*[1]; W. Postiglione[1]; H. Yun[1]; J. Jeong[1]; A. Mkhoyan[1]; B. Jalan[1]; C. Leighton[1]

1. University of Minnesota, Department of Chemical Engineering and Materials Science, USA

Owing to its high 300 K mobility, exceeding 300 $cm^2V^{-1}s^{-1}$, the wide band gap perovskite $BaSnO_3$ (BSO) is of high interest in oxide electronics. Despite rapid progress, many questions remain regarding transport mechanisms and mobility limiting factors in this material, particularly in thin films. In this work, we focus on a high-throughput, potentially scalable technique: high-pressure-oxygen (~1 Torr) sputtering. High-resolution X-ray diffraction, scanning probe microscopy, and scanning transmission electron microscopy confirm phase-pure, close to stoichiometric, smooth, epitaxial $Ba_{0.98}La_{0.02}SnO_3(001)$ grown by this method. Film thickness, growth rate, deposition temperature, and substrate (i.e., lattice mismatch) have all been systematically varied, and related to mobility. 300 K mobilities over 70 $cm^2V^{-1}s^{-1}$ at 2×10^{20} cm^{-3} are obtained, even in 380-Å-thick films without a buffer layer. Important observations include a monotonic increase in mobility with deposition temperature, carrier freeze-out and decreasing mobility at low thickness, optimal mobility around 1200 Å thickness, and remarkable insensitivity to substrate mismatch. The results provide significant insight into the structure-electronic property relationships and mobility-limiting factors in BSO films. Work supported by the UMN NSF MRSEC and the DOE CQM.

11:30 AM

(EMA-S6-005-2019) Electronic and Catalytic Behavior of Mn-based Spinels Grown by Molecular Beam Epitaxy

M. Blanchet*[1]; S. Chikara[1]; A. R. Bredar[2]; B. Farnum[2]; R. B. Comes[1]

1. Auburn University, Dept. of Physics, USA
2. Auburn University, Dept. of Chemistry, USA

Previous research on manganese-based spinel structures has shown that some exhibit strong oxygen reduction reaction catalytic behavior for water splitting in hydrogen fuel cells. However, there have been limited efforts to study these materials as epitaxial thin films which can be used for surface catalysis studies. With this in mind, thin films of spinel structures such as $MnFe_2O_4$, $CoMn_2O_4$, $NiMn_2O_4$ and Mn_3O_4 were synthesized to study the relationship of electronic properties and catalytic behavior. Films were grown using a molecular beam epitaxy system which allowed for precise control of sample stoichiometry. After growth, films were transferred to an in-situ x-ray photoelectron spectroscopy system to be examined without exposure to atmosphere. In addition, measurements characterizing the films' electronic and catalytic properties such as ellipsometry and cyclic voltammetry were also performed. The combination of these studies allows for a greater understanding of these spinels and how they might be used in future catalytic applications.

11:45 AM

(EMA-S6-006-2019) Growth of the delafossite $PdCoO_2$ by molecular beam epitaxy

M. Brahlek*[1]

1. Oak Ridge National Laboratory, USA

In this talk I will discuss the growth and transport properties of thin films of the metallic delafossite oxide $PdCoO_2$ by molecular beam epitaxy (MBE). The delafossite oxides are a unique class of oxides with layered A-BO_2-A-BO_2 structure and inplane trigonal coordination. For A=Pd, and Pt this structural motif gives a natural 2D electronic behavior with inplane conductivity rivaling that of the noble metals. The key challenges, however, for the growth of $PdCoO_2$ by MBE is twofold: (1) optimizing conditions to form oxides of Pd, and (2) maintaining the correct A:B stoichiometry. The former is especially challenging since Pd is difficult to oxidize in the reducing ultrahigh-vacuum environment of MBE, thus necessitating the use of reactive atomic oxygen. Structural and transport data will be presented that highlight these challenges and how to overcome them. Optimization of these growth conditions is the first step towards creation of a new generation of layered oxide materials.

12:00 PM

(EMA-S6-007-2019) Evidence and Influence of Copper Vacancies in p-Type $CuGaO_2$ Mesoporous Films

A. R. Bredar*[1]; M. Blanchet[1]; R. B. Comes[1]; B. H. Farnum[1]

1. Auburn, University, USA

Delafossite $CuGaO_2$ nanocrystals were hydrothermally synthesized and characterized spectroscopically and electrochemically as mesoporous thin films. The nanocrystals demonstrate a preferred orientation within the film structure, as shown by enhancement of the (00l) peaks via two-dimensional powder x-ray diffraction. Annealing conditions of low and high temperature (i.e. 100-300 ºC), with oxygen and/or argon atmospheres were investigated and the resulting effect on the thin film electrochemistry was measured. Cyclic voltammetry showed an increase in non-faradaic current with higher annealing temperatures and demonstrated a quasi-reversible redox feature ($E_{1/2}$ = 0.1 V vs $Fc^{+/0}$). This feature is assigned to a Cu^{II}/Cu^{I} redox couple associated with surface defects. X-ray photoelectron and energy dispersive spectroscopies provide evidence for surface defects in the form of $Cu^{II}(OH)_2$ and copper vacancies. Electrochemical impedance spectroscopy revealed that $CuGaO_2$ films were highly conductive with $\sigma \sim 10^{-5}\Omega^{-1}$ cm^{-1}, consistent with a large density of hole carriers induced by copper vacancies. The significance of synthesis, film preparation, and annealing conditions on the presence of surface defects and large hole densities is discussed. The prevalence of such defects in delafossite $CuGaO_2$ is expected to have a large impact on the use of this material as a hole transport layer in solar cell architectures.

Chalcogenide Semiconductors

Room: Magnolia A
Session Chair: Rafael Jaramillo, Massachusetts Institute of Technology

2:00 PM

(EMA-S6-008-2019) Chalcogenide Materials and Applications: From bulk to 2D (Invited)

K. A. Morgan*[1]; I. Zeimpekis[1]; K. C. Huang[1]; Z. Feng[1]; C. Craig[1]; E. Weatherby[1]; N. Aspiotis[1]; G. Alzaidy[1]; A. Ravagli[1]; B. Moog[1]; F. Guzman[1]; A. H. Lewis[1]; M. Delaney[1]; D. W. Hewak[1]

1. University of Southampton, Optoelectronics Research Centre, United Kingdom

In this talk, we give an overview of our chalcogenide material and device capabilities and the applications they are driving, scaling from bulk glasses to two-dimensional films. Using a melt-quench technique, we routinely manufacture a family of Ga:La:S semiconducting glasses which offer considerable advantages over commercially available chalcogenides, expanding uses in defense, medical and sensing. We use these glasses to produce optical fibers using extrusion, rod and crucible drawing. We are also developing these materials further, for example by incorporating selenium resulting in improved infrared transmission, enabling both thermal and visible imaging for object recognition. Transition metal dichalcogenides (TMDCs) are promising alternatives to graphene, with bandgaps tunable through composition and number of layers. Today's challenge remains in the fabrication of large area atomically thin TMDCs on desired substrates. We have developed chemical vapor and atomic layer deposition techniques to deposit highly crystalline TMDCs, from nanometers down to a monolayer on up to 6 inch wafers. We recently developed novel patterning techniques that result in defect free devices. Our applications range from 3D photonic crystals to photovoltaics and transistors. Finally we deposit chalcogenide thin films via sputtering and demonstrate applications which exploit their phase change and thermoelectric properties.

2:30 PM

(EMA-S6-009-2019) Mechanism and Applications of Large and Persistent Photoconductivity in CdS

H. Yin*[1]; R. Jaramillo[1]

1. Massachusetts Institute of Technology, USA

Theory has suggested that anion vacancies in II-VI semiconductors are responsible for large and persistent photoconductivity (LPPC) due to negative-U behavior, whereby two minority carriers become kinetically trapped by lattice relaxation following photo-excitation. By performing a detailed analysis of photoconductivity in CdS, we provide experimental support for this negative-U model of LPPC. We also show that LPPC is correlated with sulfur deficiency. We use this understanding to vary the photoconductivity of CdS films over nine orders of magnitude by controlling chemical activities during chemical bath deposition. We then apply our knowledge of defect physics and LPPC in CdS to design selectors for resistive processing units. We make two-terminal selector devices using hole injection layers to control the charge state of sulfur vacancies, and thereby modify the film conductivity. The fabricated devices show highly non-linear current-voltage characteristics, and potential as selectors in memristor cross-point arrays for memory and neuromorphic applications. We also discuss the role of LPPC in thin film solar cells.

2:45 PM

(EMA-S6-010-2019) Shining Light on Perovskite Chalcogenides: Semiconductors for Visible to Infrared Optoelectronics (Invited)

J. Ravichandran*[1]

1. University of Southern California, Chemical Engineering and Materials Science, USA

Perovskite Chalcogenides are a new class of semiconductors, which have tunable band gap in the visible to infrared part of the electromagnetic spectrum. Besides this band gap tunability, they offer a unique opportunity to realize large density of states semiconductors with high carrier mobility. In this talk, I will discuss some of the advances made both in my research group and in the research community on the theory, synthesis of these materials and understanding of their optoelectronic properties. First, I will discuss how structure and chemical composition in Zr-containing perovskite sulfides can tune the optical properties in the visible spectrum, with an eye towards solar energy conversion. Second, I will discuss how the band gap can be further reduced to the infrared region for Ti-containing perovskite sulfides with an unique opportunity to leverage their anisotropic optical properties to achieve large linear optical properties such as birefringence and dichroism. Finally, I will provide a general outlook for future studies on these exciting new class of materials.

3:15 PM

(EMA-S6-011-2019) Chemical bonding and electronic structure analysis of layered hexagonal $ZnIn_2S_4$

J. Lee*[1]; T. Lee[1]; W. Jang[1]; A. Soon[1]

1. Yonsei University, Materials Science and Engineering, Republic of Korea

The ternary chalcogenide, $ZnIn_2S_4$ is known to exhibit various polymorphic expressions: from the cubic spinel phase to various polytypic layered hexagonal structures, commonly known as the α-, β-, II_a-, and II_b-phase. Recently, layered II_a- and II_b-$ZnIn_2S_4$ have been actively investigated due to their outstanding photocatalytic performances. However, an accurate atomistic view of these layered structures is still lacking, and the influence of van der Waals (vdW) interactions on these polytypic layered-phases of $ZnIn_2S_4$ is not well established. In this work, we systematically perform first-principles density-functional theory (DFT) calculations to study and examine the crystal structures of layered hexagonal $ZnIn_2S_4$, considering the vdW interactions. Interestingly, we propose a revised atomic structure of the II_a-phase, disputing earlier experimental reports with the support of chemical bonding analysis. Furthermore, we report the detailed electronic structure analysis of the polymorphic phases of $ZnIn_2S_4$ to provide the basis for their potential applications as a new class of high-performance photo-catalysts.

4:00 PM

(EMA-S6-012-2019) Route to topological quantum effects via defect engineering (Invited)

S. Oh*[1]

1. Rutgers, the State University of New Jersey, USA

Since the notion of topological insulator (TI) was envisioned about a decade ago, topology has become a new paradigm in condensed matter physics, as recognized in the 2016 Physics Nobel Prize awarded to three theoretical physicists who laid foundation for the current topological boom. Realization of topology as a generic property of materials has led to numerous predictions of unprecedented phenomena such as magnetic dipoles, axion electrodynamics, resistance-free conduction etc. However, only a very small subset of these predictions have been materialized in real materials. Here, I will show that defects have been the major culprit behind this slow progress. Once we suppress these defects using various thin film engineering tricks, a series of topological quantum phenomena, including quantized Faraday/Kerr rotations as evidence for axion electrodynamics, quantum Hall effects, and topological quantum phase transitions, start to emerge above otherwise murky topological ocean. I will try to convince the audience that we are now truly entering the age of topological quantum materials, but only with the ability to control defects.

4:30 PM

(EMA-S6-013-2019) First-Principle Studies of Charged Point Defects in Two-Dimensional Semiconductors

B. Rijal*[1]; R. G. Hennig[1]

1. University of Florida, Material Science and Engineering, USA

Point defects can control the electronic and optical properties of semiconductor materials. These defects can exhibit a net charge that can be tuned by an applied external potential. The computational modeling of charged point enables the prediction of the doping of semiconductors for use in devices such as solar cells, light-emitting diodes, or transistors. However, the modeling of charged defects presents challenges, notably the unavoidable presence of implicit or explicit countercharges within the simulation cell introduces electrostatic artifacts for calculations using periodic boundary conditions. In this schoolroom, we compare and benchmark the defect formation energies of vacancies and anti-sites in two-dimensional materials (MoS2, SnSe, and P) using a FNV correction method developed by Freysoldt et al. (Phys. Rev. B 97, 205425) that is based on a surrogate model for the electrostatics. We compare the results with values for the bulk materials.

4:45 PM

(EMA-S6-014-2019) Influence of zinc sulfide shell structure on hydrogen sensing properties of zinc oxide nanorod-based gas sensor

H. Chen*[1]; Y. Tsai[1]

1. National Chi Nan University, Applied Materials and Optoelectronics, USA

In this study, ZnO/ZnS core shell nanostructures were fabricated on SiO2 gas sensing chips by hydorthermal and sulfurization methods. To optimize the sensing performance the hydrogen gas sensing properties, the thickness and the growth conditions of ZnS shell were modulated. Based on multiple material analysis techniques including field-emission scanning electron microscope (FESEM), photoluminescence (PL), X-ray diffraction (XRD), transmission electron microscopy (TEM), electron spectroscopy for chemical analysis (ESCA), the thickness and the morphologies of the ZnS shell on ZnO nanorods could be adjusted. Furthermore, electrical characaterizations and gas sensing tests indicated a capacitor-like junction structure between the ZnS/ZnO interface might be formed to induce the high electric field and enhance the carrirer mobility. In addition, the hydrogen sensing capabiltiy could be boosted by varying the morphoogy of the ZnS shell. Results also show that an appropriate thickness of the ZnS shell would be preferrable for the hydrogen gas applications because a over-thick layer of ZnS shell may lengthen the carrier transition time and worsen the gas sensing capability.

5:00 PM

(EMA-S6-015-2019) Thermal Conductivity of PbTe/PbSe Superlattice Thin Films

M. E. DeCoster*[1]; X. Chen[2]; K. Zhang[2]; H. Baumgart[2]; P. E. Hopkins[1]

1. University of Virginia, Mechanical Engineering, USA
2. Old Dominion University, USA

A significant body of research exists on the improvement of the thermoelectric properties of bulk PbTe and PbSe based materials; however, the thermal properties of structured, nano-scale, thin films are studied to a lesser extent. The concept of controlling thermal energy carriers in thin film superlattices of PbTe/PbSe grown on silicon substrates is experimentally investigated in this work. We demonstrate the use of Time Domain Thermoreflectance (TDTR) to measure the cross-plane thermal conductivity of these systems in order to understand the roll of interface and boundary scattering on the thermal conductivity of ALD grown PbTe/PbSe superlattices. The thermal conductivities of a series of thin films with varying period thicknesses and total thickness resulted in reduced conductivities that clearly demonstrate superlattice effects, where the layered periodicity of the superlattice structure increases phonon boundary scattering. Additionally, we experimentally investigate the evidence of an intrinsic localized mode within the superlattice material and its effects on the overall thermal conductivity of the superlattice. Our results indicate that the ordered structure of a PbTe/PbSe superlattice reduces the lattice thermal conductivity.

S7: Superconducting and Magnetic Materials: From Basic Science to Applications

Superconducting and Magnetic Materials IV

Room: Citrus A
Session Chair: Xingjiang Zhou, National Lab for Superconductivity

10:00 AM

(EMA-S7-013-2019) Emergent two-dimensional superconductivity in few-layer stanene (Invited)

D. Zhang*[1]

1. Tsinghua University, China

Two-dimensional crystalline superconductors attract growing interests as they exhibit rich quantum phenomena such as the Griffiths singularity and an extremely large in-plane critical magnetic field. Here we report the discovery of superconductivity in few layer stanene—the ultrathin form of gray tin (111). This finding is unexpected because bulk gray tin is semi-metallic and non-superconductive. We grow high quality stanene films on PbTe/Bi_2Te_3/Si(111) substrate via molecular beam epitaxy. Superconductivity emerges in bilayer stanene and the transition temperature increases with the film thickness. We also modulate the superconducting properties by tuning the thickness of the PbTe layer. Through transport and angle-resolved photoemission spectroscopy, we reveal the two-band nature of this two-dimensional superconductor. Our experimental studies are further supported by first-principles calculations, which suggest a topological non-trivial band structure.

10:30 AM

(EMA-S7-014-2019) Electrostatic gating as a tool for inducing superconductivity (Invited)

M. Osofsky*[1]; E. Lock[1]; J. Prestigiacomo[1]; K. Perkins[1]; A. Boyd[1]; A. Nath[1]; R. Myers-Ward[1]; P. Dev[1]; T. Reinecke[1]; D. K. Gaskill[1]

1. Naval Research Laboratory, USA

A large body of recent work has demonstrated the utility of electrostatically gating a wide variety of thin films or 2-D materials to modulate, or even induce, superconductivity by varying the carrier concentration. In this presentation we will briefly review previous work on inducing superconductivity in insulating systems and discuss the influence of proximity to the metal-insulator transition on the superconductive transition temperature. We will also demonstrate a novel functionalization approach that modifies the carrier concentration of epitaxial graphene in a manner similar to electrostatic gating so that the position of the Fermi energy can be moved towards the Dirac point resulting in the expected increase in mobility. In particular, we show that these functionalized samples exhibit the Quantum Hall Effect and Shubnikov-de Haas oscillations, which are typical for high quality exfoliated graphene flakes. The results are consistent with first principle calculations which indicate that the results are likely due to reduced sheet charge density after functionalization, derived from charge transfer from the chemical molecules to the epitaxial graphene.

11:00 AM

(EMA-S7-015-2019) 2D Magnets and Heterostructures (Invited)

X. Xu*[1]

1. University of Washington, USA

Since the discovery of graphene, the family of two-dimensional (2D) materials has grown to encompass a broad range of electronic properties. However, until recently 2D crystals with intrinsic magnetism were still lacking. Such crystals would enable new ways to study 2D magnetism by harnessing the unique features of atomically-thin materials, such as electrical control for magnetoelectronics and van der Waals engineering for novel interface phenomena. In this talk, I will describe our recent magneto-optical spectroscopy experiments on van der Waals magnets, chromium(III) iodide CrI_3. I will discuss the layered antiferromagnetic properties of atomically thin CrI_3, electrical control of 2D magnetism, and the emerging spin phenomena in van der Waals magnetic heterostructures.

11:30 AM

(EMA-S7-016-2019) Electronic properties of Ruddlesden-Popper chromium oxide perovskites (Invited)

R. Comin*[1]

1. Massachusetts Institute of Technology, Physics, USA

Chromium-based compounds realize a multitude of electronic and magnetic phases: half-metals (CrO_2), ferromagnetic insulators (CrI_3, $YCrO_3$), antiferromagnetic insulators (Cr_2Se_3, $CrSe_2$, Cr_2O_3 and $LaCrO_3$), or antiferromagnetic metals (Cr and $SrCrO_3$). These compounds, whose magnetic transitions are often near room temperature, represent a far less charted platform for emergent quantum matter compared to their other 3d transition metal siblings. Low-dimensional perovskites of tetravalent chromium with d^2 electronic configuration deserve particular attention. Antiferromagnetism is ubiquitous in these systems, but recent theoretical studies indicate the presence of proximate electronic phases, including orbital order and superconductivity. These materials are hard to stabilize structurally in bulk form and electronically in the Cr^{4+} oxidation state (with spin S=1) but could host interesting new phenomena enabled by the strong interplay of spin, charge, and orbital degrees of freedom. To explore these scientific opportunities, we have grown thin films of various members of the Ruddlesden-Popper series of chromium oxide perovskites: $SrCrO_3$, Sr_2CrO_4, and $Sr_4Cr_3O_{10}$. In this talk, I will report on the synthesis and characterization of their transport and magnetic properties, including recent investigations of spin and orbital ordering in the ground state of these materials.

Superconducting and Magnetic Materials V

Room: Citrus A

Session Chair: Michael Susner, Air Force Research Laboratory

2:00 PM

(EMA-S7-017-2019) STM studies of density wave evolution in a cuprate superconductor (Invited)

J. E. Hoffman*[1]; T. Webb[1]

1. Harvard University, Physics, USA

The strong electronic correlations of the doped antiferromagnetic Mott insulator give rise to unconventional phases beyond high temperature superconductivity in the cuprates. Multiple broken symmetries have been reported, though a complete description of their emergence and interaction is missing. At the heart of this complex phase diagram is evidence of a quantum critical point, where disconnected Fermi arcs jump inexplicably to a large Fermi surface as holes are added. Here, we use sub-unit-cell scanning tunneling microscopy and spectroscopy (STM/S) to track the d-form factor density wave throughout the phase diagram as a local fingerprint of the dominant interactions in $(Bi,Pb)_2(Sr,La)_2CuO_{6+d}$. Crucially, we use nanoscale electronic inhomogeneity as a tool to access a range of dopings within a single sample. We discover an abrupt change in the evolution of the modulation wavevector, signaling a commensurate to incommensurate transition that is coincident with the Fermi surface transition. Furthermore, the rapid growth of the wavelength on the overdoped side of the transition is at odds with a simple Fermi surface instability, providing evidence for persistent effects of strong correlations.

