Lone Pairs in the Halide Perovskites, Hidden and Otherwise
Douglas Fabini¹, Geneva Laurita², Constantinos Stoumpos³, Mercouri G. Kanatzidis³ and Ram Seshadri¹; ¹Materials, University of California, Santa Barbara, Santa Barbara, California, United States; ²Chemistry, Bates College, Lewiston, Maine, United States; ³Department of Chemistry, Northwestern University, Evanston, Illinois, United States.

The $ABX_3$ halide perovskites that have attracted so much renewed attention mostly possess $B = \text{Sn}^{2+}$ or $\text{Pb}^{2+}$, with $n^2$ lone pairs of electrons. These lone pairs are frequently hidden, in the sense that the crystal structures are not consistent with the presence of a stereochemically active lone pair that would result in certain characteristic distortions of $MX_6$ polyhedra in the structure. The influence of such hidden lone pairs can be found in numerous perovskites including the hybrids with methylammonium [$A = \text{CH}_3\text{NH}_3^+$] and formamidinium [$A = \text{CH} (\text{NH}_2)_2^+$], where the lone pairs are associated with proximal instabilities that can profoundly influence materials properties. We will discuss the understanding that we have developed from extensive real and $k$-space studies of local and average structure in these materials using synchrotron and neutron scattering. DFT calculations and NMR studies complement the structural studies to obtain a coherent picture of what is happening, and where all the red herrings are. This work was supported by U.S. DOE, Office of Science, through DE-SC-0012541.

A Study of Dynamic Tilt in Perovskites—Bridging the Gap Between Simulation and Experiment
Christopher M. Handley, Robyn Ward, Colin L. Freeman, John H. Harding and Ian M. Reaney; University of Sheffield, Sheffield, United Kingdom.

Tilting in perovskites is a well-documented structural phenomenon, which occurs due to the mismatch in the A and B site ion sizes¹. We can observe the influence of these tilts through selected area diffraction patterns (SADP), and classify them using Glazer notation². However, Glazer notation is limited as it only classifies tilt for the time-averaged system structure, and assumes that the octahedra are regular in shape. Attempts have been made to simulate transmission electron microscope (TEM) patterns for SADP for each perovskite tilting motif, but it has been limited to static simulations and assumes ideal SADPs².

We have developed a new methodology that uses a combination of commercial (CrystalMaker³) and in-house (PALAMEDES) programs, to analyse the dynamics of perovskite tilts from molecular dynamics simulations, and in turn use these simulations to simulate time averaged TEM and X-ray diffractions (XRD).

Simulations of CaTiO₃, BaTiO₃, and solid solutions of BCT and BST have been performed using DL_POLY 4⁴.

The calculated diffraction patterns and spectra for these materials compare well to experiment. In addition, we are able to use PALAMEDES, to extract
dynamic measures of structural features, such as the magnitudes and oscillations of the tilt angles, volumetric distortions, local dipoles, and the phase of the tilts - both locally and at longer ranges.

Through our methodology we are able to demonstrate the influence that temperature and dopants have on perovskite structure, in particular their dynamical traits, and how these dynamics are detected or masked by experimental TEM and XRD, and ultimately have a basis for how it is the dynamics of structural features that underpins the material properties.


8:45 AM CM01.01.03 Tunable Emission in Multinary Halides Bayrammard Saparov1, Mao-hua Du2 and Rachel Roccanov1; 1University of Oklahoma, Norman, Oklahoma, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

One of the projects in our group targets the synthesis, modeling, single crystal growth, and characterization of low cost multinary halides for light emission applications (e.g., solid-state lighting, scintillators etc.). Taking advantage of the simple processing and rich chemistry of multinary halides including hybrid organic-inorganic halides, we controllable prepared a series of 2D, 1D and 0D crystal structures featuring perovskite-derived and non-perovskite crystal structures. Tunable light emission properties of the obtained materials were characterized using UV-vis absorption, photoluminescence (emission, excitation, time-resolved, temperature-dependent, quantum yield etc.) and density functional theory calculations.

In luminescent hybrid Sn- and Pb-based halides, the inorganic Sn/Pb-halide networks (or clusters) are usually responsible for the observed luminescence due to their relatively small energy gaps of the inorganic substrates compared to those of organic molecules. The low energy gaps of the inorganic substrates in such cases are ensured by the relatively small electronegativity difference between Sn/Pb and halogen elements, which results in valence bands dominated by halogen lone pairs and conduction bands primarily made of metal orbitals. In principle, the band alignment in hybrid halides can be altered by (1) combining pairs of metal and halogen elements with large electronegativity difference to accommodate organic molecules’ frontier orbitals, or (2) by utilizing low-gap aromatic molecular orbitals. The hybrid metal halides studied in our group feature electropositive metals such as Zn and Cd, among others, and aromatic organic cations, yielding unusual band alignments at the organic-inorganic interface. Thus, we were able to obtain compounds showing type-I band alignment with bands near the band gap originating from the inorganic component, type-I band alignment based on organic molecules, and also type-II band alignment featuring both organic and inorganic states. Therefore, depending on the specifics of their band structures, highly tunable light emission of our compounds are attributed to inorganic or organic substructures, or a combination of both.

In this talk, we will provide fresh examples of highly luminescent multinary halides prepared in our group including several examples of broadband white-light emitters, and efficient deep blue emitters, both of which are sought for solid-state lighting applications. The highest room temperature photoluminescence quantum yield (PLQY) values measured in our lab include 3% for a white-light emitting hybrid zinc bromide compound, and 26% for blue-emitting all inorganic Cu halides. Importantly, this work paves the way to band alignment engineering of organic and inorganic components in hybrid organic-inorganic halides to controllably create type I and type II band alignments, and to fabricate materials where the emission originates from organic, inorganic or both components.

9:00 AM CM01.01.04 Tuning the Magnetic Anisotropy in the Layered Chromium Mixed Halides Ezael Fallah Tafhi, Mykola Abramchuk, Samantha Jaszeski, Kenenth Burch and Kenneth Metz; Boston College, Boston, Massachusetts, United States.

Magnetic anisotropy is the tendency of spins to align in a certain crystallographic direction - the easy-axis. Without anisotropy, thermal fluctuations prevent magnetic ordering in two dimensions according to the Mermin-Wagner theorem. In layered materials, the two limits of the easy-axis are in-plane (XY) and out-of-plane (Z). Recent advances in exfoliation and device fabrication have led to the discovery of ferromagnetic ordering with Ising anisotropy in CrI₃ monolayers. It is theoretically conjectured that spin-orbit coupling (SOC) provided by halide atoms on the super-exchange path yields the magnetic anisotropy. Here, we design a unique experiment to probe this idea by growing a series of CrClₓBrₓ crystals where SOC is tuned between CrClₓ with XY and CrBrₓ with Ising anisotropy. We discover a continuous rotation of the easy-axis from XY to Ising with increasing x. Remarkably, the magnetic ordering temperature, optical gap, and inter-layer spacing are also tuned linearly with x. This is the first observation of a continuous rotation of the easy-axis and the effect of SOC on the super-exchange path. Methods presented here can be extended to produce other metal mixed halides to fabricate tunable heterostructures and spintronic devices.

9:15 AM CM01.01.05 Colloidal CuFeS₂ Nanocrystals—Synthesis and Insights into the Intermediate Fe d-Band That Influences Its Optical Properties Sandeep Ghosh; The University of Texas at Austin, Austin, Texas, United States.

In this presentation, we will describe the colloidal synthesis of phase-pure nanocrystals (NCs) of a highly abundant mineral, chalcopyrite (CuFeS₂). The steady state optical extinction spectrum of these NCs offers few surprises due to Fe which introduces deep energy levels in the electronic band structure, as supported by our density functional theory (DFT) calculations. The spectrum is characterized by absorption bands centered at around 480 and 950 nm, spanning almost the entire visible and near infrared regions. These are ascribable to electronic transitions from the valence band (VB) to the empty intermediate band (IB), located in the so-called fundamental band-gap and composed predominantly of Fe 3d orbitals. We further demonstrate, through spectroscopic measurements and ab initio calculations that these NCs actually sustain metal-like quasi-static optical resonances despite the absence of free carriers in the NC ground state owing to this unique band structure. Laser-irradiation (at 808 nm) of an aqueous suspension of these CuFeS₂ NCs exhibited significant heating, with a photothermal conversion efficiency of 49%. Such efficient heating is most likely due to the carrier relaxation within the broad IB band, as corroborated by transient absorption measurements and further described by DFT calculations. The intensity absorption and high photothermal transduction efficiency (PTE) of these NCs in the so-called biological window (650–900 nm) make them suitable for photothermal therapy as demonstrated by tumor cell annihilation upon laser irradiation.

We intend to put forward the chemistry behind the synthesis of these low band-gap ternary semiconductor NCs and describe the optoelectronic properties using experimental and theoretical points of view, through this presentation. A suite of spectroscopic techniques, which include visible-infrared transient absorption, x-ray absorption and emission, resonant inelastic x-ray scattering (RIXS) were used in our analyses. The subsequent use as a photothermal...
agent is an offshoot of this understanding. The presence of the deep Fe levels constituting the IB is the origin of such enhanced PTE, which can be used to design other high performing NC photothermal agents.

References:

9:30 AM BREAK

10:00 AM *CM01.01.06 Colloidal Nanocrystals of APbX3 Perovskites [A=Cs+, CH(NH2)2+, X=Cl, Br, I]: Structural Aspects, Self-Assembly and Potential Applications Maksym V. Kovalenko1, 2; 1Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland; 2Empa–Swiss Federal Laboratories for Materials Science and Technology, Dubendorf, Switzerland

We survey the synthesis methods for colloidal lead halide perovskite nanocrystals (APbX3, NCs, A=Cs+, FA+, FA=formamidinium; X=Cl, Br, I), structural chemistry and structural dynamics, and prospects of these NCs for optoelectronic applications such as in television displays, light-emitting devices, and solar cells, emphasizing the practical hurdles that remain to be overcome. The spontaneous and stimulated emission spectra of these NCs are readily tunable over the entire visible spectral region of 410-700 nm [1-2]. The photoluminescence of these NCs is characterized by narrow emission line-widths of 12-42 nm, wide color gamut covering up to 140% of the NTSC color standard, high quantum yields of up to 100%. Cs0.81FA0.19PbI3 and FAPbI3 reach the near-infrared wavelengths of 800 nm [3]. Their processing and optoelectronic applications are, however, hampered by the loss of colloidal stability and structural integrity due to the facile desorption of surface capping molecules during isolation and purification. A new ligand capping strategy utilizing common and inexpensive long-chain zwitterionic molecules such as 3-(N,N-dimethyloctadecylammonio) propanesulfonate, resulting in much improved chemical durability had been developed [4]. Perovskite NCs also readily form long-range ordered assemblies, known as superlattices. These assemblies exhibit accelerated coherent emission (superfluorescence), not observed before in semiconductor nanocrystal superlattices [5].

L. Protesescu et al. Nano Letters 2015, 15, 3692–3696
M. V. Kovalenko et al. Science 2017, 358, 745-750
L. Protesescu et al. ACS Nano 2017, 11, 3119 –3134
G. Raimo, M. Becker, M. Bodnarchuk et al. 2018, submitted

10:30 AM CM01.01.07 First Principles Investigation of Metal-Insulator Transitions in Rare-Earth Nickelates Induced by Chemical Doping Pilsun Yoo and Peilin Liao; Purdue University, West Lafayette, Indiana, United States.

Chemical doping driven metal-insulator transitions (MIT) can be adopted for solid-state field effect devices, solid electrolytes for solid oxide fuel cells, and active broad spectrum photonic devices. The electrical conductivity of SmNiO3 decreases by ~8 orders of magnitude when it is chemically modified by hydrogen atoms. 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 Ueff = 2 eV produced results in good agreement with experiments for both insulating and metallic phases of SmNiO3. 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.

10:45 AM CM01.01.08 Exploring Tunable Persistent Luminescence in Chromium-Substituted Spinel Phosphors Erin Finley; University of Houston, Houston, Texas, United States.

Developing new persistent luminescent phosphors, which have applications ranging from emergency signage to children’s toys, requires an improved understanding of the mechanism that drives their distinctive optical properties. The current consensus is that the long luminescence lifetime stems from a relationship between the inorganic host crystal structure’s band gap and the position of defects that form electron trap states. Fortunately, investigating the crystal chemistry and electronic structures of well-known persistent luminescent phosphors based on the chromium substituted spinel ZnGa2O4 offers a platform to study this mechanism. Substituting Cr3+ into this host crystal structure produces a long lifetime red emission as a result of the spin forbidden \( ^4E \rightarrow \ ^4A_2 \) transition of the \( 3d \) orbitals. This electronic transition results in a phosphorescence emission decay that is further extended by anti-site defects that act as electron traps. Research has shown that substituting aluminum onto the gallium site can change the luminescence lifetimes by varying the size of the band gap and presence of structural defects. Therefore, this work presents the preparation and investigation of persistent luminescence in the solid solution Zn(Ga1-xAlx)2O4:Cr3+ (\( x = 0–1 \)). Employing a combination of luminescence spectroscopy, extended X-ray absorption fine structure (EXAFS) spectroscopy, and density functional theory this work provides valuable insight into the relationship between crystal chemistry and the persistent luminescence mechanism. These results provide a pathway to aid in the discovery of new persistent luminescent phosphors with a range of both emission wavelengths and luminescence lifetimes.

11:00 AM CM01.01.09 The Magnetic Properties of Triple Perovskites—Spin Glasses, Ferrimagnets and Relaxors Peter D. Battle1, Emily C. Hunter1, Chun-Mann Chin1, Yawei Tang1, Mylene Hendrickx2, Joke Hadermann1 and Maxim Avdeev3, 4; 1Oxford Univ, Oxford, United Kingdom; 2Physics, University of Antwerp, Antwerp, Belgium; 3ANSTO, Lucas Heights, New South Wales, Australia; 4The University of Sydney, New South Wales, Australia.

This contribution is centred on the magnetic properties of so-called triple perovskites having the general formula \( La_xA_2B_2'O_6 \) where \( A \) is Ca, Sr or...
Boron atoms in boron-rich materials have the tendency to form clusters or 2D sheets. As a synthesis method we have discovered that small amounts of characterization with theoretical modeling will be highlighted.

In regard to magnetism, unexpectedly strong magnetic coupling was previously discovered in dilute f-electron insulating property relationships, leading to interesting properties in thermoelectrics (TE) and magnetism. Borides are promising for high temperature TE (NIMS), Tsukuba, Japan; 2Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan.

A grand challenge in solid state materials chemistry is to achieve the same level of control over bond-making and bond-breaking as afforded by well-known organic reaction paradigms. In this talk, I will present recent work on the discovery of new organo-halide electronic materials and mineral-derived quantum spin liquids. Despite disparate synthetic approaches, these subjects are unified by having progress made through an enhanced understanding of how well Pauling’s rules perform for oxides up to today in literature. In this contribution, we will provide such an answer. To do so, all five Pauling rules are checked on thousands of oxides from the Materials Project that originally stem from the experimental database ICSD. We will start from a very recent analysis of the statistics of the coordination environments of oxides. A special focus will be on the rules describing the connections of the coordination polyhedra because the knowledge on the performance of these rules is especially sparse. Deviations from Pauling’s rules and their origins will also be discussed.

Acknowledgements: Computational resources have been provided by the Consortium des Équipements de Calcul Intensif (CÉCI).

References:
Disorder in Semiconducting Ternary Nitrides

Oxides comprise a large number of insulators or semiconductors, often with rather poor electronic properties. In contrast, nitrides have often better electronic properties, but have much smaller number of known phases, in particular regarding ternary or multinary compounds. Due to the inherent relative instability of nitrides relative to $N_2$, such ternary nitrides are often grown as thin films at relatively low temperatures, leading to crystal structures with atomic disorder. Using first principles and Monte-Carlo calculations, we investigate the effects of disorder on the electronic structure. Case studies include ZnSnN$_2$, which has attracted interest as photovoltaic material, and which tolerates large off-stoichiometry without adverse effects on the electronic properties. We discuss the possibility to remove undesirable electronic localization effects by controlling short range order, even when the material remains long-range disordered. A second example are the Mg-TM-N (TM = Ti, Zr, Hf, Nb) nitrides, which have recently been identified as a particularly stable region in the map of ternary nitrides. First principles structure search and electronic structure calculations predict rocksalt structure semiconductors with low effective masses and large dielectric constants. Disorder not only affects the electronic properties directly, but it also can tip the balance between competing structure types, thereby playing a crucial role in the phase formation and the ensuing materials properties.

Lithium Alkaline-Earth Metalide-Nitrides—From Simple to Complex

Depending on preparation conditions and composition, phases obtained in the quaternary systems Li – $AE$ – M – N (AE = Ca, Sr, Ba, M = Ga, In, Tl, Ge, Sn, Pb) range from nitridometalates (e.g. (Ca$_2$)$_3$Ga$_2$N$_3$)$_2$, (Ca$_2$)Ge$_2$N$_6$ (5)) via nitride-metalides (e.g. (Ca$_2$)Ga$_2$N$_2$ (6)), to intermetallic species without nitrogen (e.g. Li$_2$BaSn (4)). They may contain nitrogen as isolated N$^+$ anions or complex anions $[M, N, \ldots]$ of different dimensionality with coordination numbers $M$ by $N$ typically between two and four, respectively. Whereas the bonding within these complex anions and frameworks is essentially covalent, nitridometalates are stabilized by predominantly ionic bonding through counterions like alkali (4) or alkaline-earth (AE) cations. In contrast, bonding in metalide-nitrides is dominated by metallic and ionic interactions. Structural data for the majority of phases reported up to now had been derived from X-ray single crystal data, whereas single-phase powder samples had to be employed for investigation of physical properties, since no sufficiently large single crystals were available. Here we report on crystal growth experiments in lithium melts by modified high-temperature centrifugation aided filtration (HTCAF) (3), which resulted in specimens of up to $5 \text{ mm}$ in length and $50 \text{ mm}^3$ in volume. Generally, due to the mode of preparation the thermodynamically most stable phases are precipitated from the reaction mixtures of Li, Li$_3$N, $AE$, $M$, and $N$, which leads to significantly different results concerning composition of products with respect to reaction temperatures and the alkaline-earth and main-group elements involved.

A selection of cubic crystal structures illustrates the variety and complexity of the new phases: (Sr$_{1}$_{1}$_{x}$)$_{1}$Pb$[6] crystalizes in the perovskite type with a $2\times2\times2$ superstructure, Li$_{1}$S$_{1}$Sn$_{1}$Pb$_{1}$ (7) features an ordered variant of the Sr$_{1}$Ir$_{1}$ type structure, whereas Li$_{1}$S$_{1}$Sn$_{1}$Ga$_{1}$Ga$[8]$ crystalizes in a new structure type. Li$_{1}$Sn$_{1}$Ga$[9]$ is isotypic to the $\eta$-carbide Fe$_{1}$W$_{1}$C. Most phases show diamagnetic behaviour and electrical resistivities of about $1\times10^{-3}$ $\Omega$ m.

Boron tends, like carbon and silicon, to form covalent molecular as well as extended compounds, but boron’s “electron deficiency” enables the formation of multicenter B–B bonds, and therefore unexpected compounds. Boron reacts with most metals to form the large class of metal borides, ranging from the boron-richest YB$_{66}$ monochromator up to the metal-richest Nd$_{14}$Fe$_{2}$B permanent magnet. This huge composition range, coupled with the unusual chemical bonding, makes this class of materials an ideal playground for unexpected discoveries. In this seminar, I will present our recent works on “designing” new boron-richest YB$_{66}$ monochromator up to the metal-richest Nd$_{14}$Fe$_{2}$B permanent magnet. This huge composition range, coupled with the unusual chemical bonding, makes this class of materials an ideal playground for unexpected discoveries. 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in the corners of the rhombohedral unit cell, and linear chains (C-B-B or C-B-C or C-C-C) oriented along its body diagonal. According to numerous early studies, boron carbide exists as a single-phase material within a wide homogeneity range, from ~7 at. % (B4C) to ~20 at. % (B14C) of carbon. Synthesis and investigations of single crystals of boron carbide have been reported for “nearly stoichiometric B12C5”, B14C5, B13C2, and B16C7. On the basis of studies of single crystals, there is a dispute in the literature data whether there is or is not a phase transition in this material.

BULK compressibility of boron carbide compared to compressibility of icosahedra has been a matter of debate. Nelmes et al. reported the crystal structure to be more rigid than the icosahedron cluster, whereas Dera et al. observed an opposite relation.

In the present work we have studied the compressional behavior of the stoichiometric boron carbide B14C5 in the pressure interval up to 68 GPa. Unlike the previous experimental observations, our single-crystal synchrotron X-ray diffraction investigations revealed structural stability of the boron carbide in the studied pressure range. A comparison of the compressional behavior of B14C5 with that of α-B, γ-B, and B13C2 showed that it is determined by the types of bonding involved in the course of compression. Neither ‘molecular-like’ nor ‘inverted molecular-like’ solid behavior upon compression was detected that closes a long-standing scientific dispute.

3:45 PM CM01.02.06

Unexpected Origin of Strength in Mo2BC

Aria Mansouri Tehrani, Amber Lim and Jakoha Brgoch; University of Houston, Houston, Texas, United States.

In the search for new superhard materials using machine learning, we recently prepared the high hardness, ultraincompressible compound, Mo2BC. This compound is not only extremely hard but according to the calculated bulk and shear moduli ratio (G/B) it is also ductile, which is contrary to most superhard materials like diamond or ReB13. Mo2BC crystallizes in a highly anisotropic, pseudo-layered orthorhombic crystal structure containing alternating layers of boron and carbon rich planes. The complexity of this compound and its exceptional mechanical properties motivated an in-depth examination of the structure-property relationship using density functional theory. Calculating the tensile and shear stress-strain behavior to probe the ideal strength of the crystal structure reveals an unusual strain-stiffening due to the formation of pseudo-gaps with a remarkable bond-breaking and concurrent bond-formation mechanism that is not present in a typical hard material. The understanding gained by studying the electronic structure has enabled the discovery of the unique coexistence of high hardness and ductility in Mo2BC. These results provide a new perspective on the design of future mechanical materials by contrasting the notion of avoiding materials with pseudo-layered structures.

4:00 PM CM01.02.07

Understanding the Crystal Structures of InSe3

Philipp M. Konze1, Michael Küppers1 and Richard Dronskowski1, 2; 1Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, Germany; 2Juelich–Aachen Research Alliance (JARA–HPC), RWTH Aachen University, Aachen, Germany.

Phase-change memories (PCMs) are promising candidates for storage class memories, bridging the gap between traditional DRAM and Flash storage. Their targeted synthesis and characterization has therefore become an interesting field for chemists, physicists, and material scientists alike. Traditional PCMs, such as GeSb2Te5, use the differences in reflectivity or resistivity between an amorphous and a crystalline phase, where switching is performed using heat, either through radiation or Joule heating. This local melting and quenching has become a limiting factor for the energy efficiency of these materials. Switching, instead, between two closely related crystalline structures, as proposed for chalcogenide superlattices (CSLs), promises to increase their energy efficiency and reduce mechanical stress within a device. One possible candidate as a CSL is In2Se3.

InSe3 was first characterized over 100 years ago, but only recently attracted interest as a promising candidate for applications such as solar cells, photodiodes, and phase-change memories. Despite the growing interest for possible uses, its polymorphism and structures remain poorly understood.

Combining X-ray diffraction and transmission electron microscopy, we will present the crystal structures of In2Se3 and rationalize their local environments using chemical bonding analysis. We aim to understand different coordination environments through covalent, as well as ionic contributions, comparing them to prototypical structure types such as Bi2Se3. In doing so, we will highlight some new features of our chemical bonding analysis tool LOBSTER.

4:15 PM CM01.02.08

Cation-Ordering in Tri-Rutile Ternary Antimony Oxide Systems

Winnie Leung1, Elizabeth Martin1, Robert Palgrave1 and David O. Scanlon1, 2; 1Department of Chemistry, University College London, London, United Kingdom; 2Harwell Science and Innovation Campus, Diamond Light Source Ltd., Didcot, United Kingdom; 3University College London, London, Thomas Young Centre, London, United Kingdom.

The search for novel, earth abundant materials to be used as transparent conductors and/or in thermoelectric devices has resulted in recent interest in the ternary Sb(V)-oxides. A key example is ZnSb2O6, known to have an ordered tri-rutile structure which consists of MO6 octahedra (where M is Zn or Sb) and edge-sharing atoms in the order of Zn-Sb-Sb-Zn. Early reports demonstrated the potential of ZnSb2O6 as a new transparent-conducting oxide (TCO) due to its high carrier concentration in the near-IR region and wide band gap of 3.5 eV, while recent calculations by our group indicate a large thermopower and low thermal conductivity at elevated temperatures, once sufficient carrier concentrations are present, making the system of interest for thermoelectrics (TE). Pure ZnSb2O6, however, is non-conductive; hence to enhance the electrical conductivity one needs to dope it with metal ions such as Co, Ni, Cu, Al and In. Indeed, these doped systems have been shown to possess higher electrical conductivity than the nominally pure material. Nevertheless, the mechanism of doping and associated cation ordering in ZnSb2O6, upon which the structural and chemical properties are strongly dependent, remain unknown.

In this study, we have successfully doped ZnSb2O6 with various metal ions such as Ni(II), Ga(III), Cr(III), Al(III), In(III) and Nb(V), and have investigated the structural properties of these doped samples via powder x-ray diffraction (PXRD), x-ray photoelectron spectroscopy (XPS), ultraviolet and visible spectroscopy (UV-vis) and energy-dispersive x-ray spectroscopy (EDX). Where applicable, we make comparisons with computational work done within our group. Our results help elucidate the cation ordering and doping mechanisms in each case, allowing us to determine the optimum doping strategies to facilitate TCO and TE applications.

References

4:30 PM CM01.02.09

Borates as Cathodes for Li- and Mg-Ion Batteries

Sian E. Dutton; University of Cambridge, Cambridge, United Kingdom.

Polyanion materials are attractive for use as electrodes in Li-ion batteries due to their chemical stability and high operating voltages. Studies of polyanion compounds doped with Mg, typically assume that there is no Mg-ion transport and that the dopant Mg-ions are electrochemically inactive. In this talk I will
present our results on the structure and electrochemical properties of magnesium, transition-metal borates. Despite their being cation disorder between the magnesium and transition-metal sites I will show that it is possible to remove electrochemically remove Mg and subsequently intercalate Li ions. The role of the crystal structure on the ion transport will be discussed and the results of testing MgMnB$_2$O$_7$ vs. a Mg metal anode will be presented.

SESSION CM01.03: Poster Session I: Solid-State Chemistry of Inorganic Materials
Session Chairs: Ashifa Huq and Antoine Maignan
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

CM01.03.01
Solvothermal Intercalation of Iron-Amine Complexes into Iron Sulfide Layered Materials
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Recent interest in the intercalation chemistry of layered iron chalcogenides has led to the discovery of many new compounds with magnetic properties ranging from simple paramagnetism to antiferromagnetism and superconductivity. The parent superconducting compounds, mackinawite-FeS and β-FeSe, are composed of as iron-chalcogen layers stacked via van der Waals forces. These relatively weak interlayer forces make iron chalcogenides suitable candidates for intercalation studies. Numerous reports have shown that drastic changes to magnetic behavior can arise from intercalation by a variety of species, such as, simple cations, metal hydroxides, metal-amine complexes, and neutral organic molecules. Although a wide variety of intercalates are possible, their diversity can pose a challenge when trying to assess direct relationships between the intercalated species and bulk properties. One approach towards a more systematic study is to intercalate iron-chalcogenides with a coordination complex and subsequently tune the complex while assessing structural and property variations. Our study focuses systematically modifying the ligand of the previously reported [FeS$_{30}$]Fe(en)|en compound, while observing changes to the structure, stability and bulk thermodynamic properties. [FeS$_{30}$]Fe(en)|en consists of [FeS$_{30}$]$^{2-}$ layers intercalated by tris(ethylenediamine)iron(II) and a free ethylenediamine. Through solvothermal synthesis, we have made two new compounds intercalated with bidentate amines, 1,2-diaminopropane and 2,2'-bipyridine. We show that the interlayer spacing increases with the size of the coordination Fe-amine complex. This work will focus on the solvothermal synthesis, structure, and properties of the ethylenediamine, 1,2-diaminopropane and 2,2'-bipyridine-containing compounds.

CM01.03.02
Need for a SCAN+U Framework to Describe the Oxidation Energies of Transition Metal Oxides
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Transition metal oxides that can tolerate a large number of oxygen vacancies, specifically systems containing the redox-active Ce, Mn, and Fe atoms, are crucial ingredients for generating renewable fuels via two-step, oxide-based solar thermochemical reactors. However, any predictive modeling, such as DFT-SCAN+U-calculated lattice parameters exhibit marginally better quantitative agreement with experimental values. Importantly, SCAN+U predicts the right ground state polymorph for all transition metal oxides considered in this work, unlike SCAN, which yields erroneous predictions for CeO$_2$, MnO$_2$ and FeO$_2$. Hence, we conclude that the DFT-SCAN+U framework with an appropriately determined $U$ is required to describe accurate ground-state energies and qualitatively consistent electronic structures for most transition metal oxides and sulfides.

CM01.03.03
Magnetic and Dielectric Properties of Single Crystal GaFeO$_3$
Mitsuru Itoh$^1$, Shintaro Yasui$^1$, Tsukasa Katayama$^2$, Hiroki Moriwake$^3$, Ayako Komishi$^4$, Jianding Yu$^5$ and Yosuke Hamasaki$^6$; 1Laboratory for Materials and Structures, Tokyo Institute of Technology, Yokohama, Japan; 2Department of Chemistry, The University of Tokyo, Bunkyo-ku, Japan; 3Nanomaterials Research Laboratory, Japan Fine Ceramics Center, Nagoya, Japan; 4Center for Materials Research by Information Integration, Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, Tsukuba, Japan; 5Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China; 6Department of Applied Physics, National Defence Academy, Yokosuka, Japan.

α-Al$_2$O$_3$-type GaFeO$_3$ is a promising multiiferroic material due to the coexistence of a large spontaneous magnetization and polarization near room temperature. Currently, the physical properties of GaFeO$_3$ are not clearly verified, making it an interesting study. Quite recently, a study on c-Fe$_2$O$_3$ which is isomorphous to GaFeO$_3$, García-Munõz et al. (Chem. Mater. 2017, 29, 9705) unveiled a new magnetic ordering at 850 K, higher than the conventional $T_N$ at 480 K. In order to design α-Al$_2$O$_3$-type GaFeO$_3$ multiiferroics, it is essential to know the similarities in the properties between α-Al$_2$O$_3$-type 4FeO$_3$ and c-Fe$_2$O$_3$. In the current study, we present the magnetic, electric, and thermal properties of single crystalline GaFeO$_3$ (space group Pna2$_1$) and compare it with that of c-Fe$_2$O$_3$. The as-grown GaFeO$_3$ crystal was found to have modest, anisotropic electrical resistivities of 5.7×10$^3$, 3.6×10$^3$, and 5.7×10$^4$ Ωcm at room temperature along the crystallographic axes of a, b, and c, respectively. Dielectric measurements revealed that the dielectric constant is largest for the a-axis, around 31 when below 50 K, and the dielectric loss abruptly increases above 50 K. Polarization switching could not be observed even at extremely large electric field of 350 kV/cm at 77 K, due to the high coercivity, although the value of polarization by ab intio calculation is ~21 μC/cm$^2$ and polarization switching energy is ~100 meV/f.u. Magnetic measurements revealed that spontaneous magnetization appears below 540 K and 480 K for α-Al$_2$O$_3$-type FeFeO$_3$(A=Al, Cr, Ga, Fe, Rh, Sc, and In) films.
Hydrothermal Synthesis of New Pentavalent Bismuthates

Hydrothermal reactions were performed in Teflon-lined autoclaves. NaNbO₃·H₂O with Ba(OH)₂·8H₂O, Ca(OH)₂, Sr(OH)₂·8H₂O with 1:1, 1:1.1, 1:1.8 molar ratios were placed in Teflon-lined autoclaves and heated at 80 °C, 80 °C and 120 °C respectively for 2 days. Samples were filtered, washed and dried. Semi-quantitative structure was determined by XRD using monochromated CuKα radiation (RINT-2000, Rigaku). SXRPD measurements were performed using beam line BL02R2 at the SPring-8 facility. Rietan-FP and VESTA were used for crystal structure refinement and drawing respectively. The thermal stability was investigated by TG-DTA (RIGAKU Thermo Plus). Band gap were measured by diffuse reflectance spectra (JASCO V-550 spectrometer). DFT were performed using Vienna Ab initio Simulation Package (VASP). The temperature dependent electrical resistivity was measured between 300K and 1.8 K using a standard four-probe method (PPMS, Quantum Design). The photocatalytic activities were examined for the decomposition of phenol (20 ppm) under visible light from a 300 W Xe lamp (UXR-300DU, Ushio Inc.).

The XRD patterns of Ca and Sr bismuthates could be indexed with the cubic system (pyrochlore-type, Fd-3m) and that of Ba bismuthate with the trigonal system (P6₃/mmc-type, P-3m1). From the chemical analysis (ICP) Ca/Bi, Sr/Bi and Ba/Bi molar ratios were 1:1, 1:1 and 1:2 respectively. The Rietveld refinements of BaBi₂O₆, Ca₂Bi₂O₇ and Sr₂Bi₂O₇ from SXRPD data led to the final reliability (R) factors were (Rwp=5.53%, Rp=4.28% and Rwp=6.40%, Rp=4.84%) respectively. The lattice parameters of BaBi₂O₆, Ca₂Bi₂O₇ and Sr₂Bi₂O₇ were a=5.75346(6) Å, c=5.7381(1) Å, a=10.75642(6) Å and a=10.94133(6) Å respectively. Above 200 °C all the bismuthates decomposed consequently mass loss being due to the reduction of Bi₅⁺ to Bi³⁺. BaBi₂O₆ exhibited photocatalytic activity for phenol degradation under visible light. However, Ca₂Bi₂O₇ and Sr₂Bi₂O₇ showed strong oxidation property for the degradation of phenol under dark condition. This is due to the metallic behavior evidence by DOS calculation and supported by temperature dependent resistivity data indicated that these compounds possessed very low resistivity at room temperature. While BaBi₂O₆ is a semiconductor exhibited band gap energy estimation and supported by DOS calculation.
Investigating the Effects of Surface Ligand Concentration on the Magnetic Properties of Semiconductor Nanocrystals

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Semiconducting nanocrystals (NCs) have been utilized in optoelectronic devices like solar cells and laser emitting diodes and semiconductor materials have biomedical applications such as biological markers. These types of materials typically consist of an inorganic core, which dictates most of the physical properties, and an organic layer on the surface, which helps dictate chemical stability. While much work has been performed towards understanding the fundamental physics of the core NC, the surface science of these materials remains relatively unexplored. Although we stated that the surface of NCs help drive chemical stability, recent reports have suggested that the surface layer does much more, including effecting photoluminescence (PL) quantum yields, PL lifetimes, and electrical properties. Quite remarkably, the surface layer even has shown to convert nominally non-magnetic materials, such as CdSe and ZnO, into “magnetic NCs.” This result is curious, as the bulk state of these materials exhibit diamagnetic properties. These exciting results suggest that it may be possible to pair these induced magnetic properties with the inherent PL properties of these materials. This multi-functionalization of CdSe and ZnO semiconducting magnets can lead to better biomedical applications like targeted drug delivery, targeted organelle extraction, and magnetic hyperthermia treatments.

To gain further insight on how the surface layer affects the magnetic properties, this work alters the surface chemistry by controllably varying the surface ligand concentrations and by systematically varying the types of ligands (i.e. headgroup) on the surface of spherical NCs. In addition, we will study how the NC shape and interface can affect the magnetic properties by examining materials like nanowires and core/shell materials. This study will provide detailed information on how the surface ligands and interfacial layers in a NC can lead to unique magnetic properties.

CM01.03.08

Citrate-Controlled Optical Properties of Solution Deposited PbSe Thin Films

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Chemical bath deposition is an efficient method to reproduce high quality thin films. Extensive work has been done on deposition of lead chalcogenides due to their technological importance as infrared detectors and emitters [1]. Our group has previously reported on the ability to obtain desirable microstructure of lead selenide at high pH (>13) by optimizing reactants concentration, temperature and growth duration [2,3]. There is an important advantage in understanding the kinetics influencing the deposition of PbSe at relative low pH (<13) and gaining further control on film's morphological related to optical properties. Trisodium citrate (TSC) is a commonly used co-complexing agent during chemical deposition of the lead selenide, which allowed us to deposit films at lower pH, yet its exact role has not been systematically studied [3]. This work focuses on the effect of citrate and pH on the optical properties related on the deposition of PbSe and on microstructure related optical properties of the films.


CM01.03.09

High Pressure H2 and D2 Annealing Effects on the Interface Characteristics Between HfO2 and Si0.7Ge0.3

Gary Hodes, Department, NRCN, Beer Sheva, Israel.

In this presentation, we compared the electrical and interface characteristics of the HfO2 films grown on Si0.7Ge0.3 after different PMA: conventional forming gas annealing (4% H2/96% N2 at 1 atm), and high pressure H2 and D2 annealing (20 bar). Immediately after native oxide cleaning of epitaxially-grown Si0.7Ge0.3 films on Si, the HfO2 (nominally 5 nm) films were grown using atomic layer deposition at 250 °C. Following the metal electrode formation, PMA was conducted at 300 °C for 30 min, and then various electrical measurements were conducted. The detailed electrical properties of the capacitors after different PMA, including the interface state density, will be discussed. In addition, the chemical analysis results of the high-pressure H2/ D2 interlayer will be presented.


CM01.03.10

Sterically Controlled Solid-State Mechanochemistry Under Hydrostatic Pressure

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Mechanical stimuli can modify the energy landscape of chemical reactions and enable new reaction pathways, offering a complementary synthetic strategy to conventional chemistry. Mechanoochemical mechanisms under tensile stress have been extensively studied in one-dimensional polymers. In these systems, the pulling force stretches chemical bonds, initiating the reaction. Recently, it has also been shown that forces orthogonal to the chemical bonds can alter the rate of bond dissociation. However, these bond activation mechanisms have not been possible with isotropic, compressive stress (i.e., hydrostatic pressure) in three-dimensional solids. Here we show that mechanochemistry through isotropic compression is possible by molecularly engineering structures that can translate macroscopic isotropic stress into molecular-level anisotropic strain. We engineer molecules with mechanically heterogeneous components consisting of a compressible (‘soft’) mechanophore and incompressible (‘hard’) ligands. In these ‘molecular anvils’, isotropic stress leads to relative motions of the rigid ligands, anisotropically deforming the compressible mechanophore and activating bonds. Conversely, rigid
ligands in steric contact impede relative motion, blocking reactivity. We combine experiments and computations to demonstrate hydrostatic-pressure-driven reodo reactions in metal-organic chalcogenides incorporating molecular elements with heterogeneous compressibility, where bending of bond angles or shearing of adjacent chains activates the metal-chalcogen bonds leading to formation of elemental metal. These results reveal an unexplored mechanism and enable new possibilities for high-specificity mechanosynthesis. Recent results applying the molecular anvil strategy to the activation/reduction of carbon dioxide will also be discussed.

CM01.03.11
High-Mobility N- and P-Type Cu,N Thin Films Realized by Novel Direct Nitriding Synthesis and Computational Doping Design Kosuke Matsuzaki1, Kou Harada1, Yu Kumaga1, Shogo Kishiya2, Koji Kimoto2, Shigenori Ueda2, Masato Sasa1, Akihiro Maeda1, Tomofumi Susaki1, Masaaki Kitano1, Fumiyasu Oba1,2 and Hideo Hosono1; 1Tokyo Institute of Technology, Yokohama, Japan; 2National Institute for Materials Science, Tsukuba, Japan.

Copper nitride (Cu,N) has an indirect bandgap of ~1.0 eV and a high absorption coefficient of ~10^5 cm^−1 above ~2.0 eV, and therefore is considered as an earth-abundant and environmentally-benign absorber candidate in thin-film photovoltaics. Its self-doping mechanism has been discussed theoretically, but a comprehensive understanding of the doping mechanism and intrinsic behavior of pure Cu,N is still lacking owing to the low crystalline quality. We show that bipolar doping with high electron and hole mobilities in high-quality Cu,N is realized by our novel gaseous direct nitriding reaction utilizing a catalytic ammonia oxidation to form Cu,N from Cu metal. This reaction overcomes the thermodynamic constraint associated with its high positive formation enthalpy (~83.7 kJ mol^−1) and provides high-quality Cu,N films showing resistive n-type behavior. P-type conduction is realized by fluorine doping into the interstitial site as predicted by density functional theory calculations and directly proven by electron energy loss spectroscopy combined with scanning transmission electron microscopy. The electron and hole mobilities of undoped n-type and F-doped p-type films are as high as 200 and 80 cm^2(Vs)^−1, respectively. Our synthetic methodology for high quality n- and p-type films applicable to uniform and large-area deposition would open up the possibility for Cu,N as an alternative photoabsorber in thin-film photovoltaic cells.


CM01.03.12
Defects Behavior in Disordered Iron Oxide Synthesized from Grain-Oriented Iron Foils Karen A. Neri1, José Alberto Andracca Adam1, Ramón Peña1 and Roberto Bacsa2; 1Doctorate in Nanoscience and Micro-Nanotechnology, ENCB, Instituto Politécnico Nacional, Mexico City, Mexico; 2Department of Electrical Engineering, Solid State Electronics Section, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Mexico City, Mexico.

Disordered iron oxide thin-films synthesized from grain-oriented iron foils were grown on both glass and Si (100) n-type substrates by vacuum evaporation followed by thermal oxidation at low temperatures. Defects such as vacancies formation has been studied using Atomic Force Microscopy (AFM) and Raman Spectroscopy. The kinetic of oxidation as a function of surface parameters was investigated by AFM studies. The vibrational modes (bands) connected with the vacancies formation and magnetic ordering into the iron oxide structure were validated by Raman spectroscopy. Space-charge effects can be influenced by discontinuous growth of iron oxide and correlated with their structure parameters. Finally, the disordered iron oxide will be useful for the next generation of adaptive oxide devices.

CM01.03.13
Chemical, Structural and Photovoltaic Properties of Graded Cd,S,Se Thin Films Grown by Chemical Bath Deposition on GaAs(100) Ofir Friedman, Omri Moscovitch and Yuval Golan; Department of Materials Engineering and the Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beersheva, Israel.

Cd,S,Se thin films are direct band gap ternary semiconductors that can harvest photon energy in an energy range from 2.42 eV (CdS) to 1.74 eV (CdSe) by compositional tuning or chemical gradation. Growth of such films using chemical bath deposition (CBD) is advantageous due to low production costs and the ability to easily control initial bath composition.1 We have recently demonstrated monocrystalline CdS and CdSe deposited on GaAs substrates by CBD.2,3 In this work we present the chemical, structural and photovoltaic properties of Cd(S,Se) solution thin films deposited on GaAs(100) substrates by CBD. The structural and chemical properties of the films were characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM), analytical transmission electron microscope (A-TEM) and energy dispersive spectroscopy (EDS) mapping. We present evidence of chemically graded films that were formed by controlling the initial anion concentrations in the batch, which affect nucleation and growth of the films. The films are polycrystalline in nature, with a thin zinc blende layer formed directly onto the GaAs substrate, on top of which a highly oriented nano-columnar layer of wurtzite Cd,S,Se is obtained. Finally, current-voltage measurements of GaIn-eutectic/GaAs-Cd(S,Se)/In device were conducted at room temperature under 1 sun. We demonstrate the photo-response dependence on the S/Se ratio in Cd,S,Se-based photovoltaic cells.


CM01.03.14
Revealing the Atomic Arrangement of Dopants in the Layered Oxide Cathode Structure Sorosh Sharifi-Asl1, Jason Croy2, Mahalingam Balasubramanian1 and Reza Shahbazian-Yassar1; 1Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois, United States; 2Chemical Science and Engineering, Argonne National Laboratory, Argonne, Illinois, United States; 3Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois, United States.

The positive electrode of rechargeable-ion battery, which is normally a layered oxide ceramic material, is known as the bottleneck of this technology. Based on the numerous studies focused on the degradation mechanisms of cathode materials, it has been proposed that cationic doping with electrochemically-inactive metals such as Al, Ti and Mo improves the cycling stability and electrochemical performance of cathode materials. LiCoO2 is one of the most widely used cathode materials in Li-ion batteries. It has a layered hexagonal (R3m) structure, which allows for free Li-ion mobility during the electrochemical cycling. LiCoO2 has a very high theoretical capacity of 270 mAhg^−1, only half of which can be reversibly utilized to maintain a stable cycling condition. The reason is, Li intercalation higher than a certain extent results in migration of Co ions into the Li sites that leads to the layered to spinel/rock-salt phase transition, an irreversible reaction that results in rapid capacity fading. To combat this issue metal doping has been pursued as a promising direction in the literature. The electrochemically inactive cations act as stabilizing skeleton in the cathode structure and resist against the structural collapse upon high extent of Li-deintercalation. However, the dispersion of such dopant cations in the cathode structure is not truly


CM01.03.12
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Disordered iron oxide thin-films synthesized from grain-oriented iron foils were grown on both glass and Si (100) n-type substrates by vacuum evaporation followed by thermal oxidation at low temperatures. Defects such as vacancies formation has been studied using Atomic Force Microscopy (AFM) and Raman Spectroscopy. The kinetic of oxidation as a function of surface parameters was investigated by AFM studies. The vibrational modes (bands) connected with the vacancies formation and magnetic ordering into the iron oxide structure were validated by Raman spectroscopy. Space-charge effects can be influenced by discontinuous growth of iron oxide and correlated with their structure parameters. Finally, the disordered iron oxide will be useful for the next generation of adaptive oxide devices.

CM01.03.13
Chemical, Structural and Photovoltaic Properties of Graded Cd,S,Se Thin Films Grown by Chemical Bath Deposition on GaAs(100) Ofir Friedman, Omri Moscovitch and Yuval Golan; Department of Materials Engineering and the Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beersheva, Israel.

Cd,S,Se thin films are direct band gap ternary semiconductors that can harvest photon energy in an energy range from 2.42 eV (CdS) to 1.74 eV (CdSe) by compositional tuning or chemical gradation. Growth of such films using chemical bath deposition (CBD) is advantageous due to low production costs and the ability to easily control initial bath composition.1 We have recently demonstrated monocrystalline CdS and CdSe deposited on GaAs substrates by CBD.2,3 In this work we present the chemical, structural and photovoltaic properties of Cd(S,Se) solution thin films deposited on GaAs(100) substrates by CBD. The structural and chemical properties of the films were characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM), analytical transmission electron microscope (A-TEM) and energy dispersive spectroscopy (EDS) mapping. We present evidence of chemically graded films that were formed by controlling the initial anion concentrations in the batch, which affect nucleation and growth of the films. The films are polycrystalline in nature, with a thin zinc blende layer formed directly onto the GaAs substrate, on top of which a highly oriented nano-columnar layer of wurtzite Cd,S,Se is obtained. Finally, current-voltage measurements of GaIn-eutectic/GaAs-Cd(S,Se)/In device were conducted at room temperature under 1 sun. We demonstrate the photo-response dependence on the S/Se ratio in Cd,S,Se-based photovoltaic cells.

investigated and it is normally assumed that dopants will disperse uniformly into the cathode structure. In this study, we utilized aberration-corrected scanning transmission electron microscopy (AC-STEM) together with analytical electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS) to study the atomic structural arrangement of W-doped LiCoO$_2$. High angle annular dark field imaging (z-contrast imaging technique) that can distinguish between Co and W atoms is utilized in our investigation. Interestingly, our results indicate that in the W-doped LiCoO$_2$ sample, W atoms prefer to occupy a distinct Co layer and form separate LiWO$_4$ layers inside the LiCoO$_2$ matrix. The mechanism of such abnormal atomic arrangement is being investigated by computational calculations. Furthermore, structural analysis at various state of charge and cycling conditions is studied to reveal the role of W layers on the structural stability of W-doped LiCoO$_2$. In addition, to test the structural stability of such local W rich layers, controlled beam damage experiments have been carried out that demonstrate higher stability of W layers against beam knock-on damage. Overall, presenting the first atomic demonstration of dopant arrangement inside the layered-oxide cathode structures can explain many questions regarding the role of dopant on the electrochemical performance of the cathodes and can have a great contribution in designing superior cathode materials for next generation of Li-ion batteries.

**CM01.03.15**

**Towards the Application of Large Zeolite Particles as PEPT Tracers**

**Dan Parsons**$^2$, Joe Hriljac$^2$ and Andy Ingram$^1$; $^1$School of Chemical Engineering, University of Birmingham, Birmingham, United Kingdom; $^2$School of Chemistry, University of Birmingham, Birmingham, United Kingdom.

PEPT (Positron Emission Particle Tracking) is a powerful technique used to elucidate dynamics in chemical engineering processes$^{[1]}$. Visualizing dynamics with PEPT relies on incorporating tracer particles, radioactively labelled with a β$^-$-emitting isotope, into the system under study. The most commonly applied tracer particles are resin or glass beads with diameters in the range 0.1 – 4 mm. Large glass beads (> 1 mm) may be activated directly in a cyclotron, converting some oxygen in the glass to F-18; however, this is not possible for smaller glass beads and resin particles (< 1 mm), instead these are labelled by surface adsorption or ion-exchange, respectively, from aqueous solutions containing F-18$^{[3]}$. Low affinities for F-18 in existing tracers limits the ability to label particles smaller than 100 μm, hence tracer particles are often much larger than the granular material they represent, and the properties of the tracer may not also often atypical of the granular material in true systems, ultimately limiting the applications of PEPT studies and potentially the accuracy of results obtained$^{[1]}$. The aim of the current work is to develop syntheses that provide control of particle size and morphology for materials with high affinities for the β$^-$-emitting isotopes of interest.

Our work has applied established methods to successfully synthesize large crystals, or particles, of zeolites with the faujasite, LTA and mordenite structures in the size range of interest, 10 - 100 μm. Methods employed have included the addition of triethanolamine to gels, retarding the crystal growth and significantly increasing the size of crystallites, which were then labelled by exploiting the innate affinity of the material for the β$^-$-emitting β$^+$-emitting isotopes.

The most commonly used β$^+$-emitting isotopes for labelling tracers in PEPT are F-18 and Ga-68, owing to ease of production and suitable half-lives. We have demonstrated the affinity of large zeolite particles for uptake of both cationic and anionic species, viz. Ga$^{3+}$ and F$^-$, from aqueous solution by ion-exchange and adsorption, respectively.

Ultimately, we have produced crystalline tracers in the size range of interest which may be labelled by exploiting the innate affinity of the material for the species of interest. The application of crystalline tracers that are smaller than any previously used in PEPT studies have the potential to provide more accurate information on dynamics in many industrially important processes including mixing and fluidization phenomena.


$^{[3]}$ M. Aghbashlo et al., Drying Technol., 2014, 32, 1005

**CM01.03.16**

**Solid Electrolytes Particle Size Effect in All-Solid-State Batteries**

Qingsong Tu, Gerbrand Ceder and Tan Shi; University of California, Berkeley, Berkeley, California, United States.

All-solid-state battery (SSB) is a promising candidate to replace the conventional lithium ion batteries. It not only has improved safety, but also could has higher energy density by utilizing Li metal anode. However, two factors limit the cathode loading in current SSBs and lead to low energy density. 1) Large amount (30 wt% - 50 wt%) of solid electrolyte (SE) in the cathode composite is required to provide sufficient ionic diffusion pathways. 2) Cathode composite thickness is limited by the poor ionic diffusion in the cathode composite.

We address these two issues by improving the Li ion conduction network through cathode morphology optimization. Our theoretical calculation and experimental data both show the relative particle size of cathode and SE greatly modifies the ionic percolation in the cold pressed cathode composite. Through simple SE particle size optimization, we were able to reduce the SE needed in the cathode composite and increase the cathode composite thickness without sacrificing specific capacity, resulting in an increased full cell energy density.

**CM01.03.17**

**Field-Induced Magnetic Order Switching of A'-site Iron Spins in CaFe$_2$Ti$_4$O$_9$**

Midori Amano Patino$^1$, Fabio Denis Romero$^2$, Masato Goto$^1$, Takashi Saito$^1$ and Yuichi Shimakawa$^2$; $^1$Institute for Chemical Research, Kyoto University, Kyoto City, Japan; $^2$Hakubi Center for Advanced Research, Kyoto University, Kyoto City, Japan.

Materials which adopt the $A$-site-ordered quadruple perovskite structure, continue attracting significant attention due to the intriguing magnetic and electronic properties they display. In this structure, small cations such as transition-metal ions at the originally twelve-fold coordinated $A$ site of an $ABO_3$ perovskite lead to a significant tilting of the corner sharing $BO_6$octahedra and give way to square-coordinated units or "$A$ sites". In this work we got particularly interested in the quadruple perovskite phase CaFe$_2$Ti$_4$O$_9$, in which the $B$-site Ti$^{4+}$ ions are nonmagnetic therefore allowing the investigation of the unusual magnetic behaviour of the Fe$^{3+}$ spins forming the $A$'-site sublattice. We synthesized this compound using high-temperature high-pressure techniques, and characterized its magnetic properties for the first time. This phase had been previously observed, but not fully characterized$^{[1]}$. Here we confirm the presence of Fe$^{3+}$ $S = 2$ centers at the square planar $A$' sites in CaFe$_2$Ti$_4$O$_9$ from Curie-Weiss $\mathbf{S} = 2$ magnetic susceptibility and Mössbauer data. Magnetic susceptibility data show a maximum at 2.8 K suggesting AFM (antiferromagnetic)-like behaviour of the Fe$^{3+}$ spins. Interestingly, such state switches to a ferromagnetic-like behaviour under the application of magnetic fields $H \geq 1$ T. Therefore, the applied magnetic field is capable of inducing a FM-like structure on the $A'$-site Fe$^{3+}$ $S = 2$ spin sublattice. DFT calculations for the AFM and FM spin arrangements for the Fe$^{3+}$ spin sublattice in CaFe$_2$Ti$_4$O$_9$ reveal that the two states are very close in energy. We propose that the comparable energies of the AFM and FM states lead to competition between the two spin configurations.
In recent years, zirconia (ZrO$_2$) micro- and sub-microparticles gained considerable attention due to their outstanding properties, including chemical inertness, thermal stability and high refractive index. These excellent features of zirconia-based materials enable a broad variety of applications ranging from fuel cells, catalysis, sensors to electro- and bioceramics. Furthermore, zirconia (sub-)microparticles are interesting for applications as building blocks of photonic glasses for high-temperature applications, including structural colors (SC)\cite{1} and thermal barrier coatings (TBC)\cite{2,3}.

For structural colors, well-defined monodisperse core-shell particles with smooth surface and strong refractive index contrast are needed. These particles are used for structural pigments and as colorants in ceramics, paint and cosmetics. In this work, we will present the influence of aliovalent substitution of $\text{P}^{5+}$ with $\text{Si}^{4+}$ and isoelectronic substitution of $\text{Se}^{2–}$ for $\text{S}^{2–}$ on the structure-transport correlation in lithium conducting argyrodites\cite{3,4}. Structural changes arising from the substitution were monitored through Rietveld refinements of the experimental X-ray powder and neutron diffraction data, and severe changes in the lithium substructure and site ordering can be found. The found changes in the lithium substructure and site ordering cannot be explained in the Li$^+$ ionic conductivities as measured by impedance spectroscopy. This work provides an approach to a better understand structure-property relationships in solid electrolytes. The herein found correlations between the Al amount and the stabilization of the tetragonal polymorph against the destructive martensitic transition to the monoclinic phase and inhibited grain growth. Evident dopant segregation after annealing revealed by EDX mappings suggests a reduction of the propagation of grain boundaries during sintering (solute drag effect).

In this work, we will present the influence of aliovalent substitution of $\text{P}^{5+}$ with $\text{Si}^{4+}$ and isoelectronic substitution of $\text{Se}^{2–}$ for $\text{S}^{2–}$ on the structure-transport correlation in lithium conducting argyrodites\cite{3,4}. Structural changes arising from the substitution were monitored through Rietveld refinements of the experimental X-ray powder and neutron diffraction data, and severe changes in the lithium substructure and site ordering can be found. The found changes in the lithium substructure and site ordering cannot be explained in the Li$^+$ ionic conductivities as measured by impedance spectroscopy. This work provides an approach to a better understand structure-property relationships in solid electrolytes. The herein found correlations between composition, structure and functional properties contribute towards a general framework and universal strategy to design solid materials with fast ionic diffusion.

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4. Manuscript submitted

Synthesis and Characterization of ZrO$_2$@SiO$_2$/Al$_2$O$_3$ Core-Shell Particles for Application as Structural Colors and Thermal Barrier Coatings

Maik Finsel	extsuperscript{1}, Jil Rüter	extsuperscript{1}, Maria Hemme	extsuperscript{1}, Kaline P. Furlan	extsuperscript{1,2}, I. Guoliang Shang	extsuperscript{3}, Robert Blick	extsuperscript{3}, Robert Zierold	extsuperscript{3}, Rolf Janßen	extsuperscript{2}, Alexander Petrov	extsuperscript{1,4}, Manfred Eich	extsuperscript{1,4}, Horst Weller	extsuperscript{1} and Tobias Vossmeyer	extsuperscript{1}; \textsuperscript{1}Physical Chemistry, University of Hamburg, Hamburg, Germany; \textsuperscript{2}Advanced Ceramics, Hamburg University of Technology (TUHH), Hamburg, Germany; \textsuperscript{3}Center for Hybrid Nanostructures, University of Hamburg, Hamburg, Germany; \textsuperscript{4}Optical and Electronic Materials, Hamburg University of Technology (TUHH), Hamburg, Germany; \textsuperscript{5}ITMO University, St. Petersburg, Russian Federation; \textsuperscript{6}Materials Research, Helmholtz-Zentrum Geesthacht Center for Coastal Research, Geesthacht, Germany.

In recent years, zirconia (ZrO$_2$) micro- and sub-microparticles gained considerable attention due to their outstanding properties, including chemical inertness, thermal stability and high refractive index. These excellent features of zirconia-based materials enable a broad variety of applications ranging from fuel cells, catalysis, sensors to electro- and bioceramics. Furthermore, zirconia (sub-)microparticles are interesting for applications as building blocks of photonic glasses for high-temperature applications, including structural colors (SC)\cite{3} and thermal barrier coatings (TBC)\cite{2,3}.

For structural colors, well-defined monodisperse core-shell particles with smooth surface and strong refractive index contrast are needed. These requirements can be achieved by encapsulation of spherical zirconia submicroparticles with a suitable shell material. For example, to achieve the desired properties for structural colors Al$_2$O$_3$, SiO$_2$, and polymers are attractive materials to form the shell.\cite{1,2}

Most synthesis methods for such core-shell particles use organic ligands (e.g. polymer\cite{1}, citric acid\cite{2}) as adhesive layer between the core and the shell. One of the main obstacles of this approach is that it precludes high-temperature applications. Here, we developed a straightforward approach to prepare...
ZrO$_2@$SiO$_2$ core-shell composites without using additional organic coupling agents. First results show that changing the silica shell thickness varies the optical properties in the visible region. Furthermore, we demonstrate that ZrO$_2@$SiO$_2$ core-shell particles withstand temperatures up to 1000 °C whereas size-comparable zirconia particles and core-shell particles using polyvinylpyrrolidone (PVP) as interfacial layer disintegrate when heated up to 800 °C as shown by XRD, SEM and cross-sectional TEM characterization.

For thermal barrier coatings, low-thermal conductivity ceramics such as Y-stabilized zirconia (YSZ) are used to provide thermal insulation of the underlying superalloys in gas-turbine engines operated in aircrafts. One of the main obstacles of this system is the oxygen diffusion through the ceramic TBC due to oxygen vacancies, which leads to corrosion and failure of the turbine blade.