2:30 PM

(EMA-S7-018-2019) Atomic visualization of copper oxide structure in epitaxial cuprate $SrCuO_2$ films (Invited)

X. Ma*[1]

1. Tsinghua University, Department of Physics, China

Among cuprates, the infinite layer $ACuO_2$ (A = Ca, Sr, Ba) compounds have the simplest crystal structure and a stacking of alternative CuO_2 and Sr planes. The partial substitution of Sr by La introduces electrons and consequently leads to superconducting $Sr_{1-x}La_xCuO_2$ ($x = 0.05 \sim 0.15$) with a maximum transition temperature of $T_c = 43$ K. More significantly, a nodeless superconducting gap is suggested by both bulk and surface sensitive measurements in optimal doped $Sr_{0.9}La_{0.1}CuO_2$. Here we report the atomic-scale structure of epitaxial films of parent infinite-layer compound $SrCuO_2$ prepared on $SrTiO_3$ by molecular beam epitaxy. In-situ scanning tunneling microscopy study reveals a stoichiometric copper oxide (CuO_2)-terminated surface featured by 2 x 2 reconstruction, caused primarily by structural distortions of four adjacent CuO_2 plaquettes. Furthermore, the subsurface Sr atoms have been rarely discernible, showing intra-unit-cell rotational symmetry breaking. These observations can be reasonably modelled by a periodic up-down buckling of oxygen ions on the CuO_2 plane. Our study provides indispensable structural information to help understand the exotic properties of cuprate superconductors.

3:00 PM

(EMA-S7-019-2019) High-temperature interface superconductivity in bilayer cuprate films grown by pulsed laser deposition (Invited)

Y. Xie*[1]

1. Zhejiang University, Department of Physics, China

The effect of interface on superconductivity has received much attention. It has been demonstrated that superconductivity can occur at the interface of two non-superconducting materials, and the critical temperature can even be significantly enhanced compared with the corresponding single-phase samples. In this talk, I will present our recent efforts in exploring superconductivity at interfaces of copper oxides. We prepared all our samples by pulsed laser deposition (PLD). Taking La_2CuO_4-$La_{2-x}Sr_xCuO_4$ bilayer as an example, we extensively explore this interface by spanning x from 0.00 to 1.70, in which the $0.47 < x < 1.70$ range has never been explored in previous reports. High-T_c interface superconductivity was observed in a wide range of Sr doping levels up to x = 1.70. Our result demonstrates that the interface superconductivity in cuprates is robust, general, and insensitive to film quality. In addition, because PLD is costly cheap, technically easy, and versatile in growing a large number of materials with reasonable quality, our result suggests the opportunity to combine more materials using PLD and thus to search for superconductivity in new interfaces.

Superconducting and Magnetic Materials VI

Room: Citrus A
Session Chair: Jennifer Hoffman, Harvard University

4:00 PM

(EMA-S7-020-2019) Optically Triggered Microwave Emission from an Inductively Charged Superconducting Ring (Invited)

T. Bullard*[1]; J. Bulmer[2]; J. Murphy[3]; M. Ferdinandus[5]; C. Eakins[6]; D. Latypov[6]; T. J. Haugan[4]

1. UES, Inc., USA
2. University of Cambridge, United Kingdom
3. University of Dayton Research Institute, USA
4. Air Force Research Labs, RQQM, USA
5. Air Force Institute of Technology, USA
6. ARA, Berrie Hill, USA

It is well established that a current carrying superconductor will emit microwave/terahertz radiation when illuminated with a femtosecond infrared laser pulse. Typically this radiation is generated by illuminating a current biased superconducting thin film bridge. In this investigation an inductively charged superconducting annular thin film ring is considered. We believe this configuration lends itself to a simple compact microwave emitter device as the antenna plays the part of the waveguide and power supply, and contact heating between the current leads and the superconductor are now eliminated. We find that the emitted energy of this system displays a power-law dependence with increasing current and laser energy. The emitted signal shows a frequency dependence on the ring dimension as well as a well-defined polarization direction determined by the location of the laser illumination point. The in-plane radiation pattern is typical for an electrically large loop antenna while the out-of-plane pattern differs noticeably from predicted results. These results suggest a rich and complex dynamics that spans time scales commensurate with the terahertz and microwave regimes.

4:30 PM

(EMA-S7-021-2019) Linking Raman spectroscopy and transport measurements for YBCO micro bridges aiming to predict process induced degradation (Invited)

K. Lange*[1]; J. Bulmer[1]; J. Feighan[2]; T. J. Haugan[3]; W. O'Neill[1]; M. Sparkes[1]

1. University of Cambridge, Institute for Manufacturing, United Kingdom
2. University of Cambridge, Department of Materials Science & Metallurgy, United Kingdom
3. US Air Force Research Laboratory, AFRL/RQQM, USA

We are proposing to use Raman spectroscopy as a new method for quick measurements during laser processing of YBCO micron bridges to identify heat damages. We are investigating the link between changes in the Raman spectrum and transport measurements of 200 nm thin YBCO films. In the first instance this has been done by repeated heat treatments at 300 °C in air while sequentially measuring the critical current density (J_c) and Raman spectra. The goal is to use the obtained data to predict J_c losses from changes in Raman peak intensities and shifts. The limitations of this technique were investigated by applying it to laser machined YBCO bridges which were exposed to highly localised heating. They also have geometries small enough (< 10 μm) to be a potential problem in relation to the relatively large Raman probe spot size (4 μm). Results show that above certain widths a femtosecond laser (1030 nm, 300 fs) can be used to successfully machine bridges with no loss in Jc and that there is some correlation in the Raman spectra.

5:00 PM

(EMA-S7-022-2019) Role of iron in the ferromagnetic-antiferromagnetic boundary of La0.5Ca0.5Mn1-*x*Fe*x*O3+δ (0≤x≤0.5) manganites

H. A. Martinez-Rodriguez*[1]; G. Herrera-Perez[1]; F. Jurado[2]; A. Reyes-Rojas[1]

1. CIMAV, Physics of Materials, Mexico
2. Universidad Nacional de Colombia, Ciencias Exactas, Colombia

Samples of La0.5Ca0.5Mn1−xFexO3+δ (0≤x≤0.5) were synthesized using a solid-state reaction method involving a milling process and thermal treatment up to 1200 °C in an air atmosphere. Samples were characterized structurally with X-ray diffraction analysis and Rietveld refinement with morphology characterization using scanning electron microscopy. Magnetic properties were investigated using a physical property measurement system to obtain zero field cooling and the associated curves to plot hysteresis loops. Our results revealed the interplay between the structural and magnetic properties as Fe ions attached to the crystalline structure. A mechanism based on the substitution of Mn3+ and Mn4+ by low-spin Fe3+ and Fe4+ ions, respectively, was hypothesized to interpret the experimental data. More specifically, the temperature at which the transition from ferromagnetic to paramagnetic occurred increased with increasing Fe content as a result of a greater density of oxygen-mediated ferromagnetic bonds. Conversely, the magnetization weakened because the t2gelectrons were distributed in the respective *d* orbitals by adopting a low-spin configuration. Such a configuration is preferred as a result of the unit cell distortion in the milling process where the greater ionic radius of the Fe4+ ions leads to an elongated *c*-axis tetragonal symmetry and a greater unit cell volume.

5:15 PM

(EMA-S7-023-2019) Large Tunable Intrinsic Gap in Rhombohedral-stacked Tetralayer Graphene at Half-filling

S. Che*[1]; K. Myhro[2]; Y. Shi[2]; Y. Lee[2]; K. Thilahar[2]; K. Bleich[2]; D. Smirnov[3]; C. N. Lau[1]

1. Ohio State University, Physics, USA
2. University of California, Riverside, Physics, USA
3. National High Magnetic Field Laboratory, USA

Rhombohedral-stacked tetralayer (r-4LG) has a highly unusual energy dispersion, which can be approximated as $E\sim k^4$, where k is the wave vector. At half filling, the very flat energy bands in r-4LG are unstable to electronic interactions, giving rise to electronic states with spontaneous broken symmetries. Using transport measurements on suspended dual-gated devices, we observe an insulating ground state with a large interaction-induced transport gap up to 80 meV at the charge neutrality point. The energy gap is enhanced further with a perpendicular magnetic field, but closed or suppressed upon the application of an out-of-lane electric field of either polarity, increasing charge density or a critical temperature of ~40 K. This insulating gapped state is consistent to that observed in bilayer graphene and rhombohedral-stacked trilayer graphene, and therefore proposed to be a layer antiferromagnet with broken time reversal symmetry. The large magnitude of the gap also suggests that, at lease in r-4LG, the band flattening effect prevails over the increasing screening and charge de-confinement in thicker graphene, in agreement with a first principle calculation.

S8: Structure–Property Relationships in Relaxor Ceramics

Perovskite Relaxors I

Room: Magnolia B/C
Session Chairs: Dwight Viehland, Virginia Tech; Tadej Rojac, Jozef Stefan Institute

2:00 PM

(EMA-S8-001-2019) Accidental Discoveries of Relaxor Ferroelectrics (Invited)

M. Dolgos*[1]

1. University of Calgary, Department of Chemistry, Canada

Relaxor ferroelectric materials offer a wide range of useful properties that make them attractive for actuator and sensor applications. The most prevalent structure type of relaxor ferroelectrics are perovskites and perovskite-based layered structures. This is due to the compositional flexibility where the possible A- and B-site atoms include most of the cations in the periodic table and even some small molecules. Our group has synthesized a variety of novel relaxor ferroelectric materials with the perovskite and aurivillius crystal structures. Many of the new materials were initially predicted to be classical ferroelectrics such as high T_c materials or solid solutions with properties derived from a polarization extension mechanism. However, the balance between order and disorder is very delicate. Compositional and structural disorder lead to the formation of polar nanoregions which result in relaxor behavior. This talk explores several different new relaxor ferroelectric systems and focuses on their synthesis, structure, and electromechanical properties.

2:30 PM

(EMA-S8-002-2019) Bismuth Ferrite-Based Lead-Free Relaxor Ceramics and Multilayers with Large Electromechanical Strain and Recoverable Energy Density (Invited)

D. Wang*[1]; Z. Fan[2]; G. Wang[1]; W. Li[3]; D. Zhou[3]; A. Khesro[4]; S. Murakami[1]; A. Feteira[5]; X. Tan[6]; I. M. Reaney[7]

1. University of Sheffield, United Kingdom
2. Iowa State University, USA
3. Xi'an Jiaotong University, China
4. Abdul Wali Khan University, Pakistan
5. Sheffield Hallam University, United Kingdom
6. Iowa State University, Materials Science & Engineering, USA
7. University of Sheffield, Materials Science and Engineering, United Kingdom

Lead-free ceramics with high recoverable energy density (W_{rec}) and energy storage efficiency (η) are attractive for advanced pulsed power capacitors to enable greater miniaturization and integration. In our recent work, dense bismuth ferrite (BF)-based, lead-free relaxor ceramics and multilayers were fabricated. Compositional impact on the structure-property relationships, in particular on the electromechanical strain and energy storage characteristics were evaluated. Due to the enhanced breakdown field strength (BDS) and large maximum polarization (P_{max}). High recoverable energy densities W_{rec} of 1.8~2.1 J/cm^3 were achieved. Multilayers of this composition possessed both high W_{rec} of 6.74 J/cm^3 and η of 77% and were stable up to 125 °C, which are therefore considered promising candidates for lead-free energy storage applications. In addition, large electromechanical strains of 0.2~0.46% were also observed with effective d_{33}^* of 424~465 pm/V, suggesting that this family of ceramics may also have potential for high strain actuators.

3:00 PM

(EMA-S8-003-2019) Effect of A-site substitutions on dielectric and energy storage properties of $BaTiO_3$-$BiScO_3$ relaxor ferroelectrics

S. Nayak*[1]; S. Venkateshwarlu[1]; A. Setiadi[1]; M. Jørgensen[2]; K. Beyer[3]; O. Borkiewicz[3]; A. Pramanick[1]

1. City University of Hong Kong, Department of Materials Science and Engineering, Hong Kong
2. Aarhus University, Department of Chemistry, Denmark
3. Argonne National Laboratory, Advanced Photon Source, USA

Solid-solutions of the form (1-x)$BaTiO_3$-x$BiMeO_3$ [Me = metal ions] have attracted attention because of their potential as high-energy density, high temperature capacitors. Here, we report a detailed investigation of the effects of A-site substitutions on relaxor and energy storage properties of $0.095BiScO_3 – 0.905Ba_{0.78-\delta}Ca_{0.22-\delta}Sn_{2\delta}Ti_{0.96}Sn_{0.04}O_3$ (δ = 0.0025) ceramics. A combined substitution scheme of Ca^{2+} and Sn^{2+} ions at the A-site is shown to induce off-centered multisite atomic displacements, which are correlated over nanometers length-scales. Investigation of dielectric properties revealed a frequency-dispersive broad phase transition, which arises due to weak mutual coupling among the polar nanoregions (PNR). Rietveld refinement of the average crystal structure indicated transition from a high-symmetry cubic phase above T_m to a combination of cubic and tetragonal phases at lower temperatures. Investigation of the local structure using X-ray pair-distribution function (PDF) indicated short-range correlations among A- and B-site atomic displacements within the PNRs, consequently leading to relaxor behavior. The system exhibited thin hysteresis loops from room temperature to 200 °C, which is beneficial for high-density energy storage applications. A high energy efficiency (η ~ 91 %) was evaluated for these ceramics, which is one of the highest recorded yet.

3:15 PM

(EMA-S8-004-2019) Sintering and dielectric study of the pseudobinary $Pb(Fe_{0.5}Nb_{0.5})O_3$-$BiFeO_3$ system

R. Sherbondy*[1]; U. Prah[2]; H. Uršič[2]; G. L. Brennecka[1]; T. Rojac[2]; B. Malic[2]

1. Colorado School of Mines, Metallurgical and Materials Engineering, USA
2. Jozef Stefan Institute, Electronic Ceramics Department, Slovenia

$BiFeO_3$ (BFO) is a classic ferroelectric material known for being perhaps the only single-phase material exhibiting strong ferroelectric and (anti)ferromagnetic coupling at room temperature. $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN) is a material that has been increasingly studied recently owing to its notable classification as a rare relaxor multiferroic, showing rFE-FM coupling below the Neel temperature of approximately 150K. Despite interest in these end members, few studies have fabricated and analyzed members of the PFN-BFO pseudobinary system, the preliminary steps of which are presented in this work. Compositions of the (1-x)PFN-xBFO system where x=0, 0.05,0.10, 0.20 and 0.50 were synthesized by a mechanochemical activation process and found to have complete solid solubility as single-phase perovskites with slightly decreasing pseudocubic lattice parameters with increasing values of x. Increasing BFO content was also found to lower the densification temperature, and all samples were fully dense after sintering below 1100°C. The electrical resistivity was also found to exhibit a maximum with respect to changing composition for a given processing condition.

Perovskite Relaxors II

Room: Magnolia B/C
Session Chairs: Michelle Dolgos, Oregon State University; Dawei Wang, University of Sheffield

4:00 PM

(EMA-S8-005-2019) Effect of minor doping on the relaxor behaviour and electrostrain of BNT-BKT-BT ceramics

A. Feteira*[1]

1. Sheffield Hallam University, United Kingdom

Undoped BNT-BKT-BT ceramics exhibit a non-ergodic relaxor behaviour and a piezoelectric response typical for a ferroelectric, whereas Nb-doped BNT-BKT-BT ceramics show ergodic relaxor behaviour and an electromechanical response typical for an incipient piezoelectric. This minor doping also contributed to the enhancement of the room-temperature unipolar field-induced strain from 0.19% to 0.43% at 75 kV/cm and an electrostrictive response in the entire temperature range studied. Although at 40 kV/cm, doped ceramics exhibit a good temperature stability, it worsens as the electric field increases. These results may motivate further investigations on the impact of minor doping and driving electric fields on the electromechanical response of BNT-BKT-BT based ceramics.

4:15 PM

(EMA-S8-006-2019) Spontaneous relaxor-ferroelectric transition in $0.91(Na_{1/2}Bi_{1/2})TiO_3$-$0.09BaTiO_3$

L. Kodumudi Venkataraman*[1]; J. Koruza[1]; M. Hinterstein[2]; J. Rödel[1]; P. Groszewicz[3]

1. Technical University Darmstadt, Institute of Materials Science, Germany
2. Karlsruhe Institute of Technology, Institute for Applied Materials - Ceramic Materials and Technologies, Germany
3. Technical University Darmstadt, Institute of Physical Chemistry, Germany

The aim of this work is to demonstrate a spontaneous relaxor to ferroelectric transition in $0.91(Na_{1/2}Bi_{1/2})TiO_3$-$0.09BaTiO_3$ (NBT9BT) using two different approaches, viz. the composite route and quenching. In the former case, a composite with NBT9BT matrix and ZnO inclusions is formed and in the latter case, NBT9BT is quenched from the sintering temperature. In both the scenarios, a spontaneous relaxor to ferroelectric transition transition is observed as evident from the temperature-dependent permittivity and electromechanical hysteresis. These results confirm stabilization of a long-range ferroelectric order at room temperature without application of electric field. Synchrotron diffraction and nuclear magnetic resonance are used to establish the nature of the relaxor-ferroelectric transition in the composites. The observed results are explained in the light of propensity of spontaneous relaxor-ferroelectric transformation, wherein, residual stresses aid the transformation in the case of the composites, while in the case of quenching, it is influenced by the change in cation and vacancy disorder.

4:30 PM

(EMA-S8-007-2019) Temperature dependent polarization reversal mechanism in $(Bi_{1/2}Na_{1/2})TiO_3$-based relaxor ceramics

J. Glaum*[1]; H. Simons[2]; J. Hudspeth[3]; M. Acosta[5]; J. Daniels[4]

1. Norwegian University of Science and Technology NTNU, Materials Science and Engineering, Norway
2. Technical University of Denmark, Denmark
3. European Synchrotron Radiation Facility, France
4. University of New South Wales, Australia
5. University of Cambridge, United Kingdom

Morphotropic $(Bi,Na)TiO_3$-$xBaTiO_3$ ceramics exhibit macroscopically a pseudo-cubic structure in the unpoled state even though they show strong hysteretic behavior upon electric field application. This characteristic is rationalized by the appearance of an electric field induced ferroelectric phase, which, depending on composition and temperature, sustains or vanishes when the electric field is removed. The dielectric characteristics of these materials are described as relaxor-like and are associated with formation and disappearance of a long-range domain structure. Our study is concerned with the mechanism of polarization reversal. For temperatures far below the ferroelectric-relaxor transition temperature, T_{F-R}, polarization reversal is governed by ferroelectric switching, while for $T > T_{F-R}$ the reversible phase transition between relaxor and ferroelectric state is the determining mechanism. In the intermediate temperature regime an applied electric field can trigger depolarization and onset of relaxor-like behavior already well below T_{F-R}. This highlights the continuous transition from a switching based to a phase transition based polarization reversal mechanism. This transitional behavior has been studied using dielectric and piezoelectric characterization techniques as well as synchrotron diffraction. The relationship between macroscopic properties and structure will be discussed.

4:45 PM

(EMA-S8-008-2019) Piezoelectric properties of lead-free relaxor ferroelectric $Bi(Zn_{2/3}Nb_{1/3})O_3$-$BaTiO_3$ (BZN-BT) system

J. M. Marshall*[1]

1. University of Warwick, Physics, United Kingdom

Lead-free relaxor ferroelectrics based on $BaTiO_3$ have been proposed as alternatives to lead-based high-performance lead-based ferroelectrics such as $Pb(Zr, Ti)O_3$ (PZT) and $Pb(Mn, Nb)O_3$ (PMN) systems. Recently, it has been demonstrated that the $xBi(Zn_{2/3}\ Nb_{1/3})O_3$ $-(1-x)$ $BaTiO_3$ (BZN-BT) system has excellent energy storage and high dielectric constants [1-3]. The nature of relaxors and the high dielectric constant indicates this system shows potential as a lead-free piezoelectric material. Ceramics of the BZN-BT system had d_{33} values > 100 pC N^{-1} for compositions $0.03 < x(BZN) < 0.04$, peaking at $d_{33} = 110$ pC N^{-1} at $x(BZN) = 0.038$ with $\varepsilon_{max} = 3670$ at T_{max} 0= 338K. Peak d_{33} coefficients did not coincide with the dielectric maxima composition which was at $x(BZN) = 0.08$ where $\varepsilon_{max} = 5100$ at 298K within the pseudo-cubic relaxor dielectric region. XRD analysis showed the coexistence of tetragonal, cubic and rhombohedral phases at 298K, with the maximum piezoelectric coefficients coinciding with the peak in the rhombohedral phase at 298K. The tetragonal c_T/a_T ratio decreased sharply with for $x(BZN) > 0.04$ along with d_{33} with no measurable d_{33} for $x(BZN) = 0.06$, marking the transition from ferroelectric to relaxor dielectric at $x(BZN) = 0.06$. The decline in d_{33} was similarly matched with the decrease in the Curie temperature from 338K for $x(BZN) = 0.038$ to 298K for $x(BZN) = 0.048$.

5:00 PM

(EMA-S8-009-2019) Piezoelectric and Dielectric Thick Films Fabricated on Metal Substrates by Aerosol Deposition

E. A. Patterson*[1]; S. D. Johnson[1]; E. Gorzkowski[1]

1. Naval Research Lab, USA

The Aerosol deposition (AD) process was used to produce thick-film with layer thicknesses on the order of 5 to 40 micrometers that have densities greater than 95% of the bulk. The primary advantage of AD is that the deposition takes place entirely at ambient temperature. This enables film growth of systems such as perovskite oxides on to metal substrates despite their widely disparate melting temperatures. The bonding and densification of the film and film/substrate interface are thought to be facilitated by high pressure, impact and fracture of the particles, and some form of chemical bonding during deposition. The resulting nano-grained microstructures are characterized and related to the electrical properties of the film. In this talk, the dielectric and ferroelectric properties of these films are presented, including the effect of post-processing parameters on the resultant materials properties.