Here we studied ionic transport in nanocrystalline LiF and nanocrystalline LiF:Al$_2$O$_3$ composites to study interfacial ion transport properties. It is well known that the properties of materials with nm-sized structures, particularly if we consider ionic transport, can be significantly different from those of their coarse-grained counterparts. Understanding ionic diffusion in solids is a very vital topic in material science. Currently we put much effort into finding suitable materials that meet the needs to develop leading-edge energy storage devices and sensors. Besides studies driven directly by applications, also fundamentally oriented investigations are required to shine further light on the structure-property relationships determining fast ion transport.

Fast interfacial Li$^+$ diffusion in nanostructured LiF and LiF-Al$_2$O$_3$ composites as seen by NMR spectroscopy

Stefan Breuer, Veronika Pregartner and Martin Wilkening; Institute for Chemistry and Technology of Materials, Graz University of Technology, CD-Laboratory for Lithium Batteries, Graz, Austria.

Understanding ionic diffusion in solids is a very vital topic in material science. Currently we put much effort into finding suitable materials that meet the needs to develop leading-edge energy storage devices and sensors. Besides studies driven directly by applications, also fundamentally oriented investigations are required to shine further light on the structure-property relationships determining fast ion transport. LiF attracted our attention as it has known that the properties of materials with nm-sized structures, particularly if we consider ionic transport, can be significantly different from those of their coarse-grained counterparts. Understanding ionic diffusion in solids is a vital topic in material science. Currently we put much effort into finding suitable materials that meet the needs to develop leading-edge energy storage devices and sensors. Besides studies driven directly by applications, also fundamentally oriented investigations are required to shine further light on the structure-property relationships determining fast ion transport. LiF attracted our attention as it has known that the properties of materials with nm-sized structures, particularly if we consider ionic transport, can be significantly different from those of their coarse-grained counterparts. Understanding ionic diffusion in solids is a vital topic in material science. Currently we put much effort into finding suitable materials that meet the needs to develop leading-edge energy storage devices and sensors. Besides studies driven directly by applications, also fundamentally oriented investigations are required to shine further light on the structure-property relationships determining fast ion transport. LiF attracted our attention as it has known that the properties of materials with nm-sized structures, particularly if we consider ionic transport, can be significantly different from those of their coarse-grained counterparts.

References:


CM01.03.23

Microwave Synthesis of Transition Metal Oxide Nanoparticles Adsorbed on Silica Nanospheres for Energy Applications

Pierre Magni, Noura Zahir, Sara Soltani, Jean J. Gaumeret, Sébastien Diliberto, David N. McIlroy, Wen Luo and Liqiang Mai; Jean Barriol Institute, University of
SiO2 nanosprings (NS) are used not only for support and substrates in various chemical, biological and medical applications, but also for photovoltaic development and hydrogen storage depending on the choice of the coating on the NS [1,2]. SiO2 NS are now readily coated with metal oxides, which make them interesting devices for sensors based on redox processes, particularly with semiconducting elements [3]. The use of microwave (MW) chemistry has become more and more common as a means to synthesize nanoparticles, and it is now possible to model deposition of metal oxide nanoparticles on the silica NS using two joint mechanisms for heating, dipolar polarization and ionic conduction. However, to ensure the stability of the SiO2 NS, it is better to first synthesize the nanoparticles by MW reaction before adding them to the NS. In this context, we present herein some MW synthesis of transition metal oxide (TMO) and mixed metal oxide (MMO) nanoparticles (Zn, Co, V) followed by direct absorption on SiO2 NS. Defect-rich TMO and MMO nanoparticles are synthesized by preparing various metal acetylacetonate solutions in different H2O/EtOH volume ratios. After MW irradiation up to 1 h, the resulting precipitates were filtered, washed with EtOH, and dried at 80°C [4]. Finally, the nanoparticles were added to various NS in EtOH. SEM, TEM and X-Ray diffraction confirmed the presence of metal-oxide nanoparticles in a different size range and shapes depending on the solvent ratio and the MW irradiation time. The quantification of ligands originating from the precursors was determined by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). After SEM and TEM characterizations, the optical properties of the different TMO and MMO nanoparticles were carefully measured by UV-Visible photoluminescence and absorption spectroscopy. The same analytical protocol was performed after adsorption on SiO2 NS. It shows that integrity of defect-rich TMO or MMO nanoparticles (constant visible light emission for ZnO at 570 nm for example) is preserved when deposited onto the NS. Such results on this stability show the potential of using a metal-oxide shell with a silica NS core as an absorber/Emitter when connected to a metal contact.

**References**


**CM01.03.24 Impact of the Isovalent Alloying on the Thermoelectric Properties of Yb14MnSb11**

Giacomo Cerretti, Sabah K. Bux and Jean-Pierre Fleurial; Jet Propulsion Laboratory, Pasadena, California, United States.

Yb14MnSb11, with a zT of about 1.2 at 1200 K, is the highest performing p-type materials for high temperature thermoelectric applications. Structurally it belongs to the Zintl phase family A14MPn11, (where A = Ca, Sr, Ba, Eu and Yb; M = Al, Mn, Zn, Ga, Nb, In, and Cd, Pn = P, As, Sb, Bi), which is formed by 14 A+2 cations, a MPn3+ tetrahedron, a linear Pn3- trimer, and 4 Pn3- anions. This chemical configuration gives the possibility to independently manipulate the electronic and thermal transport properties of the compound by using different alloying species and adjusting their concentrations. In this contribution, we want to show how different alloying approaches affect the chemical and structural properties of the Yb14MnSb11, and how this translates into the manipulation of the thermoelectric properties. Specifically, we studied the impact of the isovalent partial substitution on the Yb and Mn sites with Sr and Co/Pd respectively. The lack of filled f-orbitals in Sr could result in large changes in the DOS due to the different nature of the chemical bonding. Additionally, the bigger cationic radius of Sr compared to Yb will reduce the bond length generating a higher chemical pressure, and in turn altering the thermal transport properties of the material. Partial substitution of the Mn2+ ions can produce changes in the electronic band structure which can improve the performance of the material. The impact of Sr/Pd substitution will be presented and discussed.

**CM01.03.25 Negative Magnetisation in A4’+3Cr2BO6 Perovskites**

Emily C. Hunter1, Peter D. Battle1, Maxim Avdeev2,3, Mylene Hendrieks4 and Joke Hadermann5; 1The University of Oxford, Oxford, United Kingdom; 2ANSTO, Lucas Heights, New South Wales, Australia; 3The University of Sydney, Sydney, New South Wales, Australia; 4Physics, University of Antwerp, Antwerp, Belgium.

This research explores the compositional sensitivity of the magnetic properties of A4’+3Cr2BO6 perovskites where A is La or Pr; A’ is Sr or Ca and B is Sb, Nb or Ta. In monophasic compounds of this type the cations occupying the B sites can be partially ordered or fully disordered. Alternatively the material can phase-separate to give regions in which the cations are ordered and ordered in other regions. Neutron diffraction and electron microscopy have shown that in compositions where there is cation order two crystallographically distinct B sites are present in a 1:1 ratio, despite the two cation species being present in a 2:1 ratio.

The extent of the cation ordering affects the magnetic properties of the perovskite. For example, LaSrCr2SbO6, which has a high degree of cation order, is a ferrimagnet while PrSr2Cr2NbO6 and PrSr2Cr2TaO6, which contain both cation-ordered and disordered regions, are spin glasses. PrSr2Cr2SbO6 still behaves as a ferrimagnet, despite containing disordered regions. We shall focus on PrCa2Cr2SbO6 and PrCa2Cr2TaO6 which are both fully disordered, adopting the space group Pnma. In these compounds the Cr cations order antiferromagnetically below ~120 K, however, magnetometry studies show that the field-cooled magnetisation becomes negative below 50 K for PrCa2Cr2NbO6 and below 80 K for PrCa2Cr2TaO6. The direction of the net magnetisation can be flipped by applying magnetic fields of 1000 Oe to PrCa2Cr2NbO6 and 3000 Oe to PrCa2Cr2TaO6 and both compounds show a large degree of hysteresis in M(H). We have studied both of these negative magnetisation materials in depth using neutron diffraction, collecting data over a range of temperatures and applied fields. In our presentation we will present the results of this study and describe the other compositions in more detail.

**CM01.03.26 A Novel Approach of Dopant Selection to Immobilize Lanthanides in Uranium-Based Metallic Fuels**

Rahil Khanal1, Nathan Jerred2,3, Indrajit Charti1, Michael Benson2, Robert Mariani3 and Samrat Choudhury1; 1University of Idaho, Moscow, Idaho, United States; 2Idaho National Laboratory, Idaho Falls, Idaho, United States.

In metallic fuels, fission products generated during operation react with the cladding materials leading to fuel-cladding-chemical interactions (FCCI). The FCCI results in degradation of the cladding wall and eventual rupture of the cladding if the fuel is operated for higher burnup. Use of a dopant in the fuel matrix, which can form intermetallic compounds with lanthanide fission products (e.g., Nd, Ce, Pr, and La), is proposed to be one of the effective ways of mitigating FCCI. Here we used ab-initio calculations based on density functional theory (DFT) to study the interactions between different possible dopants (such as Se, As, Pd, In) and the lanthanide fission products. Based on the calculations, arsenic and selenium were identified as potential dopants to arrest the major lanthanides within the uranium matrix effectively. The relative preference of identified novel dopants in binding with another fuel component, Zr, is also evaluated. Finally, we present an approach that can be used in selecting a dopant to bind a particular lanthanide inside the fuel matrix based on their intrinsic properties such as electronegativity and atomic size. The approach used in this study is generic; so it has implication in other areas of research related to alloy design. This research is being funded by DOE-NEUP, grant # DE-NE0008557.
CM01.03.27
Ozone-Mediated Synthesis of Ceria Nanoparticles Anuja Bhalkikar and Chin Li Cheung; Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

Numerous methodologies have been developed for the synthesis of cerium oxide or ceria, a commercially important lanthanide oxide. Some of the techniques employ long reaction times, elevated temperatures and/or pressures, expensive metal alkoxides and caustic alkalins. This necessitates the need to develop milder, environment friendly synthetic routes for cerium oxide generation. Herein, we report a rapid, room temperature methodology to synthesise fluorite-structured ceria nanoparticles using cerium (III) salts and ozone in the presence of short chain primary, secondary, and tertiary alcohols. This simple technique produced nanoparticles with higher oxygen vacancy compared to that of bulk ceria. Chemical species in the reaction mixtures were studied to elucidate a possible growth mechanism of these nanoparticles from ozonating alcoholic solutions of cerium salts. The catalytic activity of ceria nanoparticles towards the oxidation of carbon monoxide (CO) was further evaluated and compared with that of commercial bulk ceria.

CM01.03.28
How to In Situ Follow the Evolution of Dislocation Configurations During Mechanical Testing on Bulk Specimen? Ben Haj Slama Meriem1, 2, Hana Kriaa1, 2, Julien Guyon1, 2, Nabilal Maloufi1, 2, Jean-Jacques Fundenberger1, 2 and Antoine Guitton1, 2; 1Université de Lorraine – CNRS – Arts et Métiers ParisTech – LEM3, Metz, France; 2Labex Damas - Université de Lorraine, Metz, France.

In the aim of following the fast evolution of the industrial demands, developing innovative techniques that allow to understand and to predict the mechanical properties of materials has become a necessity for the Materials Science community. For instance, mechanical tests followed by microstructural investigations provide engineers with the necessary information to computationally predict the mechanical performance of components. In situ mechanical testing combined with microscopy techniques (SEM and TEM) [1,2] is well known for studying the instantaneous evolution of microstructures during exposure to stress. Such experiments allow capturing footprints of the deformation mechanisms responsible for the changing microstructure. For instance, in-situ testing combined with TEM is generally required for studying the instantaneous evolution of defects during exposure to stress. Today various approaches inside a TEM exist: TEM holders with a simple mechanical actuation [3], elaborated testing units that fit inside the pole pieces [4,5] or by playing with various coefficients of thermal expansion [1]. Nevertheless, in-situ TEM mechanical testing is experimentally very tough. In addition to the difficult control of the deformation conditions, the space available is generally less than one centimeter and statistics on physical mechanisms is scientifically very weak. Indeed, TEM needs an electron transparent specimen with a thickness of \( \approx 100 \) nm with a useful field of view of few \( \mu m^2 \).

Therefore, fundamental questions on the representativeness of observed phenomenon must be raised when extrapolating discussions to a millimeter-size specimen. In this framework, we have successfully combined mechanical testing of bulk specimen with an in-situ avant-gardist dislocation-scale characterization technic; the accurate Electron Channeling Contrast Imaging (aECCI) [6]. aECCI is a non-destructive groundbreaking procedure that provides, inside a SEM, TEM-like diffraction contrast imaging of sub-surface defects (at a depth of about one hundred of nanometers) on centimetric bulk specimen with still unsurpassed resolutions [7,8]. Firstly, technological challenges such as defect contrast comprehension and experiment procedure will be presented. Secondly first in-situ results will be discussed and they clearly show the full potentialities of this groundbreaking and powerful testing set-up.

References

CM01.03.29
Fundamental and Experimental Aspects of Diffraction for Characterizing Dislocations on Bulk Materials by Electron Channeling Contrast Imaging in Scanning Electron Microscope Hana Kriaa1, 2, Antoine Guitton1, 2 and Nabilal Maloufi1, 2; CNRS, Arts et Métiers ParisTech, Université de Lorraine, Metz, France; 2Labex Damas, Université de Lorraine, Metz, France.

The SEM is an easier way to use electron microscope compared to TEM essentially because of the possibility to observed centimetric bulk specimen and the larger space available in the chamber. SEM can access diffraction contrast on bulk materials with the phenomenon of electron channeling [1]. The Electron Channeling Contrast Imaging (ECCI) is a non-destructive groundbreaking technique offering the ability to provide, inside a SEM, TEM-like diffraction contrast imaging of sub-surface defects (at a depth of about one hundred of nanometers) on centimetric bulk specimen with still unsurpassed resolutions [2,3]. Electron channeling contrast is produced from electrons, that channel down the crystal planes. Strain and defects distort the crystal planes, which produce changes in backscattered electron intensity leading to a contrast on the image. Dislocations for example can be characterized by ECCI using the well-known TEM \( g \cdot b = 0 \) and \( g \cdot bxu = 0 \) extinction criteria [4] where \( g \) is the diffraction vector and \( b \) the Burgers vector. In this study, fundamental and experimental aspects of electron diffraction for characterizing dislocation by ECCI in SEM are reported [5]. The \( (g \cdot g) \) method is explored on several dislocation configurations in an Interstitial-Free steel sample. Moreover, the first detailed characterization of a dislocation dipole by ECCI [4,5] is presented.

References

CM01.03.30
Structural, Raman and Electrical Characterization of Nanocrystalline ZnSe Thin Films Deposited by Pulse Laser Deposition Pawan Kumar1, 2, Arvind Kumar3, Trilok Pathak3, Sita Dugu1, Rajesh K. Katiyar1, Alvaro Instan1 and Ram Katiyar1; 1Department of Physics, Institute for Functional Nanomaterials, University of Puerto Rico, San Juan, Puerto Rico, United States; 2Department of Physics, GuruKul Kangri Viswavidyalaya, Haridwar, India; 3Department of Physics, Kalindi College, Delhi University East Patel Nagar, Delhi, India.

Thin films of group II–VI semiconductor compounds have attracted considerable attention due to their novel physical properties. As a wide band-gap material, ZnSe is a potential candidate showing compatibility for optoelectronic devices based on the thin film technology [1, 2]. Zinc Selenide (ZnSe) thin
films were deposited by Pulse Laser Deposition (PLD) technique on Si-p type substrates at different substrate temperatures. The substrate temperatures were fixed at 150°C, 200°C, 250°C, and 300°C respectively during the growth of the samples. The stoichiometry of ZnSe was confirmed by using X-ray diffraction pattern. The surface morphology and roughness of thin films were investigated by atomic force microscopy. The atomic bond behavior at room temperature and at lower temperatures (30°C to -190°C) were studied by Raman spectroscopy. The n-ZnSe/p-Si heterojunction thin films were characterized by current-voltage (I-V) and capacitance-voltage (C-V) measurements at different temperatures (273K to 373K). These films are promising candidates for applications in solar cells and sensors.


CM01.03.31

Development of Highly Hydrogen-Sensitive Thermal Desorption Spectroscopy System—For Detection of Extremely Low Concentration Hydrogen in Oxide Semiconductors

Hidenori Hiramatsu1, Taku Hanna1, Isao Sakaguchi2 and Hideo Hosono1; 1Tokyo Institute of Technology, Yokohama, Japan; 2National Institute for Materials Science, Tsukuba, Japan.

Hydrogen is the most unavoidable and uncontrollable impurity in semiconductor devices because of the ease of contamination during fabrication processes, even under an ultra-high-vacuum (UHV) atmosphere. This impurity results in serious problems such as instability of thin-film transistors and unintentional carrier doping. The detection limit of various techniques strongly depends on the sample volumes because a larger total amount of hydrogen facilitates detection. Thus, many quantitative hydrogen analyses have been performed on ‘bulk’ samples. However, semiconductor device technology is generally based on thin-film deposition and fine-scale processing technologies, for which material purification and refinement of processing techniques have been rapidly advancing. Thus, the development of highly sensitive hydrogen detection techniques for small-volume samples such as ‘thin films’ with nanometer-scale thicknesses is critical to investigate the effects of hydrogen impurities for practical semiconductor devices.

In this study, we developed a highly hydrogen-sensitive thermal desorption spectroscopy (HHS-TDS) system to detect and quantitatively analyze low hydrogen concentrations in thin films [REF]. The system was connected to an in situ sample-transfer chamber system, manipulators, and an r.f magnetron sputtering chamber under an UHV atmosphere of ~10^-8 Pa. The following key requirements were proposed in developing the HHS-TDS: (i) a low hydrogen residual partial pressure, (ii) a low hydrogen exhaust velocity, and (iii) minimization of hydrogen thermal desorption except from the bulk region of the thin films. To satisfy these requirements, appropriate materials and components were selected, and the system was constructed to extract the maximum performance from each component. Consequently, ~2000 times higher sensitivity to hydrogen than that of a commercially available UHV-TDS system was achieved. Quantitative analysis of an amorphous oxide semiconductor InGaZnO4 (IGZO) thin film (hydrogen concentration of 4.5 x 10^17 atoms/cm^2), which is the minimum concentration among previously reported (IGZO) was demonstrated using the HHS-TDS system. This concentration level cannot be detected using UHV-TDS or secondary ion mass spectroscopy (SIMS) systems. The hydrogen detection limit of the HHS-TDS system was estimated to be ~1 x 10^8 atoms/cm^2, which implies ~2 orders of magnitude higher sensitivity than that of SIMS (~10^9 atoms/cm^2). This detection limit is the most sensitive among various conventional analysis techniques, to our knowledge, in the case of thin-film samples.

We will also discuss role of hydrogen in oxide semiconductors such as IGZO, which are practically applied to channel layers of thin-film transistors in electronic display devices such as organic light-emitting diode displays and smartphones.


CM01.03.32

Role of Surface Oxidation in the Dehydrogenation of Complex Metal Hydrides

James L. White1, Andrew J. Bowberg1, Liwen Wan1, ShinYoung Kang2, Tadashi Ogitsu3, Robert D. Kolasinski1, Josh A. Whiteley1, Timothy C. Wang1, A. A. Baker2, Jonathan R. Lee1, Y-Sheng Liu1, Lena Trotchoud1, Jinghua Guo1, Vitalie Stavila1, David Prendergast4, Hendrik Bluhm4, Mark Allendorf4, Brandon Wood4 and Farid El Gabaly1; 1Sandia National Labs, Livermore, California, United States; 2Lawrence Livermore National Laboratory, Livermore, California, United States; 3University of California, Santa Barbara, Santa Barbara, California, United States; 4Dept of Materials, Imperial College London, London, United Kingdom.

Complex metal hydrides have high hydrogen storage capacities and the potential to be employed in hydrogen fuel cell vehicles. However, many of these materials remain limited by slow kinetics in their cycling reactions between hydrogenated and dehydrogenated states. In addition, mechanisms for hydrogen formation at the surface have been postulated for several hydrides but not directly investigated during desorption. Using both operational and ex situ measurements, on several length scales, combined with ab initio simulations, we show an unambiguous view of the surface chemistry evolution in dehydrogenating NaAlH4 and Mg(BH4)2. Shifts in speciation are observed in real time during desorption using ambient pressure X-ray photoelectron spectroscopy and low-energy ion scattering, and detailed computational models provide atomistic descriptions and energetics of the observed surface processes. While adventitious oxidized species on the surface are often assumed to be inert or inhibitory for metal hydrides, we show that, instead, they participate in the release of hydrogen, in some cases with lower computed barriers than pristine, unoxidized surfaces. Hydrogen enrichment near the surface indicates that dehydrogenation in NaAlH4 is limited by surface processes, which have the potential to be improved through optimization of the extent surface processes described here.

CM01.03.33

Galore—Simulation of Photoelectron Spectra

Adam J. Jackson1, 2, Alex M. Ganose1, 2, 3, Anna Regoutz4 and David O. Scanlon1, 2, 3; 1Dept of Chemistry, University College London, London, United Kingdom; 2Thomas Young Centre, University College London, London, United Kingdom; 3Diamond Light Source Ltd, Didcot, United Kingdom; 4Dept of Materials, Imperial College London, London, United Kingdom.

Photoelectron spectroscopy (PES) is a powerful tool for the characterisation of materials by probing their electronic structure; indeed, experiments with x-ray sources in the early part of the 20th century contributed to the modern understanding of electronic structure [1, 2]. In the later part of the 20th century, computational methods become available for ab initio predictions and analysis of electronic band structure. With the widespread use of density-functional theory, it is now a routine procedure to compute an accurate density of states (DOS) for a hypothetical structure. The occupied energy levels in the DOS should map directly to the first-order transition energies observed in photoelectron spectroscopy, providing insight into valence band phenomena.[3,4]

However, additional processing is required to form a realistic simulated spectrum. There are several mechanisms causing broadening, typically modelled with Gaussian and Lorentzian functions.[5,6] In addition, relative peak intensities generally match the DOS poorly until corrected. The Gelius model assumes that the contributions of bands will be dominated by their behaviour close to atom centers.[7] This allows free-atom photoionization data to be used with a DOS which is decomposed into atomic contributions (e.g. [3]). Although the data for this process is widely available, the analysis is not performed routinely, partly because it is tedious. We have automated this process and present an open-source package to assist the community in the implementation of this analysis.[8] Free-atom data has been parametrised to enable the selection of optimal HAXPES energies and exploration of the system sensitivity before expensive synchrotron measurements are performed.

1. Rutherford, E. (1914) Phil. Mag. S. 6. 28 (165) 305-319
Influence of Surface Chemistry on the Electrocatalytic Activity of Oxygen Electrodes for Solid Oxide Fuel Cells

CM01.03.34
Synthesis, Structural and Magnetotransport Properties of Antiferromagnet-BiFeO₃: Epitaxial Thin Films Obtained by Polymer Assisted Deposition

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Bismuth ferrite (BiFeO₃, BFO) has been widely studied for its unique magnetoelectric properties at room temperature, such as antiferromagnetism coupled with ferroelectricity. It has been also shown to display various novel phenomena, e.g., an increased conductivity at specific ferroelectric domain walls, photovoltaic properties, and new structural phases in thin films. Understanding microstructure and phase evolution in multiferric BFO thin films is an important issue, because interesting physical properties with practical applications are related to the microstructure and 2D nanostructures. This microstructure is also related with the synthesis/fabrication of the thin film. In this study, we address the polymer assisted deposition synthesis (PAD), a chemical technique of deposition with high control of thickness, stoichiometry and epitaxial crystallinity. This method allows to produce a high quality epitaxial thin films of BiFeO₃ on SrTiO₃. We present a detailed investigation on the atomic structure, morphology and microstructure of BFO/STO thin films based on studied by various transmission and scanning transmission electron microscopy techniques (in particular, with a probe Cs -corrector for atomic resolution in the latter case). Correlation with magneto-transport and thermal properties of the epitaxial films are also addressed.

CM01.03.35
Influence of Surface Chemistry on the Electrocatalytic Activity of Oxygen Electrodes for Solid Oxide Fuel Cells

Clement Nicollet, Dmitri Kalaev, Chang Sub Kim, Defferriere and Harry L. Tuller; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Solid oxide fuel cells (SOFCs) offer direct conversion of hydrogen or hydrocarbon fuels to electricity with high energy conversion efficiency (>50%). In reverse electrolysis operation, powered by wind or solar generated electricity, the same devices produce H₂ for later consumption, thus serving as a valuable means of energy storage. The electrode polarization related to electrochemical reactions at the gas/solid interface of the cathode is often the dominant flux limiting mechanism. Accumulating surface impurities (e.g. Si, Na, Al, Cr, and Sr) leads to reduction of long term durability. Identifying means for overcoming the detrimental impact of surface impurity accumulation on oxygen surface exchange kinetics can be expected to result in high payoffs in both improved performance and extended operating life. Pr-doped ceria (PCO), a mixed ionic and electronic conductor with a high electrocatalytic activity toward the oxygen reduction reaction, has a strong advantage over state-of-the-art materials such as La₀.₆SrₓCa₀.₄O₃₋δ and La₀.₆SrₓCa₀.₄Fe₀.₃O₃₋δ by not containing strontium, known to readily segregate to the solid gas interface, thereby limiting catalytic activity. Silicon contamination, however, remains a problem even with Sr-free materials, given external sources such as glass sealants, or as an impurity in precursor materials used to fabricate the devices. This work focuses on Si contamination of PCO cathodes, observed to reduce electrode kinetics by as much as several orders of magnitude. By controlling the levels of Si contaminant applied to PCO thin films by wet chemical methods, it becomes possible to systematically study its impact on the oxygen reduction reaction by an in-situ optical transmission relaxation method. We also further investigate the feasibility of using lanthanum as an efficient Si getter [1], and extend this strategy to study the effect of various single valence oxides on the oxygen surface exchange rates of PCO.

CM01.03.36
Probing Luminescence in Undoped and Eu³⁺ Doped La₂Zr₂O₇ Nanocrystals—An Effort to Differentiate Its Optical Properties from La₂Hf₂O₇

Yuanbing Mao 1, Santosh Gupta 1, Jose Zuniga 1, Maya Abdou 1 and Partha Ghosh 2; 1The University of Texas at Rio Grande Valley, Edinburg, Texas, United States; 2Bhabha Atomic Research Centre, Trombay, India.

Probing the origin of multicolor emission in La₂Zr₂O₇ nanoparticles (NPs) is crucial for their applications as tunable phosphors and assessing the effects of doping, varying particle size and other factors on its optical properties. In this work, the effect of doping has been explored by making size tunable La₂Zr₂O₇:Eu³⁺ (LZO) NPs by varying the concentration of precipitating agent in molten salt synthesis. The effect of such changes has been explored on structure, surface area, photoluminescence, radioluminescence, lifetime and quantum yield of LZO NPs. Furthermore, the effect of changing B site ions by replacing Zr⁴⁺ with Hf⁴⁺ on optical properties of undoped NPs and europium ion doped NPs is investigated to find suitable pyrochlore host for phosphor and scintillator applications. Photoluminescence spectroscopy on undoped La₂Zr₂O₇ (LZO) and La₂Hf₂O₇ (LHO) NPs shows violet-blue emission from the LHO NPs whereas the LZO NPs display both violet-blue and red emission upon UV irradiation. Such differences has been explained based on density functional theory (DFT) calculated density of state (DOS), which presented different energetics of ionized oxygen vacancies in LHO and LZO. The differences in luminescence spectroscopy on undoped LZO and La₂Hf₂O₇:Eu³⁺ (LHOE) NPs highlighted higher quantum yield, emission output, photoluminescent intensity and luminescence lifetime from the LHOE NPs which could be highly beneficial in newer pyrochlore materials for red phosphors, scintillators and fluorimmunoasays.
a structural phase transition in oxyhydrides [2]. The presence of chalcogenides anions (e.g., Se\(^{2-}\)) with greater compressibility than oxide anions leads to extensive control of metal-oxide distance, leading to unusual spin state [3].


8:30 AM CM01.04.02
Learning Solid State Chemistry from Atomic Fluctuations—A Statistical Physics and Machine Learning Approach
Rama K. Vasudevan, Lukas Vlcek and Sergei V. Kalinin; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

A key aspect of statistical physics is that the fluctuations of a system encode information about the response of the system to changing thermodynamic variables. However in most studies, structural and chemical fluctuations in materials characterization are seen as a hindrance, that complicates analysis. Here, we present a method to take advantage of atomic-scale fluctuations of chemical and structural fluctuations and use them to build a generative model that can be used to predict the phase diagram of the system in a finite temperature and composition space. We show the example for understanding cationic segregation in a manganese thin film (La\(_3\)SxCas\(_3\)MnO\(_{3-x}\)) where a combination of in-situ atomic imaging via scanning tunneling microscopy as well as bulk measurements of composition as a function of layer (via angle-resolved x-ray photoemission spectroscopy) enables constraining the generative model.

Through use of a recently developed statistical distance framework, the fluctuations in the system are inherently captured (as opposed to averaged out). The model leads to the prediction of weak segregation forces in bulk (attributable to elastic effects) and weak de-segregation forces in the surface (attributable to electrostatic interactions), which agree with recent quantum-chemical calculations (J. Am. Chem. Soc. 135, 7909 (2013)), but which are derived entirely from experiment. We further extend this approach to mapping atomic dynamics observed with scanning transmission electron microscope, providing insight into solid state chemistry on a single-defect level. This approach can be applied to a large array of systems, wherein the observed fluctuations can be exploited to understand the interactions between the constituent components of the system.

The work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division (R. K. V., S. V. K., L. V.). Research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

8:45 AM CM01.04.03
A Structural Characterization Challenge Using Atomic Pair Distribution Function Based on Electron Diffraction
Elson R. Leite\(^1\), Jefferson Bettini\(^2\) and Gustavo Azevedo\(^3\); \(^1\)Physics Department, Federal University of Amazonas (UFAM), Manaus, Brazil; \(^2\)LNNano-CNPEM, Campinas, Brazil; \(^3\)Chemistry Department, Federal University of São Carlos, São Carlos, Brazil; 4LNLS-CNPEM, Campinas, Brazil.

In this work, we intend to investigate the extent of information about the size-dependent structure of nanoparticles from the atomic pair distribution function (PDF) method. However, we intend to use the PDF method in an innovative way. Instead of using x-ray and neutron powder diffraction data, we will use electron diffraction data acquired from a conventional transmission electron microscope (TEM), that we will call PDFe. We will show results regarding the characterization of reference materials (amorphous Carbon and gold nanoparticle) in order to establish a protocol of characterization and to confront the results obtained by electron diffraction with results (from the literature) obtained by other scattering techniques. Another important point of our work is to use the PDFe to characterize nanoparticles, more specifically, we performed the accurate determination of atomic-scale structure and structural defects of Zinc Oxide (ZnO) nanoparticles synthesized by different sol-gel routes, considering the tetragonal and monoclinic phases. The advantages and disadvantages of using electron diffraction (using a transmission electron microscope) will also be presented to obtain the PDF.

9:00 AM CM01.04.04
Expanding the Toolset for Colloidal Synthesis and Integration of Functional Inorganic Nanomaterials
Dimitri V. Talapin; Department of Chemistry and James Franck Institute, University of Chicago, Chicago, Illinois, United States.

The synthesis of inorganic nanomaterials has seen impressive developments, both in the fundamental understanding of nucleation, growth and surface chemistry of inorganic phases, and in the ability to prepare functional materials with precisely engineered optical and electronic properties. However, the lack of atomic precision in nanomaterial synthesis restricts our ability to harness all the power of this broad and diverse class of matter. Heterogeneity introduces broadening of the absorption and emission spectra, reduces charge carrier mobility in nanocrystal solids, and generally restricts our ability to engineer nanomaterials. I will discuss new approaches for colloidal synthesis of nanomaterials with minimal, ideally no, size distribution. The concept is inspired by gas-phase atomic layer deposition (ALD) widely used in microelectronics. Our studies show that the ALD concept can be successfully implemented in solution and, when applied to nanomaterials, enables layer-by-layer growth of crystalline lattices with close-to-atomic precision. I will also discuss recent advances in the surface chemistry of semiconductor nanostructures. Molecular inorganic species can be designed to electronically couple individual nanostructures into nanocomposite materials with high electron mobility. By making surface ligands photochemically active, we introduce a general approach for photoresist-free, direct optical lithography of functional inorganic nanomaterials (DOLFIN). Examples of patterned materials include metals, semiconductors, oxides, and magnetic and rare earth compositions. No organic impurities are present in the patterned layers, which helps achieve good electronic and optical properties. The ability to directly pattern all-inorganic layers using a light exposure dose comparable to that of organic photoresists opens up a host of new opportunities for additive nanomanufacturing.

9:30 AM BREAK

10:00 AM CM01.04.05
Structures, Magnetism and Soft Chemistry of Layered Oxide Chalcogenides and Oxide Pnictides
Simon Clarke; University of Oxford, Oxford, United Kingdom.

Oxide chalcogenides and oxide pnictides have become of increasing interest following the discovery of the iron-based pnictide and chalcogenide superconductors. In this presentation we will discuss the synthesis (using high-temperature and soft techniques), crystal structures and physical properties of a series of layered oxide arsenides and oxide chalcogenides will be described and the changes in magnetic ordering and other physical properties will be described as functions of temperature and composition, and related to changes in crystal structure. Examples will include the complex magnetic ordering in Sr\(_2\)Fe\(_3\)Se\(_2\)O\(_3\), the changes in magnetic structure of A\(_2\)Cr-O\(_2\)Cr\(_2\)As\(_2\) (A = Sr, Ba) as a function of layer (via angle-resolved x-ray photoemission spectroscopy) enables constraining the generative model and the changes in magnetic structure in the series Sr\(_{2-x}\)Co\(_{2}\)O\(_2\)Cu\(_2\)As\(_2\)S\(_2\). We will show results regarding the characterization of reference materials (amorphous Carbon and gold nanoparticle) in order to establish a protocol of characterization and to confront the results obtained by electron diffraction with results (from the literature) obtained by other scattering techniques. Another important point of our work is to use the PDFe to characterize nanoparticles, more specifically, we performed the accurate determination of atomic-scale structure and structural defects of Zinc Oxide (ZnO) nanoparticles synthesized by different sol-gel routes, considering the tetragonal and monoclinic phases. The advantages and disadvantages of using electron diffraction (using a transmission electron microscope) will also be presented to obtain the PDF.

10:30 AM CM01.04.06
A Soft Chemistry Route to Control the Oxidation States of Dopants in Inorganic Phosphors
Romain Gautier; Centre National de la Recherche...
A series of new ternary graphite intercalation compounds (GICs) containing alkaline earth metal cations (M=Mg, Ca, Sr, Ba) and ethylenediamine (en) are reported. These GICs are deep blue to green in color and can be prepared as phase pure compounds by the direct reaction of graphite powder and the metal in liquid ethylene at mild temperatures (25-100 °C) under an inert atmosphere. X-ray diffraction and thermal analyses were employed to determine the structural and composition. [Mg(en)]_x[LiH]_y[O_3]_z (0 ≤ x ≤ 1, 0 ≤ y ≤ 1) oxyhydrate materials. However, little is known about the H^− diffusion mechanism in this new material and its unique structure. The origin of such exceptional H^− conduction in the oxide-based materials is of great interest. Using first-principles calculations, we studied the energetics and diffusion mechanisms of H^− ions as a function of structures and compositions in this oxyhydrate system. Our study identified that fast H^− diffusion is mediated by H^− vacancies and that the fast two-dimensional or three-dimensional H^− diffusion is activated by different anion sublattices in different compositions. In addition, novel doping was predicted from ab initio computations to increase H^− conductivity in these materials. The unique two-anion-site feature in this structural framework enables highly tunable lattice and minimizes the blocking of anion diffusion by oxygen sublattice, allowing high mobile-carrier concentration and good diffusion network. This conclusion offers general guidance for future design and discovery of novel oxide-based anion conductors. This study has been published in ACS Applied Energy Materials.[1]


Photoluminescence properties are important for different applications such as solid-state lighting, sensors, and display devices. Among the materials exhibiting such properties, doped phosphors are of particular interest owing to their high thermal stability and potentially high quantum efficiency. Interestingly, the photoemission of such doped materials differs according to the multistate states of the dopants. The reduction under controlled atmosphere or the co-doping with other cations enable to target dopants in specific oxidation states but this control is usually poor.

In this context, we carry out a soft chemistry route to reduce the dopants of inorganic phosphors by heating the solid-state compounds at low temperature with oxygen getters in glass tubes sealed under vacuum. This soft reduction enables to control the ratio Ni^{3+}/Ni^{2+} in SrTiO_{3}:Ni and Eu^{3+}/Eu^{2+} in SrAl_{2}O_{4}:Eu or (CaMg)(NaSc)_{1-x}Si_{2}O_{6}:Eu [1-3]. The optical properties could also be tuned according to these ratio. The control of the ratio Ni^{3+}/Ni^{2+} in SrTiO_{3}:Ni allowed the tuning of IR photoluminescence vs. optical absorption which could have potential applications in biomedicine. For SrAl_{2}O_{4}:Eu or (CaMg)(NaSc)_{1-x}Si_{2}O_{6}:Eu, the photoemission corresponding to the 4F-4I transition of Eu^{3+} dopant vs. the photoemission corresponding to the 4F-5d transition of Eu^{2+} dopant can be tuned to control the photoluminescence color of these compounds. In the specific case of (CaMg)(NaSc)_{1-x}Si_{2}O_{6}:Eu, the additional modification of the solid-solution composition enables to design a white phosphor for potential applications in solid-state lighting.


Preparation and Characterization of Graphite Ternary Intercalation Compounds Containing Alkaline Earth Metal Cations and Ethylenediamine Wei Xu and Michael Lerner; Department of Chemistry, Oregon State University, Corvallis, Oregon, United States.

A series of new ternary graphite intercalation compounds (GICs) containing alkaline earth metal cations (M=Mg, Ca, Sr, Ba) and ethylenediamine (en) are reported. These GICs are deep blue to green in color and can be prepared as phase pure compounds by the direct reaction of graphite powder and the metal in liquid ethylene at mild temperatures (25-100 °C) under an inert atmosphere. X-ray diffraction and thermal analyses were employed to determine the structural and composition. [Mg(en)]_x[LiH]_y[O_3]_z (0 ≤ x ≤ 1, 0 ≤ y ≤ 1) oxyhydrate materials. However, little is known about the H^− diffusion mechanism in this new material and its unique structure. The origin of such exceptional H^− conduction in the oxide-based materials is of great interest. Using first-principles calculations, we studied the energetics and diffusion mechanisms of H^− ions as a function of structures and compositions in this oxyhydrate system. Our study identified that fast H^− diffusion is mediated by H^− vacancies and that the fast two-dimensional or three-dimensional H^− diffusion is activated by different anion sublattices in different compositions. In addition, novel doping was predicted from ab initio computations to increase H^− conductivity in these materials. The unique two-anion-site feature in this structural framework enables highly tunable lattice and minimizes the blocking of anion diffusion by oxygen sublattice, allowing high mobile-carrier concentration and good diffusion network. This conclusion offers general guidance for future design and discovery of novel oxide-based anion conductors. This study has been published in ACS Applied Energy Materials.[1]


Materials Science and Application of Inorganic Electrides Hideo Hosono; Tokyo Institute of Technology, Yokohama, Japan.

Electrides are rare ionic compounds in which an electron does not occupy an atomic orbital but rather acts as an anion. This electron is expected to behave differently to those occupying the valence state of standard materials, making electrides desirable as electron emitters,[1] nonlinear optical switches,[2] superconductors,[3] battery anodes,[4] and catalysts for applications ranging from compound synthesis to CO2 splitting.[5]

We use high-throughput screening and advanced calculations to identify undiscovered electrides among all known inorganic materials. Our method recovers the more than 60 previously unknown electrides along with 4 already known, significantly expanding this class of industry-relevant materials. We use high-throughput screening and advanced calculations to identify undiscovered electrides among all known materials. Our method recovers the more than 60 previously unknown electrides along with 4 already known, significantly expanding this class of industry-relevant materials.


11:30 AM *CM01.04.10
Materials Science and Application of Inorganic Electrides Hideo Hosono; Tokyo Institute of Technology, Yokohama, Japan.

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We use high-throughput screening and advanced calculations to identify undiscovered electrides among all known materials. Our method recovers the more than 60 previously unknown electrides along with 4 already known, significantly expanding this class of industry-relevant materials.


11:30 AM *CM01.04.10
Materials Science and Application of Inorganic Electrides Hideo Hosono; Tokyo Institute of Technology, Yokohama, Japan.
We have examined to apply C12A7:e- to electronic devices (Adv. Mat. 2004, JPCC 2007), and chemistry such reducing regent (Org Lett 2007) usable in aqueous media. The representative examples are: Ru-loaded C12A7:e- works an effective catalyst for ammonia synthesis at mild conditions (Nat. Chem. 2012) and is free from hydrogen poisoning which is known as a common drawback of Ru-catalysts (Nat. Comm. 2015). Amorphous C12A7:e- thin film with low work function and high optical transparency is promising as an electron injection layer, an obstacle, in organic light emitting diodes (PNAS 2017). C12A7:e- may be regarded as Oh-electrode viewed from dimensionality of anionic electrons. The concept of electrode was extended to 1D and 2D materials. CaN was confirmed to be the first 2D electrode in 2013 (Nature 2013). Subsequently, we screened material candidates for 2D electrodes by computation (PRX 2014, Inorg. Chem. 2014) and experimentally demonstrated 2D electronic nature for Y2C (Chem. Mat. 2014, PRB 2017) and Tb3C (Phys. D 2016). For 1D electrodes, Substitution of O in the channel with hydride ion and subsequent photo-ionization of H realized apatites:e- (JPCL 2015, PCCP 2016). Several 1D/2D electrode materials such as Y3Si (JACS 2016) and LaScSi (Adv. Mat. 2017) were found by extending the system to intermetallics. Sr3P2 is a 0D electrode material with Mott insulating nature (JACS 2017) and is a new phase predicted to exist by computation and verified by experiment.

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1:30 PM *CM01.05.01
Multiple Bonding in Intermetallic Compounds Yuri Grin; Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany.


2:00 PM CM01.05.02
Exploring New Inorganic Clathrates for Thermoelectric Application Jian Wang1, 2 and Kirill Kovnir1, 2; 1Iowa State University, Ames, Iowa, United States; 2 Ames Lab, Ames, Iowa, United States.

Recent years have witnessed growing in the research of thermoelectric materials, which are capable to directly convert waste heat into electrical power and vice versa. Thermoelectric materials exhibit high potential in improving our society energy efficiency. Achieving high performance thermoelectric materials is proved to be a challenging question due to the intrinsic correlation between electrical and thermal properties in solids. Clathrate compounds are good candidate for thermoelectric applications, with intrinsically low thermal conductivity. Thus, the research efforts can be mainly focused on tuning charge transport properties of clathrate. The origin of intrinsic low thermal conductivity is mainly from the “rattling” behavior of guest atoms in large oversized cages. Applying solid state chemistry to discover new inorganic clathrates is of scientific and practical importance. New pnictide-based (P, As, Sb) clathrates were discovered by solid state reactions. The vertical Bridgman method was also applied to grow single crystals of new clathrate for investigating the intrinsic physical properties. The crystal structure and thermoelectric properties of new discovered clathrate will be discussed.

2:15 PM CM01.05.03
Drastic Changes of Physical Properties Through H and C Insertion into CeSeSi-Type Phases Frédéric Gauvin, Tadhg Mahon, Bernard Chevalier and Sophie Tence; ICMCB, CNRS, Université de Bordeaux, Pessac, France.

Only a few intermetallics crystallize with the tetragonal CeSeSi-type structure which has strong relationship with the CeFeSi-type. In both structural types, layers of empty [Ce4] tetrahedra are observed. In the case of the CeFeSi-type structure, the [Ce4] tetrahedra can be fully filled by hydrogen. This induces a very interesting modulation of the physical properties [1]. It is worth pointing out that these new hydrides RETX (RE = rare-earth, T = transition metal, X = Si or Ge) adopt the ZrCuSiAS-type structure which is also observed for LaFePO [2], the first member of the new family of iron-based superconductors. Very recently the new superconductor LaFeSiH (Tc = 11 K) has been discovered in our group after hydrogen insertion in the pristine phase LaFeSi with CeFeSi-type structure [3].

This work is devoted to the study of the insertion of hydrogen or carbon into the series of intermetallics RETX (RE = rare-earth, T = Sc or Ti, X = Si or Ge) crystallizing with the CeSeSi-type structure (an ordered variant of the La5Sb-type [RE5] tetrahedral and [T,RE] octahedral sites are available for the insertion of light element. According to the nature of the rare-earth and of the light element (i.e. H or C) different composition can be achieved. The
examples of GdScGeH₁₀, REScSiHₓ and REScSiCₓₓ (RE = Ce, Nd) will be presented. The insertion of the light elements induces a strong modulation of the magnetic properties of the pristine compound. For instance, we evidenced that hydrogenation strongly reduces the Curie temperature of NdScSi from Tᵥ = 175 K to Tᵥ = 4 K in NdScSiH₁₀, the H (or D) atoms being located in both interstitial sites[4]. A significant change in the transport properties can be also induced. In the case of GdScGe, for instance, a transition from metallic to non-metallic behavior is observed[5]. Density functional theory (DFT) calculations were performed using the PAW method as implemented in the VASP code with GGA+U or HSE06 approach. It appears that GdScGe is a half-metal ferromagnet, with 3D electron conduction, whereas GdScGeH is a semiconductor or poor metal with, at Fermi level, low DOS and 2D electron density distribution. The latter indicates possible low-dimensional electron conduction. In the case of NdScSi and CeScSi phases it has also been possible to insert, in two different sites, both C and H as interstitial atoms leading to interesting variation of the magnetic properties. Neutron diffraction experiments have been performed to determine the magnetic structures of these new insertion compounds.


2:30 PM BREAK

3:00 PM CM01.05.04
Harnessing Chemical Frustration Toward the Creation of Modular Intermetallic Phases
Daniel Fredrickson; Univ of Wisconsin-Madison, Madison, Wisconsin, United States.

The intermetallic phases offer immense opportunities for the creation of new materials, with their crystal structures ranging from simple packings to complex arrangements that lead one to invoke cells containing thousands of atoms or higher-dimensional axes. However, navigating this structural diversity is made challenging by the need for predictive principles relating composition, structure, and properties. In this presentation, we will derive lessons from some of the most complicated intermetallic structures toward the development of one such principle: chemical frustration. A common theme that can be perceived in complex intermetallics structures is microscopic segregation between competing interactions. Using the results of theoretical calculations, we will develop mechanisms that will be derived by which competition between segregation and attraction between incompatible structural motifs can emerge in these phases. For example, in the epitaxial stabilization mechanism, structures with strains of opposite signs in the interactions between the majority elements have to opportunity for the cancellation of these strains at interfaces between them. Similarly, in the electron-hole pairing scheme the potential for electron transfer across interfaces is viewed means of stabilizing multi-domain character. Based on these mechanisms, the chemical pressure schemes and non-optimal electron counts of simple but geometrically distinct compounds are used as measures of their potential reactivity toward intergrowth. New crystal structures that have been encountered in our synthetic attempts to induce frustration in intermetallic systems following these and other approaches will also be presented and analyzed.

3:30 PM CM01.05.05
Synthesis, Structure and Properties of New Inorganic Clathrates
Kaya Wei² and George Nolas¹; ¹Univ of South Florida, Tampa, Florida, United States; ²National High Magnetic Field Laboratory, Tallahassee, Florida, United States.

The chemistry and physics of the group 14 elements such as silicon and germanium have been extensively studied, largely due to their fundamental importance in the development of semiconductor electronics. In addition to their ground state configurations, these elements can crystallize in metastable expanded frameworks of elemental, binary, ternary and quaternary compositions, known collectively as clathrates. The common structural feature of all clathrate materials is an open-structured host framework that has the ability to encage guest atoms or molecules. We will report on the synthesis and crystal growth of new single-crystal compositions with frameworks comprised of tin, and others comprised of arsenic, that exhibit unique physical properties. We employ conventional, synchrotron and inelastic neutron single-crystal X-ray diffraction techniques in investigating their structural features, as well as electrical resistivity, thermopower, thermal conductivity and heat capacity measurements. In addition, first principles calculations of the electrical properties, including Fermi surface, electron localization and charge transfer, will be discussed, thus enabling an in-depth understanding of the fundamental properties of these new materials.

3:45 PM CM01.05.06
FeSi as New Conductive Layer for Fe-Based Superconductors
Sophie Tence² and Andres Cano¹; ¹Institut Néel, Grenoble, France; ²Institut de Chimie de la Matière Condensée de Bordeaux, Bordeaux, France.

Since the discovery of unconventional superconductivity in Fe-based materials in 2008³, Fe-based superconductors (Fe-SC) have attracted much attention and have been the subject of intense and systematic investigations. To date, in high-Tc, Fe-SC, iron is invariably associated to toxic pnictogen or chalcogen elements (P, As and S, Se, Te respectively) in the conductive layer. This circumstance raises the important fundamental question about the link between Fe-based superconductivity and the apparent need of these pnictogens and chalcogens. Besides, Fe-SC are usually obtained by solid state reaction with elements (P, As and S, Se, Te respectively) in the conductive layer. This circumstance raises the important fundamental question about the link between Fe-based superconductivity and the apparent need of these pnictogens and chalcogens. Besides, Fe-SC are usually obtained by solid state reaction with possibly the use of high pressure.

In this context, we have recently synthesized the new silicide hydride LaFeSiH by solid-gas hydrogenation of the precursor LaFeSi. Preliminary results show that this hydride is isostuctural to the 1111 Fe-SC compounds (s.g. PmPm). Interestingly, LaFeSiH displays onset of superconductivity at 11 K as evidenced notably on the resistivity measurement on single-crystal⁴. This hydride also presents other structural, magnetic and electronic similarities with the previously reported Fe-SC compounds, similarities that will be presented in this talk. Therefore, LaFeSiH can be considered as the first Fe-SC obtained by solid-gas hydrogenation and free from toxic pnictogen and chalcogen elements. This is the first member of a new class of materials with which we have surpassed traditional pnictide and chalcogenide compounds and promoted, for the first time, original Fe-based silicides to unconventional high-temperature superconductors.

3:45 PM CM01.05.06
Exploiting Controlled Nanoarchitecture to Study Structure-Property Relationships in [(SnSe)₅]₀.₅[TiSe₂]ₓ Thin-Film Heterostructures
Danielle M. Hamann¹, Sage Bauers¹ and David C. Johnson¹; ¹Chemistry, University of Oregon, Eugene, Oregon, United States; ²National Renewable Energy Laboratory, Golden, Colorado, United States.
Recent research on monolayers and their heterostructures has led to the discovery of numerous emergent properties. These can be markedly different from those of the respective bulk materials and are not always additive, making the properties of heterostructures difficult to predict. Self-assembly of designed precursors with composition profiles that mimic the desired product allows for the synthesis of superlattice heterostructures with controllable stacking sequences between the layers, or “nanoarchitecture”. Using this unique control, homologous series of compounds are prepared where the layer thickness of a single constituent is changed with unit-cell precision, allowing the study of properties as a function of material thickness or stacking order. One family of compounds with properties dependent on nanoarchitecture is \([\text{SnSe})_{1+\delta}\] \([\text{TiSe}_2]\), where \(n\) and \(\delta\) can be individually varied. These compounds exhibit thickness-dependent structural distortions, degree of interlayer templating, and transport properties. Interestingly, distortions in the SnSe constituent are a result of a surface area to volume competition and are influenced by interfaces with TiSe2. When single layers of TiSe2 and SnSe are interleave there is an accidental lattice match between constituents that results in regions of alignment in an otherwise rotationally disorder system. Coupled with the structural distortions are changes in resistivity, Hall, and Seebeck coefficients. Measurements suggest competition between n-type TiSe2 and p-type SnSe, with the specific properties dependent both on the constituent ratios as well as their dimensionality. The ability to study the properties in these heterostructures is a result of precise layer control through synthesis of systematically varied compounds. Using this technique to gain advanced knowledge about the source of emergent properties in heterostructures will facilitate future “materials by design” approaches to target and optimize a desired property for a specific application.

4:15 PM CM01.05.08
From Quasicrystals to Crystals and Superconductors in Ca/Y–Au–Al
Joyce Pham1, 2, Walter Schnelle1, Gadran Auffermann1, Claudia Felser1 and Gordon J. Miller2, 3; 1Max-Planck Institute for Chemical Physics of Solids, Dresden, Germany; 2Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa, United States; 3U.S. Department of Energy, Ames Laboratory, Ames, Iowa, United States.

In the Au-rich region of the Ca–Au–Al system, an icosahedral quasicrystal (i-QC) CaAu3SnAl1.27 was discovered and shown to irreversibly transform into the cubic 2/1 crystalline approximant (CA) Ca3(SnSe)7.96A12.04 (space group (no. 205); Pearson symbol: cP172; \(a = 23.8918(2)\) \(\text{Å}\) via \(n\)-Stills, high-energy, variable-temperature powder X-ray diffraction, thereby providing direct experimental evidence for the relationship between QCs and their associated CAs. The 2/1 CA crystalizes in a Tsai-type structure and, following the polar intermetallic depiction, the atoms of different electronegativities, viz., electronegative Au+Al+ and formally electropositive Ca, are arranged in concentric shells. As part of an overarching chemical pressure and valence electron count investigation, the cubic 1/1 CA Y3Au16(0.62)Al4(0.38) (space group (no. 204); Pearson symbol: cP192; \(a = 14.662(2)\) \(\text{Å}\)) was discovered and shown to also crystalize in the Tsai-type, and in which preliminary magnetization data show potential surface superconductivity behavior below \(T_c\) around 3.7 K. The QC-CA transformation, crystallographic structure, and atomic site preference analysis of Ca–Au–Al along with the crystal and electronic structures, chemical analysis, and preliminary transport properties, including resistivity and specific heat, of the 1/1 CA Y3Au16(0.62)Al4(0.38) will be presented for discussion.

4:30 PM *CM01.05.09
Complex Intermetallic Alloys Anja V. Mudring: Stockholm University, Ames, Iowa, United States.

The design of new materials with desired chemical and physical characteristics requires thorough understanding of the underlying composition–structure–property relationships and the experimental possibility of their modification through the controlled involvement of new components. From this point of view intermetallic phases, a class of compounds formed by two or more metals, present an endless field of combinations that produce several chemical compound classes ranging from simple alloys to true ionic compounds. Polar intermetallics (PICs) belong to the class that is electronically situated in the middle, between Hume-Rothery phases and Zintl compounds and possessing an \(n/e\) (valence electron per atom) values around two. In contrast to the latter, where logical rules of formation and classification systems have been developed decades ago, polar intermetallics remain a dark horse with a huge diversity of crystal structures, but unclear mechanisms of their formation. Partial incorporation of structural and bonding features from both nonpolar and Zintl compounds is commonly observed here. A decent number of PICs can be described in terms of complex metallic alloys (CMAs) following the Hume-Rothery electron counting schemes, but, exhibit electronic structure changes that cannot be explained by the latter. For that reason, research efforts are aiming at the discovery and synthesis of new polar intermetallic compounds, their structural characterization and properties’ investigation in line with the analysis of the principles connecting all these components. Understanding of the basic structural tendencies is one of the most anticipated outcomes of this analysis and systematization of the available knowledge is the initial and the most important step. The occurrence of different structure types for PICs ranging from commonly encountered AlB12 or BaAl14 types in line with the recently discovered diamond-like homoatomic metal networks, formation of local five-fold symmetry, different types of tunneled structures and more complex intergrown multicomponent structures will be discussed.

SESSION CM01.06: Poster Session II: Solid-State Chemistry of Inorganic Materials
Session Chairs: Ashila Huq and Corey Thompson
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

CM01.06.01
Novel Heteroleptic Tin Precursors for Atomic Layer Deposition of Tin Oxide Thin Films Applications Seong Ho Han1, 2, Bo Keun Park1, 2, Chang Gyuon Kim3, 4, Seung Uk Son5 and Taek-Mo Chung2, 3; 1Thin Film Materials Research Center, Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); 2Department of Chemistry, Sungkyunkwan University, Suwon, Korea (the Republic of); 3Department of Chemistry, Pohang University of Science and Technology, Daejeon, Korea (the Republic of); 4Advanced Materials and Chemical Engineering, Seoul National University, Seoul, Korea (the Republic of).

Over the past decade, oxide semiconductor materials have attracted significant interest as important materials for various applications, including thin film transistors (TFTs), gas sensors, lithium batteries, and solar cells. Particularly, p-type tin(II) monoxide (SnO) has generated considerable research attention owing to its wide optical band gap energy (2.7-3.0 eV), which can translate into the possibility of completely transparent electronic devices. Moreover SnO based TFT recently showed a record hole mobility of \(-1.87\) cm²/Vs and Hall mobility of \(-6.75\) cm²/Vs and Hall mobility of \(-6.75\) cm²/Vs. The other hand, tin(V) dioxide (SnO2) which is an n-type material, with a wide band gap energy of \(-3.6\) eV and excellent optical, electrical, and chemical properties is also constantly under investigation to improve upon its properties for various applications. SnO2 is transparent under visible light and has a resistivity that can extend over a wide range depending on the deposition process and the growth conditions. Doped SnO2 films has also demonstrated good performance as transparent conducting oxides for solar cells. Generally, chemical vapor deposition (CVD) and atomic layer deposition (ALD) are the preferred growth methods for uniform and conform thin films. Moreover, SnO and SnO2 can be selectively deposited by controlling the oxidation state of the Sn(II) precursor and the oxygen source. In the case of ALD,
several attempts have been made to grow SnO or SnO2 films using different Sn precursor/reactant combinations. Unfortunately, most of the attempts have only resulted in n-type SnO films. Only few reports have shown the successful deposition of SnO films including a recent publication from our lab.  

Recently, the importance of heteroleptic precursors with improved properties have been highlighted by a number of reports. Most common precursors exist as homoleptic type in nature, where identical ligands are bonded to a metal center. In contrast, a heteroleptic precursor is a metal complex with two or more distinct ligands attached to the metal center. Reports have shown that heteroleptic precursor design through suitable ligand selection could result in several improved properties in comparison to the homoleptic precursors. Even though the selection of suitable ligands for heteroleptic metal precursors is as challenging as designing a new ligand for homoleptic precursors, the heteroleptic precursors are advantageous because of the availability of several ligands and their complexes with well-known properties to choose from.

To develop novel tin(II) precursors for thin film applications, we have synthesized new tin complexes using tin(II) chloride as starting material. The resulted complexes were characterized by various analysis equipments such as nuclear magnetic resonance (NMR), elemental analyses (EA), thermogravimetric analysis (TGA), and single crystal X-ray diffraction. The detailed applications of thin films by ALD will be shown in the presentation.