S9: Ion–Conducting Ceramics

Oxygen Conducting Ceramics

Room: Citrus B
Session Chairs: Yingge Du, PNNL; Hui Xiong, Boise State University

10:00 AM

(EMA-S9-017-2019) The Dual Tales of Ionic Electrolyte Gating: Pushing Electrochemical Transformations and Restoring Electrostatic Doping in Functional Oxides (Invited)

H. Zhou*[1]

1. Argonne National Laboratory, Advanced Photon Source, USA

The very high charge density induced by an electric double layer formed at the solid-liquid interface has recently been used to induced or "gate" exotic phase transitions, therefore electronic ground states of multifunctional oxides in the interfacial region, via the subtle interplay between electrostatic doping (electronic phenomena) and chemical redox effects (field-driven ionic motion) depending on field polarity and defect instability. It is highly expected that leveraging ionic electrolyte gating would be fertile ground for exploration in a broad range of functional oxides. In this talk, I will present two developing frontiers of ionic electrolyte gating within two contrasting mechanistic frameworks by illustrating most recent in-situ and real-time X-ray studies to deliver fundamental understanding of structural and chemical basis and their inherent links during gating on representative functional oxide heterostructures. In one end, we drive forward the limits of electrochemically emergent transformations by manipulating ionic defects (e.g. vacancy formation and distribution) during gating; in the other end, we create a new paradigm of highly efficient ionic gating toward sub-voltage operation regime (e.g. restoring electrostatic carrier doping) by designing redox actuatable poly-ionic-liquids.

10:30 AM

(EMA-S9-018-2019) Preparation of Highly Conductive Lanthanum Silicate-Based Oxide Ion Conductor

A. Mineshige*[1]; M. Momai[1]; S. Yagi[1]; H. Hayakawa[1]; Y. Takayama[1]; Y. Kagoshima[1]; T. Yazawa[1]

1. University of Hyogo, Japan

Recently, it is strongly expected to develop high performance solid oxide fuel cells (SOFCs) since they are clean and sustainable energy systems with high conversion efficiency from chemical to electrical energy. The oxyapatite-type lanthanum silicate ($La_{9.33+x}Si_6O_{26+1.5x}$, LSO), found by Nakayama et al., is one of the candidates as an electrolyte material used in the intermediate-temperature SOFCs. We have reported that its ionic conductivity largely depends on its chemical composition, firing conditions, and intentional transition metal additions. Especially, additional La incorporation, cation doping into its Si-site, and firing at very high temperature (1973 K) are important to design the highly conducting electrolyte. However, since its conduction mechanism has not been fully clarified yet, activation energy (Ea) for conduction as well as its conductivity (s) in the obtained data could not be explained quantitatively so far. In addition, in La-rich composition, chemical instability resulting in conductivity degradation is an also important issue. In the present study, its conducting properties were reinvestigated in detail aiming at obtaining highly conductive LSO specimen with high chemical stability.

10:45 AM

(EMA-S9-019-2019) Fast Oxygen Ion Conduction in $Bi_4Ti_3O_{12}$

L. Li*[1]; M. Li[2]; D. C. Sinclair[1]

1. University of Sheffield, Materials Science & Engineering, United Kingdom
2. University of Nottingham, Department of Mechanical, Materials and Manufacturing Engineering, United Kingdom

Fast oxygen ion conductors have drawn significant interest due to their important technical applications in electrochemical devices. The Aurivillius oxide $Bi_4Ti_3O_{12}$ (BiT) is a well-known high-temperature lead-free ferroelectric material with an undesirable leakage current. BiT adopts the monoclinic space group B1a1 and undergoes a structural phase transition to tetragonal I4/mmm around 675 °C. Zhou and Kennedy (Chem. Mater. 2003, 15, 5025-5028) suggested the phase transition around T_C is via an intermediate orthorhombic phase exists between 670 and 695 °C. Here we report BiT exhibits a mixed ionic and p-type electronic conduction at lower temperatures but a nearly pure oxygen ion conduction with an ionic transport number (t_{ion}) close to unity near Curie temperature (T_C). The temperature range of maximum t_{ion} in BiT coincides with the above mentioned intermediate orthorhombic phase. The t_{ion} of BiT has shown to be strongly coupled to T_C and can be improved at lower temperatures by stabilised the high temperature phase to lower temperature via A-site doping. The oxygen ion conduction of BiT can be further enhanced by acceptor doping or suppressed by donor doping.

11:00 AM

(EMA-S9-020-2019) Reducing operating temperatures of ionic conductors using vertically aligned nanocomposite thin film approaches, experiment and modelling (Invited)

J. MacManus-Driscoll*[1]; B. Zhu[1]; G. Schusteritsch[1]; C. J. Pickard[1]

1. University of Cambridge, Dept. of Materials Science, United Kingdom

Vertically aligned nanocomposites (VAN) typically have pillar-matrix nanostructures combining two distinct phases. Up to two orders of magnitude increase in out-of-plane ionic conductivity was observed using Sm-doped CeO_2 (SDC) /$SrTiO_3$ (STO) VAN films grown on STO substrates compared to plain SDC films. ~10-20 nm SDC pillars were observed, grown by vertical epitaxy with the STO matrix. Similar enhancements in ionic conductivity were also observed using VANs consisting of YSZ and STO. To investigate the roles of vertical interfaces, we used random structure searching to construct an atomistic model of the vertical interface. The structures were found to not contain any features that promoted interfacial oxygen diffusion. Instead, they suggested that vacancy movement may be suppressed near the interface due to the existence of trapping sites. Based on both experimental and modelling results, the enhanced ionic conductivity is consistent with high crystallinity in the fluorite-structured ionic conducting pillars rather than enhanced diffusion along the vertical interfaces.

11:30 AM

(EMA-S9-021-2019) Demonstration of the Cold Sintering Process for the Bi-based Ceramics

K. Tsuji*[1]; T. De Beauvoir[1]; C. Randall[1]

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

This work demonstrates the feasibility and challenges of the Cold Sintering Process (CSP) for the low-temperature densification in a bismuth based ceramics. The CSP was performed on the Bi_2O_3 and Y-doped- Bi_2O_3. The density reached ~ 90 % of the theoretical density (T.D.). The ionic conductivity of the Y-doped- Bi_2O_3 at 500 °C reached to > 1 mS/cm, which is comparable to the conventionally sintered Y-doped- Bi_2O_3. The structure-property relationship will be discussed for the cold-sintered Bi_2O_3 based ceramics using the impedance spectroscopy, XRD, SEM, EDS and TEM.

S10: Current Challenges in Microstructural Evolution: From Basic Science to Electronic Applications

Grain Boundary Structure, Mobility and Characterization

Room: Cypress B
Session Chair: Yanhao Dong, Massachusetts Institute of Technology

2:00 PM

(EMA-S10-001-2019) Grain Boundary Atomic Structures, Segregation and Properties in Electronic Materials (Invited)

Y. Ikuhara*[1]

1. University of Tokyo, Institute of Engineering Innovation, Japan

Grain boundary (GB) atomic structures are dependent on the GB characters such as misorientation angle and GB planes. In addition, GB structures are also influenced by the segregated dopants and vacancies to form the relaxed and stable structures. It is therefore needed to investigate the sites of vacancies and dopants segregated at GB, depending on the GB characters, to fully understand GB atomic structures, which are related to the material's properties. In this study, various types of GBs in electronic materials were systematically fabricated for doped and pristine Al_2O_3, ZrO_2, ZnO, CeO_2, $SrTiO_3$ by the bicrystal techniques, and the structures were characterized with an atomic scale by aberration-corrected STEM, EELS and EDS. Based on the experimental results, the role of segregated dopants and vacancies to change the GB structures and macroscopic properties were investigated by first principles calculation.

2:30 PM

(EMA-S10-003-2019) Tailoring grain boundary mobility in zirconia ceramics (Invited)

Y. Dong*[1]; J. Li[1]; I. Chen[2]

1. Massachusetts Institute of Technology, Nuclear Science and Engineering, USA
2. University of Pennsylvania, Materials Science and Engineering, USA

Microstructural control of ceramics relies on the rational design of grain boundary mobility within the applicable processing window. In the model system of zirconia, we show the ability to tailor grain boundary mobility over orders of magnitude, using state variables such as temperature, atmosphere and applied electric field. Specifically, we found (electro-) chemical reduction can enhance grain boundary mobility >1,000 times, suggesting hugely accelerated cation diffusion and novel electron-phonon interactions on cation kinetics from our first-principles calculations. Meanwhile, an apparent mobility transition has been observed in cubic zirconia at 1300 °C, suppressing grain growth at lower temperature and enabling two-step sintering for nano-grain ceramics. A generalized mean-field growth theory agrees with our results, pointing out the hidden contribution from multi-grain junctions. In summary, we believe there is plenty of room in ceramic processing and microstructural control, where mechanistic understandings from continuum to atom level are critical.

3:00 PM

(EMA-S10-004-2019) Disconnections, Grain Growth and Grain Boundary Chemistry (Invited)

H. Sternlicht*[1]; W. Rheinheimer[2]; A. Mehlmann[3]; A. Rothchild[3]; M. J. Hoffmann[4]; N. P. Padture[1]; W. D. Kaplan[3]

1. Brown University, School of Engineering, USA
2. Purdue University, School of Materials Engineering, USA
3. Technion - Israel Inst of Tech, Dept. of Materials Engineering, Israel
4. University of Karlsruhe, Institute for Applied Materials (IAM-KM), Germany

Understanding the mechanism of grain boundary motion is important for both fundamental and applied issues related to microstructural evolution of materials, such as controlling the grain size of polycrystalline material systems in order to optimize their engineering properties. In this work it will be shown that the motion of disconnections is very likely associated with the mechanism of grain growth in $SrTiO_3$. This is done by combining in- situ and ex- situ transmission electron microscopy (TEM) focusing on the characterization of general grain boundaries. In addition, it will be shown that the chemistry of grain boundaries in $SrTiO_3$ can be associated with microstructural changes. Changes in the chemistry of grain boundaries which can be correlated to microstructure will be demonstrated for other systems as well.

4:00 PM

(EMA-S10-005-2019) The Grain Boundaries of Strontium Titanate that Facilitate Anti-thermal Grain Growth (Invited)

A. R. Krause*[1]; A. Roti Roti[2]; M. Harmer[2]

1. University of Florida, Materials Science and Engineering, USA
2. Lehigh University, Materials Science and Engineering, USA

Strontium titanate exhibits anti-thermal or non-Arrhenius grain growth behavior, where the grain growth rate appears to decrease as the temperature increases from 1350 °C to 1425 °C. The mechanism for this desirable grain growth behavior remains unknown. Previously, the grain growth change has been correlated with a change in grain boundary energy, which may indicate a grain boundary complexion transition. Such a transition in the grain boundary structure and/or chemistry may have important implications for other transport phenomenon. Therefore, the atomic structure and chemistry of the grain boundaries from samples heat treated at different temperatures, both inside and outside of the anti-thermal regime, have been investigated with an aberration-corrected scanning transmission electron microscope (STEM) equipped with an energy-dispersive x-ray spectroscope (EDS). Other observations including bulk chemistry changes, the population of special boundaries, and other grain growth studies will be discussed to help elucidate the anti-thermal grain growth behavior of strontium titanate.

4:30 PM

(EMA-S10-006-2019) Diffusional drag in $SrTiO_3$

W. Rheinheimer*[1]; K. Karra[1]; R. García[1]; M. J. Hoffmann[2]

1. Purdue University, School of Materials Engineering, USA
2. University of Karlsruhe, Institute for Applied Materials (IAM-KM), Germany

The present study investigates the impact of acceptor dopants on grain growth in strontium titanate. While undoped microstructures show normal grain growth at low temperatures (<1350°C), doped microstructures evolve bimodally: with increasing acceptor dopant concentration an increasing population of small grains arises. At a concentration of 5 mol% Fe, hardly any grain growth is evident and the grain size stays close to the powder particle size (~300nm). It was shown before via TEM and EDS that Fe segregates to the interfaces due to its negative charge and a positive boundary potential. Thus the experimental findings seem to be well explained by the theory of solute drag: the diffusion of segregated defects ('solutes') at interfaces can retard grain boundary migration. This retardation depends on the defect concentration and on the local driving force. Possible implications for the grain growth transition of strontium titanate are discussed.

S11: Electronic Materials Applications in 5G Telecommunications

Electronic Materials Applications in 5G Telecommunications I

Room: Cypress C
Session Chair: Geoff Brennecka, Colorado School of Mines

10:00 AM

(EMA-S11-001-2019) What is 5G and how can materials help?

N. Orloff*[1]; T. Birol[2]; L. Cai[3]; G. L. Brennecka[4]

1. National Institute of Standards and Technology, Communications Technology Laboratory, USA
2. University of Minnesota, Chemical Engineering and Materials Science, USA
3. Corning Incorporated, USA
4. Colorado School of Mines, USA

Demand for mobile data, the implementation of new wireless devices, and an explosion of mobile users has stressed our current telecommunications infrastructure to its limits. In response to this demand, the Federal Communications Commission released new bands for telecommunications above 28 GHz, commonly referred to as 5G. Meanwhile, engineers have pushed many existing devices to the limit of their frequency operation, and must now design new architectures to work at these new bands. These same architectures must also work with more complicated channel access methods to address this multifaceted capacity and application problem. With the march to higher frequencies and evolution of frequency agile components and urgency to capitalize on these new bands, there is a growing clamor that conventional materials are not up to the challenge. Hence, materials science engineers have an opportunity to develop new materials that answer the call of 5G. In this presentation, I will introduce the session and 5G, discuss device topologies that require new materials, and most importantly how materials can help.

10:10 AM

(EMA-S11-002-2019) BAW Filters for 5G (Invited)

R. Aigner*[1]

1. Qorvo, Acoustic R&D, USA

The application space for BAW filter is growing significantly with the launch of 5G mobile. BAW is in particular well suited for the new radio bands below 6 GHz. Many of the new bands feature an exceptionally wide passband which calls for larger coupling coefficients than traditional thin-film piezolayers provide. This challenge is addressed by innovative new materials and processes. The presentation gives an overview and describes recent trends for high frequency bands, wide bandwidth filters, miniaturization and thermal management. Evolution of RF content and the challenges of developing complex RF modules are discussed.

10:40 AM

(EMA-S11-003-2019) How an understanding of the loss mechanism in microwave ceramics can be used to enhance their performance and develop switchable microwave devices (Invited)

N. Newman*[1]; J. Gonzales[1]; S. Gajare[1]

1. Arizona State University, Materials Program, USA

5G cellular systems will require low-loss temperature-compensated microwave ceramics with moderate dielectric constants. I will summarize my group's progress in understanding what determines the microwave properties of these materials in the 4-15 GHz range and how this understanding can be used to optimize 5G microwave dielectric materials. The dominant loss mechanism in commercial Ni-doped $Ba(Zn_{1/3}Ta_{2/3})O_3$ and Co-alloyed $Ba(Zn_{1/3}Nb_{2/3})O_3$ based-materials at reduced temperatures is shown to result from spin excitations of unpaired transition-metal d electrons in exchange coupled clusters. Extrinsic loss at near room temperature and higher is shown to involve polaron conduction. I will highlight how this understanding has allowed us to switch a low-loss microwave dielectric to a high-loss material using small (<75 g) magnetic field at frequencies up to 13 GHz. This enables high performing microwave dielectric resonators and filters to be switched between a high-Q on-state and low-Q off-state electronically. Our modeling efforts show that it is possible to further optimize the performance of these switchable device potentially up to room temperature through a material selection process. It also shows that improved switching will be more readily achieved in the 35-50 GHz range, compared to that at lower frequencies.

11:10 AM

(EMA-S11-004-2019) Nonlinear polarization dynamics in the tens of GHz

A. Hagerstrom*[1]; E. Marksz[1]; S. Das[2]; C. Long[1]; R. Ramesh[2]; L. W. Martin[2]; N. Orloff[1]

1. National Institute of Standards and Technology, Communications Technology Laboratory, USA
2. University of California, Berkeley, Materials Science and Engineering, USA

Recently, the combination of advances in film deposition techniques and mesoscale modelling has enabled the design and fabrication of novel nonlinear dielectric materials. For example $PbTiO_3/SrTiO_3$ superlattices can display toroidal polar order. The behavior of these polar structures under an applied electric field is still not fully characterized. In this talk, we present linear permittivity measurements of $PbTiO_3/SrTiO_3$ superlattice films at microwave frequencies. We also discuss our recent work on nonlinear dielectric characterization and describe a new measurement technique that achieves wide bandwidth and absolute phase and amplitude resolution. We used this technique to characterize the second order nonlinear permittivity of a $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) thin film from 5 GHz to 40 GHz. These measurements agree with a phenomenological theory of the nonlinear permittivity of relaxor ferroelectrics and indicate that the same description of the relaxation dynamics accounts for both the linear and nonlinear frequency dependence. Our technique offers a new avenue to characterize the dynamics of nano- and microscale polar order including polar vortices, polar nano-regions and domain walls.

11:30 AM

(EMA-S11-005-2019) Enabling tunable, low-loss millimeter-wave electronics through the stabilization of strain-engineered oxide superlattices

E. Marksz*[1]; A. Hagerstrom[3]; N. Dawley[2]; I. Takeuchi[1]; D. Schlom[2]; N. Orloff[3]

1. University of Maryland, Department of Materials Science and Engineering, USA
2. Cornell University, Department of Materials Science and Engineering, USA
3. National Institute of Standards and Technology, Communications Technology Laboratory, USA

Tunable millimeter-wave devices and materials have important applications for reconfigurable electronics, beamforming, and full duplex. However, at mm-wave frequencies, current state-of-the-art tunable dielectrics suffer from energy-dissipating losses due to the presence of defects. Previous work found that $SrTiO_3$-based strained Ruddlesden-Popper superlattices on $DyScO_3$ achieved high tunability, while mitigating defects to reduce loss. Yet, few device implementations using these materials exist. In part, there are few examples because total device tuning is limited by the achievable film thickness. It is not possible to grow these films more than some critical thickness, beyond which lattice relaxation occurs and electrical properties degrade. Here, we explore periodic substitution of

$BaTiO_3$ layers into the $SrTiO_3$ Ruddlesden-Popper phases, allowing for much thicker films and increased total device tuning. We used our broadband dielectric spectroscopy techniques to extract the electrical properties of 100 nm thick $(SrTiO3)_{n-1}(BaTiO3)_1SrO$ (n = 6) films from 10^2-10^{11} Hz. At high frequencies relevant to 5G, films maintain relatively low losses and tunability of almost 50%. This result provides a path toward the implementation of low-loss tunable dielectrics in new, frequency-agile 5G microwave components.

11:50 AM

(EMA-S11-006-2019) Determining orientation and alignment of multi-layer carbon fiber composites using waveguides

N. Popovic*[1]; D. B. Knorr[3]; J. Booth[2]; E. Garboczi[2]; C. Long[2]; N. Orloff[2]

1. University of Colorado, Boulder, Electrical Engineering, USA
2. National Institute of Standards and Technology, USA
3. US Army Research Laboratory, USA

Carbon-fiber composites are integral to many applications, where mechanical properties such as physical strength and durability is paramount. A typical composite is composed of multiple layers of aligned fibers to enhance the strength. To ensure material quality, materials engineers perform destructive mechanical tests on the end-product; these tests are destructive, difficult, and time consuming. Mechanical properties directly correlate to the alignment and orientation of the fibers in their matrix. We illustrate a simple, one-port measurement technique for determining the alignment and orientation of multi-layer composites. The goals of the technique are to determine misalignment of fiber orientation. We demonstrated our technique on 4-layer carbon-fiber composites, where the carbon fibers are on the order of micrometers in diameter. For these experiments, we measured four samples that unknown at the time of test. We determined the orientation and alignment with an open rectangular waveguide mounted flush to a carbon-fiber sheet, measuring the scattering parameters as a function of waveguide angle with respect to the sheet. An ellipse fit the angular scattering parameter data, which we used to calculate the orientation, alignment of the fibers, and the misaligned layer. Our technique is a simple, generalizable method to quantify composite anisotropy.

12:10 PM

(EMA-S11-007-2019) Characterization of extremely small nonlinearities in the dielectric response of glass-ceramics in the microwave range

F. Bergmann*[1]; H. Maune[2]; G. Jakob[3]; M. Letz[1]

1. Schott AG, R&D, Germany
2. Technical University Darmstadt, Germany
3. Johannes Gutenberg University, Germany

Recent mobile network solutions require better microwave circuit performances than ever before. Material solutions need to tackle the challenge of intermodulation between high power signals, e.g. the sending channels of a microwave base station. Intermodulated signals can interfere with the receiving channel with orders of magnitude lower intensity. Therefore, also these very weak passive intermodulation (PIM) levels need to be controlled. One source of intermodulation is the nonlinear response of dielectrics to the electric field. While there is a lot of data on nonlinearity of ferroelectricity and piezoelectricity, only few experimental data exists on the characterization of nonlinear dielectrics in the GHz frequency range with a sensitivity necessary for mobile communication solutions. Following a resonator method exciting eigenresonances of three coupled cylindrical dielectric resonators enables to measure nonlinear behavior at high field strengths and allow isolating the resonators' material nonlinearities from other intermodulation sources. For the first time, the nonlinearity of a dielectric glass-ceramic is measured and is compared to previously measured sintered ceramics.

Electronic Materials Applications in 5G Telecommunications II

Room: Cypress C
Session Chair: Nate Orloff, NIST

2:00 PM

(EMA-S11-008-2019) Technical Panel on 5G (Invited)

N. Orloff*[1]; T. Birol[2]; L. Cai[3]; G. L. Brennecka[4]

1. NIST, Communications Technology Laboratory, USA
2. Rutgers University, USA
3. Corning Incorporated, USA
4. Colorado School of Mines, USA

In this open panel discussion, leaders from industry, academia, and government will discuss 5G technologies, challenges, and opportunities. In the first half of the session, the panel will discuss prepared questions. Next the panel will discuss selected topics and then the floor will be open for discussion. The goal of this panel discussion is to provide the audience with a variety of informed perspectives about 5G and to address two primary questions: 1) how materials can help the advancement of 5G, and 2) what topics of research can impact this important new application space for electronic materials and their applications. The authors of this abstract will be the moderators of the panel discussion, rather than panelists themselves. The panelists will be noted on the itinerary outside the session.