**CM01.06.02**  
**Physical and Structural Properties of High Quality LaCuOSe1-xSex Prepared by Novel Solid State Solution Method**  
**Nengduo Zhang; National University of Singapore, Singapore, Singapore.**

Transparent conducting oxides (TCOs) have been a very hot topic over the past few decades due to their great importance in electronic industries including touch screen display, organic light emitting diodes (OLED) and liquid crystal displays (LCD). However, the majority of TCOs used currently all belong to N-type TCOs. The lack of high performance P-type transparent conducting oxides (TCOs) presents a huge problem in many optoelectronic applications ranging from organic light emitting diodes (OLED) to transparent electronics. Oxysulfide based P-type TCOs are very promising due to the recent outstanding results in terms of P-type conductivity and transparency. Oxysulfide with the basic form of LnCuOCh have layered structure consisting of alternating [LnO] layers and [CuCh] layers, which allows more degrees of variation. LaCuOS with the band gap 3.10eV has lower conductivity than LaCuOSe of band gap 2.5eV. In this work, LaCuOS has been firstly prepared via our novel solid state reaction without using commonly used toxic gas H2S. The LaCuOS prepared in this shows high conductivity due to the absence of hydrogen atoms in the process. Then LaCuOSe was doped with Se via solid state reaction to prepare LaCuOSe1-xSex without any impurities. The optical properties of the polycrystalline samples were studied by UV-Vis spectroscopy, and the chemical states of the aforementioned five elements in films with varying concentration of Se were examined by using X-ray photoelectron spectroscopy (XPS). The electrical properties were measured by four point probe method. The detailed atomic structures and doping sites of the LaCuOSe1-xSex samples were analyzed by scanning transmission electron microscopy (STEM).

**CM01.06.04**  
**Brownmillerite Type SrCoO2.5 for Oxygen Enrichment—Optimization of Absorption Parameters**  
**Aswathy M. N and Arun M. Umarji; Materials Research Centre, Indian Institute of Science, Bengaluru, India.**

Ternary oxides are known for many applications like solid oxide fuel cells, catalysis and gas sensing. These oxides can be oxygen non-stoichiometric if transition metals with variable oxidation states are present. This can be regarded as a functionality when the extent of oxygen vacancies inside the lattice is very high. They can transport oxygen through the lattice if a partial pressure gradient of oxygen is applied. This is normally exploited in case of oxygen separation membranes and solid oxide fuel cells.  

Perovskite oxides (general formula ABO3) are promising candidates as they can exist in a variety of oxygen non-stoichiometric forms by varying temperatures and oxygen partial pressures. SrCoO2 (Perovskite, Pm-3m) is one such material which reversibly transforms to SrCo2O4 (Brownmillerite, Ima2) phase at 623 K.  

Here in we report the application of Brownmillerite SrCoO2.5 for oxygen enrichment. Brownmillerite (BM) SrCoO2 phase has been stabilized to date only by liquid nitrogen quenching. We report a cost-effective method of quenching for the stabilization of the BM SrCoO2. The solution combustion synthesized powder was calcined and sintered at 1223 K in pellet form. This pellet was quenched to 473 K using Al foil pads to stabilize the intact ceramic with Brownmillerite phase. A simple home-built volumetric setup has been fabricated for studying the oxygen storage property of the material. The sample was pre-treated with a higher partial pressure of oxygen at 673 K to form the oxygen-rich perovskite phase and this phase was heated at lower pressure to study the desorption characteristics. The pressure change observed when sample releases oxygen is used to find the oxygen storage capacity. The effects of partial pressure of oxygen, time and temperature of pre-treatment on oxygen storage capacity have been investigated. The results indicate that the pressure and temperature of pre-treatment has a profound effect on the oxygen holding capacity.

**References**


**CM01.05.05**  
**Evolution of Dealloyed PdBi2 Nanoparticles as Electrocatalysts with Enhanced Activity and Remarkable Durability in Hydrogen Evolution Reactions**  
**Shreya Sarkar; Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India.**

**Abstract:** The development of non-Pt based electrocatalysts for the hydrogen evolution reaction (HER) is a pre-requisite for the generation of hydrogen, a feasible and cost-effective source of hydrogen. Structural transitions and generating metal deficiency are the effective ways of manipulating the d-band centre of a metal surface which enhances the catalytic activity of metal nanoparticles towards the HER. Charge-transfer from in situ generated oxide species to the metal centre also leads to an enhancement in catalytic activity towards the HER. In the present work, we report a facile colloidal synthesis of PdBi2 nanoparticles using sodium borohydride as the reducing agent. Upon annealing the as-synthesized nanoparticles, a phase transition from the lower symmetry monoclinic phase to the higher symmetry tetragonal phase has been observed, and hence a change in morphology from agglomerated to core-shell nanoparticles. Potential electrochemical cycling of both monoclinic and tetragonal PdBi2 leads to the formation of a Pd-rich PdBi2 alloy with enhanced catalytic activity (onset potential: −11 mV and −18 mV vs. the RHE; 20 mA cm−2 current density at an overpotential of ~140 mV and ~207 mV for monoclinic and tetragonal phases, respectively). The low coordination number of Pd active sites formed by the dissolution of Bi alters the d-band symmetry monoclinic phase to the higher symmetry tetragonal phase has been observed, and hence a change in morphology from agglomerated to core–shell nanoparticles. Cyclic voltammetry of the monoclinic PdBi2 shows the formation of Bi–O species after potential cycling. Electron transfer from the Bi–O centre of Pd, and hence the optimal energy required for hydrogen adsorption leading to enhanced activity. Although the obtained composition after cycling resulted complexes were characterized by various analysis equipments such as nuclear magnetic resonance (NMR), elemental analyses (EA), thermogravimetric analysis (TGA), and single crystal X-ray diffraction. The detailed applications of thin films by ALD will be shown in the presentation.

The chemistry of vanadium is very prominent in both biological and technological systems. Metal vanadates have been paid enormous interest owing to their environment benignity, excellent redox and electrochemical properties. Hence, they have been used in many potential applications such as batteries, luminescent materials, semiconductors, ceramics, magnetic materials, catalysis and photocatalysis. Lanthanides occupy unique positions in the periodic table and they exhibit interesting properties for many applications. They have magnetic, catalytic and optic properties and are also used in biological applications. Upconversion nanocrystals emerges as a novel class of compounds which presents exceptional properties, namely large anti-Stokes shifts, sharp emission spectra, long excited-state lifetimes and high photoconvertibility. These characteristics allow its use for cancer therapy, in vivo labelling/imaging, biomarker detection and so on. Among the vanadates, Rare Earth orthovanadates (REVO₄, RE = Y,La-Lu) have been attained enormous interest due to their good electrical properties, high surface area, thermal stability, optical, magnetic and luminescent properties. Despite of many Luminene and Upconversion nanomaterials exploited until now, methods for making materials with tunable size and shape as well as desirable surface characteristics that are compatible with biological environments are still necessary. YVO₄,RE (RE = Eu, Tb, Sm and Yb/Er) nanocrystals were efficiently synthesized by the Hydrothermal Microwave method without any further heat treatment. This method allows fast, efficient and cheap synthesis of nanomaterials as well as control of morphology and size. X-ray powder diffraction patterns show all peaks can be indexed to the pure desired phases. It was also observed defined and sharp Raman modes as well as characteristic luminescence peaks for all the samples due to f-f transitions. The morphology was confirmed by FE-SEM showing structures in the nanosized range. These results show possible application of these materials to suppress the demand for next-generation luminescent biomarkers as well as new optical devices.

Hydrothermal Incorporation of Silver into Three Types of Potassium Niobates

Josué Esaú Romero-Ibarra¹ and Roberto Sato³; ¹IIM, Universidad Nacional Autonoma de Mexico, Mexico, Mexico; ²IF, Universidad Nacional Autónoma de México, Mexico, Mexico; ³ICAT, Universidad Nacional Autónoma de México, Mexico, Mexico.

Three types of Ag-incorporated potassium niobates; a layered K₄Nb₆O₁₇·nH₂O, a pyrochlore-type (K,H)NbO₃·nH₂O, and a perovskite-type KNbO₃, were synthesized via a hydrothermal reaction. The products were identified using X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The chemical environment of the doped Ag atom was studied by Extended X-ray Absorbance Fine Structure (EXAFS) measurement. The photocatalytic activity was evaluated by analyzing the kinetics of the decomposition of a 20 ppm phenol solution under UV light irradiation.

Novel Copper Precursor Based-Deposition of Cu₂O and CuO Thin Films Using Atomic Layer Deposition

Copper oxide has been attracted considerable attention because of its favorable intrinsic characteristics such as environmental-friendly, low-cost and reconfigurable electronic structure. Among various copper oxides, cuprous oxide (Cu₂O) and cupric oxide (CuO) are well known for many kinds of applications due to their attractive electrical characteristics. For example, Cu₂O and CuO show the n- and p-type characteristic when they have crystalline structure of cubic and monoclinic, respectively, and their combination can be utilized in various applications such as gas sensor, photodiode, anode materials in batteries, thin film transistor (TFTs), solar cells, and photo-catalysts. Until now, however, atomic layer deposition (ALD) based thin film fabrication of Cu₂O and CuO have not been seriously studied yet.

In this research, Cu₂O and CuO thin films were successfully deposited by ALD technique using novel copper precursor, (bis(1-dimethylamino-2-methyl-2-butoxy)copper) (Cu(dmamb)₂) for copper source, and H₂O and O₃ for oxygen source, respectively. To clarify the structural and electrical characteristics of individual thin films, X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray fluorescence (XRF) analyses were performed. All the analyses results demonstrated that Cu₂O and CuO thin films have cubic and monoclinic structure with low C-impurity in it. The XPS measurement also showed consistent result with XRD analysis. The electrical characteristic was investigated using UV-Visible (ultraviolet-visible) spectroscopy, and it revealed that each thin film has favorable optical band-gap. The more detailed experimental procedures and physical/chemical characterization results of thin films will be discussed in presentation.
Our group are interested in reproducing, some superconducting materials reported. Found, that most of these materials have not reported a thermodynamic study. So this has led us to find the relationship, of the crystalline structure, with the magnetic and electric properties. The polycrystals were prepared by solid-state reaction. So these were dehydrated in an oven, around 10 min at 100 C to observe, if exist a weight loss. It is an approach to guarantee, that stoichiometry is not lost. Dry and wet techniques were used to manufacture nano-crystals. Single crystals were prepared by fusion. Each reagent and product was analysed by powder XRD, to get the crystal structure, purity and amorphous. Characterizations techniques used: SDT simultaneous technique (TGA-DSC), RAMAN (with two cells: -190 to 500 C and 20 to 1200 C), HRTEM and SQUID (ZFC-FC curves were obtained at 2 - 300 K with an applied field of 100 Oe). For (K,Sr)2CrO4, x = 0.10-0.50 system poly, nano and single crystals. A SrSO4 solid solution was formed at room temperature with x = 0.50. At high temperature with x = 0.10, 0.15, 0.50 a K,Sr,CrO2 solid solutions were formed at 665 C. Diffractograms show (hkI) displacements in: (110), (113), (202), (116), (125) and (300), K,Sr,CrO2 compound presents a rhombohedral crystal structure. Nano-crystals size was 4-12 nm, until 520 min in mechanical milling (MM). The single crystals melting at 900 C and crystallized at 660 C/72 h, keeping a solid solution with x = 0.50. This system is an insulator and shows a weak ferromagnetic behaviour. Zn,MgO2 achieve a Tc 1.52 K, studying it, its detect the formation of two solid solutions: ZnO, it was found a greater displacement on: (100), (002), (101), (102), (103) and (110) being able to ensure that in those coordinates the substitution of cations is carried out. MgO, a shift was found on (111), (200) and (220), derived from the formation of periclide solid solution. RAMAN shows, the vibrations of the tetrahedral crystalline structure. Magnetic measurements get the blocking temperatures (TB) reaching maximum at 280 K for Zn,MgO2. The polycrystals in Bi-2212:2:2:3 and (Bi,Pb)-2223 compounds, with the possibility to reproduce it, and later prepared the nano-crystals, by wet technique. Our problem was that copper oxide reagent, have a mixture of Cu2+ and Cu+. Decreasing the melting point and appears Bi-2212 10 K, Bi-2223 80 K in XRD. The SQUID detected the different superconducting phases. Analysis K,Cu2SeO4 composition by DSC in air, near 197 C notice an exothermic comportment, that is the property of Se metal oxidation. Usual with N2 flux it is not appear, the Se oxidation process. Also in air it is possible to manufacture K,Cu4(SeO3)2 compound at 400 C. With N2 flux the formation was at low temperature. Then it is formed in air at atmospheric pressure, K,Cu4(SeO3)2 at 300 C/12h and K,Cu2(SeO3)4 at 400 C/12h, faster and lower T process, that the ones reported. TB reaches a maximum at 150 K.

CM01.06.10
Substitutional Solute Atom Effect on Dislocation Motion in BCC Iron Alloys—An Atomistically Informed Kinetic Monte Carlo Study Shubhi Shinzato1, Masato Wakeda2 and Shigenobu Ogata1,3; 1Osaka University, Osaka, Japan; 2National Institute for Materials Science, Tsukuba, Japan; 3Kyoto University, Kyoto, Japan.

Solute atom changes the mechanical strength of alloys, which is known as solid solution strengthening and softening. This solute atom effect is widely used to control the mechanical strength of alloys. In this work, we analyze the solute effect on screw dislocation motion in BCC iron, which dominates plastic deformation in BCC iron, using an atomistically informed Monte Carlo (kMC) model. The kMC model represents dislocation motion via kink-pair nucleation and kink migration, and all of the necessary kMC parameters, such as activation energies of kink-pair nucleation and migration and its stress dependency, are computed using atomistic methods based on developed interatomic potential. We successfully predicted the solute effects on dislocation velocity, temperature dependent yield strength, and activation volume of dislocation motion.

CM01.06.11
A Comparative Study on Ca-Doped and Sr-Doped Gd2Ti2O7 for Microwave Absorption Applications Qimlong Wen1,2, Wancheng Zhou1, Fa Luo1, Dongmei Zhu1 and Yongmin Liu3,4; 1State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, China; 2Department of Mechanical & Industrial Engineering, Northeastern University, Boston, Massachusetts, United States; 3Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts, United States.

With the development of communications industry, unexpected and harmful electromagnetic waves have raised concerns about the impact on communication devices, aircraft, and human beings. A wide variety of microwave absorption materials (MAMs) have been investigated based on magnetic, dielectric, semiconducting and conductive materials. Most of the conventional absorbers are 1-5 mm thick, which degrades their practical applications. In order to reduce the thickness of MAMs, we need to judiciously engineer the complex permittivity of the absorber. Towards this goal, we have doped Gd2Ti2O7 with Ca and Sr, and systematically investigated their dielectric and microwave absorption properties in the frequency range of 8.2-12.4 GHz (X-band). The samples were prepared by hot press method according to the chemical formulas Gd_{x}Ca_{y}Sr_{z}Ti_{4}O_{7} (M = Ca, Sr; x = 0; 0.03, 0.06, 0.09 and 0.12). The XRD patterns of Gd_{x}Ca_{y}Sr_{z}Ti_{4}O_{7} show typical pyrochlore-type crystal structure. There exist oxygen vacancies in all the samples according to the thermogravimetric analysis, which have significant effects on the electric conductivity and dielectric properties. When the Ca doping concentration is less than 9wt%, there are no big influences on the dielectric properties. When it reaches 12wt%, the real part of permittivity increase from 66 (without doping) to 76 at 8.2GHz. However, the Sr-doped Gd2Ti2O7, the real part of permittivity increases gradually from 66 to 114 at 8.2 GHz as the Sr doping concentration rises. At the same doping concentration, the Sr-doped Gd2Ti2O7 has higher complex permittivity. The calculated reflection loss suggests that the Sr-doped Gd2Ti2O7 absorber is thinner than the Ca-doped counterpart. The optimal thickness of the Sr-doped Gd2Ti2O7 is 0.74 mm with an effective absorption bandwidth of 2.7 GHz, surpassing the existing MAMs. In the next stage, we will plan to modify the frequency dispersion characteristics to broaden the effective absorption bandwidth and further reduce the thickness by adjusting doping concentration and combining with other ceramics. These doped Gd2Ti2O7 and related composite ceramics would be very good candidates for microwave absorption applications in the future.

CM01.06.12
Superstructures Driven Through Ordered Chemical Bonding in Unconventional Clathrates—Cs8Zn18Sb28 and Cs8Cd18Sb28 Bryan Owens-Baird1,2, Shannon J. Lee1,2, Oleg Lebedev3 and Kirill Kounin1,2; 1Iowa State University, Ames, Iowa, United States; 2Aames National Laboratory, Ames, Iowa, United States; 3Laboratorie CRISMAT, Caen, France.

Unconventional clathrates, whose frameworks are composed of late row transition metals and pnictide elements (e.g. M = Ni, Cu, Zn, Au; Pn = P, As, Sb), are a promising class of materials for thermoelectric applications. Previous studies have shown that many unconventional clathrates show a disorder to position their frameworks into larger supercells due to the difference in chemical bonding between framework elements. This framework ordering often minimizes bonding interactions within the framework, e.g. M-M interactions. The previously reported clathrates, Cs2ZnSb28 and Cs2CdSb28, were described to have the arystotype cubic clathrate-1 structure in which all framework sites were mixed occupied by metal and antimony. In our study of these clathrates, we show that the frameworks order into discrete metal and antimony sites, reducing Cd-Cd and Zn-Zn interactions. Cs2CdSb28 adopts an 8-fold volume increase into a centered cubic superstructure, space group (No. 206), doubling the unit cell length to 24.3027 Å. The structure of Cs2ZnSb28 has been to be more complex and not easily solved through single crystal X-ray diffraction experiments at 2 - 300 K with an applied field of 100 Oe. For (K,Sr)2CrO4, x = 0.10-0.50 system poly, nano and single crystals. A SrSO4 solid solution was formed at room temperature with x = 0.50. At high temperature with x = 0.10, 0.15, 0.50 a K,Sr,CrO2 solid solutions were formed at 665 C. Diffractograms show (hkI) displacements in: (110), (113), (202), (116), (125) and (300), K,Sr,CrO2 compound presents a rhombohedral crystal structure.
In this study, the sintering behavior of zinc oxide (ZnO) under dc field was analyzed. The performed method is called as flash sintering where the assistance of electric field reduces sintering temperature much lower than traditional sintering temperatures. Non-isothermal condition runs under 50V/mm electric field and 250°C/min heating rate led us to the rapid increase in power absorption by specimen between 5880°C to 830°C in less than a minute and densification of the specimen increased to >95%. No appreciable grain growth was observed in ex situ SEM analyses. While flash-sintering has been demonstrated in a variety of oxide material systems including ZnO, the mechanism behind this technique is not still fully understood. Here, we report on the results of an in situ time-resolved EDXRD study as a function of electric field and temperature. The densification phenomena of ZnO particulate system has been analyzed at the unit cell level over times scales by using polychromatic x-rays with photon energies up to 200 keV.

CM01.06.15
Hexagonal Molybdenum Trioxide (h-MoO₃) as a Multi-Functional Material for Energy Storage, Optoelectronics and Photocatalytic Applications
Paloma Almodóvar1, María Luisa López2, Carlos Diaz-Guerra1, Julio Ramírez Castellanos2, José María González Calbet1, Marco Pérez1, 4, Katharina Lorenz2, 4, Silvia Suárez2 and Benigno Sánchez2; 1Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Madrid, Spain; 2Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Madrid, Spain; 3IFCN, Instituto Superior Tecnico, Universidade de Lisboa, Bobadela, Portugal; 4Instituto de Engenharia de Sistemas e Computadores-Microsystems and Nanotechnology (INESC-MN), Lisboa, Portugal; 5FOTOAIR-Ciemat, Unit of Analysis and Photocatalytic Treatment of Pollutants in Air, Avda, Madrid, Spain.

Molybdenum oxides are considered exceptionally functional and adaptable optical and electronic oxides due to their unique physical properties. In particular, molybdenum trioxide (MoO₃) is a polymorphic material. The thermodynamically stable orthorhombic α-phase is a well-known semiconductor with important applications in catalysis, sensors, solar cells technology, electrochronic systems and field emission devices. Known for almost one century and still a source of findings, hexagonal MoO₃ (h-MoO₃) is a metastable material with, as yet, poorly known structure and physicochemical properties. In this work, undoped and Ag-doped h-MoO₃ microrods have been synthesized by a scalable soft chemistry method based on the precipitation of ammonium heptamolybdate, while composites of h-MoO₃ microrods and graphene or graphene oxide (GO) were synthesized by a slightly different route. In addition, highly crystalline h-MoO₃ nanoparticles were obtained by ball-milling of the as-grown microstructures. All the obtained samples were thoroughly characterized by a wide set of complementary techniques including monochromatic X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), UV-Vis spectroscopy, micro-Raman, micro-photoluminescence, X-ray photoemission spectroscopy (XPS) and X-ray absorption (XAS) with synchrotron radiation.

In this study, the sintering behavior of zinc oxide (ZnO) under dc field was analyzed. The performed method is called as flash sintering where the assistance of electric field reduces sintering temperature much lower than traditional sintering temperatures. Non-isothermal condition runs under 50V/mm electric field and 250°C/min heating rate led us to the rapid increase in power absorption by specimen between 5880°C to 830°C in less than a minute and densification of the specimen increased to >95%. No appreciable grain growth was observed in ex situ SEM analyses. While flash-sintering has been demonstrated in a variety of oxide material systems including ZnO, the mechanism behind this technique is not still fully understood. Here, we report on the results of an in situ time-resolved EDXRD study as a function of electric field and temperature. The densification phenomena of ZnO particulate system has been analyzed at the unit cell level over times scales by using polychromatic x-rays with photon energies up to 200 keV.

CM01.06.16
Electrochemical Li-Ion Intercalation for Control of Electronic Phases in Transition-Metal Oxide Epitaxial Films
Takuto Soma1, Kohei Yoshimatsu1 and Akira Ohtomo1, 2; 1Department of Chemical Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan; 2Materials Research Center for Element Strategy (MURES), Tokyo Institute of Technology, Yokohama, Japan.

In this study, we have focused on epitaxial films as host materials, which are advantageous to Li-ion intercalation owing to well-defined structural transition and superconductivity. Nevertheless, due to a hurdle for homogeneous intercalation to bulk materials, it is limited to apply electrochemical intercalation for control of physical properties. In this study, we have focused on epitaxial films as host materials, which are advantageous to Li-ion intercalation owing to well-defined structural transition and superconductivity. Nevertheless, due to a hurdle for homogeneous intercalation to bulk materials, it is limited to apply electrochemical intercalation for control of physical properties.

CM01.06.17
Grain and Grain Boundary Properties of ZnO-Zn₂BiVO₆-Co₃O₄-Cr₂O₃-CaCO₃ Ceramics Using Dielectric Functions
Yeun-Woo Hong, Man-Jin Ha, Jong-Hoo Paik, Jeong-Ho Cho, Young-Hun Jeong and Ji-Sun Yun; KICET, Jinju, Korea (the Republic of).

ZnO has been applied to various electrical and optical applications such as gas sensors, piezoelectric transducers, phosphors, transparent conducting films, and varistors. To control the figure of merits of these devices it is essential to understand the behavior of defects and interface states in doped ZnO, especially in ZnO varistor. All of these applications are either affected by, or depend on, defects and grain boundary properties according to various dopants (Bi, V, Pr, Mn, Cr…oxides). It is known that cobalt oxide doped to ZnO improves the nonlinear current-voltage characteristics, which is presumably due to the formation of the Schottky-type double barriers at the grain boundaries. Also it is found that the presence of a large Bi, V or Pr ions induces the concentration of native defects of acceptor type in the grain boundary of doped ZnO. However, it is not known about the relationship between the defects and grain boundary properties in the simple five component system ZnO-Zn₂BiVO₆-Co₃O₄-Cr₂O₃-CaCO₃ (ZZCCCa) revealed good nonlinear
current-voltage characteristics. In this study, we investigated the effects of CaCO₃ and Zn₂BiVO₄ (newly synthesized liquid phase sintering aid by us for varistor application) additives in ZnO-CaO-CrO (it’s a new varistor system developed by us) in terms of defects and grain boundary properties using dielectric functions (Z*, M*, ε*, Y*, and tanθ). It will provide information about the relationship between the formations of donor or acceptor defects at the grain or grain boundary for the double Schottky barrier. Experimentally ZZZCCa sintered at several temperatures in air have two kinds of defects (Zn interstitial and O vacancy) according to its sintering temperatures, a single grain boundary (apparent activation energy Ea=0.90–1.2 eV), and a good varistor properties (nonlinear coefficient α~80). The origin of varistor behavior in this system has been discussed in relation to grain boundary traps and defect chemistry based on the experimental results.

CM01.06.18
Materials Discovery by Chemical Analogy—Role of Oxidation States in Structure Prediction
Daniel W. Davies, Keith Butler, Alexandr Isayev, and Aron Walsh

The concept of oxidation states has, for many decades, been integral to the way in which chemists think about the coming together of elements to form molecules and extended solids. Oxidation states continue to be a useful heuristic tool across all areas of the chemical sciences. By treating elements in given oxidation states as species in their own right, it is possible to use these as building blocks to create chemically feasible compositions.[1] Oxidation states also play a crucial role in approaches to structure prediction: Tabulated sources like Shannon’s radii and coordination environments as well as recent data-mined probabilistic models,[2] can predict the likelihood of a given crystal structure occurring.

In this work, we carry out a statistical analysis of the occurrence of oxidation states in 25,000 ordered, inorganic compounds. These results demonstrate that a large number of elements are only likely exhibit certain oxidation states when other, particular elements are present.

We use the information gleaned from this analysis to construct a screening process that ascribes a likelihood score to suggested element compositions. This screening procedure is implemented in this work to efficiently explore the enormous search space for new ternary transition metal halide compositions. We show how a large number of otherwise sensible looking compositions can be discounted from such a search using our method.

Structure prediction is then carried out for some candidate compositions using a probabilistic model as implemented in the Pymatgen code,[3] in which oxidation states also play a crucial role. Finally, we carry out global structure searches for these compositions using an evolutionary algorithm and compare the energies of the structures found with those suggested by the probabilistic model, in order to assess its performance. Overall, we show how careful consideration of the occurrence of oxidation states can be used as part of a materials design methodology. Our methodology can be applied in a range of contexts and is an important tool in the quest for accelerated materials discovery.

References

CM01.06.19
Perovskite Electron Emitters—Computational Prediction and Preliminary Experimental Assessment of Novel Low Work Function Cathodes
Tianya Ma, Lin Lin, Ryan Jacobs, Dane Morgan and John Booze; University of Wisconsin–Madison, Madison, Wisconsin, United States.

Commercial W-based thermionic electron emission cathodes have been used in high frequency, high power vacuum electronic devices for decades. However, there is an ongoing need for the development of new thermionic cathode materials that don’t suffer from the shortcomings of traditional W-based cathodes, such as limited emission lifetime due to the continual evaporation of volatile Ba during high temperature operation and non-uniform emission throughout the cathode surface.[1]

Our recent work explored a representative set of 20 perovskite oxides as potential new electron emitting materials by conducting Density Functional Theory (DFT) calculations of the surface work function using accurate hybrid HSE functionals, where we discovered that pure and Ba-doped SrVO₃ could exhibit low work functions of about 1.9 and 1.1 eV, respectively.[2] Given the well-known compositional flexibility of perovskites, the question naturally presented a significant challenge.

In this work, we have used high-throughput DFT calculations enabled by the MAterials Simulation Toolkit (MAST)[3] to computationally screen over 3100 perovskite oxides in search of new thermionic electron emitters. We screened materials in search of candidates with (1) low predicted work function values using high temperature heat treatment in a reducing atmosphere. Additionally, we pressed and sintered the SrVO₃ powders into cathode test pellets and obtained low work function surfaces that are also stable and are thus expected to be present on the surface of a real cathode. From this computational search, we have identified 6 new perovskite compounds that are promising new thermionic cathode materials.

In addition to our high-throughput computational search for low work function perovskites, it is crucial to experimentally synthesize and test these promising materials. We successfully synthesized >95% phase pure polycrystalline SrVO₃ powders using solution-based precursor salts and high temperature heat treatment in a reducing atmosphere. Additionally, we pressed and sintered the SrVO₃ powders into cathode test pellets and obtained low work function surfaces using high temperature electron emission measurements and X-ray photoelectron spectroscopy (XPS). These experimental results demonstrate the promise of SrVO₃ as a low work function thermionic emission cathode.

References

CM01.06.20
Fracture Detection of Ceramic Substrates Utilizing an Acoustic Emission Method and Frequency Analysis of the Elastic Wave
Takuya Ono.
Yusuke Daiko, Sawao Honda and Yuji Iwamoto; Nagoya Institute of Technology, Nagoya, Japan.

From the strong demand of both higher efficiency and energy saving of the power semiconductor, material shift from conventional silicon (Si) to silicon carbide (SiC) was gradually seen since the late 1980s [1,2]. SiC-based power devices have various advantages including high frequency operation, high thermal conductivity, high breakdown voltage and temperature operating capability higher than 200 °C owing to its wide bandgap compared with silicon [3]. High temperature operation leads to decrease the volume of heat sink (cooling system). Ceramics with high thermal conductivity such as AlN and SiC have been used for the insulating substrate. Because of their high power/current densities and wider range of the operating temperature, thermal fracture at those insulating ceramic substrates during prolonged operation is a serious problem. In addition, since the power module consists of various components including a ceramic insulating substrate, Cu electrode and polymer molding, understanding of the start-point of the thermal fracture, e.g. whether at the ceramic substrate itself or at Cu electrode/ceramic interface etc. also becomes a significant issue. Acoustic emission (AE) has been widely used to detect fractures, and frequency of the elastic wave can be obtained by Fourier analysis. Here we show the relationship between the frequency of the acoustic wave and elastic modulus of various substrates. Frequency of the acoustic wave was obtained using a three-point bending method for crack generation, serious noise due to the friction between substrate and AE sensor was also detected. On the other hand, characteristic frequencies for each substrate were observed using the IRH method with a good reproducibility especially in the frequency ranging from 200 to 300 kHz. A good linear relationship between the Young’s modulus of substrates and corresponding frequency was successfully obtained. We also confirmed the start-point of the fractures at both AlN substrate AlN/Cu interface from the AE frequency shift. These results will be discussed together with a heating/cooling cycle test.

The extensive field of application of magnetic nanoparticles (NPs) makes them a wide, popular and attractive class of materials that receives evergoing development, with different compositions and morphologies being proposed to improve the NPs’ magnetic features. In regards to this, cation exchange (CE) could represent a promising approach to obtain complex, modulated magnetic nanostructures, but its application to this class of materials has been sporadic and not always consistent. To this aim we studied the effect of a post-synthetic CE approach on same-sized magnetite and wüstite NPs by performing in-depth morphological, structural, spatially resolved chemical and magnetic behavior analyses, finally obtaining bi-magnetic core/shell NPs with mixed Fe/Mn and Fe/Co ferrite shells that still maintained the initial shape and size. The combination of such diverse techniques evidenced unanimously this unexpected result, while also shedding light on the role of the NPs’ crystal structure for CE reactions: given the common size and shape of the initial NPs, the crystal structure of the two phases (non-defective for magnetite, defective for wüstite) was the only variable among the NPs populations that affected the CE and was responsible for the higher percentage of doping cation (Co or Mn) present in the post-CE wüstite NPs. Then, the experimental evidence provided what needed to clarify the mechanisms that drive CE processes in this class of materials, while also offering a solid basis for the interpretation of the dramatic variations observed in the magnetic features of the post-CE NPs. In particular, the evolution of the magnetic features could be attributed to the combination of three separate factors: the formation of well-defined shells, the introduction of different magnetic cations and the presence of two distinct crystal structures in the cores. The first factor was the main cause of exchange bias effects, while the introduction of Mn or Co in the shell modulated the net magnetic hardnes of the core/shell NPs, leading to magnetically softer or harder NPs, respectively, with respect to the initial NPs. Finally, the presence of ferrimagnetic (magnetite) or antiferromagnetic (wüstite) cores in the core/shell NPs has a major influence in the net magnetic hardness and saturation magnetization of the final NPs. These results give a new insight on the mechanisms that command CE of nanosized magnetic oxides, while providing a clearer picture over the possible capabilities of CE approach to develop novel, complex magnetic nanostructures.

CM01.06.21
The Influence of Crystal Structure in the Development of Complex Nanosized Mixed Iron Oxides by Cation Exchange
Alberto Casu1, Sergio Lentijo Mozó1, Davide Deiana2 and Andrea Falqui1; 1Biological and Environmental Sciences and Engineering (BESE), King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia; 2Centre Interdisciplinaire de Microscopie Electronique, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

The rational design and interfacing of semiconductor heterostructures comprising light harvesting (charge donor) and wide-bandgap semiconductor (charge acceptor) elements is imperative for solar energy conversion within PEC cells wherein incident solar radiation is converted and stored as a chemical fuel. Such heterostructures need to be carefully designed to efficiently harvest a large portion of the incident solar radiation, which requires precise control of energetic offsets (governing the thermodynamic driving forces for charge separation) and the kinetics of charge transfer (determined in large measure by interfacial properties). I will discuss the design of V2O5/quantum-dot heterostructures that simultaneously optimize thermodynamics and kinetics. The

reference

CM01.06.22
Rational Design of Semiconductor Heterostructures for Energy Conversion
Junsang Cho1, 2, Erick Braham1, 2 and Sarbajit Banerjee1, 2; 1Department of Chemistry, Texas A&M University, College Station, Texas, United States; 2Department of Materials Science and Engineering, Texas A&M University, College Station, Texas, United States.

Lead halide perovskites have rapidly emerged as promising next-generation candidates for photovoltaics, light-emitting displays, and other optoelectronic applications owing to their desirable electronic and optical properties. Dimensional control provides a means to tune the optical, electronic, and magnetic properties of semiconducting materials as a result of quantum confinement effects. Ligand-mediated colloidal synthesis methods allow for control over nucleation/growth kinetics and enable precise modulation of nanocrystal dimensions through variation of reaction parameters such as the precursor concentration, reaction temperature, and the electronic and steric parameters of passivating ligands. I will focus on synthetic efforts at establishing dimensional control of semiconductor nanostructures with a particular emphasis on the ligand-mediated synthesis of two dimensional (2D) lead halide perovskite nanocrystals guided by elucidation of crystal growth mechanisms. I will further discuss the design of semiconductor heterostructures for photocatalytic water oxidation that couple multiple polymorphs of vanadium oxide (V2Ox) nanowires with semiconductor nanocrystals. The alkyl chain length, branching, ligand concentration, and temperature greatly influence the dimensional modulation of 2D perovskite nanoplatelets (MAPbBr3, CsPbBr3). Our recent work demonstrates that the crystalline order of the ligand-shell assembly, as dictated by the length of the alkyl chains, the degree of branching, the reaction temperature, and ligand concentration, strongly influences the extent of dimensional confinement attainable for the perovskite nanoplatelets. The denticity, steric bulk, and concentration of the added alkylamine ligands further provide a means of modulating structural dimensions from 3D CsPbBr3, to 2D CsPbBr3 structures. Machine learning approaches for navigating synthetic landscapes have further been developed and provide control over layer thickness down to a single layer.

The rational design and interfacing of semiconductor heterostructures comprising light harvesting (charge donor) and wide-bandgap semiconductor (charge acceptor) elements is imperative for solar energy conversion within PEC cells wherein incident solar radiation is converted and stored as a chemical fuel. Such heterostructures need to be carefully designed to efficiently harvest a large portion of the incident solar radiation, which requires precise control of energetic offsets (governing the thermodynamic driving forces for charge separation) and the kinetics of charge transfer (determined in large measure by interfacial properties). I will discuss the design of V2O5/quantum-dot heterostructures that simultaneously optimize thermodynamics and kinetics. The
Re Segregation at Interfacial Dislocation Network in a Nickel-Based Superalloy Jixue Li, Qingqing Ding, Qian Yu and Ze Zhang; Zhejiang University, Hangzhou, Alabama, United States.

The distribution of Rhenium (Re) in a Ni-based single-crystal superalloy is studied by sub-angstrom resolution transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy. It is found that Re atoms segregate at the tensile stress regions near the interfacial dislocation cores, and the segregation process is facilitated by dislocation pipe diffusion. In situ TEM and scanning electron microscopy (SEM) straining studies reveal that the Re-decorated dislocation networks along the phase boundaries act as mechanical walls that effectively block dislocation motion and crack propagation. Furthermore, the degree of Re segregation can be regulated by thermal treatment; the slower the cooling rate, the higher the concentration of Re at the local composition strain of Re and the dislocation strains, leading to significantly stabilized interfacial dislocation networks. These results provide a new perspective on understanding the origin of the Re effect on mechanical properties in Ni-based superalloys and will benefit to both improving creep properties of Ni-based superalloys and designing high-performance Re-free superalloys.

Sequential Charge Transitions in $\text{Ca}_x\text{Bi}_3\text{Fe}_2\text{O}_6$ and the Electronic Consequences of B-Site Substitution Fabio Denis Romero1, 2, Takashi Saito1, J. Paul Attfield1 and Yuichi Shimakawa1; 1Institute for Chemical Research, Kyoto University, Kyoto, Japan; 2Hakubi Center for Advanced Research, Kyoto University, Kyoto, Japan; 3University of Edinburgh, Edinburgh, United Kingdom.

Transition metal oxides with unusually high-valent cations often show unusual structural, magnetic, and transport behavior as a result of their inherent charge instabilities. Additionally, the charge transitions via which these instabilities are relieved often lead to coupling of several fundamental properties. For example, CaFeO$_3$ shows charge disproportionation of the unstable Fe$^{4+}$ cations ($2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$) which leads to a structural phase transition due to ordering of the disproportionated cations and a metal-insulator transition.[1] In addition, competing magnetic interactions in the charge disproportionated phase lead to the emergence of incommensurate magnetic order.[2] In BiNiO$_3$, there is an inter-site charge transfer transition ($\text{Bi}^{3+}\text{Ni}^{3+}\text{O}_3 \rightarrow \text{Bi}^{3+}\text{Bi}^{5+}\text{Ni}^{2+}\text{O}_3$) which is accompanied by significant structural modifications due to the co-mingling ordering of the Bi$^{3+}$ and Bi$^{5+}$ cations.[3]

Recently, we reported the synthesis of Ca$_{0.8}$Bi$_{0.5}$Fe$_{2}$O$_6$, which shows sequential charge transitions of the unusually high valent Fe$^{3+}$: first at 250 K there is charge disproportionation from Ca$_{0.8}$Bi$^{3+}$Bi$^{5+}$Fe$_{2}$O$_6$ to Ca$_{0.8}$Bi$^{3+}$Fe$_{5+}$Fe$^{3+}$Fe$_{2}$O$_6$ with accompanying charge and magnetic ordering and then at 200 K there is inter-site charge transfer between Bi and Fe to form Ca$_{0.8}$Bi$^{3+}$Bi$^{5+}$Bi$_{0.25}$Fe$_{2}$O$_6$.[4] These charge transitions are accompanied by significant changes to the structural, magnetic and transport properties of this material.[5] This material is tolerant to substitution of the iron for cobalt enabling the formation of the full Ca$_{0.8}$Bi$_{0.5}$Fe$_x$Co$_{1-x}$O$_6$ solid solution. Results in an initial sharp suppression of the charge disproportionation transition at $x = 0.03$ due to the broadening of the oxygen hole band while the inter-site charge transfer transition remains up to approximately $x = 0.67$.

References:

Influence of Nanoparticle on Microstructure and Magnetic Properties of Bi-Substituted LiZnTi Ferrites with Low Sintering Temperature Fang Xu and Huaiwu Zhang; University of Electronic Science and Technology, Chengdu, China.

Microstructural changes including grain growth and densification in ceramic materials, either through liquid phase sintering or by lowering reaction energy, have a profound effect on the material properties. In this work, Li$_{1-2x}$Bi$_{2x}$Fe$_{2}$O$_6$ nanoparticles (LZNs) with $x = 0.05$–0.15 were prepared by sol-gel method. HRTEM image of the LZNs showed that the spinel structure nanoparticles with ~6 nm average particle size were obtained. As a reaction additive, the LZNs were introduced into a Bi-substituted Li$_{1-2x}$Bi$_{2x}$Fe$_{2}$O$_6$ (LiZnTiBi) ferrite ceramic to control abnormal grain growth and enhance magnetic properties (sintering temperature is ~920 °C). XRD patterns demonstrated that a pure spinel phase structure composite ceramics were synthesized. This indicated the LZNs can further react with LiZnTiBi ferrite ceramics. Also, SEM images showed that adding LZNs can obviously control abnormal grain growth and reduce pores between grains. More importantly, results of ferromagnetic resonance (FMR) linewidth ($\Delta H$) showed that optimized LZNs additives can reduce $\Delta H$ of the LiZnTiBi ceramics. Meanwhile, saturation magnetization ($4mM$) of the ceramics can be improved by adding moderate LZNs. The doping method reported in this study also provides a referential experience for other low temperature sintering ceramics.

Magnetocaloric Materials Based on Binary and Ternary Mn Compounds—Screening and Testing Joya Cooley1, Joshua D. Bocarsly1, 2, Matthew Horton3, Kristin A. Persson4 and Ram Seshadri1, 2, 3; 1Materials Research Laboratory, University of California, Santa Barbara, Santa Barbara, California, United States; 2Materials Department, University of California, Santa Barbara, Santa Barbara, California, United States; 3Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4Materials Science and Engineering, University of California, Berkeley, California, United States; 5Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California, United States.

Magnetic refrigeration is accomplished through the magnetocaloric effect (MCE) associated with a reversible temperature change upon application of a magnetic field. The effect originates from cycling materials between two different magnetic states with high and low entropies. In recent decades, this technology has been proposed as an environmentally friendly alternative to traditional vapor-compression technology, obviating the need for chlorofluorocarbon or hydrochlorofluorocarbon refrigerants, and potentially capable of greater efficiency.1–3 The figure of merit for magnetocalorics is the magnetic entropy change ($\Delta S_M$), and it has been recently proposed that compounds with high $\Delta S_M$ can be screened using a density functional theory (DFT) based proxy called the magnetic deformation ($\Sigma_\theta$) – a measure of the deformation between relaxed structures with and without spin polarization.1 Several useful Mn-containing binary and ternary compounds have been identified as potential magnetocalorics. We will discuss the synthesis, characterization, and magnetic property measurement of some of these candidate materials.

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Research Science and Engineering Center at UCSB (MRSEC NSF DMR 1720256) is gratefully acknowledged. The UCSB MRSEC is a member of the NSF-supported Materials Research Facilities Network (www.mrfn.org).


CM01.06.27
Polymer-Derived Synthesis of Refractory Ceramic Composites

Boris Drachkin,1 William K. Edelen,1 Tristan Butler1, Syed Qadri2 and Matthew Laskoski1; 1Chemistry, U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 2Materials, U.S. Naval Research Laboratory, Washington, District of Columbia, United States.

Refractory ceramics, such as metal carbides, metal nitrides, and metal borides offer superior thermal, electrical, and mechanical properties that significantly outpace metal alloys, oxide-based ceramics, and other comparable materials. The outstanding temperature stabilities (over 3,000 °C) and high hardness (over 30 GPa) of these ceramics and ceramic matrix composites (CMCs), therefore, offer significant promise for ballistic protective armor, industrial tools, and hypersonic engine applications. However, conventional synthesis and composite fabrication methods involve expensive and energy-intensive carothermal synthesis or sintering that is neither safe nor industrially scalable for mass production. Furthermore, since intrinsic ceramics are brittle and require incorporated reinforcements in order to adequately perform, their processing adds significant engineering complexity and remains poorly optimized for refractory carbides.

We rely on blends of metals and phenolic resins to synthesize near net shape refractory ceramic using a single-step in situ reactive melt infiltration/reaction bonding method in which no pressure is required to compact and densify the composites. The polymer source, which is an inexpensive thermoset with a high char yield and zero oxygen-containing groups, reacts with metals at low temperatures (700 – 1,400 °C) under flowing Ar in a tube furnace and requires 75% less energy input than conventional ceramics synthesis methods. A similar method employs a melamine-rich resin and requires on flowing N2 to synthesize metal nitride monoliths. To date, our approach has successfully yielded TiC, SiC, NbN, B4C, ZrC, ZrN, ZrB2, and TiB2, composites in preformed shapes (discs, cones, spheres, etc.). The resulting structures exhibit nanocrystalline grains and high density, and the ceramic monoliths demonstrate high toughness and durability in harsh environments. We reinforce these composites with metals, carbon allotropes, and secondary ceramics in a bottom-up approach in order to enhance their oxidation stability, thermal stress mitigation, and fracture toughness. The resulting customizable and inexpensive refractory composites offer a number of solutions for vital applications in the aerospace, military, transportation, and tooling industries.

SESSION CM01.07: Solid-State Catalysis

Session Chairs: Amy Prieto and Dmitri Talapin
Wednesday Morning, November 28, 2018
Hynes, Level 2, Room 203

8:00 AM **CM01.07.01
Designing Catalysts for Water Splitting Based on Electronic Structure Considerations
Sarbajit Banerjee; Texas A&M University, College Station, Texas, United States.

Water splitting involves the synergistic operation of water oxidation and hydrogen evolution half-reactions and remains a considerable challenge since it requires the concerted transfer of four electrons and four protons. Catalysts that can facilitate both of the half-reactions at low overpotentials are imperative to avoid squandering free energy harvested using a semiconductor in a photoelectrochemical cell, or provided directly in the form of current in a water electrolyzer. Photocatalytic water splitting requires the operation of light harvesting, charge separation, charge transport, and redox catalytic steps that must outcompete charge recombination. As such, it requires the precise tunability of energetic offsets to establish optimal thermodynamic driving forces for charge transfer and control of interfaces to mediate kinetics of charge transfer. I will discuss the design of compounds with the composition M,3V2O5 where M is a post-transition metal cation with lone-pairs characterized by intercalative mid-gap states that can accept holes from photoexcited semiconductor quantum dots. Such compounds, accessible through topochemical intercalation of metastable polymorphs of V2O5, have facilitated the design of semiconductor heterostructures with energetic offsets primed to facilitate effective hole transfer upon photoexcitation of the heterostructures, thereby mitigating the longstanding challenge of the anodic photocorrosion of quantum dots. Interfacial design further provides a means of modulating the dynamics of hole transfer, which occurs at <1 ps timescales. The second half of my talk will focus on discussing the specific electronic structure characteristics of edge sites of MoS2 that enable them to function as catalysts for the hydrogen evolution reaction. Interfacial hybridization of MoS2 with n-C60 provides a means to modulate the electronic structure and enhance catalytic activity. Finally, I will discuss ternary heterostructures that are capable of catalyzing both reactions.

This work was supported by the National Science Foundation under NSF 1627197.

8:30 AM CM01.07.02
Disordered MoTe2 with Self-Enhanced Catalytic Activity for Hydrogen Evolution
Alexey Ganin and Jessica Meghymn; University of Glasgow, Glasgow, United Kingdom.

Sunlight is widely distributed geographically and provides enough energy in one hour to supply the world’s energy demands for a full year. However, this form of renewable energy is intermittent; thus current solar energy technologies must be fed into the grid or are otherwise wasted. Recent efforts have therefore been focused on the conversion of excess solar energy into a fuel in the form of hydrogen via water electrolysis. Subsequent oxidation of the hydrogen would allow for the release of energy (and water) without the need for fossil fuels. Due to the diffuse nature of solar power, a relatively modest current density of 10 mA cm−2 has been proposed as a benchmark for the comparison of hydrogen evolution reaction (HER) electrocatalysts, which roughly equates to a 10% efficient solar-to-fuels device. [1] Layered transition metal dichalcogenides (TMDs) can offer a viable solution for achieving appreciable conversion rates in low currents due to intrinsic and useful feature of any layered material, namely two-dimensionality. [2] The 2D nature of TMDs enables a maximum output from the entire surface of a catalyst and allows a simplistic and cheap design of future devices, for example, in form of atomically thin films. A semimetallic 1T’-MoTe2 with the monoclinic structure stands out among chalcogenides of molybdenum due to its remarkable ability to...
accommodate excess of electrons and thus, presenting an excellent prototype for studies of the role of electrochemical activation on catalytic properties of a 2D material. [3, 4] Herein, we report the synthesis, structure and properties of a new disordered MoTe2 material with self-enhanced catalytic activity for HER that reaches the overpotential value of ~187 mV at j = 10 mA cm−2 after short potential cycling in 1 M H2SO4. The optimisation is coupled with a five-fold increase in turnover frequency and reduced charge transfer resistance as the HER progresses, all while preserving the electrochemically active surface area. By applying a solid state approach to the synthesis of the disordered MoTe2, we can exclude stoichiometry defects as the cause of the enhanced activity and conclude, in conjunction with electron microscopy, spectroscopy and X-ray diffraction experiments that the improved electrocatalytic performance is due to the intrinsic activation of the basal plane. The outcome of the studies on optimisation of MoTe2 thin films using the in operando cycling protocol is discussed as well in connection with how appreciable gains in future energy conversion and storage via HER may be achieved.


8:45 AM +CM01.07.03
Faceted Oxide Nanoparticles as Catalyst Supports Kenneth R. Poeppelmeier1,2, Ryan J. Paull1, Zachary R. Mansley2 and Laurence D. Marks2; Chemistry, Northwestern Univ, Evanston, Illinois, United States; 2Materials Science & Engineering, Northwestern University, Evanston, Illinois, United States.

Our focus has been on understanding how the metal/oxide interface can modify the activity and selectivity of supported noble metal catalysts. To this end, metal/support interfaces on faceted oxide perovskite supports have been examined. Specifically, we utilize the variable strength of interaction between different perovskite oxide supports and noble metal catalysts. Support particles can be produced through sol-gel or hydrothermal methods. Lanthanide scandates (LnScO3) were produced through a low-temperature heat treatment of stoichiometric hydroxide gel in a humid environment. Water vapor was necessary to preserve the higher diffusivity of the gel, but an excess of water vapor led to the formation of secondary phases. The temperature of the reaction was used to tune the Gibbs free energy of reaction and kinetics of particle growth to produce faceted nanoparticles. The lattice parameters of LnScO3 match well with several noble metals, which allows for a systematic study of how certain support properties (lattice parameter, acidity, etc.) can affect the catalytic performance of these metals. The support synthesis paves the way for different surface morphologies or to be obtained, which further influence the metal/support interface. Hydrothermal synthesis of SrTiO3, for example, may produce materials that are controllably terminated with either SrO-rich [100], TiO2-rich [100], or SrO2-rich [110] surfaces. Pt nanoparticles showed a higher selectivity in acrolein hydrogenation towards allyl alcohol when the Winterbottom shape had a higher ratio of facets to edges or corners, as was the case when supported on SrTiO3 rather than BaTiO3, and exploiting the Strong Metal-Support Interaction further improves the selectivity. This library of the different support oxides with controlled surface morphology allows for better control of specific active sites of several noble metals.


9:15 AM CM01.07.04
Electrochemically Driven Non-Congruent Phase Transitions in Ordered Intermetallic Pd-Bi Electro catalysts Shoji Hall, Du Sun and Yunfei Wang; Johns Hopkins University, Baltimore, Maryland, United States.

The conversion of O2 to H2O is an important fuel cell reaction for the recovery of renewable electricity from chemical fuels. Alloys of Pt-group metals (PGMs) with transition metals have emerged as catalysts with enhanced activity and durability for the oxygen reduction reaction (ORR). To date, most studies focus exclusively on alloys that adopt a Face-centered cubic (FCC) or Face-centered tetragonal (FCT) crystal lattice. Under ORR operating conditions, these materials evolve from alloys to Pt core-alloy shell materials, in these systems both the alloy core and Pt shell retain the FCC or FCT type crystal structure. Generally, PGM alloys belonging to the lower symmetry FCT structure usually exhibit higher activity than FCC-type alloys of the same composition. However, materials with lower symmetry than FCT crystal structures are not often explored as catalysts, hence there is wide open opportunity to explore new materials. Here we present the synthesis and interrogation of low-symmetry Pd-Bi based ordered intermetallics for ORR. We found that under ORR operation conditions, Pd-Bi (J/4mmm space group) which adopts a tetragonal lattice, transforms to a-PdBi (Pnma space group) which adopts an orthorhombic crystal structure; this transformation is enabled by oxidative Bi corrosion under potential cycling. To the best of our knowledge, this is the first report of a material that exhibits an electrochemically driven, non-congent phase transition across materials with different crystal structures. The resulting phase-converted Pd-Bi is stable and exhibits high performance for ORR. Phase-converted Pd-Bi outperform Pt and Pd metal, reaching mass activities of 2.6 A/mgPd, which is nearly 10X higher than Pt/C (~0.3 A/mgPt) and Pd/C (~0.2 A/mg) at 0.9 V vs the Real Hydrogen Electrode (RHE). The mass activity of Pd,Bi decreases by ~38% after 10,000 cycles, indicating that it is stable. Activation energy (Ea) determined by temperature dependent electro-kinetic measurements indicates that the activity enhancement on phase-converted Pd,Bi originates from anion-poisoning resistant behavior. These results establish that PGMs-based ordered intermetallics with low-symmetry crystal structures can be highly active and durable electrocatalysts.

9:30 AM BREAK

10:00 AM +CM01.07.05
Chemical Control of Nanostructured Transition Metal Phosphides Electrocatalysts for Water Electrolysis Yury V. Kolenko; International Iberian Nanotechnology Laboratory, Braga, Portugal.

Hydrogen plays an important role in clean energy technology, complementing intermittent solar/wind power. Remarkably, lightweight hydrogen has the highest specific energy of any known non-nuclear fuel, and it can be used for both energy generation and storage purposes. More importantly, hydrogen is an environmentally friendly fuel, since only energy and water are the end products of the reaction between hydrogen and oxygen, giving rise to the emerging fuel cell technologies and devices. An interesting way to generate hydrogen is offered by water electrolysis, wherein water is simply decomposed to hydrogen and oxygen by applying a voltage bias. Notably, the water electrolysis is a kinetically controlled process characterized by slow charge transfer and insufficient chemical reaction rates, and in reality, a significantly higher overpotential than the standard potential of the water electrolysis (~1.23 V at 25 °C) needs to be applied to drive
the reaction. Therefore, electrocatalysts are used to facilitate water electrolysis by reducing the value of the applied overpotential to conduct cathodic water reduction, known as hydrogen evolution reaction, and anodic water oxidation, known as oxygen evolution reaction, which are the key half reactions of electrochemical water splitting.

Whereas the best electrocatalysts for water electrolysis are platinum group metals (PGMs), their main drawback is obvious: they are critical and expensive, thus limiting the viability of PGMs for widespread applications. Hence, the current research trend is aiming at searching for alternatives to PGMs. In this talk, I will first introduce transition metal phosphides as an emerging Earth-abundant class of electrocatalysts for water electrolysis, followed by our approaches in modeling, synthesis, chemical modification, and electrocatalytic understanding. I will then showcase our recent progress in using these electrocatalysts for water reduction and oxidation.

10:30 AM CM01.07.06 Laboratory-Based Hard X-Ray Photoelectron Spectrometer for the Study of Advanced and Complex Materials Anna Rapoutz1; Manfred Mascheck2; Christopher Liljenberg3; Kornelius Tetmner4; Benjamin Williamson4; David O. Scanlon5 and Paul Palmgreen2; Imperial College London, London, United Kingdom; 2Scienza Omicron, Taunusstein, Germany; 3Scienza Omicron, Uttarala, Sweden; 4University College London, London, United Kingdom.

The success of solid-state chemistry as a field is partly based upon the development and application of a range of highly advanced characterisation methods. Hard X-ray photoelectron spectroscopy (HAXPES) has traditionally found its application in the core topics of condensed matter physics, but the slowly growing number of beamlines worldwide has widened its appeal to other interest groups. HAXPES uses X-rays in the 2-10 keV range to excite photoelectrons, which are used to non-destructively study the chemical environment and electronic structure of materials. As its soft X-ray counterpart (SXPS or simply XPS) it delivers qualitative and quantitative information on elemental distributions, chemical states, and electronic structure.

In contrast to the very surface-sensitive XPS, HAXPES is much more bulk sensitive. This makes it applicable to bulk materials and structured samples, e.g. layered samples and heterostructures. In addition, its bulk sensitivity means that realistic samples can be investigated without the need of prior surface preparation. Furthermore, results can easily be correlated to a whole range of other bulk-sensitive characterisation results, and therefore to structural information and material properties. However, the number of existing HAXPES systems is very small and they are predominantly located at synchrotrons (approx. 20 beamlines worldwide) due to low photoionization cross sections necessitating high X-ray intensities, limiting their availability to users and applications.

This work presents a new laboratory-based instrument capable of delivering monochromated hard X-rays with an energy of 9.25 keV and a focused 30x45 μm² X-ray spot, giving excellent energy resolution of <0.5 eV. Systematic reference measurements are presented outlining the systems capability, including energy resolution, X-ray and signal intensity, and stability. Results from a rutile TiO₂ bulk sample show the wide range of possible signals that can be collected, such as shallow and deep core levels, Auger lines, and valence bands. The valence band measurements are benchmarked against theoretical results from density functional theory. Beyond pure bulk measurements a range of metal oxide multilayer structures, as are used in transistor and diode applications, is investigated to showcase the system’s ability to detect signals from buried layers and to analyse them for their local chemical states.

Ultimately, this spectrometer presents an alternative to synchrotron-based endstations and will help to expand the number and range of HAXPES experiments performed in the future. HAXPES is a cutting edge characterisation method and the advancement of this technique will tremendously increase the potential to study an ever increasing range of inorganic materials and beyond.

10:45 AM CM01.07.07 Synthesis, Crystal Structure and Electrochemical Properties of AVPO₄F (A = Li - Rb) Cathode Materials for Rechargeable Batteries Stanislav Fedotov; Skolkovo Institute of Science and Technology, Moscow, Russian Federation.

In contrast to oxides, polyanion compounds adopting sophisticated polyhedral structures with a variety of connectivity types and topologies provide a large playground for searching new cathode materials and tuning their electrochemical properties. [1, 2, 3] We recently designed and synthesized a novel series of vanadium-based AVPO₄F (A = Li, Na, K, Rb) cathode materials adopting the unique KTP-type (KTP) structure using different soft-chemistry approaches including hydrothermal and freeze-drying techniques. The peculiarities of the KTP-type “VPO₄F” framework enabled excellent rate capability particularly demonstrated in Li cells [4]. The material exhibited remarkable capacity retention maintaining more than 75% of the initial specific capacity in Li-ion cells at 40C and an average potential of 4.0 V vs Li/Li⁺. The structural evolution during Li de/intercalation was studied using in-situ synchrotron diffraction and ex-situ electron tomography. The material was found to undergo a sequence of phase transformations with the change of a non-centrosymmetric space group to a centrosymmetric one.

The materials also support reversible intercalation of Na⁺, K⁺ and even Rb⁺ ions maintaining the host structure. The observed electrochemical behaviour and ion transport properties were quite different for Li⁺, Na⁺, K⁺ and Rb⁺ ions. Alkalii ion diffusion coefficients measured by PITT were found the lowest for Li⁺ (10⁻¹⁰ – 10⁻¹⁲ cm²/s) and highest for K⁺ (10⁻¹⁴ – 10⁻¹⁵ cm²/s). [5] Moreover, the full de/intercalation of K⁺ in KVPO₄F occurs at the highest potentials comparing to Li⁺, Na⁺ and Rb⁺ exceeding 4.6 V vs K/K⁺, which states KVPO₄F as the most high-voltage cathode material for K-ion batteries studied so far. DFT studies revealed extremely low energy barriers for K⁺ and Rb⁺ migration of less than 0.2 eV along the c-axis, which are in accordance with experimentally observed fast ion transport properties.

Thus, the KTP-type “VPO₄F” framework that exhibits an ability to de/intercalate four types of alkalii ions opens up new opportunities in designing polyanion-based cathodes for metal-ion batteries. We will focus on our recent activities on KTP-type fluoride-phosphates considered as promising cathode materials for metal-ion rechargeable batteries.

References:

11:00 AM CM01.07.08 Structural and Physical Properties of Novel Double Perovskites, BaLaBO₆, Andrew Bowser and Corey Thompson; Purdue University, West Lafayette, Indiana, United States.