2:40 PM

(EMA-S11-009-2019) Epitaxial Growth of ScAlN for High Power Millimeter Wave Transistors and Resonators (Invited)

M. T. Hardy*[1]; B. P. Downey[1]; N. Nepal[1]; E. Jin[2]; D. Storm[1]; S. Katzer[1]; D. Meyer[1]

1. Naval Research Laboratory, Electronic Science and Technology Division, USA
2. National Academcy of Science National Research Council Postodctoral Scholar Residing at the U.S. Naval Research Laboratory, USA

Alloys of scandium with AlN have recently received significant attention owing to the large increase in reported piezoelectric response with increasing ScN fraction, up to a six-fold increase for $Sc_xAl_{1-x}N$ with x = 0.41 deposited by sputtering, and predicted 1.6× increase in the spontaneous polarization relative to AlN with x = 0.18. Epitaxial growth of ScAlN enables high-electron mobility transistors (HEMTs) with very high polarization charge, leading to improved output power even for scaled barrier-layer thicknesses required for millimeter wave frequency operation. The advent of electronic-grade ScAlN also allows for unique acoustoelectric device topologies, which could utilize a ScAlN piezoelectric layer underlying a III-nitride channel to produce acoustoelectric amplification in an RF filter. The challenges and opportunities for ScAlN based high frequency, high power devices will be discussed. In addition, the development of molecular beam epitaxial growth of ScAlN with x = 0.18 for HEMTs and x = 0.33 for acoustoelectrics will be presented, as well as device simulations and transport measurements in initial ScAlN/GaN HEMT samples.

3:10 PM

(EMA-S11-010-2019) The Use of MEMS and PCM Technologies in the Design of Tunable RF Devices (Invited)

R. Mansour*[1]

1. University of Waterloo, ECE Department, Canada

The essential elements of RF technology to enable 5G are: massive MIMO, beamforming, millimeter-wave and full duplex. RF switches are key components needed in the realization of tunable antenna impedance matching networks for massive MIMO, phase shifters for beamforming networks and delay lines and variable attenuators for full duplex systems. There are several technologies available to realize RF switches. The list includes semiconductor, Micro-Electro-Mechanical Systems MEMS and Phase Change Material (PCM).

This talk will focus on the use of MEMS and PCM switches in the realization of a wide range of tunable devices such as tunable filters, variable attenuators, delay lines and impedance matching networks.

4:00 PM

(EMA-S11-011-2019) Material Optimizations in Chalcogenide-Based Phase-Change RF Switches for 5G Applications (Invited)

N. El-Hinnawy*[1]

1. Jazz Semiconductor, USA

RF switches are one of the most common circuit elements in wireless communication systems. To push towards the higher wireless data rates required in 5G and next generation wireless systems, RF switches need to be improved along with other components in order to make these systems a reality. Chalcogenide-based phase-change material (PCM) RF switches are one of the only candidate devices that can offer extremely low switching loss across a very broad frequency spectrum, including multiple 5G frequency bands. In order to meet and surpass a variety of 5G RF specifications (insertion loss, isolation, power handling, linearity, power consumption, switching speed, integration, reliability, etc.), device performance needs to be increased even further. These performance increases need to come from the incorporation of advanced and optimized materials. In this presentation, the relationship between materials, device performance, and circuit performance will be discussed, as well as how some of these problems are solved in modern PCM RF switches. The material requirements and knowledge of critical layers will also be discussed, with a roadmap to future device performance with the incorporation of advanced or optimized materials.

4:30 PM

(EMA-S11-012-2019) Multiphysical Design Approach for RF BAW Modules on a SiCer Substrate (Invited)

A. Hagelauer*[1]; V. Chauhan[1]; V. Silva[1]; U. Stehr[2]; M. Fischer[2]; J. Müller[2]; R. Weigel[1]

1. Friedrich-Alexander-University Erlangen-Nuremberg, Institute for Electronics Engineering, Germany
2. TU Ilmenau, Germany

Nowadays, primarily acoustic wave MEMS devices are used for filtering in front ends of modern mobile transceivers. An increasing number of frequency bands of operation, combined with more complex modulation schemes are proposed to satisfy the steady demand for higher channel capacities and data rates. This trend leads to more and more heterogeneous integration concepts with the increasing challenge to retain the excellent properties of the components in the final module. We describe a carrier substrate, targeting applications, which combine MEMS components and microelectronic devices at RF frequencies. It combines a LTCC substrate with a silicon wafer, therefore called Silicon-Ceramics, or shortly, SiCer-substrate. Furthermore, we describe a multiphysical design approach for designing such heterogeneous modules.

5:00 PM

(EMA-S11-013-2019) Material, Device, and Integration Challenges for High-Frequency Piezoelectric Microresonators (Invited)

C. D. Nordquist*[1]; M. Henry[1]; D. W. Branch[2]; G. Esteves[1]; A. Siddiqui[1]; M. Eichenfield[1]; R. W. Reger[1]; A. Edstrand[1]; K. Knisely[1]; T. A. Friedmann[1]; T. Pluym[1]; B. A. Griffin[1]

1. Sandia National Laboratories, Microsystems Science and Technology Center, USA
2. Sandia National Laboratories, Nano and Micro Sensors, USA

Contour-mode piezoelectric resonators offer frequency-diverse miniature high-Q filters and frequency references on a single die. These devices use surface electrodes to excite in-plane acoustic waves in micromachined thin piezoelectric films, lithographically defining the frequency and increasing interaction of the electric and acoustic fields. However, several challenges must be addressed prior to incorporation in future microwave systems. For increased bandwidth, devices using scandium-aluminum nitride alloys or lithium niobate demonstrate increased figure-of-merit compared to aluminum nitride. Scaling to higher operating frequencies requires improved fabrication control, while electric-field or mechanical tuning provide promising tuning approaches. Integration with electronics, coupled with wafer-level packaging, provides miniaturization and protection for integration into next-level assemblies. Addressing these and other challenges will allow these devices to provide a technical solution to the increasing filter requirements for future wireless systems. Sandia National Laboratories is a multimission 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.

5:30 PM

(EMA-S11-014-2019) Embedded standards for 5G and millimeter-waves (Invited)

J. A. Drisko*[1]; R. Chamberlin[1]; X. Ma[1]; A. D. Feldman[1]; F. Quinlan[1]; J. Booth[1]; N. Orloff[1]; C. Long[1]

1. National Institute of Standards and Technology, USA

Calibrations are essential for accurate characterization of materials and devices at 5G frequencies and to optimize the energy efficiency of 5G integrated circuits. For many 5G applications, these circuits are combined and incorporated into larger systems, prohibiting the individual test and evaluation required to optimize a single circuit. Furthermore, systematic errors from the measurement setup dominate any given measurement of these circuits. Calibrations are necessary to correct these systematic errors and extract the true behavior of the device or material under test so that it can be accurately understood and modeled. Here, we describe recent progress on embedded calibration standards as well as on-wafer calibrations. Specifically, we will discuss a photoconductive device as a multi-state calibration artifact and an optimal resistor for the series resistor calibration. Such a multi-state device might enable calibration artifacts to be integrated into larger 5G systems and allow for individual measurements of specific integrated circuits. More efficient, reliable, and accurate calibrations will facilitate faster development of materials and devices for the 5G industry and beyond.

S13: From Basic Science to Agile Design of Functional Materials: Aligned Computational and Experimental Approaches and Materials Informatics

High-throughput Computational/Experimental Approaches/Functional Perovskite

Room: Magnolia B/C
Session Chair: Lan Li, Boisie State University

10:00 AM

(EMA-S13-012-2019) Discovery of 2D Half-Metals and Other Low-Dimensional Magnets by Materials Informatics (Invited)

R. G. Hennig*[1]

1. University of Florida, Materials Science and Engineering, USA

The rapid rise of 2D materials presents the exciting opportunity for materials science to explore an entirely new class of materials. I will present our data-mining, chemical substitution, and evolutionary algorithm approaches to identify novel low-dimensional materials that are sufficiently stable and show how unexpected structures and properties emerge when a material is reduced to sub-nanometers in thickness. We identify several 1D and 2D compounds with ferromagnetic order at temperatures accessible to experiments and show that some exhibit an easy-plane for the magnetic moment and hence a Berezinsky-Kosterlitz-Thouless transition to a magnetically ordered low-temperature phase, while others display an easy magnetization axis and thus an actual ferromagnetic ground state. Furthermore, we identify a family of three magnetic 2D materials with half-metallic band structures. Their purely spin-polarized currents and dispersive interlayer interactions should make these materials useful for 2D spin valves and other spintronic applications. These new 2D materials provide the opportunity to investigate the interplay of magnetic order and reduced dimensionality and may provide materials suitable for optoelectronic and spintronic applications. The structures and other calculated data for all 2D materials are available in the MaterialsWeb database at https://materialsweb.org.

10:30 AM

(EMA-S13-013-2019) High throughput ab initio and machine learning for screening perovskites (Invited)

D. Morgan*[1]; R. Jacobs[1]

1. University of Wisconsin, Madison, USA

This talk will summarize recent work from our group screening perovskites for use as solid oxide fuel cell cathode, electron emitter cathodes, and photovoltaics. We will highlight the use of simple correlations of surface exchange coefficients and work function with oxygen p-band to guide screening. We will also explore how machine learning can be applied to relevant properties such as stability and band gap to greatly expand that space of compounds that can be practically explored.

11:00 AM

(EMA-S13-014-2019) Orientational disorder matters: Thermodynamic stability and electronic structure of hybrid organic-inorganic perovskites

S. R. Xie*[1]; M. Sexton[1]; S. R. Phillpot[1]; J. Xue[1]; R. G. Hennig[1]

1. University of Florida, Materials Science and Engineering, USA

In recent years, interest in lead-free hybrid organic-inorganic perovskites has rapidly grown due to the toxicity and instability of the otherwise-promising organolead halide perovskites, which have been used to great success in perovskite solar cells. To screen the chemical space for stable perovskites, density functional theory can be used to predict the enthalpies of decomposition of different materials. However, we find that energy calculations can vary by hundreds of meV depending on the rotational configuration of organic components in hybrid perovskites and their competing phases. We develop a workflow to sample this orientational disorder and explore its effect on thermodynamic stability and electronic structure in hybrid organic-inorganic perovskites. We demonstrate our workflow on (CH3NH3)2KBiCl6 and (CH3NH3)2AgBiBr6, which have been synthesized in experiment. Across their competing phases, we find that total energy and band gap may change by up to 150 meV/molecule and 0.8 eV, respectively, with orientational disorder.

11:15 AM

(EMA-S13-015-2019) Accelerated Discovery and Design of Perovskite-Based Advanced Functional Materials (Invited)

K. Yang*[1]; J. Cheng[1]; Y. LI[1]

1. University of California San Diego, Department of NanoEngineering, USA

As a rapidly growing area of materials science, high-throughput computational materials design is playing a crucial role in accelerating the discovery and development of novel functional materials. In this talk, I will introduce the strategy of high-throughput first-principles computational materials design, and take several research examples to show the usage of this approach in the accelerated design of functional materials. In particularly, I will talk about our recent research progress on the perovskite-based functional materials: perovskite-based two-dimensional electron gas (2DEG) and hybrid organic-inorganic perovskites for optoelectronics.

11:45 AM

(EMA-S13-016-2019) Two-Dimensional Organic-Inorganic Hybrid Perovskites (Invited)

L. Dou*[1]

1. Purdue University, Chemical Engineering, USA

Semiconductor quantum wells are usually fabricated through metal-organic chemical vapor deposition or molecular beam epitaxy, are key building blocks in modern optoelectronics. The ability to simultaneously realize defect-free epitaxial growth and to individually fine-tune the chemical composition and band structure of each layer is essential for achieving the desired performance. Such structures are challenging to realize using organic or hybrid materials because of the difficulty of controlling the materials growth. In this talk, I will present a molecular approach to the synthesis of high-quality organic-inorganic hybrid perovskite quantum wells through incorporating widely tunable organic semiconducting building blocks. Single crystalline organic-perovskite hybrid quantum wells and superlattices can be easily obtained via one-step solution-processing. Energy transfer and charge transfer between adjacent organic and inorganic layers are extremely fast and efficient, owing to the atomically-flat interface and ultra-small interlayer distance. The 2D hybrid perovskite superlattices are surprisingly stable, due to the protection of the bulky hydrophobic organic groups. The molecularly engineered 2D semiconductors are promising candidates for use in next-generation nanoelectronics, optoelectronics, and photonics.

Friday, January 25, 2019

S2: Advanced Electronic Materials: Processing Structures, Properties, and Applications

Advanced Electronic Materials: Lead free III

Room: Orange A
Session Chair: Zuo-Guang Ye, Simon Fraser University

8:30 AM

(EMA-S2-035-2019) Defect Chemistry of ABO_3 Ceramics (Invited)

S. Lee*[1]; J. Kim[1]; J. U. Rahman[2]; M. Kim[1]

1. Changwon National University, School of Materials Science and Engineering, Republic of Korea
2. Korea Institute of Ceramic Engineering and Technology (KICET), Republic of Korea

Nonstoichiometric ABO_3 ($BaTiO_3$ and $BiFeO_3$) ceramics were investigated through high temperature equilibrium conductivity (HiTEC) and in-situ impedance measurements at various equilibrium conditions. Contribution of mobile oxygen vacancies and volatile metal vacancies has been determined by HiTEC measurement as a function of oxygen partial pressure. The dominant defect and minor carrier types with different nonstoichiometric conditions were intensively investigated as well combining with Seebeck coefficient measurement. In the $SrTiO_3$ ceramics, to control the Schottky barrier at the grain boundaries, doping strategy has been used widely. In this work we investigated the reduced grapheme oxide (RGO) effects at the grain boundaries in $SrTiO_3$ ceramics with different sintering techniques. The electrical and thermal properties will be discussed in terms of defect chemistry.

9:00 AM

(EMA-S2-036-2019) Fractal Nature as a Bridge Between Ceramics Structures and Energy (Invited)

V. Mitic*[1]; G. Lazovic[3]; V. Paunovic[2]; S. Veljkovic[2]; B. Vlahovic[4]

1. Serbian Academy of Sciences, Institute of Technical Sciences, Serbia
2. University of Nis, Faculty of Electronic Engineering, Serbia
3. University of Belgrade, Faculty of Mechanical Engineering, Serbia
4. North Carolina Central University, USA

In science and technology, tools are always adjusted to the problem, i.e. orderly packed atomic structures suits Euclidian geometry, which is not suitable for rather characterized particles flows and irregular structures. It is fact that energy transformations are permitted on a small scale. The modern Material Science faces new frontiers priorities which opens directions within deeper structure knowledge down to nano and towards new and alternative energy sources. Through our research, we recognize that BaTiO3 and other ceramics have fractal configuration nature based on three phenomena. Ceramic grains fractal shape, so called “negative space” (pores), Brownian fractal particles motions. The stress in this note is set on super inter-granular capacity in function of higher energy harvesting and energy storage. Constructive fractal theory recognize micro-capacitors with fractal electrodes. The method is based on iterative process of interpolation. Intergranular permeability is a function of fundamental thermodynamic parameters (temperature, Gibbs free energy, …).

9:30 AM

(EMA-S2-037-2019) Electric field and pressure induced defect chemistry in lead free potassium sodium niobate piezoelectrics

P. Vilarinho*[1]; R. Pinho[1]; M. Costa[1]; I. M. Reaney[2]; J. Noudem[3]

1. University of Aveiro, Department of Materials and Ceramics, Portugal
2. University of Sheffield, Materials Science and Engineering, United Kingdom
3. IUT-Caen, CRISMAT, France

Producing monophasic stoichiometric dense lead free piezoelectric potassium sodium niobate ((K1-xNax)NbO3, KNN) is still challenging. Dense KNN ceramics require relative high sintering temperatures, not compatible with the high partial pressure of alkaline elements and alternative processing techniques are required. Spark Plasma Sintering (SPS), an electric current activated / assisted sintering (ECAS), that combines the application of pressure and electric current directly on the sample, enabling high heating rates due to Joule heating of conductive dies, is some of the possible alternatives. In this work we have used a derivative method of SPS, Spark Plasma Texturing (SPT) defined as an edge-free SPS. The deformation of the material in the radial direction in SPT, similarly to Hot Forging, results in particles neck destruction, particle rearrangement, destruction of agglomerates improving density and limiting grain coarsening of KNN ceramics. Consequently, SPT KNN presents improve functional performance d33 (125 pC.N-1), g33 (24.5×10-3 Vm.N-1), Pr (43.3 μC cm-2) and Ec (15.0 kV cm-1). HRTEM combined with impedance spectroscopy allowed to establish the defect concentration profile and its relation to defect chemistry, dependence on the grain growth and electrical performance

9:45 AM

(EMA-S2-038-2019) Impact of process optimization and composition on thin film BNKT microstructure, ferroelectric and piezoelectric response

K. M. Grove*[1]

1. Oregon State University, Materials Science, USA

One lead-free piezoelectric material system which bulk research has identified as a potential candidate for replacing PZT in actuator applications is (100-X)$Bi_{0.5}Na_{0.5}TiO_3$-X$Bi_{0.5}K_{0.5}TiO_3$ (BNKT). Difficulties, however, have arisen in the development of marketable high-quality thin film BNKT. The majority of BNKT research has been done near the observed MPB composition of 80$Bi_{0.5}Na_{0.5}TiO_3$-20$Bi_{0.5}K_{0.5}TiO_3$ due to its characteristically large piezoelectric response. Characterizing films of other compositions provides insight into compositional changes that occur due to cation volatilization during high temperature processing. Three separate compositions were evaluated: 40BNT-60BKT, 60BNT-40BKT, and 80BNT-20BKT. Dielectric loss is considerably lower in 40BNT-60BKT (tan δ = 0.02-0.05) than at the MPB (tan δ = 0.05-0.1). d_{33} increases closer to the MPB ranging from 30-40 pm/V at 40BNT-60BKT, 50-60pm/V at 60BNT-40BKT, and 60-90pm/V at the MPB. Polarization loops show more linear polarization response in compositions further from the MPB which displays a more traditional ferroelectric response. The impact and optimization of process conditions including cation excess, and annealing conditions on dielectric, ferroelectric, and piezoelectric response of BNKT films as a function of composition will also be introduced.

Advanced Electronic Materials: Characterization

Room: Orange A

Session Chair: Dragan Damjanovic, Swiss Federal Institute of Technology in Lausanne - EPFL

10:30 AM

(EMA-S2-039-2019) Deconvolved intrinsic and extrinsic contributions to electrostrain in high performance, Nb-doped PZT piezoceramics near the MPB (Invited)

C. Zhao[1]; D. Hou[2]; C. Chung[2]; H. Zhou[2]; A. Kynast[4]; E. Hennig[4]; W. Liu[1]; S. Li[1]; J. L. Jones*[2]

1. Xi’an Jiaotong University, School of Electrical Engineering, China
2. North Carolina State University, Dept. of Materials Science & Engineering, USA
4. PI Ceramic GmbH, Germany

Lead zirconate titanate (PZT) is the base compound for the highest performing piezoelectric compositions. When doped with Nb, PZT has superior electrostrain and piezoelectric properties. However, the origin of that electrostrain involves both intrinsic and extrinsic contributions which have been challenging to deconvolute. In the present work, we utilize high-energy, synchrotron X-ray diffraction (XRD) in combination with an area detector to measure the response of 1% Nb-doped $PbZr_xTi_{1-x}O_3$ (PZT, $0.50 \le x \le 0.56$) piezoceramics to electric fields. Using analysis involving micromechanics-based calculations and pair distribution functions (PDFs), it is found that both the intrinsic and extrinsic contributions are important for realization of high electrostrain. In the compositions nearest the morphotropic phase boundary (MPB), the relative contributions of the intrinsic response increase. The interdependence of crystal symmetry (tetragonal and rhombohedral), spontaneous strain, and the extent of non-180° domain switching are also elucidated. An orientation dependence in the field-induced lattice strain is observed and attributed to extrinsic effects, i.e., the intergranular interaction between domain switching and lattice strain.

11:00 AM

(EMA-S2-040-2019) Structures and Properties of Bismuth-Based High-T_C Piezo-/ferroelectrics (Invited)

Z. Ye*[1]

1. Simon Fraser University, Canada

In order to understand the complex phase symmetry and phase transitions, and to illustrate the microscopic mechanisms of high piezoelectricity, single crystals of a new ternary complex perovskite system, $Pb(Mg_{1/3}Nb_{2/3})O_3$-$Bi(Zn_{2/3}Nb_{1/3})O_3$-$PbTiO_3$, are grown by the high temperature solution growth method and their domain structure, dielectric and ferro-/piezoelectric properties, and phase transformation behavior are investigated by various techniques. Different phase symmetries including the rhombohedral, tetragonal and monoclinic are found in these crystals, indicating that the composition of the crystals is close to the morphotropic phase boundary (MPB) region. Most interestingly, unusual phase transformation sequences of rhombohedral → monoclinic → cubic, and monoclinic → cubic are directly observed by polarized light microscopy and confirmed by the dielectric and birefringence results. Moreover, an ultrahigh piezoelectric coefficient $d_{33}\approx$ 2000 pC/N is obtained in these crystals, making these crystals useful for applications as electromechanical transducers. The unusual phase transformation sequences and the high piezoelectric response are explained from the polarization rotation mechanism, which has been evidenced in this work. Based on these results, a temperature-composition phase diagram is established, which illustrates the complex phases present and their transformation behavior.

11:30 AM

(EMA-S2-041-2019) Local structure studies of ferroelectrics by X-ray fluorescence holography (Invited)

K. Hayashi*[1]

1. Nagoya Institute of Technology, Japan

X-ray fluoresce holography (XFH) is a structural analysis method, which provides 3D atomic images of middle-range local structures around specific elements. Unlike ordinary X-ray diffraction, XFH can record both the amplitude and phase information of scattered waves from atoms. So, using XFH, we have revealed local structures of many functional materials. In particular, XFH is useful for clarifying nano-scale heterogeneous structures, which play a crucial role in the appearance of gigantic susceptibilities and the associated novel phenomena in solids. In this context, we applied perovskite ferroelectrics such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Zr_{1-x}Ti_x)O_3$ (PZT). The XFH experiments were carried out at BL22XU of SPring-8. The 3D local environment around each element was reconstructed using a Fourier-transformation-based algorithm. The XFH result of PMN revealed acute and obtuse rhombohedral structures of the crystal unit cells, which forms a body-center-like $2a_0\times2a_0\times2a_0$ superlattice. On the other hand, the XFH result of PZT showed quite different environments around Zn and Ti, respectively. That is, strong correlation between Zr atom and nearest neighbor Pb atom was observed, while Ti atom does not show such a specific correlation to other atoms.

12:00 PM

(EMA-S2-042-2019) Study of an hourglass-shaped high-temperature piezoelectric vibration energy harvester based on $BiScO_3$-$PbTiO_3$ (BSPT) piezoceramics

W. Chen*[1]; A. Gurdal[1]; S. Tuncdemir[1]; C. Randall[2]

1. Solid State Ceramics, Inc, USA
2. Pennsylvania State University, Materials Science and Engineering, USA

In this study, an hourglass-shaped piezoelectric energy harvester operating in an d_{31} mode and aiming for reliable mechanical vibration energy harvesting in a high temperature environment are considered. This design is composed of a plate-shaped piezoceramics, a tip mass, and low thermal expansion Invar metal foils assembling together. The piezoceramics is based on $BiScO_3$-$PbTiO_3$ ceramic with a piezoelectric coefficient of 450pC/N and a high Curie temperature point T_c of about 450°C. Experimental results show that the harvesters work effectively in a wide temperature range from room temperature up to 250°C. Moreover, device showed functional and higher output power at 250°C. The shifting of resonance frequency is 12.7% from 25 to 250°C. The decrease of maximum output power is 22.8% from 25 to 250°C. The proposed harvester has the potential for applications as a self-power source in high temperature environment. This study of their high temperature vibration responses will enable us to focus on some important aspects that are essential to improve electro-mechanical properties in future higher temperature energy harvesting piezoelectric systems.

12:15 PM

(EMA-S2-043-2019) Effects of Post-irradiation Annealing on Structural Changes in Ferroelectric Thin Film Capacitors

H. Zhou*[1]; M. Liu[1]; S. Williams[2]; L. Griffin[2]; C. Cress[3]; M. Rivas[4]; R. Rudy[4]; R. G. Polcawich[4]; E. Glaser[3]; N. Bassiri-Gharb[2]; A. Hawari[1]; J. L. Jones[1]

1. North Carolina State University, USA
2. Georgia Institute of Technology, USA
3. Naval Research Laboratory, USA
4. US Army Research Laboratory, USA

Ferroelectric materials are considered ideal for operation in hostile radiation environments as remote sensors and logic devices. However, ionization and displacement events induced by irradiation can increase defect concentrations and interaction between defects and domain wall motion, which influences the performance of the device. Heavy-ion radiation-induced structural changes in $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin film capacitors have been studied using Doppler Broadening Spectroscopy (DBS) and X-ray diffraction (XRD). The results suggest that defect concentration increases as the radiation fluence level increases. Furthermore, the concentration of Zr/Ti- related defects is enhanced by radiation at a greater rate than defects associated with the Pb-site. In order to understand the recovery of radiation-induced defects, the heavy-ion-irradiated PZT capacitors were annealed at several temperatures. The XRD results demonstrate that the radiation induced structural changes can be recovered to the level before irradiation when the samples are annealed above the Curie temperature.

S4: Complex Oxide Thin Film Materials Discovery: From Synthesis to Strain/Interface Engineered Emergent Properties

Functionality: Ferroic III

Room: Orange B

Session Chairs: Roman Burkovsky, Peter the Great St. Petersburg Polytechnic University; Sean Smith, Sandia National Laboratories

8:30 AM

(EMA-S4-036-2019) Magnetic Frustration Engineering Through Stereochemical Disorder in Single Crystalline Entropy-Stabilized Oxides

P. B. Meisenheimer*[1]; L. Williams[1]; E. Kioupakis[1]; J. Heron[1]

1. University of Michigan, Materials Science and Engineering, USA

A unique benefit to entropic stabilization is the increased solubility of elements, which opens a broad compositional space with subsequent local chemical and structural disorder resulting from different atomic sizes and preferred coordinations of the constituents. It is unknown, however, to what degree this structural disorder contributes to material functionalities. In the antiferromagnetic entropy-stabilized oxides studied here, we see that by tuning the concentration of local structural frustrations caused by Jahn-Teller active cations, we induce or reclaim a large degree of disorder in the magnetic lattice of the material. This effect can be utilized to tune the anisotropy and magnetic structure of the oxide to approach that of an isotropic spin glass, yet still in a single crystalline material. Our results reveal that the unique characteristics of entropy stabilized materials can be utilized to realize novel magnetism in oxide thin films.

8:45 AM

(EMA-S4-037-2019) Co-existence of ferromagnetism and superparamagnetism in thin films of $La_{0.7}Sr_{0.3}MnO_3$

M. B. Holcomb*[1]; N. Mottaghi[1]; R. Trappen[1]; S. Kumari[1]; A. Penn[2]; C. Huang[3]; S. Yousefi[1]; G. Bhandari[1]; J. LeBeau[2]; M. Seehra[1]

1. West Virginia University, Physics, USA
2. North Carolina State University, Materials Science & Engineering, USA
3. West Virginia University, Mechanical & Aerospace Engineering, USA

Superparamagnetism is the ability of some magnetic nanoparticles to randomly flip direction under the influence of temperature. We observe evidence of a similar effect in $La_{0.7}Sr_{0.3}MnO_3$, a strongly correlated ferromagnetic system that is proposed for magnetoresistance applications. Utilizing many techniques (bulk magnetometry, neutron reflectometry and resonant x-ray magnetic scattering), we observe magnetic competition between different magnetic phases in many samples under various growth conditions. This competition results in inverted hysteresis loops (common in superparamagnetic nanoparticles) and negative remanent magnetization. While scanning transmission electron microscopy shows pristine epitaxial growth, the data supports that there are regions of different magnetic order. This results in interesting magnetic measurements, that share similarities with ferrimagnets with competing magnetic lattices. Sample growth and optimization were supported by NSF (DMR-1608656), national facility measurements and theory were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0016176, and optical measurements by American Chemical Society (PRF #56642-ND10). We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work.

9:00 AM

(EMA-S4-038-2019) Epitaxial Multiferroic Superlattices Combining Hexagonal and Cubic Ferrites (Invited)

M. E. Holtz*[1]; R. Steinhardt[1]; D. Muller[4]; R. Ramesh[3]; J. Mundy[2]; D. Schlom[1]

1. Cornell University, Materials Science and Engineering, USA
2. Harvard University, Physics, USA
3. UC Berkeley, Materials Science and Engineering, USA
4. Cornell University, Applied and Engineering Physcis, USA

Hexagonal rare earth ferrites offer a promising but relatively unexplored area for multiferroic materials design. A recent approach was to grow epitaxial superlattices that combine the ferroelectric hexagonal $LuFeO_3$ with the ferrimagnetic $LuFe_2O_4$ using oxide molecular beam epitaxy. While these lutetium ferrite superlattices demonstrated magnetoelectric coupling up to 320 K, for device applications we seek materials that have stronger magnetism well above room temperature. Here, we use a similar technique to combine h-$LuFeO_3$ with cubic spinel ferrites, such as $CoFe_2O_4$ which has a ferrimagnetic moment up to 860 K. Depending on growth conditions, the spinel can form as surface polycrystalline precipitates, 3D epitaxial structures, or well-ordered superlattices. The resulting superlattices show both strong magnetic moment and polarization above room temperature, which is promising for device applications. Characterization by scanning transmission electron microscopy investigates the interfacial reconstruction between the two materials as well as the ferroelectric polarization atom-by-atom in the $LuFeO_3$. Multiferroic properties such as magnetoelectric coupling are currently under investigation.

9:30 AM

(EMA-S4-039-2019) Strain effects in ferroic superlattices

M. El Marssi*[1]; J. Belhadi[1]; B. Carcan[1]; H. Bouyanfif[1]; Y. Gagou[1]; F. Ravaux[2]; M. Jouiad[2]

1. Université de Picardie Jules Verne, LPMC, France
2. Masdar Institute of Science and Technology, United Arab Emirates

Perovskites are known to be very sensitive to even small distortion and their properties can be modified by mechanical constraints within the superlattice (SL). The lattice strain variations within the constituent layers of the artificial SL may change profoundly properties of each layer. Stress effects govern physical properties of thin films and SLs and better understanding of these factors is obviously required to achieve reliability of ferroic properties desirable for device engineering. Ferroic bicolor $[ABO_3]_{(1-x)\Lambda}/[A'B'O_3]_{x\Lambda}$ SLs grown by pulsed laser deposition with the modulation period Λ varied between 16 and 1008 Å for x=0.5 and for a fixed period, x was varied between 0.15 and 0.85. X-ray diffraction, Raman spectroscopy, dielectric spectroscopy and Transmission Electron Microscopy (TEM) were used to understand peculiarities of the ferroic phases in SLs resulting from the lattice mismatch between the constituent layers. The strain effects on the polarization orientation and the frequency shift of the soft mode with respect to bulk crystal and thin films were studied in different SLs. Reduction of the disorder and a critical period Λc, above which the strain relaxation in the SLs due to misfit dislocations is energetically preferable, were observed. A stress profile in SL constituents was discussed and possible ferroic phase transitions in SLs discussed.

9:45 AM

(EMA-S4-040-2019) Well-Ordered Stripe Domains in $BiFeO_3$ grown on $TbScO_3$ by Molecular-Beam Epitaxy

A. B. Mei*[1]; D. Schlom[1]

1. Cornell University, Materials Science & Engineering, USA

Bismuth ferrite $BiFeO_3$ layers, ~200-nm-thick, are deposited on $SrRuO_3$-coated $DyScO_3(110)o$ substates in a step-flow growth regime via adsorption-controlled molecular-beam epitaxy. Structural characterizations establish phase-pure films of high structural perfection with substrate-limited mosaicity (0.012° x-ray diffraction ω-rocking curve widths) and atomically smooth surfaces (0.2 nm root-mean-square height fluctuations) consisting of 260-nm-wide $[-111]_o$-oriented terraces and unit-cell-tall (0.3 nm) step edges. The combination of interfacial and step-edge templating promotes two monoclinically-distorted $BiFeO_3$ ferroelectric variants, r1 and r2, sheared along $[-11-1]_o$ and $[1-1-1]_o$, respectively. The domain variants self-assemble into $[001]_o$-oriented 290±4-nm-wide one-dimensional striped patterns of unprecedented long-range order and distinguished periodicity.

Functionality: Optical

Room: Orange B

Session Chairs: Qian Li, Argonne National Laboratory; Hyoungjeen Jeen, Pusan National University

10:30 AM

(EMA-S4-041-2019) Complex Oxide Thin Films as Alternative Plasmonic Materials (Pioneer talk) (Invited)

P. K. Petrov*[1]; M. Wells[1]; R. Bower[1]; B. Zou[1]; A. Mihai[1]

1. Imperial College, Materials, United Kingdom

Current opto-electronic devices are rapidly approaching their theoretical maxima in terms of both speed and bandwidth capabilities. Also, the light diffraction limits their miniaturisation and integration with the modern nanoelectronic devices. Therefore, the plasmonic phenomena have been proposed as enabling means for enhancement of wide range of technologies, ranging from energy harvesting, optical and chemical sensing, to high-speed computing.

The traditional plasmonic materials, gold and silver, are subject to a number of inherent limitations e.g. lack of performance tunability, and crucially, incompatibility with conventional silicon-based electronics. Here we will discuss several complex oxide materials, namely strontium ruthenate ($SrRuO_3$), strontium molybdate ($SrMoO_3$) and strontium niobate ($SrNbO_3$), which have recently been proposed as new plasmonic materials that offer better temperature stability than conventional plasmonic metals and control field localization with a choice of plasma frequencies in a wide spectral range. Thin films and multilayer structures of these materials, were deposited by pulsed laser deposition and were comprehensively characterised by means of spectroscopic ellipsometry, XRD, AFM, SEM, and SIMS, along with DC resistivity and AC Hall effect measurements. The results of these experiments confirmed the suitability of these materials for visible to near infrared plasmonic applications.

11:00 AM

(EMA-S4-042-2019) $SrNbO_3$/Metal composites for chiral optics plasmonics devices

A. Mihai*[1]; M. Wells[2]; B. Zou[2]; P. K. Petrov[2]; S. Maier[1]

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

Controlling the flow of light with nanotphotonic optical devices has the potential of transforming integrated information processing. Because of the strong transverse confinement of guided photons, their internal spin and their orbital angular momentum get coupled. Using this spin-orbit interaction of light once can imagine optical devices that take advantage of spin orbit coupling such as vaweguides. Photonic integrated circuits also require various optical materials with versatile optical properties and easy on-chip device integration. To address such needs, a we designed nanoscale metal-oxide metamaterial, (i.e. Metal nanoparticles embedded in $SrNbO_3$ thin films) with controllable optical response. Specifically, epitaxial $SrNbO_3$ (SNO) thin films with tailored metal nanoparticle morphologies (i.e., various nanoparticle sizes and densities), have been grown by a pulsed laser deposition (PLD) method. SEM, XRD, Hall Effect, 4-probe Resistivity and Ellipsometry were used for analysis. Optical measurements present surface plasmon resonance and dramatically varied dielectric permitivity, attributed to the plasmonic character of $SrNbO_3$ enhanced by the presence of strong s-o effects -coupled with plasmonic effects found in the metal nanoparticles. The hybrid Metal-SNO metamaterial thin films provid a novel platform for tunable optical materials and their future on-chip integrations in photonic based integrated circuits.

11:15 AM

(EMA-S4-043-2019) Plasmonic Transition Metal Oxide Nanoarrays: Fabrication and Characterisation

R. Bower*[1]; M. Wells[1]; A. Mihai[1]; B. Zou[1]; P. K. Petrov[1]

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

Conductive transition metal oxides (TMOs) have recently been suggested as alternative materials to the noble metals gold and silver for plasmonic applications. We have previously characterised the optical and physical properties of TMO thin films including strontium ruthenate (SRO), strontium molybdate (SMO) and strontium niobate (SNO). The increased thermal stability and broad spectral tunability of these TMOs indicate that they are suitable candidates for use within optical and plasmonic devices, with applications ranging from epsilon-near-zero components to plasmonic local heat generation. We present the properties of TMO plasmonic devices with critical dimensions ranging from 200nm-1μm. Colloidal lithography and e-beam lithography were used. SRO, SNO and SMO thin films with thickness 50-100nm grown by pulsed laser deposition were used to fabricate nanodisc arrays and nanostructures. Spectroscopic characterisation of these devices will also be presented and related to the properties of the parent materials.

11:30 AM

(EMA-S4-044-2019) Multiferroic bandgap tuning in (001) ordered $Bi(Fe,Cr)O_3$ heterostructures

M. Walden*[1]; G. L. Brennecka[1]; C. Ciobanu[2]

1. Colorado School of Mines, Materials Science, USA
2. Colorado School of Mines, Mechanical Engineering, USA

Ferroelectric materials are of potential use in solar energy applications due to the bulk photovoltaic (BPV) effect, which bypasses efficiency limits that apply to conventional junction-based photovoltaic devices. However, there are many material challenges which limit the efficiency of BPV-based devices, perhaps chief of which is the large bandgap of many ferroelectric materials. In this study, we explore the $Bi(Fe,Cr)O_3$ (BFCO) system, a perovskite ferroelectric wherein bandgap may be tuned via B-site cationic ordering. We use density-functional theory to model a series of (001) layered BFCO heterostructures consisting of integer numbers of $BiFeO_3$ (BFO) layers and $BiCrO_3$ (BCO) layers, determining how the Fe/Cr ratio and interface density affect bandgap, as calculated using the local density approximation (LDA). As is typical in LDA, our calculated bandgaps are systematically underestimated. We have corrected these bandgaps using consideration of spin via a Hubbard-type model. Using this set of calculated bandgaps, we have developed a quantitative predictive model for the bandgap of BFCO in terms of the compositional and ordering parameters we have investigated.

11:45 AM

(EMA-S4-045-2019) Interfacial perturbation of Epsilon Near Zero (ENZ) Modes in Cadmium Oxide Thin Films

E. L. Radue*[1]; E. L. Runnerstrom[2]; K. Kelley[2]; J. Maria[3]; P. E. Hopkins[1]

1. University of Virginia, Mechanical and Aerospace Engineering, USA
2. North Carolina State University, Material Science and Engineering, USA
3. Pennsylvania State University, Materials Science, USA

The transparent conducting oxide, Cadmium Oxide, has been a promising gateway for mid-IR plasmonics, due to its high mobility and relatively low carrier concentration. In addition, as opposed to traditional plasmonic metals, CdO's resonances are tunable via doping and are not lossy in the infrared regime leading to very strong plasmonic absorption. We attempt to manipulate the epsilon-near (ENZ) zero modes of CdO thin films deposited on Pt using femtosecond optical pulses in a pump-probe configuration. We pump the Pt with a visible pulse and measure the CdO's ENZ mode with a tunable output from an optical parametric amplifier, allowing us to spectrally and temporally monitor the shifts in the ENZ mode over time. I will be discussing how the interplay between the exited Pt and the CdO leads to significant, nanoseconds long, perturbations in the IR-ENZ mode.

12:00 PM

(EMA-S4-046-2019) Tailorable Au nanoparticles embedded in epitaxial TiO_2 thin films for tunable optical properties

S. Misra*[1]; L. Li[1]; J. Jian[1]; J. Huang[1]; X. Wang[1]; D. Zemlyanov[4]; J. Jang[2]; F. H. Ribeiro[3]; H. Wang[1]

1. Purdue University, Materials Engineering, USA
2. Ulsan National Institute of Science and Technology, Republic of Korea
3. Purdue University, Chemical Engineering, USA
4. Purdue University, Birck Nanotechnology Center, USA

The unique property of plasmonic materials to localize light into deep sub-wavelength regime has greatly driven various applications in the field of photovoltaics, sensors and photocatalysis. Here, we demonstrate a one-step growth of oxide-metal hybrid thin film incorporating well dispersed gold (Au) nanoparticles (NPs) with tailorable particle shape and diameters (ranging from 2 to 20 nm) embedded in highly epitaxial TiO_2 matrix, deposited using pulsed laser deposition. Incorporation of Au NPs reduces the band gap of TiO_2 and enhances light absorption in the visible regime owing to the excitation of localized surface plasmons. Optical properties including the plasmonic response and permittivity, and photocatalytic activities of the Au-TiO_2 hybrid materials are effectively tuned as a function of the Au NP sizes. Such optical property tuning is well captured using full field simulations and effective medium theory for better understanding of the physical phenomena. The tailorable shape and size of Au NPs embedded in TiO_2 matrix present a novel oxide-metal hybrid materials platform for optical property tuning and highly efficient plasmonic properties for future oxide-based photocatalytic sensors and devices.

S5: Mesoscale Phenomena in Ferroic Nanostructures: Beyond the Thin–Film Paradigm

Mesoscale Phenomena in Ferroic Nanostructures: Beyond the Thin–Film Paradigm II

Room: Citrus B

Session Chairs: Seungbum Hong, Argonne Nat Lab; Serge Nakhmanson, University of Connecticut

8:30 AM

(EMA-S5-009-2019) Tomographic Atomic Force Microscopy of $BiFeO_3$: Ferroelectricity and Electrical Conductivity Resolved in Three Dimensions (Invited)

J. Steffes*[1]; R. Ramesh[2]; B. Huey[1]

1. University of Connecticut, Materials Science and Engineering, USA
2. University of California, Berkeley, Materials Science and Engineering, USA

Tomographic atomic force microscopy (AFM) is presented as a novel technique for the measurement of the size-dependence of functional properties in multiferroic BiFeO3. By combining tomographic AFM with piezoresponse force microscopy (PFM) and conductive AFM (CAFM), three-dimensional imaging of ferroelectric domains and conductive defects has been achieved in epitaxial $BiFeO_3$. Tomographic AFM provides a platform for quantifying the thickness dependence of the local spontaneous polarization, ferroelectric coercive field, and electrical conductivity in $BiFeO_3$ across two decades of thickness to below 5 nm. Thickness-resolved ferroelectric properties of $BiFeO_3$ strongly correlate with both Landau-Ginzburg-Devonshire theory and the semi-empirical Kay-Dunn scaling law for ferroelectric coercive fields, providing an unambiguous determination of a stable and switchable polar state in $BiFeO_3$ below 5 nm. Combined tomographic PFM and CAFM data reveals reconfigurable, one-dimensional, electrically conductive defects in $BiFeO_3$, which are probed a function of film thickness and show strong agreement with the Schottky emission model of electrical conduction. Along with complementary transmission electron microscopy (TEM) analysis, this work provides new insights into the relationship between thickness and ferroelectric properties in heteroepitaxial multiferroics.

9:00 AM

(EMA-S5-010-2019) What happens at the surface of ferroelectrics?