Double perovskite oxides, A₂BB'O₆ and AA’BB’O₆, are a well-studied set of compounds in solid state chemistry. Their importance in both fundamental
and technological research is mainly due to the wide variety of properties they exhibit, and the ability to incorporate nearly any element into their structure. The $\text{Ba}_2\text{BO}_6\text{O}_{10}$ compounds have been underexplored until recently, with only limited structural data reported. Interestingly, according to current literature, several of these compounds have been reported to adopt either a hexagonal ($P6_3/mmc$ or $P-3m1$) or cubic ($Pm-3m$) structure, dependent on reaction conditions. Recently, magnetic and physical property studies upon hexagonal-$\text{Ba}_2\text{Fe}_{12-8x}\text{O}_{36-8x}\text{O}_x$, synthesized under ambient solid-state conditions have revealed ferrimagnetic behavior with a magnetic ordering temperature of ca. 370 K. Whereas, cubic-$\text{Ba}_2\text{NiO}_3\text{O}_6$, synthesized under high-pressure show properties of a Dirac-Mott insulator with a magnetic ordering temperature at 100 K. In both these cases, the properties observed can be traced to 3d5d interactions within the B-site sublattice. We have recently synthesized several novel double perovskite compounds, and their structure and physical properties will be presented.

11:15 AM CM01.07.09
Local Atomic Rearrangement Around the Superconducting CuO$_2$ Planes Upon Oxidation in the M-1212 Cuprates (M <> Fe, Mo & W) Miguel Angel Alario-Franco, Sara Lopez Paz, Xabier Martinez de Irujo and Emilio Moran-Miguelz; Facultad de Química, Universidad Complutense, Madrid, Spain.

Superconductivity in cuprates is achieved when holes are doped to an antiferromagnetic Mott insulating parent compound [1]. However, not only a high concentration of holes is required but also an effective charge transfer process from the Charge Reservoir Layer to the superconducting planes [2]. As a result, the critical temperature (Tc) is very sensitive to subtle changes in both local structure and charge distribution between the planes and the charge reservoir block [3].

The M-1212 phases, resulting from total or partial substitution of copper in the chains in the YBCO model compound by other transition metals, are suitable candidates in studying this charge transfer process [4, 5]. In this communication we will present the effect of iron, molybdenum and tungsten substitutions, resulting in Fe-1212, Mo-1212 & W-1212 phases with $\text{FeSr}_2\text{YCu}_2\text{O}_y$, $\text{MoSr}_2\text{YCu}_2\text{O}_y$ and $\text{WSr}_2\text{YCu}_2\text{O}_y$ compositions. We have studied the subtle influence of charge balance and compositional order/disorder in both the anion and cation sub-lattices. Besides, we have explored the local atomic rearrangement around the superconducting CuO$_2$ planes as a function of the oxidation treatment. The ensemble of these results will be presented and discussed.

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References

11:30 AM CM01.07.10

Among various semiconductor electrodes (photoelectrodes) that have been investigated for solar fuel production, oxide-based photoelectrodes have the possibility of significantly lowering the materials processing costs while also being more stable in aqueous media. However, oxide-based photoelectrodes typically suffer from low carrier conductivity and their photon-to-current conversion efficiencies have been considerably lower than their theoretically expected efficiencies based on their bandgaps. In this presentation, we discuss charge transport mechanisms in oxide-based photoelectrodes (e.g. small polaron hopping and spin polaron hopping) and present strategies to improve their carrier conductivities. A few selected photoelectrode systems that will be discussed in this presentation include n-type BiVO$_4$, p-type CuO, and p-type LaFeO$_3$. BiVO$_4$ has emerged as one of the most promising photoanodes in the field of photoelectrochemical water splitting, and its ideal bandgap and band edge positions to perform overall solar water splitting. Investigation of these photoelectrode systems will provide new understanding and strategies to improve the photoelectrochemical properties of oxide-based photoelectrodes.

SESSION CM01.08: Advances in Magnetism
Session Chairs: Simon Clarke and Corey Thompson
Wednesday Afternoon, November 28, 2018
Hynes, Level 2, Room 203

1:30 PM CM01.08.01
Exotic Magnetic Orders in Novel Two-Dimensional Manganese Vanadate Systems Vasile O. Garlea; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The structural versatility of the tetrahedral vanadate (VO$_4$)$^{3-}$ bridging group provides the opportunity to systematically examine a wide range of low-dimensional magnetic systems with a broad assortment of spin values. The structural and magnetic properties of several novel layered magnetically frustrated manganese vanadate systems will be discussed. Magnetic lattices with mixed corner-sharing and edge-sharing triangular units have recently been found in $\text{K}_{2}\text{Mn}(\text{VO}_4)\text{O}_2\text{OH}_2$, $\text{Mn}_5\text{(VO}_4)\text{O}_2\text{(OH}_4$ and $\text{Mn}_5\text{V}_8\text{O}_{16}$. The arrangement of triangular $[\text{Mn}_3\text{O}_4]$ building blocks in $\text{K}_2\text{Mn}(\text{VO}_4)\text{O}_2\text{OH}_2$ create a Kagome strip lattice. $\text{Mn}_5(\text{VO}_4)\text{O}_2\text{OH}_4$ contains two unique triangular $[\text{Mn}_3\text{O}_4]$ units formed by the presence of the additional Mn atom, such that every other row of hexagons has an additional Mn atom in the center of each hexagon creating two-dimensional striped triangular lattices. The structure of $\text{Mn}_5\text{V}_8\text{O}_{16}$ differs from the other two structures, by containing Mn in two valence states $2^+$ and $3^+$ distributed over two types of magnetic layers that are alternately stacked in the crystal structure. One layer contains Mn$^{2+}$ in a Kagome strip lattice and the other contained a mixture of Mn$^{2+}$ and Mn$^{3+}$ that form a triangular lattice. For all these systems, neutron diffraction measurements revealed the onset of very complex antiferromagnetic orderings, while inelastic
data confirmed the strong two-dimensionality of the magnetic interactions. Experimental data provides evidence of magnetic ground-states characterized by multiple ordering vectors, coexisting short-range and long-range orders, or incommensurate spin structures. K2Mn3V4O24CO3 is another interesting vanadate system that contains alternately stacked triangular and honeycomb magnetic layers that act as nearly independent magnetic sublattices. This compound exhibits a complex magnetic phase diagram that includes three phase transitions associated with sequential long range magnetic ordering of the different sublattices. Applied magnetic fields induce exotic ordered phases characterized by various spin-stacking sequences of triangular layers that yield bilayer, three-layer or four-layer magnetic superstructures. Because the observed magnetic superstructures cannot be explained in the frame of any existing theories based only on nearest-neighbor interlayer coupling, they compel a closer look at effective second-nearest-neighbor interactions, mediated by fluctuations of the magnetic moments in the honeycomb sublattice, that become crucial at finite-temperatures and intermediate fields.

2:00 PM CM01.08.02
Understanding Metallicity and Magnetism in \( AB_4Q_3 \) Defect Spinel Systems

**Emily C. Schueller**, 1, 2, Julia Zuo, 1, 2, Stephen Wilson 1, 2 and Ram Seshadri 1, 2

1 Materials, University of California, Santa Barbara, Santa Barbara, California, United States; 2 Materials Research Laboratory, University of California, Santa Barbara, Santa Barbara, California, United States; 3 Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California, United States.

The family of \( AB_4Q_3 \) compounds, where \( A \) is Al, Ga, or Ge, \( B \) is an early transition metal like V, Mo, or Ta, and \( Q \) is a chalcogen like S or Se have been studied since the 1970s.1 They crystallize at room temperature in the \( F\bar{4}3m \) defect spinel structure and display a fascinating array of magnetic and electronic properties. Some materials in this family undergo metal-insulator transitions and others host exotic magnetic spin textures such as skyrmions.2,3 These properties can be related to clustering of the \( B \)-site atom, crystalline anisotropy, and the electronic correlations present. We study two of these materials, GaV\(_4\)Se\(_8\) and GaMo\(_4\)Se\(_8\), using a combination of experimental techniques including high-resolution X-ray diffraction and magnetic measurements, and density functional theory calculations of structural, electronic, and magnetic ground states. We examine the interplay between electronic structure, crystal structure, and magnetic/electronic properties in these systems and develop insights into chemical tuning to optimize functionality.

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References:

2:15 PM CM01.08.03
Predictive Many-Body Theory for Formation and Migration of Oxygen Defects in Highly-Correlated Transition-Metal-Oxide Materials

Juan A. Santana-Palacio1, 2, Kayahan Saritas1, Rohan Mishra1, 2, Albina Borisevich1, Sokrates Pantelides1, 2, Paul Kent1 and Fernando A. Reboredo1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Department of Chemistry, University of Puerto Rico at Cayey, Cayey, Puerto Rico, United States; 

Strong electronic correlations, interfaces, defects, and disorder each individually challenge the theoretical methods for predictions of materials properties. These challenges are all simultaneously present in complex transition-metal-oxides (TMOs). TMO’s interfaces and superlattices are known to exhibit unique and unusual properties caused by multiple coupled degrees of freedom and strong electronic correlations. The computational treatment of TMOs remains an outstanding challenge due to the multivalent character of the metal species and the predominant role played by many-body effects (electronic correlations). This challenge is increased at TMO interfaces and superlattices, where the transition-metal ion valence varies sharply. Computational costs due to the TMO oxide chemistry make it difficult to test old conventional quantum chemistry methods. On the other hand, the commonly used Density Functional Theory (DFT) approximations, e.g., Local Density (LDA) and semilocal Generalized Gradient (GGA), are not sufficiently accurate and transferable to account for all experimental observations without adjustable parameters. We show [1] that a fundamentally different approach, ab initio diffusion Monte Carlo (DMC), is now a practical solution of the many-electron problem for the full complexity of these systems. Within a single nonempirical theoretical approach, we unambiguously establish the site-specific stability of oxygen vacancies in the (LaFeO3)(2)/(SrFeO3) superlattice, accounting for experimental data, and predict their migration pathways. In addition, we will describe a number DMC calculations which are currently capable of playing a major role in the elucidation of many-body phenomena complex oxides previously out of reach of theories without adjustable parameters.


2:30 PM BREAK

3:30 PM *CM01.08.04
Muon Spin Rotation/Relaxation Studies of Geometrically Frustrated Magnetism

Graeme Luke1, 2; 1Physics & Astronomy, McMaster University, Hamilton, Ontario, Canada; 2TRIUMF, Vancouver, British Columbia, Canada.

Geometrical frustration provides an exciting route to generating new exotic magnetic ground states with unconventional properties and excitations. Examples of these ground states include classical and quantum spin liquids and spin icies. Excitations in these systems include a wide variety of emergent quasiparticles with spin charge separation (spinons and holons), magnetic monopoles and Majorana fermions (which their own anti-particles). Identifying and understanding this wide range of phenomena requires a variety of experimental tools. Muon spin relaxation/rotation provides a powerful microscopic magnetic technique to probe materials. I will describe our recent work on pyrochlores such as Dy2Ti2O7 and Yb2Ti2O7, whose corner-sharing tetrahedral lattice is an ideal motif for the study of frustration, as well as our search for a spin liquid state in ErMgGaO4 which has a stacked triangular lattice.

4:00 PM CM01.08.05
Strain-Enhanced Topotactic Hydrogen Substitution in SrTiO3

Dai Kutsuzawa1, Yasushi Hirose1, Akira Chikamatsu1, Shoichiro Nakao1, Yumi Watanuki2, Isao Harayama2, Daichihiro Sekiba3 and Tetsuya Hasegawa2; 1The University of Tokyo, Tokyo, Japan; 2University of Tsukuba, Ibaraki, Japan.

Recently, transition metal oxyhydrides have attracted attention due to the interesting properties originating from specific features of H-. For example, high
lability of $H^-$ in BaTiO$_3$H, enables exchange of anion species such as H$^-$/N$_3^-$, which leads to its catalytic activity for ammonia synthesis from N$_2$ molecule [1]. Heavy electron doping achieved by hydrogen substitution for oxygen in ATO$_3$ (A = Ca, Sr, Ba and Eu) indicates significant potential of H$^-$ as n-type dopant for oxides [2].

Thus far, transition metal oxyhydrides have been prepared by topotactic hydrogen substitution of precursor oxide using metal hydrides or high temperature high pressure synthesis. The former method is applicable to samples in both fine powder and epitaxial thin film forms, being suitable for investigating the intrinsic electrical transport properties of oxyhydrides. Moreover, it is expected that use of epitaxial thin films as precursors for topotactic hydrogen substitution can modify the physical and/or chemical properties of oxyhydrides due to epitaxy-related effects, such as biaxial strain from the substrate. However, no attempts have been made to conduct a research of the strain effects on the chemical composition and physical properties of epitaxial oxyhydrides thin films synthesized by topotactic hydrogen substitution.

In this study, we synthesized SrTiO$_3$H, epitaxial thin films on various substrates with different lattice constants and evaluated their anion compositions and electrical transport properties. At first, SrTiO$_3$ epitaxial thin films as precursors were prepared by a pulsed laser deposition method. Then, SrTiO$_3$H, epitaxial thin films were synthesized via low temperature topotactic hydrogen substitution of the precursor films using CaH$_2$. The hydrogen content $x$ in the SrTiO$_3$H thin film was increased from 0.56 to 0.87 by applying tensile strain, while $x$ was suppressed to 0.16 by compressive strain probably owing to enhanced oxygen diffusion. Furthermore, the heavily hydrogen substituted film showed a negative temperature coefficient of resistivity, being a characteristic of an insulator, is contrary to lightly substituted films indicating metallic behavior. These results demonstrate the potential of “strain-engineering” as an approach to modify the chemical and physical properties of transition metal oxyhydrides.

Reference


4:15 PM CM01.08.06

Temperature-Dependent Elastic and Inelastic Neutron Scatterings of Mullite-Type PbMBO$_4$ (M = Fe, Mn) Compounds Manoel Murshed$^{1,2}$, Mathias Gogolina$^{1,2}$, C. M. Naveen Kumar$^2$, Ashfia Huq$^1$, Michael M. Koza$^1$ and Thorsten M. Gesing$^{1,2}$; 1Institute of Inorganic Chemistry and Crystallography, University of Bremen, Bremen, Germany; 2MAPEX Center for Materials and Processes, University of Bremen, Bremen, Germany; 3Chemical and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 4Jülich Centre for Neutron Science (JCNS), Forschungszentrum Jülich GmbH, Outstation at SNS, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 5Institut Laue-Langevin, Grenoble, France.

The Mullite-type PbMBO$_4$ (M = Fe, Mn) [1,2] compounds have been considered as an excellent playground to understand the Goodenough–Kanamori–Anderson spin rules between the antiferromagnetic (AFM) and ferromagnetic (FM) microscopic features. In the Heisenberg 1D uniform chain model, PbFeBO$_4$ and PbMnBO$_4$ are AFM ($T_{N} = 125 ~K$ and 280 K) and FM ($T_{C} = 31 ~K$), respectively. Interestingly, the magnetic susceptibility anisotropy was observed even in the paramagnetic regime of PbFeBO$_4$ [3]. Neutron elastic scattering data showed axial negative thermal expansion both in the paramagnetic and as magnetic regions. The lattice thermal expansion was modeled using the Debye-Einstein-Anharmonicity model [2]. Debye temperatures extracted from two different approaches is explained in terms of phonon density of states (PDOS). The inelastic neutron scatterings spectra were collected both in the Stokes and anti-Stokes sides. The temperature-dependent evolutions of the respective dynamic structure factor $S(Q,E)$ reveals considerable changes of the phonon dynamics across the $T_{N}$. The INS profile of PbFeBO$_4$ also shows steep magnon excitations up to $E=10 ~meV$ at the momentum transfer of $q=0.11(1), 0.16(1)$ and 0.27(1) nm$^{-1}$, which are corresponding to acoustic spin-waves centered at (010), (111) and (113) ABM Bragg reflections, respectively. An AFM spin wave velocity at $d = 0.57(1) ~nm$ is estimated to be $2.7(1) ~meV ~nm$. Analysis of some optical phonon maxima shed light to understand the axial negative thermal expansion of the materials. $ab initio$ dynamical calculations of PDOS enables microscopic interpretations of the observed data. The calculations well reproduce the observed vibrational features and provide also the partial atomic vibrational components.

References:


4:30 PM CM01.08.07

Nitrile Tuning of Transition Metal Perovskites Amparo Fuertes; Institute of Materials Science of Barcelona (ICMAB-CSIC), Bellaterra, Spain.

Substitution of nitrile for oxo anions is an important method for tuning materials properties in transition metal perovskites, for example, Ca$_{1-x}$La$_x$TaO$_3$, NiO colour, LaTiO$_3$N photocatalytic activity, BaTiO$_3$-$N_{2/3}$ ferroelectrics, BaTaO$_4$N-$Sr$TaO$_3$N dielectrics, and EuNbO$_3$, EuWO$_1+x$N$_{2-x}$ colossal magnetoresistance. (1) This talk will present recent research of selected perovskite oxynitrides focusing on the relationships between the synthesis conditions, the oxidation states of the metals, the nitrogen contents, the ordering of anions (2,3) and cations, and the physical properties. Simple and double transition metal perovskite oxynitrides with antiferromagnetic and photocatalytic properties have been investigated. RCoO$_x$Ni$_y$(R=rare earth) with nitrogen contents up to x=0.59 are prepared by ammonolysis of RCoO$_2$ precursors. (4) Hole doping through O$^2-/N^3-$ substitution in antiferromagnetic RCrO$_3$ decreases $T_N$ less drastically than R$^{3+/2+}$ (A=alkaline earth metal) cation substitutions because of the greater covalency of metal-nitride bonds. (3) Photochemical ammonolysis of Sr$_n$FeWO$_6$ leads to salt-cation ordered Sr$_n$Fe$_{2n-1}$N$_2$O$_{4n-1}$ which is antiferromagnetic with $T_N = 13 ~K$ and represents the first example of a double perovskite oxynitride with both high cation order and nitrogen content. (5) The new hafnium perovskite oxynitrides HfO$_2$N with GdFeO$_3$-type structure are prepared by solid state reaction between R$_2$O$_3$ and Hf$_2$O$_3$ which is antiferromagnetic under $T_N < 30 ~K$. They are semiconductors with band gaps of 3.35, 3.40 and 2.85 eV and relative dielectric constants of 30, 16 and 28 for R=La, Nd and Sm respectively, (6) and show photocatalytic activity in water oxidation and reduction under visible light irradiation.

References

CM01.09.01

**Growth Mechanisms of α-FeO₃ Nanocubes and Their Influence on Magnetic Properties**

Gabriel D. Rocha¹, Marcelo A. Martinho², Marco A. Cordeiro³ and Edson R. Leite⁴; ¹Materials Engineering Department, UFSCar, São Carlos, Brazil; ²Chemistry Department, UFSCar, São Carlos, Brazil; ³LNNano, Campinas, Brazil.

One of the main branches of nanoscience deals with the tailoring of nanoparticles (NPs) shape (e.g., spheres, octahedral, cuboctahedral, cubic structures) due to the possibility of tuning several properties as electrical, optical and magnetic. Likewise, hematite (α-Fe₂O₃) NPs have a series of fascinating polyhedral structures, which magnetic properties are ruled by NP shape and size, finding fundamental applications in many fields including ferrofluid technology, biomedicine, catalysis and magnetic storage. Accordingly, in this study we provide some insights into the growth process of hematite NCs in the colloidal state, as well as the parameters that affect crystal growth and morphology, which are essential for designing new hematite-based nanostructured functional materials. Many shape and size oleate-capped α-Fe₂O₃ NPs were synthesized by hydrothermal route under microwave heating. By fine-tuning the amount of surfactant (sodium oleate) and reaction time (5-180 min), three main structures: spheres, polyhedral, diamond and cubic-like shapes were identified by high-resolution transmission electron microscopy (HRTEM). According to HRTEM observations, the proposed mechanism for the formation of cubic-like NPs from spheres is based on a three-step growth process, with the initial formation of a seed or nucleus, and then sphere particles (7-17 nm). With the progress of the synthesis, those spheres grow under the oleate groups action and polyhedral NPs are obtained (~12 nm). The second part of the growth mechanism is the oriented attachment of polyhedral NPs, mainly by the coupling of (220) exposed facets, resulting in diamond-like shapes (25-30 nm). Although it was possible to identify many oriented attachments in progress by HRTEM, these structures were only found in a small-time gap (20-25 min of synthesis). Finally, the diamond-like NPs reshape, resulting in the formation of a cubic shape, with small size increasing from monomers in solution. According to the particle shape evolution, we also investigated the dependence of magnetic properties by using a superconducting quantum interference device (SQUID) that reveled the role of NPs shape and size in the magnetic properties of the α-Fe₂O₃ NPs. This knowledge provides fundamental improvements in chemical preparation protocols for the reproducible production of NCs with specific properties and high yields.

CM01.09.02

**Investigation of the Potentiality of Antimony Oxide as Impurity in Polycrystalline Hematite and Its Influence in Electrical Properties**

Fabricio B. Destro¹, Cipriano Gozzo², Mario R. Soares³ and Edson R. Leite⁴; ¹Department of Materials Engineering, Federal University of Sao Carlos (UFSCar), Sao Carlos, Brazil; ²Department of Chemistry, Federal University of Sao Carlos (UFSCar), Sao Carlos, Brazil; ³Brazilian Nanotechnology National Laboratory (LNNANO), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, Brazil.

Photoelectrochemical cells are a feasible way of harvesting solar energy by converting it into chemical fuels. One form of producing photocathodes is through the use of semiconductor oxides. Hematite (α-Fe₂O₃) - an n-type semiconductor, non-toxic, with low bandgap and chemically stable – is considered the most promising material as a photoanode. However, it presents huge challenges such as poor electrical conductivity. To overcome this, doping is widely studied, with metalloid elements such as Si, Ge and Sn. Antimony (Sb), another metalloid element and neighbor to Sn in the periodic table, can be considered a potential candidate as an impurity for the hematite structure. The possibility of different oxidation states (between +3 and +5) could result in a suitable dopant element. We perform an investigation in polycrystalline ceramic of hematite doped with Sn₂O₃ in different concentrations, up to 5% w/w, sintered at two different temperatures, 1100 and 1300 °C. Preliminary results show relative density is around 98%, independent of the sintering temperature. To evaluate densities, we used Archimedès’s method. XRD data show that for samples sintered at 1100 °C, only one phase is found until 1% w/w. A secondary phase of FeSb₂O₆ (PDF#74-4558) was indexed from 2% w/w on. For the samples sintered at 1300 °C, the solubility was reached until 4% w/w, and the 5% w/w concentration shows that the secondary phase was also indexed as FeSb₂O₆. SEM analysis show that average grain sizes are 2 μm for 1100 °C and 30 μm for 1300 °C. Electrical measurements were performed after the electroceramics were heat treated in N₂ atmosphere at 850 °C by 20 minutes. The results show that for 1100 °C, resistivity reaches 10¹¹ Ω cm, while for the higher temperature, it lowers by 2 orders of magnitude. These results suggest that possibly the reaction between the precursor oxides is facilitated at higher temperatures, which favor the electrical properties of hematite. The resistivities values found are comparable with those obtained with Sn-doped hematite, therefore showing the potential of Sb as a dopant.

CM01.09.03

**Solventless Synthesis of Copper Antimony Sulfide Materials from Reactive Melts of Metal Xanthate Precursors**

Tahani Alqahtani, David J. Lewis and Paul O'Brien; University of Manchester, Manchester, United Kingdom.

In recent years, ternary copper antimony sulfides show considerable promise as alternative absorber materials for cost-efficient and scalable photovoltaics due to their high absorption coefficients, optimum band gap and consist of cheap, low-toxicity and earth-abundant elements. The Cu-Sb-S system exist in four ternary phases, which are Cu₄SbS₄ (chalcostibite), Cu₅Sb₂S₈ (tetrahedrite), Cu₆SbS₄ (skeletonite) and Cu₃SbS₄ (fematinite). Chalcostibite has been considered as an alternative absorber to the Cu₃SbS₄ because of the comparable optical properties required for solar absorber materials, with the advantage that antimony is earth-abundant element and less expensive than indium. Tetrahedrite has been recently attracted a huge amount of attention due to its potential for energy conversion applications. It is highly suitable for thermoelectric materials because of its unique feature in its crystal structure as it has naturally low lattice thermal conductivity. Furthermore, it is an attractive candidate for solar absorber materials as it displays strong absorption in wide spectral range. Partially substituting on the copper, antimony and chalcogen sites has been an active area of research to optimize the thermoelectric properties. These dopants could lead to additional and interesting optical and magnetic properties.

In this work, we report a facile simple solvent-less route for the preparation of chalcostibite and tetrahedrite nanostructure phases using metal xanthes. One feature of this approach is the absence of a solvent, which gives the melt route a potential environmental and economic advantage as compared to other solution-phase routes. The use of metal xanthes is advantageous because they already contain the sulfur required for the preparation of the metal sulfide. Another important advantage of metal xanthes is that they have low decomposition temperature and the by-products of the decomposition are volatile, allowing the clean formation of Cu-Sb-S materials using mild temperature without impurities. The compositions of the obtained materials were adjusted by varying the molar ratio of the copper and antimony xanthate precursors. In addition, zinc and bismuth xanthes were also used for the preparation of the Zn and Bi-doped tetrahedrite. The results obtained from XRD indicate that the solventless pyrolysis of the metal xanthes is advantageous in that it has demonstrated successful formation of the single-phase chalcostibite and tetrahedrite of high purity in short amount of time. Furthermore, incorporation of dopants into the tetrahedrite crystal structure has shown to form the pure phase of tetrahedrite. As the dopant content increase in the samples, the diffraction peaks gradually shifted toward lower angle. The lattice parameter increases linearly with increasing the dopants content in the samples. In addition, the morphology,
Magnetic Properties of Novel Tellurides, Tl₁₋ₓAₓFe₃Te₃

CM01.09.05
Multimodal Chemical and Functional Imaging of Materials via Combined AFM/ToF-SIMS Platform

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Polarization switching in ferroelectric materials underpins a broad gamut of applications ranging from random access memory, tunneling barriers, data storage, and ferroelectric ceramics. Classically, the polarization switches due to a co-existence of energetically equivalent crystallographic states, that can be altered with an external electric field. To stabilize polarization, charge discontinuity at surfaces and interfaces requires compensation, or screening, to avoid long-range electrostatic fields that destabilize the ferroelectric phase. Most studies consider polarization screening to be chemically inert; leaving the composition of the ferroelectric intact. However, analysis of extant ferroelectric phenomena suggests higher complexity. It is well known that multiple polarization switching cycles can accumulate damage at interfaces, dubbed “ferroelectric fatigue.” Typically, tens or hundreds of thousands switching events are required, and the exact mechanisms remain controversial. Furthermore, polarization-dependent photovoltaic effects in perovskites suggest that even under optimal screening conditions a considerable electric field remains in the material. Thus, switching is associated with high fields, which can chemically alter material composition.

Here we utilize multimodal approach combining time of flight secondary ion mass spectrometry (ToF-SIMS) with atomic force microscopy (AFM) to explore the structure property interplay of ferroelectrics during polarization switching in lead zirconate titanate (PZT, Pb(Zr₀.₅₂Ti₀.₄₈)O₃) thin films. Using this multimodal imaging platform, we demonstrated that chemical phenomena plays significant role in ferroelectric switching process. Specifically, we found that local ferroelectric switching by the AFM tip, significantly alters the chemical composition in the 3-nm-thick surface layer of the sample, forming reversible concentration wave, of Pb⁺ ions. Furthermore, investigations of the polarization cycling in the PZT sample with copper electrodes, showed penetration of the copper cations into the structure of PZT. This explains ferroelectric fatigue phenomenon, leading to decrease in spontaneous polarization with sample cycling.

Altogether, explored chemical phenomena associated with ferroelectric switching will enhance fundamental understanding of ferroelectric phenomena and aid in the practical application of ferroelectrics in devices.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility, and using instrumentation within ORNL’s Materials Characterization Core provided by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

CM01.09.09
Magnetic Properties of Novel Tellurides, Thₐ₋ₓAₓFe₃Te₃

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Materials with a pronounced magnetocaloric effect (MCE) are promising candidates for magnetic refrigeration technology. The intermetallic TlFe₃Te₃ phase has several characteristics that make it an ideal system to study. These include a moderate MCE at near room transition temperature (Tc = 220 K), low thermal and magnetic hysteresis, and a low dimensional structure consisting of pseudo-1D chains composed of iron telluride clusters. To become commercially feasible, replacement of thallium with non-toxic elements and a higher magnetic ordering temperature (>300 K) are desirable. Partial substitutions of earth-abundant alkali metals for thallium have been successful. These substitutions have a substantial effect on the magnetic properties, which can be tuned based on the choice of alkali metal. Their interesting structural and magnetic properties will be presented.

CM01.09.09
Study the Synthesis, Crystal Structure, Morphology and Magnetic Properties in the BaO-MgO-V₂O₅ and SmO₂-MgO-Sb₂O₃ Systems

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Our interest is to study the thermodynamic properties on two systems of oxide materials to reproduce the Sn₄(Sb₄Te₄)Ba₂V₄Mg₂O₁₀ and Sn₄(Sb₄Te₄)Ba₂V₄Mg₂O₁₀ supersolidors reported in the web site www.superconductors.org.

The two systems BaO-MgO-V₂O₅ and SmO₂-MgO-Sb₂O₃ were synthesized, by solid-state reaction at 880 C. It is observed the formation of ternary and binary phases after reaction. Powder X-ray diffraction (XRD) was used to identify those phases.

CM01.09.09
Thermal Analysis characterization was used to know on what range of temperatures the reaction could occur.