Y. Ivry*[1]; M. Barzilay[1]; A. Hershkovitz[1]; R. Weinstook[1]; C. Saguy[1]

1. Technion - Israel Institute of Technology, Israel

The unique electric, mechnaical and electro-mechanical properties of ferroelectrics originate from picometer displacements of ions in the bulk. The surface of a ferroelectric has thus to enable a sharp transion in such properties: from zero polarization and no strain in the vacuum to high polarization and large strain release in the bulk. Using advanced TEM and AFM methods we show that the surface of ferroelectrics undergo substential chemical, electrical and mechanical deformation that arise to support ferroelectricity.

9:15 AM

(EMA-S5-011-2019) First-principles parameterization of Landau energy functionals for multiferroic GaV_4Se_8

J. Mangeri*[1]

1. Institute of Physics, Czech Academy of Sciences, Dielectrics, USA

Multiferroic materials are expected to be paramount for a number of next-generation applications, that is, if they can be successfully engineered into devices miniaturized down to mesoscale dimensions. Since such devices or individual device components can range from a few nm to hundreds of μm in size, a number of different theoretical and computational tools are needed to predict and evaluate their behavior. The phase-field method is one such useful approach because it coarse-grains the materials physics into the order parameter description of many atoms. This allows simulations of properties that are not restricted by the structure's length-scale. However, parameterization of these models is difficult, costly, and time consuming to perform experimentally. In this talk, I will demonstrate the use of DFT-based atomistic simulations to extract thermodynamic potentials for the ferromagnetic-ferroelectric GaV_4Se_8, a compound in a materials family known to host exotic magnetic skyrmion phases. The model underpins not only information about the spontaneous polarization, but also the magnetic ordering and elastic strains. The development of such a multiscale-multiferroic modeling approach will be useful for next-generation device design incorporating not-yet discovered novel materials as well as basic science research on the materials microstructure and order parameter topologies.

9:30 AM

(EMA-S5-012-2019) Conducting Domain Walls for Ephemeral Nanocircuitry (Invited)

M. Gregg*[1]

1. Queen's University Belfast, School of Maths and Physics, United Kingdom

The discovery of conducting domain walls in ferroelectrics and multiferroics has opened a new and interesting area for fundamental materials physics, building nicely on insight and experience gained, for example, in LaAlO3-SrTiO3 interface studies. The fact that domain walls can be moved, created and destroyed, under applied fields, has generated particular excitement, prompting visions of mobile nanoscale interconnects for agile circuits. We have been trying to push this paradigm even further, by seeking to build devices within domain walls which could also be moved, created and destroyed, thus presenting the possibility of entirely ephemeral nanocircuits which could be created in one moment, erased and made new in a completely different format the next. A primary building block for such ephemeral devices might be a domain wall p-n junction. We have been studying naturally formed domain wall junction structures in ErMnO3, where head-to-head (H-H) and tail-to-tail (T-T) domain walls meet. Using Kelvin Probe Force Microscopy, we have demonstrated that T-T walls show p-type conduction, while H-H walls are n-type, such that, at the domain wall junction points 1D p-n junctions are fully expected. The characterisation of these diode junctions will be discussed, along with the potentially memristive behaviour resulting from controlled injection of conducting walls in LiNbO3-based devices.

10:30 AM

(EMA-S5-013-2019) Nanoscale functionality of bismuth ferrite domain walls and ferroelectric skyrmions (Invited)

J. Hlinka*[1]

1. Academy of Sciences of the Czech Republic, Institute of Physics, Czechia

Recently, bismuth ferrite domain walls have raised a considerable attention. Their potential functional properties involve challenging phenomena like multiferroicity or photoinduced transport. I would like to present my personal view on few on-going and published experimental and theoretical studies of bismuth ferrite domain walls to which I had chance to contribute directly. In the second part of my talk, I will address flavors of the ferroelectric skyrmion concept with a special attention to the lacunar-spinel-type skyrmion.

11:00 AM

(EMA-S5-014-2019) Mesoscale-level Modeling of Light Transmission through Polycrystalline Ceramics

L. Kuna*[1]; J. Mangeri[2]; J. Wollmershauser[3]; E. Gorzkowski[3]; S. Nakhmanson[4]

1. University of Connecticut, Physics, USA
2. Institute of Physics, Czech Academy of Sciences, Czechia
3. U.S. Naval Research Laboratory, USA
4. University of Connecticut, Department of Materials Science and Engineering, USA

Recent advances in polycrystalline ceramic synthesis have established straightforward fabrication routes for producing dense ceramics with grain size on the order of few nanometers. The light transmission properties and, specifically, the high transparency of such small grain sizes cannot be physically captured by classical geometrical optics theory. In the present work, we developed a finite element method based numerical model for predicting the refractive index variation in polycrystalline piezoelectrics that is combined with Raman wave-retardation theory to describe real in-line transmission through nanocrystalline materials. This approach demonstrates excellent agreement for the transmission evaluation as a function of crystalline grain size in Al_2O_3 and MgF_2, suggesting that sophisticated optical properties predictions for nanocrystalline ceramics can now be explored. The developed modeling framework can also simulate applied elastic and electric fields, which allows us to study the influence of photoelastic and electro-optic effects on the behavior of nanocrystalline materials.

11:15 AM

(EMA-S5-015-2019) Light-Matter Interactions in Low Symmetry Nanocrystalline Ceramics near the Mie Scattering Limit

E. Gorzkowski*[1]; J. Wollmershauser[2]; J. Drazin[3]; B. Feygelson[1]; G. Beadie[1]

1. Naval Research Lab, USA
2. U.S. Naval Research Laboratory, USA
3. ASEE, USA

Optical non-cubic (i.e., birefringent) ceramics with grain sizes around 40 nanometers sit at the edge of two regimes of light-matter interactions for visible light wavelengths. In ceramics with grain sizes smaller ~40 nanometers, the grain boundary periodicity is <10x smaller than the wavelength of incident light and Mie scattering can be neglected. However, for ceramics with grain sizes greater than ~40 nanometers, light-matter interactions for visible light wavelengths can be described by a Rayleigh-Gans-Debye model developed by Apetz and van Bruggen, where the crystal birefringence (Δ_n) modulates the degree of diffuse scattering. For small Δ_n, such as in α-alumina (sapphire structure), diffuse scattering is minimized and non-cubic ceramics can exhibit high degrees of in-line transmission. In this work, nanocrystalline alpha-alumina ceramics were synthesized via Environmentally Controlled Pressure Assisted Sintering (EC-PAS) from milled nanopowders and light-matter interactions were evaluated by characterizing the transmitted wave front quality and degree of diffuse scattering. Implications for controlling light transmission in non-centrosymmetric ferroelectrics will be discussed.

S6: Complex Oxide and Chalcogenide Semiconductors: Research and Applications

Electron Microscopy of Oxides and Chalcogenides

Room: Magnolia A
Session Chair: Steven Spurgeon, Pacific Northwest National Laboratory

8:30 AM

(EMA-S6-016-2019) In situ biasing and 4D STEM of Relaxor Ferroelectric Complex Oxides (Invited)

J. LeBeau*[1]; R. Dhall[1]; M. J. Cabral[1]; A. Kumar[1]

1. North Carolina State University, Materials Science & Engineering, USA

With the introduction of 4D scanning transmission electron microscopy, new methods to directly connect structure and properties have been made possible. For example, quantitative measurement of electric/magnetic fields, high S/N ratio imaging of light elements, and phase retrieval are on their way to becoming routine. While the speeds to capture 4D STEM data (~1 ms/probe position) is still slower than conventional imaging (~1 μs/probe position), in situ experiments significantly benefit from this 4D data. In this talk, I will present our recent in situ 4D STEM studies using an electric field applied to the relaxor ferroelectric PMN-PT. As a first step, I will discuss our approach that overcomes these limitations by combining microfabrication techniques with conventional TEM sample preparation. The most important consequence of this scheme is the high degree of uniformity of the resulting electric field distribution between wired electrodes and allows us to extract representative device characteristics. As a demonstration of the approach, I will show how 4D STEM analysis of field-induced changes to the atomic structure and domain orientation provide rapid insights into the behavior of relaxor ferroelectric materials as the applied field is varied.

9:00 AM

(EMA-S6-017-2019) Atomic-scale characterization of complex oxides using Scanning Electron Microscopy Transmission Electron Microscopy (Invited)

D. Kepaptsoglou*[1]; F. Azough[3]; T. Mizoguchi[2]; R. Freer[3]; Q. Ramasse[1]

1. SuperSTEM, United Kingdom
2. University of Tokyo, Institute of Industrial Science, Japan
3. University of Manchester, Materials, United Kingdom

Perovskite oxides are widely studied for a variety of applications, from thermoelectric heat conversion to fuel cell and solar cell applications. Part of the attraction lies in the fact that perovskite ceramics are relatively easy to dope chemically over a wide range of compositions allowing for their physical properties and functionality to be efficiently tailored. Precise control of local ordering and local or extended defects can alter the local electronic structure, affecting for instance electron transport behaviour, while the precise growth control of multilayer heterostuctures can give rise to emergent properties within the interior of the multilayer structure. However, as these effects are dependent on small structural details, such as atomic arrangements at the sub-angstrom scale they are often too minute, to be detected or sufficiently characterized by bulk techniques. In this respect electron microscopy and in particular Scanning Electron Microscopy Transmission Electron Microscopy (STEM) in tandem with Electron Energy loss Spectroscopy (EELS) is probably the ultimate research tool for such systems, as it allows to probe simultaneously structural and chemical/bonding information at the atomic level. Here, we probe the effect of local chemistry and presence of defects the electronic structure of oxide systems for thermoelectric applications

9:30 AM

(EMA-S6-018-2019) In-situ characterization of multi-functional materials at atomic-resolution using aberration-corrected STEM (Invited)

R. F. Klie*[1]; X. Rui[1]; X. Hu[1]

1. University of Illinois at Chicago, Department of Physics, USA

The last few years have seen a paradigm change in the way we characterize materials, with unprecedented improvements in both spatial and spectroscopic resolution being realized in TEM. When multi-modal X-ray and electron imaging is combined with density-functional theory (DFT) calculations, the effects of defects, dopants or strain at grain boundaries or interfaces can now be directly determined and correlated to electronic/thermal transport properties. While spatial and energy resolutions better than 60 pm and 10 meV have been reported, aberration-corrected TEM has also enables a large variety of in-situ experiments at close to atomic resolution. Using this approach, the intercalation of multi-valent ions into cathode materials, the dynamics of vacancies, and the interactions between gases and nano-particles can now be directly observed, to only mention a few examples. In this presentetion, I will demonstrate how in-situ multi-modal characterization and DFT modeling can be used to unravel the fundamental structure-property relationship of complex oxide thin films as well as 2-dimensional transition metal dichalcogenides. Using in-situ heating and cooling experiments, the low temperature phase transisitions in perovksite oxides wil be examines. The thermal conductivity and expnsion of low dimensional materials will also be discussed using in-situ heating experiments.

Emerging Oxides

Room: Magnolia A
Session Chair: Matthew Brahlek, Oak Ridge National Laboratory

10:30 AM

(EMA-S6-019-2019) Data-Driven Informatics Approaches for Rational Design of Complex Oxides (Invited)

P. Balachandran*[1]

1. University of Virginia, Materials Science and Engineering, USA

I will discuss our recent informatics efforts that have rationally guided experiments in search of novel perovskite oxides with targeted properties. I will focus on the chemical space of Bi-based $PbTiO_3$ solid solutions and demonstrate the efficacy of a two-step machine learning approach that have successfully guided experiments and have led to the synthesis of new perovskite compositions with high ferroelectric Curie temperature. The problem is challenging because the search space is vast, spanning ~61,500 compositions and only a fraction are experimentally studied. Further, not every composition can be synthesized in the perovskite phase. Our approach finds six perovskites out of ten compositions synthesized, including three compositions in the previously unexplored chemical space, with $0.2Bi(Fe_{0.12}Co_{0.88})O_3$–$0.8PbTiO_3$ showing the highest measured Curie temperature of 898 K among them.

11:00 AM

(EMA-S6-020-2019) Real-space imaging of the spin cycloid in $BiFeO_3$ (Invited)

V. Garcia*[1]

1. CNRS/Thales, France

While ferromagnets are at the heart of daily life applications, the large magnetization and energy costs for switching bring into question their suitability for low-power spintronics. Non-collinear antiferromagnetic systems do not suffer from this problem and often possess remarkable functionalities: non-collinear spin order may break space-inversion symmetry and allow electric-field control of magnetism, or produce emergent spin-orbit effects which enable efficient spin-charge interconversion. To harness these unique features, the equivalent nanoscale control and imaging capabilities, now routine for ferromagnets, must be developed for antiferromagnetic systems. Here, using a non-invasive scanning magnetometer based on a single nitrogen-vacancy (NV) defect in diamond, we demonstrate the first real-space visualization of non-collinear antiferromagnetic order in a magnetic thin film, at room temperature. We image the spin cycloid of a multiferroic $BiFeO_3$ thin film and extract a period of 70 nm, consistent with values determined by macroscopic diffraction. In addition, we use the magnetoelectric coupling present in $BiFeO_3$ to manipulate the cycloid propagation direction with an electric field. Finally, we investigate the coupling between strain and magnetic order in strain-engineered samples of $BiFeO_3$. These results highlight the unique potential of NV magnetometry for imaging complex antiferromagnetic order at the nanoscale.

11:30 AM

(EMA-S6-021-2019) Current-density implementation for calculating flexoelectric coefficients for cubic oxides (Invited)

C. E. Dreyer*[1]

1. Stony Brook University and Flatiron Institute, Physics and Astronomy, USA

The flexoelectric (FxE) effect, where polarization is induced by a strain gradient, is universal in all insulators. As devices shrink to the micro and nano scale, large strain gradients can occur, and therefore the FxE effect can play a significant role in their electrical and mechanical properties; also, the FxE effect can be exploited for novel device design paradigms such as piezoelectric “meta-materials” constructed from nonpiezoelectric constituents, or mechanical switching of ferroelectric polarization. One of the crucial limitations to understanding and exploiting the FxE effect is the lack of an efficient first-principles methodology to calculate all of the components of the bulk FxE tensor; the clamped-ion transverse and shear components in particular are problematic. In this work we develop such a methodology based on density functional perturbation theory to calculate the full bulk, clamped-ion FxE tensor from a single unit cell, by calculating the current-density response to the adiabatic displacement of atoms from a long wavelength acoustic phonon. In this talk I will outline our methodology, and apply it to calculate the clamped-ion flexoelectric constants for a variety of technologically important cubic oxide materials.

12:00 PM

(EMA-S6-022-2019) Discovery of non-Fermi liquid behavior in $SrVO_3$ (Invited)

R. Engel-Herbert*[1]; M. Brahlek[2]; J. Roth[1]; T. Birol[3]

1. The Pennsylvania State University, Materials Science and Engineering, USA
2. Oak Ridge National Laboratory, USA
3. Rutgers University, USA

The synthesis of ultraclean materials has been instrumental to explore the intrinsic electronic properties of materials. This is particularly interesting for strongly correlated electron systems to explore the phenomena arising from the presence of a sizeable electron interaction strength. $SrVO_3$, generally assumed to be a Fermi liquid, is an archetypical correlated electron system due to its simplicity, given the cubic structure, absence of long-range magnetic order, absence of a superconducting ground state, and single electron occupancy in the d orbital forming the conduction band. The presence of two cations has made it difficult to control cation stoichiometry during film growth, which has resulted in material with a sizable defect concentration. In this talk we present transport anomalies observed in ultraclean $SrVO_3$ films grown by hybrid MBE, which are in stark contrast to the conventional Fermi liquid picture. A new low temperature electronic phase is identified, which violates the Luttinger count suggesting that $SrVO_3$ is not a conventional Fermi liquid. In-depth analysis of the low field magnetotransport revealed a strong wave vector dependence of electron scattering times at low temperatures. These anomalies are absent for $SrVO_3$ films with a high defect concentration, suggesting a more complex nature of the electron correlation than captured by the Fermi liquid theory and previous experiments.

12:30 PM

(EMA-S6-023-2019) Effect of strain on the metal-insulator transition and orbital polarization in strongly covalent $CaFeO_3$ (Invited)

P. C. Rogge*[1]; S. May[1]

1. Drexel University, USA

Ferrate perovskites that contain the unusually high Fe^{4+} oxidation state, such as $CaFeO_3$ and $SrFeO_3$, host a collection of novel physical properties including coupled structural and electronic phase transitions, helical magnetism, and negative charge transfer physics. The ability to make epitaxial films enables studies of how these phenomena can be altered through strain. We have synthesized $CaFeO_3$ films using oxygen plasma-assisted molecular beam epitaxy. Transport measurements reveal that the metal-insulator transition (MIT) temperature is suppressed under compressive and tensile strain. X-ray spectroscopy measurements across the MIT show changes to the oxygen-derived electronic structure, but not to the iron-derived states, consistent with a bond disproportionation model in which oxygen ligand holes play a central role in the electronic phase transition. X-ray linear dichroism measurements reveal an inverted orbital polarization: Although multiplet ligand field theory analysis confirms that the energetic ordering of the Fe 3d orbitals is consistent with previously reported strain-induced behavior, we find that the nominally higher energy orbital is more populated than the lower. We attribute this behavior to an anisotropic bandwidth response to strain in a compound with nearly filled bands. This work is supported by the Army Research Office, grant number W911NF-15-1-0133.

S7: Superconducting and Magnetic Materials: From Basic Science to Applications

Superconducting and Magnetic Materials VII

Room: Citrus A

Session Chair: Xucun Ma, Tsinghua University

8:30 AM

(EMA-S7-024-2019) Self-assembled vertically aligned Ni nanopillars in CeO_2 with anisotropic magnetic and transport properties for energy applications (Invited)

J. Huang*[1]; Z. Qi[1]; L. Li[1]; H. Wang[1]; S. Xue[1]; B. Zhang[1]; X. Zhang[1]; H. Wang[2]

1. Purdue University, USA
2. Purdue University, School of Materials Engineering, USA

Self-assembled vertically aligned metal–oxide (Ni–CeO_2) nanocomposite thin films with novel multifunctionalities have been successfully deposited by a one-step growth method. The novel nanocomposite structures presents high-density Ni-nanopillars vertically aligned in a CeO_2 matrix. Strong and anisotropic magnetic properties have been demonstrated, with a saturation magnetization (Ms) of ~175 emu cm^{-3} and ~135 emu cm^{-3} for out-of-plane and in-plane directions, respectively. Such unique vertically aligned ferromagnetic Ni nanopillars in the CeO_2 matrix have been successfully incorporated in high temperature superconductor $YBa_2Cu_3O_7$ (YBCO) coated conductors as effective magnetic flux pinning centers. The highly anisotropic nanostructures with high density vertical interfaces between the Ni nanopillars and CeO_2 matrix also promote the mixed electrical and ionic conductivities out-of-plane and thus demonstrate great potential as nanocomposite anode materials for solid oxide fuel cells and other potential applications requiring anisotropic ionic transport properties.

9:00 AM

(EMA-S7-025-2019) An Old Frontier with New Opportunities: Magnetocaloric Materials and Magnetic Refrigeration (Invited)

Z. Turgut*[1]; M. McLeod[2]; J. Horwath[1]; B. Majumdar[3]

1. US Air Force Research Laboratory, USA
2. University of Dayton Research Institute, USA
3. New Mexico Tech, Materials and Metallurgical Engineering Department, USA

Magnetic refrigeration is a rapidly developing technology that offers more efficient and robust cooling systems with a smaller carbon footprint compared to gas compression systems. Maximum Carnot cycle efficiencies of such systems reach to 60 percent which is about 33 percent higher than that of gas compression systems. A permanent magnet field source and materials with appreciable magnetocaloric effect near room temperature are two main components of magnetic refrigeration. Among a handful of other magnetic systems, Ni–Mn–X, (X=Ga, Sn, Sb and In) based Heusler alloys are one of the actively studied materials systems that exhibit giant magnetocaloric effect (MCE). This study reports our progress on enhancing MCE and tuning phase transformation temperatures of Ga and Sn based Heusler alloys by compositional modifications, interstitial doping and stress assisted thermal cycling.

Superconducting and Magnetic Materials VIII

Room: Citrus A

Session Chair: Xiaoli Dong, Institute of Physics, CAS

10:00 AM

(EMA-S7-026-2019) Update on Aircraft Electric Propulsion and Impact of Superconducting and Cryogenic Technology (Invited)

T. J. Haugan*[2]; M. Susner[1]

1. Air Force Research Laboratory, USA
2. U.S. Air Force Research Laboratory, AFRL/RQQM, USA

The aerospace field is the last transportation industry to implement hybrid-electric technology for propulsion. Hybrid-electric or all-electric propulsion has well understood advantages to increase energy efficiency up to 2-5x, and also provide many other benefits such as regen energy capture, greatly reducing noise and CO_2 emission, better enabling use of regional and city-size hubs, and reduced machine and maintenance costs. Electric propulsion for aircraft has increased exponentially in recent years, involving 20-30 companies 2-3 years ago to over 300 the past year. This paper will summarize recent progress in this field, and present how superconducting/cryogenic is the only demonstrated technology to overcome fundamental limitations of 'conventional' technologies for energy efficiency and power density. Electric drivetrain components to be discussed include generators and motors, power transmission cables, power storage devices including Li-batteries and superconducting magnetic energy storage (SMES), power electronics including inverters, and cryogenic technologies. Properties of cryogenic systems and components will be compared to 'conventional' technology, and the effect of different cooling options may be considered.

10:30 AM

(EMA-S7-027-2019) Atomic Layer Deposition of Ultrahin Al_2O_3 Tunnel Barriers for Metal-Insulator-Metal Tunnel Junctions (Invited)

J. Wu*[1]

1. University of Kansas, USA

Metal-insulator-metal tunnel junctions (MIMTJs) are fundamental building blocks in microelectronics. Magnetic tunnel junctions for spintronics and fast access nonvolatile magnetic memory and Josephson tunnel junctions for magnetometers and qubits are examples. Since coherent tunneling decreases exponentially with the thickness of the insulating tunnel barrier, producing a pinhole-free, low defect insulating tunneling barrier of sub-nm thickness is essential to future MIMTJs. In this work, we report the first successful in situ fabrication of ultrathin (0.1 nm-1.0 nm) Al_2O_3 tunnel barriers using atomic layer deposition (ALD) on superconducting Al and ferromagnetic Fe films and in situ characterization of electronic tunneling using scanning tunneling spectroscopy. Fundamental differences in tunnel spectra characteristics, barrier height, and breakdown behavior were observed between ALD Al_2O_3 and the thermal AlOx tunnel barriers. Crucially, the barrier height of the ALD Al_2O_3 was found to be about twice that of the industry-standard thermal AlO_x formed via oxygen diffusion and remains approximately constant in the barrier thickness range of 0.1 nm-1.2nm. These characteristics indicate a significantly reduced defect density in the ALD Al_2O_3 tunnel barrier, compared to its thermal counterpart, which is supported by electrical transport study of the MIMTJs at cryogenic temperatures.

11:00 AM

(EMA-S7-028-2019) Terahertz emission from the intrinsic Josephson junctions in a thin slitted annular microstrip antenna of the high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Invited)

R. A. Klemm*[1]; S. Bonnough[1]; N. Shouk[1]; R. Shouk[1]

1. University of Central Florida, Physics, USA

We studied the electromagnetic standing waves generated from the ac Josephson effect arising from a dc voltage applied across the intrinsic Josephson junctions in a thin slitted annular microstrip antenna of the high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$. The annulus has inner and outer radii of ρ_1 and ρ_2, respectively, with a slit crossing the annulus at the azimuthal angle $\varphi = 0$. The standing waves can be excited when the frequency of the ac Josephson currents matches that of the antenna, which behaves as an electromagnetic cavity satisfying Neumann boundary conditions for the transverse magnetic modes [1,2]. The uniform Josephson current source radiation and the cavity mode-enhanced emission patterns are calculated and presented in detail. We generalized this model to the case of multiple identical slitted annular pieces, which placed together within an overall wavelength of the modified emission wave length, could produce a combined output power in the 1 mW range, sufficiently high for many useful applications.

11:30 AM

(EMA-S7-029-2019) The Effect of Growth Temperature on the Artificial Pinning Center Landscape in $BaHfO_3$ and Y_2O_3 Doped $YBa_2Cu_3O_{7-x}$ Thin Films

M. Sebastian*[1]; B. Gautam[2]; C. Ebbing[1]; J. Huang[3]; H. Wang[3]; J. Wu[4]; T. J. Haugan[5]

1. University of Dayton Research Institute, USA
2. University of Kansas, Department of Physics and Astronomy, USA
3. Purdue University, School of Materials Engineering, USA
4. University of Kansas, USA
5. Air Force Research Laboratory, Aerospace Systems Directorate, USA

The addition of different insulating, non-reactive nano-phases to $YBa_2Cu_3O_{7-\delta}$ superconductor thin films improves current density by combining different flux pinning mechanisms. Barium Hafnate (BHO) 1D APCs can be tuned by the addition of secondary yttrium oxide (Y_2O_3) 3D APCs, leading to a different pinning landscape. Thin films are grown via pulsed laser deposition (PLD) by the adsorption of adatoms on a substrate surface. The adsorbed adatoms' mobility results from their kinetic energy and arrival rate at the substrate surface, and along with film-substrate interaction energies, and film-film interaction, dictates growth mode. This paper systematically compares the growth temperature (T_g) effect on BHO 1D APCs by measurement of magnetic and transport current densities, critical temperatures, and microstructure observations via SEM and TEM. Nanocomposite films on $LaAlO_3$ and $SrTiO_3$ substrates were produced via PLD with a target consisting of 4 vol.% BHO +3 vol.% Y_2O_3 doped YBCO, while varying the growth temperature from 790 C to 825 °C. Varying the growth temperature affects the microstructural defects within the film, which in turn impacts the pinning strength, current density, and critical temperature. The pinning force density (F_p), and maximum field (H_{max}) of the APCs, are increased with T_g at its optimum growth temperature.

S8: Structure–Property Relationships in Relaxor Ceramics

Applications of Relaxors

Room: Magnolia B/C

Session Chairs: Marco Deluca, Materials Center Leoben Forschung GmbH; Antonio Feteira, Sheffield Hallam University

8:30 AM

(EMA-S8-010-2019) Fatigue and Excessive Heating during Electrocaloric Cycling of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ Ceramics (Invited)

A. Bradesko[1]; M. Vrabelj[1]; L. Fulanovic[1]; A. Hedl[1]; M. Otonicar[1]; H. Uršič[1]; Z. Kutnjak[2]; A. Henriques[3]; C. Chung[3]; J. L. Jones[3]; B. Malic[1]; T. Rojac*[1]

1. Jozef Stefan Institute, Electronic Ceramics Department, Slovenia
2. Jozef Stefan Institute, Condensed Matter Physics, Slovenia
3. North Carolina State University, Dept. of Materials Science & Engineering, USA

In cooling devices, electrocaloric (EC) materials will not only have to be efficient but will have to exhibit a stable EC response over a high number of electric-field cycles. This leads to two questions. First, do we know if one of the most promising EC ceramic materials, i.e., the relaxor-ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$–PbTiO3 (PMN-PT), can withstand such cycling conditions? Second, how does cycling at typical device frequencies (Hz range) affect the heating of the material considering the inherent hysteresis losses? In this presentation, we will discuss these issues by exploring the EC fatigue behavior of relaxor PMN and by investigating the excessive heating during static and dynamic field loading. We observed an emergence of excessive Joule heating in PMN during EC cycling, which significantly reduces the cooling efficiency of the sample. Using a combination of macroscopic and nanoscopic electrical measurements along with in situ X-ray diffraction, we will propose a mechanism linking the fatigue behavior to an electric-field induced relaxor-to-ferroelectric phase transformation. The occurrence of the fatigue will be tentatively explained considering the electric-field–temperature phase diagram of PMN. The problem of excessive heating will be further extended to PMN-PT and hard and soft $Pb(Zr,Ti)O_3$ variants to illustrate the importance of hysteresis losses during EC operation.

9:00 AM

(EMA-S8-011-2019) Nanodomain distribution, texture, and apparent symmetry (Invited)

D. Viehland*[1]

1. Virginia Tech, Materials Science and Engineering, USA

We have performed structural studies of $Pb(Mg_{1/3}Nb_{2/3})TiO_3$-x at%$PbTiO_3$ (PMN-PT) single crystals and textured ceramics. Investigations of crystals with nano-graded electrodes by x-ray reciprocal space mapping demonstrated a transverse broadening along the (H00) direction that was quite different from that of either rhombohedral (R) or monoclinic A (Ma) phases. The results evidence that the nanodomain distribution is significantly altered by nonuniform electric fields, resulting in changes in the average (apparent symmetry). Investigations of poled textured ceramics (with conventional planar electrodes) revealed a Ma lattice symmetry by XRD line scans, but a pseudo-cubic (C) texture symmetry by pole figure scans. The results evidence that the nanodomain distribution is altered by grain texture and electric fields. Our findings demonstrate the important role of the nanodomain distribution upon the average symmetry.

Non-Perovskite Relaxors and Advanced Multiscale Modeling and Characterization

Room: Magnolia B/C
Session Chairs: Igor Levin, NIST; Andrew Rappe, University of Pennsylvania

10:00 AM

(EMA-S8-012-2019) The importance of disorder in tetragonal tungsten-bronzes (Invited)

E. Buixaderas*[1]

1. Institute of Physics, Czech Academy of Sciences, Dielectrics, Czechia

Dielectric properties are considerably affected by disorder in ferroelectric materials. One important effect is the breaking of the long-range ferroelectricity, transforming well-arranged ferroelectric domains into very small polar regions, and changing a sharp ferroelectric phase transition into a diffuse transition, accompanied by an smaller increase of permittivity over a wide range of temperatures and frequencies, what is called relaxor behaviour. Disorder in relaxors is mainly created by cationic substitution and the consequent distortions in the crystal lattice. Many relaxor materials belong to the perovskite family, but the tetragonal tungsten bronze (TTB) structure also produces relaxor behaviour due to its built-in disorder. One of the main difference with perovskites is that the crystallographic structure is not isotropic but uniaxial, and this induces anisotropy in almost all properties of the material. Disorder in TTBs influences many properties, like the dielectric response, as well as the nature of the structure itself due to the presence of discommensurations. The origin of disorder in TTBs will be discussed, comparing the dielectric behaviour of several crystals with different cationic substitution, as well as its influence on the ferroelectric-relaxor transformation, where different correlation lengths plays role.

10:30 AM

(EMA-S8-013-2019) Relaxor behaviour and disorder in tetragonal tungsten bronzes (Invited)

F. D. Morrison*[1]

1. University of St Andrews, Chemistry, United Kingdom

The majority of studies of ferroelectrics focus on perovskites (ABO_3); the closely-related tetragonal tungsten bronzes (TTBs), have been much less studied. General formula $A1_2A2_4B1_2B2_8C_4O_{30}$, TTBs offer a similarly wide degree of compositional modification, but in additional also offer degrees of freedom due to non-degenerate A- and B- crystallographic sites and also a high degree of non-stoichiometry. This mixture of structural and compositional flexibility results in equally complex crystallography including simple loss of inversion symmetry, orthorhombic and monoclinic distortions involving very large unit cells, and also incommensurately modulated structures. The result is a range of electrical properties including dipole glass, relaxor ferroelectric and 'normal' ferroelectric behaviour – often in the same composition as a function of temperature. I will discuss a recent examples of TTB materials which exhibit both relaxor and 'normal' ferroelectric behaviour and where long-range, "average" structural data, as determined by "conventional" synchrotron and neutron diffraction, was insufficient to rationalise the macroscopic electrical properties and a combination of selected area electron diffraction and total neutron scattering was required to probe an order-disorder crossover in these materials.

11:00 AM

(EMA-S8-014-2019) Different origin of relaxor behavior in hetero- and homo-valent substituted $BaTiO_3$: Raman spectroscopy and ab initio modeling perspectives

M. N. Popov[1]; J. Spitaler[1]; V. Veerapandiyan[1]; M. Deluca*[1]

1. Materials Center Leoben Forschung GmbH, Austria

Barium titanate is a well-studied ferroelectric material that upon doping can also exhibit relaxor behavior. The latter is characterized by a diffuse phase transition smeared over a wide temperature range as opposed to the sharp transition observed in ferroelectrics. The most recognizable property of relaxors is the frequency dispersion of dielectric permittivity over the transition range. Despite the high industrial relevance of relaxor ceramics, the understanding of this class of materials is not yet satisfactory. In particular, it is not yet clear as to what atomic mechanisms underlie the relaxor behavior and how doping with either hetero- or homo-valent ions causes a ferroelectric to turn into a relaxor. In this contribution, we report the results of an ab initio study of $BaTiO_3$ (BT) doped with either Zr^{4+} (homo-valent) or Nb^{5+} (hetero-valent). Using density functional theory (DFT), we calculate the simulated Raman spectra of pristine and doped BT-ceramics, discuss the spectral features induced by substitution, and elaborate on their atomistic origin. Comparison with experimental Raman spectra allows then to infer on the local polar and chemical order/disorder induced by substitution.

11:15 AM

(EMA-S8-015-2019) First-principles study of piezoelectric $(Ba,Ca)TiO_3$-$Ba(Ti,Zr)O_3$ solid solutions (Invited)

D. Amoroso*[1]; A. Cano[2]; P. Ghosez[1]

1. University of Liege, Belgium
2. Institut NEEL, CNRS, France

Despite intriguing properties of $BaTiO_3$-based solid solutions have been known since the early sixties, these systems did not attract a lot of attention until recently, appearing as some of the most promising lead-free candidates to replace $Pb(Zr,Ti)O_3$ in piezo-devices. There have been several experimental investigations of $(Ba,Ca)(Ti,Zr)O_3$-systems and different theoretical attempts in modeling their structure-composition-property relationships. Nevertheless, the microscopic mechanisms behind their properties are still under debate. Additionally, no systematic theoretical studies, purely based on first-principles, have been carried out yet. Here, we analyze from Density Functional Theory calculations the evolution with composition of the ferroelectric, piezoelectric and related properties of the binary systems $(Ba,Ca)TiO_3$ and $Ba(Ti,Zr)O_3$ in order to compare the role of individual atomic substitutions at the A and B sites of $BaTiO_{3.}$ We discuss their properties in relationship to those of the parent compounds, with a focus on the ferroelectric properties and lattice dynamics. In particular, $(Ba,Ca)TiO_3$ exhibits a gradual transformation from B-type to A-type ferroelectricity due to steric effects that largely determine the behavior of the system. Different behaviors characterize $Ba(Ti,Zr)O_3$, where the appearance of ferroelectricity is strongly dependent on the local atomic arrangements and composition.

11:45 AM

(EMA-S8-016-2019) Different models for the polar nanodomain structure of relaxor ferroelectrics and their effect on the diffuse scattering patterns (Invited)

R. T. Welberry*[1]; M. Pasciak[2]

1. Australian National University, Research School of Chemistry, Australia
2. Czech Academy of Sciences, Institute of Physics, Czechia

The diffraction patterns of a wide range of relaxor ferroelectrics display broadly similar features. In particular they contain sets of diffuse streaks or rods of scattering running along $\langle 110 \rangle$directions. The intensity along the rods tends to increase towards the Bragg positions but may extend over the whole Brillouin zone to the next Bragg peak. At the intersection of these rods, surrounding the Bragg positions, there are distinctive 'X-' or 'butterfly-shaped' regions of stronger scattering. The distribution of intensity shows transverse polarization – i.e. the rods passing through the origin have zero intensity. In this paper we use computer simulation of model systems to investigate how the different features may arise and what influences their detailed appearance. Two contrasting models are considered. The first assumes that the structure is comprised of essentially 2 dimensional 'pancake-shaped' nanodomains distributed throughout the crystal. The second assumes that the nanodomains are 3 dimensional and that it is the boundaries between these domains that give rise to the oriented rods of diffuse scattering. In both models it is assumed that the basic origin of the observed scattering is the fact that Pb ions are displaced away from their average site at the centre of their coordination shell in order to satisfy their bond-valence.

Local Structure of Relaxors

Room: Magnolia B/C
Session Chairs: Elena Buixaderas, Institute of Physics, Czech Academy of Sciences; Richard Welberry, Australian National University

2:00 PM

(EMA-S8-017-2019) Nanoscale Atomistic Models of Relaxor Ferroelectrics from Diffraction Data (Invited)

I. Levin*[1]

1. NIST, USA

Relating structure to function in materials that exhibit correlated nanoscale disorder requires adequately large atomistic models which today are obtained mainly via theoretical simulations. Here, we exploit our recent advances in structure-refinement methodology to demonstrate how such models can be derived directly from diffraction data, and we use this approach to elucidate the contentious nanoscale atomic correlations in the classical relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN). Our results uncover details of the partial ordering of Mg and Nb and reveal a hitherto unsuspected hierarchical structure of polar nanoregions associated with the cation displacements. This work highlights a broadly-applicable nanoscale structure-refinement method and provides insights into the structure of PMN that require rethinking its existing models.

2:30 PM

(EMA-S8-018-2019) Relaxor physical properties controlled via compressive epitaxial strain (Invited)

J. Kim[2]; H. Takenaka[3]; Y. Qi[1]; A. M. Rappe*[1]; L. W. Martin[2]

1. University of Pennsylvania, Chemistry, USA
2. University of California, Berkeley, Materials Science and Engineering, USA
3. University of Nebraska, Lincoln, Physics, USA

To understand local structure in relaxors has been of scientific interest and technical importance to elucidate the origin of their extraordinary physical properties and to improve and optimize their properties in practical applications. In the latter case, while improvements via transition metal dopants in ternary relaxor solid solutions have been achieved, the more complex compositions have more muddled interpretations of their local structure and properties. Here, we report both experimental and theoretical investigations of the effect of compressive epitaxial strain on local features in the binary $(1-x)Pb(Mg,Nb)O_3-(x)PbTiO_3$ to propose our unprecedented approach to manipulate the properties. Diffuse scattering studies demonstrate conventional butterfly-shaped and unconventional disc-shaped patterns under 0.5% and 1.0%, respectively, and further increasing the strain to 1.5% diminishes the disc-shaped nature all correlating to an increase in correlation length with increasing strain. Analysis of local structures reveals structural phase transitions from sub-nanometer multiple domains at low strain to nanometer cylinder-like domains at high strain. The local structure with the higher strains increases the coercive field and maximum dielectric response temperature, while degrading the magnitude of the dielectric constant. Interestingly, the intermediate strain also improves piezoelectric response.

S10: Current Challenges in Microstructural Evolution: From Basic Science to Electronic Applications

Properties of Interfaces

Room: Cypress B
Session Chair: Wolfgang Rheinheimer, Purdue University

8:30 AM

(EMA-S10-007-2019) Correlative Nanoscale Quantification of Grain Boundary Microstructures (Invited)

D. R. Diercks*[1]

1. Colorado School of Mines, USA

Ceramic materials play a prominent role in advanced materials applications such as batteries, fuel cells, and separation membranes. A major limitation is that cost-effective production methods of most ceramics result in polycrystalline materials. The resulting grain boundary (GB) regions can differ substantially from the bulk material both in composition and structure. The end result can include vastly different properties at the GBs than in the interiors of the crystals, often reducing performance. Also, GBs are not homogeneous. The materials used in these applications predominantly have three-dimensional (3-D), random high-angle GBs. Therefore, the quantitative characterization of the 3-D GB nature is indispensable for the understanding and development of advanced ceramic materials. With continuing improvements, scanning transmission electron microscopy (TEM) is unsurpassed in imaging GB structure, particularly for well-controlled GBs and interfaces. However, quantification in TEM using spectroscopic techniques has limitations in terms of the detectable elements, sensitivity, and 3-D variation. These challenges in measuring the 3-D composition over such a small region makes atom probe tomography (APT) the only method available for direct quantification. In this talk, the correlative application of TEM and APT to targeted quantitative analysis of ceramic grain and phase boundaries is presented.

9:00 AM

(EMA-S10-008-2019) Effect of Processing Parameters on the Microstructure and Electrical Properties of Ceramics (Invited)

R. A. Gerhardt*[1]

1. Georgia Institute of Technology, Materials Science and Engineering, USA

Ceramic materials are challenging to work with because they are difficult to process. One of the most important goals is to achieve full densification in order to minimize the built-in flaws that prevent these materials from being used in structural or thermal applications. As a result, a number of creative solutions have been put forth over the years. For many years usage of nanoparticles was touted as an ideal solution due to the increased surface areas until it was realized that nanoparticles tend to agglomerate and this can lead to decreased densification. The use of additives to promote liquid phase sintering has also been often used but it has never been made clear as to whether the liquid phase enhances or downgrades the properties of the resultant materials. Furthermore, many modifications to the sintering protocols have been made such as the addition of uniaxial pressure, the addition of electrical or magnetic fields, or combinations of all of these methods. The main goal is usually to obtain the highest density possible without regard to the thermal history experienced by the samples. In this talk, it will be demonstrated that one cannot randomly change the composition or the sintering parameters without affecting the resultant microstructure and the desired properties. Examples from the presenters own work and that of others will be used to illustrate these important points.

9:30 AM

(EMA-S10-009-2019) Probing the Influence of Surface Charges on Amorphous Salt Electrolyte (Invited)

M. A. Gulgun*[1]; S. Shawuti[1]; A. Benli[1]; H. D. Batili[1]; C. Ow Yang[1]; M. Sezen[1]

1. Sabanci University, FENS, Turkey

Nanocomposites of an amorphous carbonate salt matrix and nm-scale oxide particles appear to provide a candidate electrolyte for Intermediate temperature (IT) range FCs. The IT performance in these nanocomposites are better than expected. Surface charges are suspected to be active parts. Studies claim that the most significant part of ionic transport in hybrid electrolytes happens at the interface between the particles and the matrix phase. Research with oxide particles of different sizes (different specific surface areas) revealed the interplay between the interface area and the ionic conductivity. Studies conducted on composites with dispersed nano-particles of different and controlled surface charges provided evidence for the influence oxide particles in dissociation of the matrix salt molecules. Depending on the sign of the surface charge different counter-ions will be adsorbed on the oxide surface influencing the total ionic conductivity. We attempted to image this electrostatic interaction with the help of Energy Filtered Imaging of the solid composites post mortem. Nanocomposite made up of an amorphous salt matrix with dispersed insulating oxide particles may not be very different than the “soggy sands” of the wet ion battery technology. The nanocomposite electrolytes appear to have a nanometer scale distribution of various ions and ion complexes around oxide particles.

10:30 AM

(EMA-S10-010-2019) Metalorganic vapor phase epitaxy of CdTe thin films on graphene and mica through chemical and van der Waals mixed interactions

X. Sun*[1]; D. Mohanty[1]; Z. Lu[1]; Y. Xiang[1]; Y. Wang[1]; L. Zhang[2]; K. Kisslinger[2]; J. Shi[1]; L. Gao[3]; M. Washington[1]; G. Wang[1]; T. Lu[1]; I. Bhat[1]

1. Rensselaer Polytechnic Institute, USA
2. Brookhaven National Laboratory, USA
3. University of Science and Technology Beijing, China

Quality heteroepitaxy of CdTe is challenging due to lattice mismatches of CdTe with many substrates. Herein, we demonstrate the epitaxial growth of single crystalline CdTe films on graphene and mica using metalorganic chemical vapor deposition, regardless of large in-plane lattice mismatches between CdTe(111) and graphene and between CdTe(111) and mica(001). X-ray diffraction, reflection high-energy electron diffraction, electron backscatter diffraction (EBSD), and transmission electron microscopy coherently suggest that CdTe is epitaxially aligned with graphene and mica: out-of-plane CdTe(111)//graphene base plane, CdTe(111)//mica(001); in-plane CdTe [-12-1]//graphene [10], CdTe [-12-1]//mica [010]. Grain size in excess of 250 μm is observed by EBSD in CdTe films on mica, larger than most observations reported in the literature. The interface interactions between CdTe and graphene and between CdTe and mica are examined by density functional theory. Calculations indicate that the former case is van der Waals interaction dominating, however, in the latter case, chemical interaction contributes ~80% of the total interfacial energy. We conclude that the nature of interface interactions dictates crystal quality of CdTe films. The demonstrated epitaxy of semiconductors on van der Waals substrates suggest potential for flexible optoelectronic devices.

10:45 AM

(EMA-S10-011-2019) Linking Surface Anisotropy to Equilibrium Crystal Shape in NiO-MgO

D. A. Lowing[1]; J. Blendell*[1]; W. Rheinheimer[1]

1. Purdue University, MSE, USA

The equilibrium crystal shape was determined for NiO-MgO alloys from faceting behavior of surface grains. NiO-MgO in an isomorphous system with complete solid solubility that’s faceting behavior with has been observed to change with composition, changing from (100) dominated to (111) dominated. Homogenous samples with varying compositions were produced using a citrate route and sintered at 1500°C. Surface grain faceting was analyzed using EBSD and AFM techniques. The data was used to produce n-diagrams for multiple alloys of NiO-MgO. The effect of composition changes on the Wulff shape and faceting behavior was quantified, identifying the dominate facets, relative surface coverage and Wulff shape rough region development.

11:00 AM

(EMA-S10-012-2019) Surface Faceting of Barium Strontium Titanate Alloys with Changing Composition

M. J. Michie*[1]

1. Purdue University, Materials Engineering, USA

The effect of alloying barium titanate (BTO) with strontium titanate (STO) on relative surface energy is being investigated. AFM surface facet data is collected and used to calculate the facet normals. Normals are plotted on a stereographic projection and rotated based on collected EBDS data. Stereographic projections are then compare across compositions. Transitions in the surface faceting behavior as a function of composition has implications for interfacial energy and grain growth.

11:15 AM

(EMA-S10-013-2019) The role of point defects and defect gradients in flash sintering of perovskite oxides

W. Rheinheimer*[1]; X. Phuah[2]; H. Wang[1]; F. Lemke[3]; M. J. Hoffmann[3]; H. Wang[1]

1. Purdue University, School of Materials Engineering, USA
2. Purdue University, USA
3. University of Karlsruhe, Institute for Applied Materials (IAM-KM), Germany

The present study investigates the impact of point defects and their redistribution on flash sintering. Strontium titanate was chosen as a model system. Different acceptor dopant concentrations were considered. The onset of flash sintering was found to be dependent on the acceptor dopant concentration, as expected by the increasing conductivity. A gradient in the microstructure was found after flash sintering with larger grain sizes at the negative electrode. TEM-EDS measurements indicated Ti enrichment at the positive electrode for undoped strontium titanate and strong acceptor segregation for doped strontium titanate. At the negative electrode the boundaries were found to be stoichiometric for the undoped case and the acceptor segregation was less obvious for the doped case. Based on these results and the space charge behavior of strontium titanate, we infer that a gradient of the oxygen vacancy concentration is induced by the electric field during flash sintering: at the positive electrode the oxygen vacancy concentration is higher than at the negative electrode. For strontium titanate it is well known that a high oxygen vacancy concentration reduces the space charge and, acceptor segregation, which agrees well with the experimental findings. Overall, the present study highlights the importance of point defect gradients and space charge for flash sintering.

11:30 AM

(EMA-S10-014-2019) FLASH sintering of KNN in different atmospheres

A. M. Senos*[1]; R. Serrazina[1]; E. Ndehkordi[1]; P. Vilarinho[2]

1. University of Aveiro/ CICECO, Materials and Ceramic Engineering, Portugal
2. University of Aveiro, Department of Materials and Ceramics, Portugal

FLASH is an electric field assisted sintering technique, where a significant decrease in sintering time and temperature can be achieved. There is a direct improvement on the sintering process sustainability and new routes for materials densification can be open. This is the case of potassium sodium niobate, $K_{0.5}Na_{0.5}NbO_3$ (KNN), a relevant lead-free piezoelectric, which is not trivial to produce by conventional sintering, due to alkali evaporation at high temperatures. In this work, KNN was sintered by FLASH and the effect of different atmospheres (Ar, N_2 and O_2, with and without water) on the consolidation process was investigated. We have observed that the FLASH temperature, Tf, is highly dependent on the sintering atmosphere and, in this case, can be as low as 270 C, if reducing conditions are used. A dwell-gas-FLASH was experienced, in which the specimens were exposed to a constant temperature slightly over Tf, for 2 h; more homogeneous densification was favored in this case. Structural and microstructural characterization (XRD, SEM and TEM) and electric and dielectric response (dielectric and impedance spectroscopy) were accessed. The relation between FLASH conditions and conduction mechanisms sheds light on the role of atmospheres together with electric field for the densification of KNN. Our results contribute also to the current body of knowledge on FLASH as an alternative sintering technique.

11:45 AM

(EMA-S10-015-2019) Modeling long term behavior of PbTe-based thermoelectric generators

Y. Sadia*[1]; D. Ben Ayoun[1]; Y. Gelbstein[1]

1. Ben-Gurion University of the Negev, Material Engneering, Israel

Thermoelectric materials can show high performance of energy conversion. Many models predict this behavior, however in long term operation many problems arise such as degradation due to sublimation. This might mean that long term operation at high temperature needs to be modeled with real numbers representation degradation in order to predict long term efficiency. In the current research a model was developed using both the evaporation rates at the high temperatures and the material degradation at high temperature to model the long term operation of such a device. The device was modeled for 60°C cold side to 600°C hot side operation using PbTe based materials showing the differences between 0 hour degradation to 456 hour degradation. This was investigated both experimentally and theoretically. Surprisingly to the opposite nature of some of the effects only small degradation to the maximal electrical power and efficiency was observed. This shows that degradation is only a moderate effect in such devices.

Interfaces in Organohalide Solar Cells

Room: Cypress B

Session Chair: Hadas Sternlicht, Brown University

2:00 PM

(EMA-S10-016-2019) The Optoelectronics of Organohalide Perovskite Solar Cells (Invited)

P. Meredith*[1]

1. Swansea University, Physics, United Kingdom

The organohalide perovskites or ‘perovskites’ as has now become common nomenclature have shot-to-stardom as the new best candidate for solution processed photovoltaics. Power conversion efficiencies > 23% at the laboratory scale have been reported and verified, and mini-modules of > 17% prove that scaling of this technology could be possible. The perovskites are hydrid organic-inorganic molecular materials but with solid state physics sometimes more akin to the crystalline inorganic compound semiconductors, they represent an intriguing new optoelectronic platform with substantial technological potential - not just in photovoltaics, but also for LEDs and photodetectors. The optoelectronic physics of the perovskites is now becoming a little clearer - in their 3D form they are definitely non-excitonic materials, but the 2D forms seem to have significant exciton branching fractions at room temperatrure. They have high dielectric constants and appear to possess hybrid electronic-ionic conduction properties. Strange semiconductors indeed. In my talk I will explore some of these intriguing features and in particular describe the current state-of-the-art in understanding why the perovskites are such efficient photovoltaic materials.

2:30 PM

(EMA-S10-017-2019) Ferroic domains regulate photocurrent in single-crystalline CH3NH3PbI3 films self-grown on FTO/TiO_2 substrate (Invited)

J. Li*[1]

1. University of Washington, Mechanical Engineering, USA

Photovoltaic conversion efficiency (PCE) of halide perovskite solar cells has risen spectacularly, yet the very crystalline structure of CH3NH3PbI3 remains ambiguous after extensive researches, and its polar nature remains hotly debated. Here we present compelling evidences that CH3NH3PbI3 crystals self-grown on FTO/TiO2 substrate consist of ferroic domains with alternating polar and nonpolar orders, in contrast to previous experimental and theoretical expectations, and polar domains possess reduced photocurrent. It is found that polar and nonpolar orders of CH3NH3PbI3 can be distinguished from their distinct lateral piezoresponse, energy dissipation, first and second harmonic electromechanical couplings, and temperature variation, even though their difference in crystalline lattice is very subtle, and they possess two-way memory effect through cubic-tetragonal phase transition. We hope these findings resolve key questions regarding polar nature of CH3NH3PbI3 and its implication on photovoltaics, reconcile contradictory data widely reported, and point a direction toward engineering ferroic domains for enhanced PCE.

3:00 PM

(EMA-S10-018-2019) Ferroelectric domains in methylammonium lead iodide perovskite solar cells

H. Roehm[1]; T. Leonhard[1]; M. J. Hoffmann[1]; A. Colsmann*[1]

1. Karlsruhe Institute of Technology, Germany

Among the emerging photovoltaic technologies, perovskite solar cells stand out with remarkable power conversion efficiencies (PCEs) and low-cost solution processability, rivaling established technologies. However, arguably, the toxic and water-soluble lead compound may be an obstacle on their way to market. Searching for alternatives, the scientific community controversially discusses the importance of ferroic properties for the exceptional performance of methylammonium lead iodide ($MAPbI_3$) light-harvesting layers, including claims of non-ferroelectricity, anti-ferroelectricity, ferroelectricity and ferroelasticity. In this work, we performed a comprehensive AFM study including Piezo-response Force Microscopy (PFM) and Kelvin Probe Force Microscopy (KPFM). On large flat crystals, we find 90 nm wide ferroelectric domains of alternating in-plane polarization. Symmetry considerations let us conclude that this polarization is oriented 45° towards the grain boundaries. In high-performance $MAPbI_3$ solar cells, only very few grains show different domain patterns. Altogether, these investigations provide micro-structural target properties for $MAPbI_3$ thin-film deposition. We discuss the formation of ferroelectric domains upon layer deposition from solution and their importance for the solar cell operation.

3:15 PM

(EMA-S10-019-2019) Probing the Microstructure of Methylammonium Lead Iodide Perovskite Solar Cells

T. Leonhard*[1]; A. Schulz[1]; H. Roehm[1]; S. Wagner[1]; F. Altermann[1]; W. Rheinheimer[2]; M. J. Hoffmann[1]; A. Colsmann[1]

1. Karlsruhe Institute of Technology, Germany
2. Purdue University, USA

The microstructure of absorber layers is pivotally important for all thin-film solar technologies. Despite its unprecedented performance development in recent years, little is known about the microstructure of metal-halide perovskites and its effect on the macroscopic device performance. In this work, we report on the spatial investigation of methylammonium lead iodide (MAPbI3) grain properties by electron backscattered diffraction (EBSD) with high resolution. We resolve diffraction pattern ambiguities that are related to the close-to-cubic perovskite unit cell, and develop a comprehensive three-dimensional picture of the crystal orientation. We identify predominant orientation directions and observe orientation cross-talk between neighboring grains. The local crystal information correlates with ferroelectric and electronic properties that we probe with piezoresponse force microscopy (PFM) and kelvin probe force microscopy (KPFM) measurements. This allows to draw conclusions about the microstructure from ferroelectric features and, likewise, to derive the ferroelectric polarization from crystallographic observations. Hence, these characterization tools are indispensable for the future relation of the microscopic structure to the optoelectronic properties of perovskite devices as they allow to monitor device optimization and to understand fundamental processes of perovskite solar cells.

S11: Electronic Materials Applications in 5G Telecommunications

Electronic Materials Applications in 5G Telecommunications III

Room: Cypress C
Session Chair: Nate Orloff, NIST

8:30 AM

(EMA-S11-015-2019) All-Oxide BST-Components for Reconfigurable Communication Systems (Invited)

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2. Technische Universität Darmstadt, Advanced Thin Film Technology, Germany

Ferroelectrics have been under investigation for a long time now. In recent years, milestones have been passed, which allow an integration of ferroelectrics into tunable devices and components for microwave applications. Hence, first Barium-Strontium-Titanate (BST) thin film components are already commercialized. However, these varactors are stymied by the absence of suited compatible electrode materials on the micrometer scale, resulting in degraded performance especially at frequencies above 3 GHz. Considering oxide electronics, there has been tremendous progress in the recent years in growing interface engineered oxide materials with various functionalities and control on the nanoscale comparable to semiconductor technology. Thin films of the conducting oxide SrMoO3 (SMO), which affords a bulk conductivity higher than Platinum, could be realized. Additionally, their successful integration into first varactors has been presented recently. We show that our approach, encompassing several orders of magnitude in film thickness scale whilst maintaining atomic layer control, enables the fabrication of a varactor based on a merely 50 nm thin BST layer with highest quality factor and unprecedentedly high tunability at Li-ion battery voltage level. The increased quality of the BST layer paves the way for the realization of varactors for all important mobile communication bands up to 10 GHz, at least.

9:00 AM

(EMA-S11-016-2019) Ceramic Oxide Magnetic and Dielectric Materials for 5G Wireless Communications (Invited)

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5G Communications will use two distinct frequency bands: 3-6 GHz and mm-waves (20-100 GHz). The role of magentic oxide materials in devices for wireless communciations is vastly different for each of these frequency ranges. The nature of the magnetic oxide materials as well as the architecture of the devices will be discussed for both the sub-6GHz band as well as for applications at 28 GHz and above. High dielectric constant bismuth substituted ferrite garnets and nickel zinc ferrite materials are useful in the low and high frequency bands respectively. In additon, dielectric materials will play a significant role as well, both in integrated isolators and circulators as well as in mm-wave filtering applications. The nature of the optimal dielectric material will depend on the frequency of use as well as the nature of the device. Results on investigations of ultra-low loss microwave dielectric materials as well as low dielectric constant microwave dielectric materials will be presented. Early results at component integration onto ceramic substrates will also be discussed.

9:30 AM

(EMA-S11-017-2019) mmWave Material Characterization for 5G and automotive applications in AIST (Invited)

M. Horibe*[1]; Y. Kato[1]; R. Sakamaki[1]; I. Hirano[1]

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Millimeter-wave frequency signals is going to be used in 5G applications. Material characterization is most important in order to known material properties for design of device, circuit and system. AIST researches and develops three key measurement method for material characteristics. Scanning Microwave Microscopy provides to understand the nanoscale electronic structure, Balanced Circular Disk Resonator method gives dielectric permittivity constant at mmWave, and using on-wafer based material characterization technique can estimate an effective dielectric permittivity constant in the integrated circuits. We present latest research achievements in AIST, Japan.

10:00 AM

(EMA-S11-018-2019) Lithium Niobate Thin Films for Resonators and Filters at 5G Frequencies (Invited)

S. Gong*[1]

1. University of Illinois at Urbana-Champaign, ECE, USA

5G resorts to higher frequencies for wider bandwidths and high data rates so that it can fulfill its potential as the next technology revolution reshaping the landscapes in data, autonomy, and energy. The frequency scaling presents unique challenges to RF front-end components as some of them either are not readily available at 5G frequencies or do not have comparable performance to their 4G counterparts. Filters and resonators, which serve to selectively allow access and reject interference in front-ends, are an example of such. This talk will first discuss the challenges in constructing piezoelectric MEMS filters to meet the requirements of 5G bands in both center frequency and bandwidth, and then demonstrate how these system-level challenges can be addressed by material level innovations via the adaption of lithium niobate thin films as a resonator and filter platform.

10:30 AM

(EMA-S11-019-2019) Study Dielectric Properties of Polymer-Ceramic Composites at Microwave Frequencies

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The drive toward faster data transmission has deepened interest in microwave characterization of ceramics and polymers. Ferrolectric-based multilayer ceramic capacitors operate in the MHz-GHz frequency range for decoupling of high-speed microprocessors. Polymers and ceramics for electronic packaging and antenna structures for 5G telecommunications and automotive guidance systems will need to function from 10 to 100 GHz range. In this research work polymer-ceramic composites were developed using epoxy as a merix with fillers such as $Ba_{0.6}Sr_{0.4}TiO_3$, BN and Co(III)-acac.

Differen methods of electrical measurements such as impedance analyzer, network analyzer connected to co-axial cable and split cavity techniqe were performed to investigate the electrical properties of polymer-ceramic composites at microwave frequencies. The results showed that the mobility of polar groups in the polymer matrix at high frequency (10 GHz) ceased, and dielectric property of polymer-ceramic composite became independent of the polymer type. In addition, effect of crosslink density on dielectric properties of polymer – ceramic composites in microwave frequency was studied. Our finding revealed that the composite with higher crosslinking agents has higher dielectric permittivity and lower dielectric loss due to the restriction of the polarizations of the main chain and some pendant groups.

10:50 AM

(EMA-S11-020-2019) Glass ceramics for MW applications

I. M. Reaney*[1]

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

Glass ceramics have been touted as potential substrates for MW circuits and antennas since Whatley (1989) reported a series of compositions based on MgO-SiO_2-Al_2O_3-TiO_2 in which ‘CMA6’ (permittivity = 6.4) gave similar gains to alumina for modules operating at 6–18 GHz. Since, there have been a few significant attempts to demonstrate glass ceramics for MW applications, with attention given to increasing permittivity to reduce the dimensions of devices for satellite navigation. Mirsaneh et al (2008) developed a Bi_2O_3-Nb_2O_5 based composition (permittivity = 17, quality factor, Qf = 15,000) for use as substrates for dielectrically loaded antennas and Braun et al (2017) fabricated and patented (Schott AG) compositions based on La_2O_3–TiO_2–SiO_2 for similar applications. 3G and 4G mobile technologies (frequency 2 – 6 GHz) have not yet recognized the potential of glass-ceramics for MW applications, preferring to use a combination of low-cost polymeric substrates such as FR4 and high permittivity ceramics with ultra-high Qf such as $CaTiO_3$-$NdAlO_3$ (permittivity = 45, Qf = 45,000GHz). However, there is renewed interest in this topic through the advent of 5G technology (frequency >20GHz) which requires lower permittivity for antenna substrates to prevent loss of bandwidth through the puck dimensions becoming too small. This paper will review the latest work on glass ceramics for 5G applications and discuss a potential roadmap for their development.

11:10 AM

(EMA-S11-021-2019) DFT+DMFT study of optical properties of metallic double perovskite Sr_2VNbO_6

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1. University of Minnesota, Chemical Engineering and Material Science, USA

Transparent conductors with a large DC electrical conductivity and optical transparency in the visible range have drawn recent attention thanks to their wide range of applications. Correlated metallic perovskite oxide $SrVO_3$ is a promising transparent conductor due to (a) the enhancement of carrier effective mass originating from correlations of electrons reduces the plasma frequency below the red end of visible spectrum, (b) enormously large carrier concentration compared to any semiconductors, and (c) suppressed interband absorption occurs in the red side of the spectrum. Replacing V atom in $SrVO_3$ by a larger Nb atom results in wider bands and very weakly correlated electrons, which in turn result in shifting the screened plasma frequency towards into the blue end. Double perovskite Sr_2VNbO_6 might bring together the advantages of either compound, and thus be the superior transparent conducting oxide. In this work, we utilize the first-principles DFT+DMFT approach to investigate the electronic and optical properties of double perovskite Sr_2VNbO_6, which has both 3d (V) and 4d (Nb) electrons with different localization tendencies. We show an unexpected but robust transfer of one electron from wider Nb 4d bands to narrower V 3d bands due to electronegativity difference between these ions. We also reveal that the optical properties of Sr_2VNbO_6 are unusual compared to its parent compounds $SrVO_3$ and $SrNbO_3$.

11:30 AM

(EMA-S11-022-2019) Ultrafast control of material properties through non-linear lattice dynamics from first principles (Invited)

G. Khalsa*[1]; N. A. Benedek[1]

1. Cornell University, USA

The development of intense ultrashort mid and far infrared laser sources has created an opportunity for functional materials based on the direct excitation of infrared active phonons. Strong excitation of infrared active phonons can produce sizable unidirectional distortions of crystal structure through non-linear coupling to other phonons. Complex oxide ceramics provide an important testground for this experimental approach due to their diversity, strong coupling to optical fields, and demonstrated connection between subtle structural changes and functional properties. Our recent theoretical efforts in perovskite oxides explore selective control of functional properties that exploit nonlinear lattice dynamics induced by the excitation of infrared phonons. Using first-principles techniques we predict that ultrafast optical control of magnetism is experimentally accessible in rare-earth titanates and show that, when combined with strain, this optical technique exposes a magnetic phase inaccessible in the equilibrium phase diagram.

12:00 PM

(EMA-S11-023-2019) Computational studies of dielectric loss in relaxor ferroelectrics

J. Mangeri[1]; P. Ondrejkovič*[1]; D. Zhu[4]; N. Orloff[3]; A. Hagerstrom[2]; K. Co[4]; P. Alpay[4]; S. Nakhmanson[4]

1. Institute of Physics, Czech Academy of Sciences, Dielectrics, USA
2. National Institute of Standards and Technology, USA
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4. University of Connecticut, Materials Science and Engineering, USA

In this work, we investigate the relaxation dynamics and dielectric tunability in the $Ba_xSr_{1-x}TiO_3$ system which has already seen integration into prototype devices for 5G electronics. To probe dielectric response, we employ an advanced finite element tool to elucidate possible influences on the loss curves, including Sr concentration, inhomogeneous fields such as epitaxial or residual strain, or the polar domain structure. Alongside these calculations, we also examine the dielectric tunability using a quasi-analytic approach and find good agreement with both theoretical methods and the available experimental data.

S14: Failure: The Greatest Teacher

Failure: The Greatest Teacher

Room: Orange B
Session Chair: Geoff Brennecka, Colorado School of Mines

4:00 PM

(EMA-S14-001-2019) Failures: The stepping stones to success

A. J. Bell*[1]

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n/a

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*** Denotes Presenter**

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