One way to study the thermodynamic properties is the comparison of reaction with the formation of a high-alumina (Mg₂O₃) crucible, because implies a slow cooling, with the reaction into a Platinum crucible cooled into an ice bath. When the cooling of the products is made into an ice bath (4 C) media, a different effect from the air (for the alumina crucible) in the formation of crystalline phases is observed, having a wider range of different crystalline phases in the case a high alumina crucible. The cooling velocity effect was observed in the x-ray diffractograms; for the products cooled in ice bath, some displacements of the experimental x-ray patterns related to the powder diffraction files (PDF) were observed, and in the case of the alumina crucible, results were aligned with PDF files. For the case of the platinum crucible, an isostructural compound related with Ba₂(VO₄)₂ structure was obtained; also, the formation of an isostructural solid solution (Sc₂(Sb₄O₈) in the planes: (110), (101), (200), (111), (210), (211), (220), (002) and (112), with rutile type structure. Due to the size of the cubic unit of Sc₂O₃ and SrO a cationic substitution of Sr by Sc ions forms the solid solution. Cooling rate had a great effect in the stability of the solid solution since when the samples were cooled into the high alumina crucibles this phase disappeared by the lack of conditions to its stability.

A magnetic characterization helped to know the behavior of the system, so the reaction products cooled into the ice bath were studied with an SQUID. The samples cooled into the ice bath were analyzed by Raman spectroscopy to know the oxidation states and the coordination number of the atoms involved in the solid solution.

A variation of composition for the system SmO₂-MgO-Sb₂O₃ was studied too, SnₓMg₃SbO₉. Two compositions were used, x = 0.15 and x = 0.20. XRD was performed to characterize the products and a thermal analysis.

Changes in weight were found during the reaction period. After XRD, a change in the oxidation state of Sb. An oxide phase formed between Sb and Mg ions was found, MgSb₁ₓOₓ, with other antimony oxide (Sb₂O₃), in both cases. The increase in weight is due to the change in the oxidation state of Sb and to an amount of oxygen entered to the system. Thermal analysis detected the total change in weight.

CM01.09.09
Temperature Dependence of the Ionic Conduction in the DyₓScₓTaO₃ (0 < x < 0.2) Solid Solution

Jesús E. Ortega, José Francisco Gómez; Universidad Nacional Autónoma de Mexico, Ciudad de Mexico, Mexico.

The defect fluorete related crystal structures poses a very wide variety of interesting properties, like structural and electronic [1], some compounds with this
crystal structure are ionic conductors. The recent interest in novel ionic conductor materials has been increased in recent years due to the development of new devices for e.g., applications like gas sensors or in electronic industry. The novel polycrystalline solid solution Dy₂₅Sc₂₅TaO₆ (0 ≤ x ≤ 0.15) was obtained by standard solid state reaction technique and single-phase compositions formation were confirmed by X-ray diffraction studies. Structural characterization of compounds was made using Rietveld refinements. The electrical measurements were carried out using complex impedance spectroscopy in a wide range of frequencies (102 – 107 Hz) in the 250 °C – 650 °C temperature range, also the electrical measurements were carried out in dc experiments to compare the data. The impedance spectra were modeled using equivalent circuits and the dc conductivity shows an Arrhenius-type behavior. The frequency dependence of the ac conductivity obeys the Jonscher universal power law. The results of the activation energy values obtained for the dc measurements and the behavior of the critical exponent show that the mechanism of electrical conduction is ionic and the charge carrier is the (O₂⁻) oxygen ion. Also, we have found two temperature regions of ionic conduction, the intrinsic and the extrinsic region, differentiate by a change in the activation energy and the critical exponent value.

References:

CM01.09.09
Effect of Cl on the Hydroxylated Cr₂O₃ Protective Layer of Stainless Steel
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Stainless steel are important materials for nuclear industry applications and is extensively used in light water reactor systems (LWR). The corrosion resistance of stainless steel is attributed to presence of chromium which segregates to the surface to form Cr₂O₃, a strong passive layer that provides corrosion protection for the material. Understanding the surface chemistries of these oxide layers in different conditions provides a critical insight into the stability of these protective layers. Chlorides and other aggressive ions are often part of the water chemistry surrounding stainless steel, but these ions can lead to a breakdown and loss of passivity. In this work, we used density functional theory (DFT) to examine the interactions of chlorine (Cl) and adsorbed water on α-Cr₂O₃ (0001) passive film to better understand these breakdown mechanisms. The interactions of Cl with different α-Cr₂O₃ (0001) terminations with and without implicit water solvent were calculated. The inclusion of implicit water increases the Cl-surface interactions on the Cr₂O₃ layer and also affects the order of the most to least stable configurations. The inclusion of implicit water increases the Cl-surface interactions on the Cr₂O₃ layer and also affects the order of the most to least stable configurations. These studies provide important insights into the initial steps of depassivation of Cr₂O₃, which can be used to design improved corrosion inhibitors and new alloys.

CM01.09.10
Sintering Behavior, Microstructure and Microwave Dielectric Properties of Novel Temperature Stable Li₃Mg₂NbO₆–TiO₂ Composite
Ceramics Gang Wang and Huaiwu Zhang; State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu, China.

A novel series of temperature stable Li₃Mg₂NbO₆–xTiO₂ ceramics were prepared by the conventional solid-state route. The effects of TiO₂ addition on the sintering behavior, phase composition, microstructure and microwave dielectric properties were investigated systematically. The dense microstructure could be obtained in low TiO₂ content (x<0.1) samples sintered at 1100 °C. The dielectric constant εr was attributed to the bulk density and TiO₂ content. The variation in Q × f values is related to the bulk density, and improved Q × f values could be obtained for Li₃Mg₂NbO₆–0.15TiO₂ ceramics. The quality factor (Q×f) has a maximum for x=0.1 and the temperature coefficient of resonant frequency (τf) value shifted towards positive direction with the increase of TiO₂ addition. Notably, Li₃Mg₂NbO₆–0.15TiO₂ ceramics sintered at 1100 °C possessed excellent microwave dielectric properties: εr=15, Q×f>74,000 GHz, τf=-3.4 ppm/°C, which made the ceramics as promising low loss and temperature stable candidates for millimeter-wave applications.

CM01.09.11
Ternary Vanadium Oxide Bronzes as a Palette for Imaging Metastable Cathode Materials with Improved Multivalent-Ion Storage Capacities
Justin L. Andrews and Sarbajit Banerjee; Texas A&M University, College Station, Texas, United States.

The discovery and investigation of metastable materials has only sparsely sampled the available design space. In this contribution, we explore a systematic approach to identifying metastable phases of interest in the vanadium-oxide system. In particular, we report on the successful stabilization of several novel polymorphs and discuss their subsequent utilization as cathode materials in Li- and multivalent-ion batteries. A detailed elucidation of structure-function relationships that underpin their much-improved performance over the thermodynamically stable bulk of the system, V₂O₅, has been performed based on structural characterization, elucidation of first-principles calculations of diffusion pathways. The first example, ζ-V₂O₅, can be topochemically stabilized from the ternary quasi-1D β-MₖV₂O₅ tunnel bronze and has been demonstrated to be far superior to its thermodynamically stable counterpart as a cathode material in both Li- and Mg-ion batteries. In particular, metastable ζ-V₂O₅ overcomes several challenges associated with α-V₂O₅, mitigating irreversible structural transitions and polaronic confinement effects that are a severe constraint on electrode applications of the thermodynamically stable phase. Mitigating these challenges allows for the unprecedented, fully reversible insertion of up to 3 Li⁺ per V₂O₅ as well as the highly reversible insertion of 0.33 Mg per V₂O₅ at moderately high operating voltages. In a second example, metastable γ-V₂O₅ can be stabilized from the ternary γ-LiV₂O₅ phase and shows promising initial results as a cathode in both aqueous and non-aqueous Mg- and Ca-ion batteries. The role of metastability is central to explaining the improved performance of these metastable polymorphs and thereby insight gleaned from a fundamental evaluation of the origins of this behavior provides a glimpse into the importance of structure-function relationships and crystal structure motifs as they relate to metastability, further establishing the potential use of metastable materials as synths for accessing underexplored compositional phase space.

CM01.09.12
Interfacial Oxidation and the Photoluminescence of InP-Based Core/Shell Quantum Dots
Mickael Tessier2, Edwin Baquero1, Dorian Dapon2, Valeremia Gregi2, Yannick Coppé1, Zeger Hens3, Celine Navrá1 and Fabien Delpech1; 1Laboratory of Physics and Chemistry of Nano-Objects, INSA Toulouse, Toulouse, France; 2Ghent University, Ghent, Belgium; 3Laboratoire de Chimie de Coordination, Toulouse, France.

CdSe based QDs have been intensively studied, however, due to their toxicity Cd-based materials are not acceptable for real-life applications. Indium phosphide (InP) based QDs represent the most advanced alternative without toxic heavy metals. Nevertheless, for industrial applications, the photoluminescence quantum yield (PLQY) and the emission linewidth (FWHM) of InP QDs have to be significantly improved. The analysis of InP
specifications shows that in contrast to their CdSe analogues, the InP QDs suffers from a high oxophilicity. This leads a strong tendency to oxidize and results in the formation of an amorphous phosphate layer at the surface of the InP QDs either during the synthesis or the shelling (often with ZnS). The role and the influence of this oxidation on the optical properties (PLQY and FWHM) is still a matter of controversy and the definitive answer has so far been precluded because of the lack synthesis method allowing the access to comparable oxide-free samples. In this presentation, we will describe our new approach to prepare oxide-free InP core and InP/ZnS core/shell QDs. Then, we will compare the structural (using XRD, TEM, MAS NMR) and the optical properties (UV-Vis and PL) of oxidized vs. oxide-free samples. The use of the same InP QDs core for the preparation of the samples provides fully comparable data and will thus allow unraveling for the first time the influence of phosphate at the core/shell interface.

CM01.09.13
Characterization of Crystalline Defects Studied by STEM-in-SEM Chunyang Zhang1, Jean-Claude Menard2, Julien Guyon1, Jean-Jacques Fundenberger1, Yudong Zhang1, Emmanuel Bouzy2, Cécile Hebert2 and Antoine Guittion1, 2, 3
1Université de Lorraine, CNRS, Arts et Métiers ParisTech, Metz, France; 2AHEAD Microscopy, Bois d'Arcy, France; 3Labex Damas, Université de Lorraine, Metz, France; 4EPFL-LSME, Lausanne, Switzerland.

Mechanical tests predicted by microstructural investigations provide engineers information to computationally predict the mechanical performance of components. Electron microscopy is one of the most well-known techniques for analyzing deformation features of materials allowing understanding their response to external solicitations [1]. Two kinds of electron microscopes are generally used and bring complementary information: at macro/meso-scopic scale, Scanning Electron Microscopy (SEM) and at micro/nano-scale, Transmission Electron Microscopy (TEM) [2,3]. Weak Beam Dark Field (WBDF) is a TEM technique allowing fine characterization of dislocations [4]. Such comprehensive dislocation studies at microscopic scale bring valuable information for understanding macroscopic mechanical response of materials [5].

Full characterization of dislocations is not only synonym of TEM experiments. SEM can access diffraction contrast with SEM information for understanding macroscopic mechanical response of materials [6].

References:

CM01.09.14
Computationally Aided Discovery of Layered Quinary Oxychalcogenide P-Type Transparent Conductors Benjamin A. Williamson1, 2, Gregory J. Limbourn3, Geoffrey Hyett1 and David O. Scanlon1, 2, 4
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Despite the major advances in n-type transparent conducting oxides (TCOs), the scarcity and performance of an equivalent p-type TCO has been a stumbling block for the opto-electronics industry for decades. Solid design principles such as the ‘chemical modulation of the valence band’, where the Cu 3d states mix with the Cu 3d states has been a more facile task allowing new materials such as [Cu5S6][Sr3Sc2O5] to surface as potential candidates. [Cu5S6][Sr3Sc2O5] has shown to have a wide optical band gap (~3.1eV) and has claims of high hole mobilities ~150 cm2 V-1 s-1 despite the relatively low carrier concentrations of 1017 cm-3[1][2]. Using chemical intuition for designer cation choice in the perovskite layer ([Sr3Sc2O5]), we have screened 24 variants of this structure type using high throughput density functional theory. Our calculations have uncovered 8 new thermodynamically stable semiconductors, with applications ranging from transparent conductors to photovoltaics. Our predictions have been validated by experimental synthesis of a new p-type TCO, with a conductivity superior to all known p-type TCOs.

References:

CM01.09.15
Carbon-Based Nanocomposites—2D Organic Materials within a 3D Lattice Ivryna Polishchuk; Materials Science and Engineering, Technion–Israel Institute of Technology, Haifa, Israel.

Composite materials usually exhibit the combined physical properties of their constituents. The result is a material that is superior to conventional monolithic materials. Advanced composites are used in a variety of industrial applications and therefore attract much scientific interest. Here we report on the formation of novel carbon-based nanocomposites via incorporation of graphene oxide (GO) into the crystal lattice of single crystals of calcite (1). Incorporation of a 2D organic material into single-crystal lattices has never before been reported. The resulting nanocomposites were characterized using state of the art characterization techniques such as high-resolution synchrotron powder X-ray diffraction, electron microscopy, aberration corrected high resolution transmission electron microscopy, fluorescence microscopy and nanoindentation tests.

Our results show that GO sheets can indeed become incorporated into calcite single crystalline hostst, allowing for the fabrication of graphene-based composite materials with enhanced properties. A detailed analysis reveals a layered distribution of GO sheets entrapped within the calcite host. Moreover, the optical and mechanical properties of the calcite host are altered when a carbon-based nanomaterial is introduced into its lattice. Carbon-based calcite single crystals exhibit new optical properties: in contrast to pure calcite, the hybrid crystals become fluorescent and are spectroscopically characterized by the presence of three lifetimes, one of which is considerably longer than that observed for bare GO in solution. Nanoindentation tests demonstrated that relative to pure calcite the composite GO:calcite crystals exhibit lower elastic modulus and higher hardness.

The results of this study demonstrate that the incorporation of a 2D material within a 3D crystal lattice is not only feasible but can also lead to the formation of hybrid crystals exhibiting novel properties.
Effects of Excess Electrons on the Structure of BiVO₄

Observations.

Formation energies, migration energy barriers and optical absorption peak position due to defects. The results are then used to explain the experimental substitutional configurations in different charge states, as well as the possible participation of oxygen and strontium vacancies. We present results for calculations based on density functional theory (DFT) we investigate possible mechanisms behind the PPC effect. We consider both interstitial and strontium titanate single crystals under sub band gap light excitation [M. C. Tarun, F. A. Selim, and M. D. McCluskey, Phys. Rev. Letters, 111, 187403 (2013)].

Synthesis, Characterization and Magnetic Behavior of α-Fe₂O₃ and α-Cr₂O₃ Nanoparticles and Their Composites with Graphite, Graphene and Graphene Oxide—Memory and Exchange Bias Effects

The role of hydrogen in the persistent photoconductivity in strontium titanate [Zhiqiang Zhang1 and Anderson Janotti1; 1Department of Physics and Astronomy, University of Delaware, Newark, Delaware, United States; 2Department of Materials Science and Engineering, University of Delaware, Newark, Delaware, United States.

Strontium titanate (SrTiO₃ or STO) is a wide band-gap material (3.25 eV at room temperature) with potential applications in oxide-based electronic devices, such as resistive switching memory. Extremely long persistent photoconductivity (PPC) at room temperature has been observed in annealed strontium titanate single crystals under sub band gap light excitation [M. C. Tarun, F. A. Selim, and M. D. McCluskey, Phys. Rev. Letters, 111, 187403 (2013)].

Annealing studies indicate that hydrogen impurities are well oxygen and strontium vacancies are involved in this effect. Using electronic structure calculations based on density functional theory (DFT) we investigate possible mechanisms behind the PPC effect. We consider both interstitial and substitutional configurations in different charge states, as well as the possible participation of oxygen and strontium vacancies. We present results for formation energies, migration energy barriers and optical absorption peak position due to defects. The results are then used to explain the experimental observations.
Among the available photoelectrochemical materials, BiVO$_4$ has huge potential to be utilized as a cheap and efficient material. Precisely knowing its band gap and understanding of electron transport in BiVO$_4$ are crucial for improving its performance, but both aspects of the material are debated, mainly due to its two extant different phases which have similar structures and are close in energy. We use density functional calculations with the PBE, meta-GGA SCAN, and hybrid functionals to study the stability of the different phases of BiVO$_4$, the effects of excess electrons in its conduction band, changes in local structure with excess electrons, and the possibility of carrier localization through electron-small polaron formation. The obtained results are compared to previous calculations and available experimental data.

CM01.09.20

Mayenite (12CaO·7Al$_2$O$_3$ or C12A7), a typical electrical insulator, can be converted into an electro-active functional material, i.e., mayenite electride (C12A7·2e$_-$), with a low work function, chemical inertness, and superconductivity at low temperatures. Mayenite electride has attracted extensive interests due to its application as inexpensive thermionic emission sources. However, pure mayenite electride exhibits brittleness, low fracture strength, and poor machinability. Thus, it is in demand to explore composite materials, such as a mayenite electride-titanium (Ti) composite, that will overcome these drawbacks while retaining the low work function characteristic of the mayenite electride. In the present work, C12A7·2e$_-$ - Ti composites (50:50 wt%) were synthesized in a single step via electric field assisted sintering (EFAS). The microstructures of the composite consist of some other calcium aluminate phases (e.g., Ca$_6$Al$_2$O$_9$) in addition to C12A7·2e$_-$ and Ti phases. The work function of the composite is approximated 2.5 eV evaluated by thermionic emission current measurement.

CM01.09.21
Structural and Magnetic Behavior in Rhenium-Based Double Perovskites Fang Yuan and Corey Thompson; Purdue University, West Lafayette, Indiana, United States.

Double perovskites, A$_2$B'Bo$_6$ have been intensively studied due to their interesting chemical and physical properties. The different B-site cations combination allows for a wide range of novel materials with unique magnetic behavior, from ferromagnets to spin glasses. Our current work is focused on the synthesis, structure, and magnetic properties of Re-based double perovskites, La$_3$B'ReO$_6$ (B' = Mg, Co, and Ni). All phases adopt the monoclinic P2$_1$/c crystal structure and are paramagnetic above room temperature. The Co- and Ni-analogs are ordered below 250 K, while the Mg-analog shows no magnetic phase transition down to 2 K. These results and a comparison to their ruthenium and osmium analogs will be presented.

CM01.09.22
Phase Transformation Kinetics and Apparent Symmetry Breaking in Pb$_5$CdS Core-Shell Nanocrystals Andrew Nelson and Richard Robinson; Materials Science and Engineering, Cornell University, Ithaca, New York, United States.

The quantification of atomic transport processes such as solid-state diffusion is important for controlling the processing, properties, and stability of solids in general. Measurements on bulk solids have provided a wealth of information on the nature of diffusing species (vacancies, interstitials, etc.) and their mobility, but it is uncertain to what extent these properties may be extrapolated to the nanoscale. The relative dearth of experimental methods for determining these properties in nanostructures complicates this question.

In this work we use the Pb$_5$-to-CdS cation exchange reaction to quantify the kinetics of ion diffusion in core-shell nanoparticles. Pb$_5$ nanocrystals (NCs) provide an ideal model system due to their well-established synthetic chemistry and their relatively simple structure, which facilitates structural interrogation. Using in-situ x-ray diffraction of 7 nm-diameter Pb$_5$ NCs as they undergo cation exchange to CdS, we have identified that three processes are important in the conversion of the NCs: an initial surface reaction (chemisorption of Cd) which imposes significant inhomogeneous strains on the underlying PbS; the exchange of the first underlying atomic layer(s) of the NC; and a diffusion-controlled growth of a thick zincblende-phase CdS shell. Quantitation of the kinetics of shell growth based on a shrinking-core model show that the activation energy for chemical diffusion of the rate-limited species lies in the range of 110 kJ mol$^{-1}$. This is in good agreement with prior measurements of the energy of interstitial self-diffusion in bulk CdS. This suggests that, at least for diffusion lengths longer than 1-2 nm, energies of motion for point defects in these simple ionic solids may not be greatly perturbed by the presence of a nearby surface, even under large chemical potential gradients.

Finally, we also discuss some structural peculiarities of these NCs. Previous suggestions of the existence of a metastable rocksalt CdS phase during shell formation are not supported by our experimental results, as we observe a monotonic change in the relative diffraction intensities to those consistent with underlying PbS@CdS NCs (loss of cubic structure) is evidenced by anomalous peak shifts in the diffraction patterns. We show this phenomenon does not indicate a true distortion of the unit cells, and account for it in terms of the kinematical diffraction theory supported by Debye scattering equation simulations. The interference of diffracted waves from octahedral Pb and tetrahedral Cd sublattices, which are displaced relative to each other by a non-integer multiple of their two extant different phases which have similar structures and are close in energy. We use density functional calculations with the PBE, meta-GGA SCAN, and hybrid functionals to study the stability of the different phases of BiVO$_4$, the effects of excess electrons in its conduction band, changes in local structure with excess electrons, and the possibility of carrier localization through electron-small polaron formation. The obtained results are compared to previous calculations and available experimental data.

CM01.09.23
Dynamic Structural Changes upon Hydrogenation and Dehydrogenation of Mg-Nanoparticles by In Situ Transmission Electron Microscopy and Electron Tomography Jochen A. Kammerer1, Xiaoyang Duan1,2, Frank Neubrech1,2, Rasmus Schroeder1,2, Laura Na Liu1,2, and Martin Pfannmuller1; 1Center for Advanced Materials, Heidelberg University, Heidelberg, Germany; 2Kirchhoff-Institute for Physics, Heidelberg University, Heidelberg, Germany; 3Max Planck Institute for Intelligent Systems, Stuttgart, Germany; 4Cryo Electron Microscopy, Heidelberg University Hospital, Heidelberg, Germany.

A theoretical capacity of 7.6 wt% hydrogen and favorable hydrogen desorption kinetics turn Mg-based nanomaterials into promising candidates for solid state hydrogen storage$. Furthermore, the excellent plasmonic properties of Mg and the transition to dielectric MgH$_2$ enable dynamic photonic applications$. Hydrogenation and dehydrogenation are accompanied by large volumetric expansion and shrinking lead to drastic structural changes and thus alter (de)hydrogenation kinetics and plasmonic properties. To be able to steer Mg behavior it is of utmost importance to understand these changes at nanoscale and below. Here, we use Mg nanoparticles (NPs) prepared by electron lithography, which are reproduceable in size and shape. This allows a meaningful comparison of pristine and dehydrogenated NPs depending on size. We demonstrate that radiation induced dehydrogenation and accompanied structural alterations lead to long-term reorganization of the Mg nanostructure. Time resolved electron energy loss spectroscopy and electron diffraction in the transmission electron microscope were used together with time and spatially resolved electron spectroscopic imaging to visualize the dynamic changes of MgH$_2$ and Mg from characteristic bulk and surface plasmon excitations. Furthermore, three-dimensional analysis by electron
tonography enables the detailed observation of voids that are formed during dehydrogenation. We investigated Mg NPs with diameters from 100 nm to 350 nm and 40 nm in thickness covered by 2 nm Ti and 3 nm of catalytic Pd. Volume expansion during hydrogenation and mechanical constrains in y/z-direction frequently cause twinning in the hydride state, especially in large NPs. Interestingly, the size of the twins clearly exceeds the grain size of pristine NPs. Shrinkage during dehydrogenation is accompanied by the formation of faceted cavities, visualized through the excitation of surface plasmons within the NPs. Surface energy reduction driven coarsening of the initially fine cavity network continues for several days at room temperature after complete dehydrogenation. Thereby, ripening of the network slows down in small NPs faster than in large ones. The transformation to Mg is observed to be rather governed by a large number of small nuclei with a low growth rate than a small number of fast growing nuclei. Our results contribute to understanding the influence of defect structures and orientation relationship between Mg and MgH$_2$ on the structure of the corresponding NPs. The presented methodology and results will enable defined experimental designs to reveal the dynamic processes in MgH$_2$ particles and related structures. Such insights will crucially influence the optimization of materials parameters that determine applications in nanophotonics and hydrogen storage.


**CM01.09.24**

**DFT+DMFT Study on the LaTiO3/LaAlO3 Superlattice—Magnetic Properties near Metal-Insulator Transition**

Jae-Hoon Sim$^1$, Hanpyo Lee$^2$ and Myung Joon Han$^3$; $^1$Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); $^2$School of General Studies, Kangwon National University, Samcheok-si, Korea (the Republic of).

The strongly correlated electron system is of central importance in the condensed matter physics. Among the correlated materials, transition-metal oxide superlattices are extensively studied, due to their novel characteristics and potential applications. The electronic and magnetic properties can be significantly different from their bulk counterpart, showing unexpected interface phenomena, e.g., magnetism, high-temperature superconductivity, correlation induced metal-insulator transition. Importantly, due to the strong couplings in TMO between the charge, spin, orbital, and lattice degrees of freedom, the material properties can be controlled by external perturbations, e.g., pressure, electric/magnetic field, or strain.

Motivated by the previous experiment and density functional theory-$U$ (DFT-$U$) results [1, 2], we have studied LaTiO$_3$-LaAlO$_3$ superlattice. From the previous theoretical study, it was found that the magnetic transition from the ferromagnetic-spin/antiferro-orbital order to the antiferromagnetic-spin/orbital ground state is induced by epitaxial strain. This magnetic transition is not observed in the bulk LaTiO$_3$ compound. While the standard DFT and DFT-$U$ are successful methods to describes real materials, correlated materials are not properly treated with this method, especially near the transition point. To overcome the technical limitation, we performed dynamical mean-field theory calculations combined with the density functional theory, which is one of the successful approaches to study these systems. Under epitaxial tensile strain, we observed unexpected insulator-to-metal transition, followed by magnetic transition [3]. Our findings demonstrate that not only magnetic but transport properties can be controlled by strain. We also present the implemented DFT+DMFT method based on the non-orthogonal pseudo-atomic orbitals (PAOs) basis DFT code, OpenMX [4]. Newly developed methods for analytic continuation, so-called maximum quantum entropy method [5], is applied to obtain resulting spectral functions.

**References**


**CM01.09.25**

Highly-Ordered Hollow Nanochanneled-Silica Nanospheres Prepared Using Sacrificial Copolymer Nanospheres

Yong Ku Kwon, Hyun Jun Lim, Seho Kwon, Minkee Lee and Tae-Yang Jeong; Inha Univ, Incheon, Korea (the Republic of).

Monodisperse hollow mesoporous silica nanospheres were synthesized based on the cationic colloidal polymeric nanospheres. The nanospheres were prepared by the surfactant-free emulsion copolymerization of styrene and butyl acrylate in the presence of a cationic monomer, methacryloxyethyl trimethyl ammonium chloride using azoisobutyrimidodine hydrochloride as an initiator. The charged polystyrene nanospheres were dispersed in water and mixed with cetyltrimethylammonium bromide and ammonium hydroxide in ethanol. Tetraethylorthosilicate as a negatively charged silica precursor was then added dropwise to achieve rapid hydrolysis onto the cationic surfaces of colloidal particles and allow mesoscopic ordering of the co-self-assembly template, resulting in monodisperse hollow mesoporous nanospheres. These nanospheres were characterized by transmission electron microscopy, scanning electron microscopy, X-ray diffraction.

**CM01.09.26**

Synthesis, Optical and Structural Properties of Copper Sulfide, Cadmium Sulfide and Lead Sulfide Nanocrystals for Use in Quantum Dot Sensitized Solar Cells

Peter A. Ajibade; University of KwaZulu-Natal, Pietermaritzburg, South Africa.

Quantum dot sensitized solar cells (QDSSC’s) have attracted numerous research interest in the past decades as alternative to silicon based photovoltaic devices. It has emerged as promising agent in solar energy conversion due to its size-dependent optoelectronic characteristics, facile and low cost fabrication techniques. Their tunable bandgaps, high extinction coefficients, multiple exciton generation effect and large intrinsic makes QDSSC’s distinctive solar cells. In this paper, copper(I), cadmium(II) and lead(II) diiodocarbamate complexes were synthesized and characterized by elemental analysis, thermal gravimetric analysis, mass spectrometry, $^{1}H$ and $^{13}C$-NMR spectroscopy. The complexes were used as single source precursors to prepare oleyamine, TOPO and HDA capped quantum dots at three different temperatures. The structural properties of the quantum dots were established using FeSEM, HRTEM, FTIR, EDS and XRD. Absorption and photoluminescence spectroscopy was used to study the optical properties of the as prepared quantum dots. HRTEM images shows quantum dots with particle size in the range 4–9 nm. The potential of the quantum dots as sensitizers in solar cells fabrication are being evaluated.

**References**

Computational Discovery of Novel Structural and Functional Heusler Compounds Christopher Wolverton; Northwestern University, Evanston, Illinois, United States.

Heusler compounds are being widely studied for their potential usage in spintronics, shape-memory devices, superconductors, thermoelectrics, topological insulators, etc. The crystal structure and its variants are ubiquitous, with more than 1000 Heusler compounds being reported. However, the phase space for possible Heusler compounds is orders of magnitude larger, raising the real possibility that many new, stable Heusler compounds are still awaiting discovery. We demonstrate a high-throughput computational DFT screening approach for ~200,000 potential Heusler compounds, and use this method to predict hundreds of new stable and metastable Heusler compounds, which we further examine for interesting functional properties. We highlight three distinct examples of computational discovery of Heusler compounds, demonstrating the extraordinary diversity of properties possible with this single structure type: efficient thermoelectrics, off-stoichiometric semiconducting Heuslers, and strengthening precipitates in bcc metals.

Energetic Upper Bound for Synthesis of New Materials Muratahan Aykol, Shyam Dwaraknath, Wenhao Sun and Kristin A. Persson; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Laboratory synthesis of new functional inorganic materials, in particular the metastable ones, designed or discovered on the computer or suggested by theorists is a significant hurdle in materials science. To bridge this gap between computational and experimental worlds, we introduce a new thermodynamic upper bound on the energy scale for the creation of metastable crystalline polymorphs that is based on the entropic dominance of amorphous form of materials. This “amorphous limit” can be computed from first-principles and is found to be remarkably accurate and very sensitive to chemistry and composition in classifying hundreds of inorganic materials in the Materials Project database, from oxides to nitrides to sulfides, as synthesizable or not. The limit is expected to replace common constant, heuristic energetic limits or intuition often used as guidelines in filtering computed materials in materials screening for functional applications.

References:

Structural and Thermodynamic Effects in High Entropy Oxides Colin Freeman1, Gautam Anand2, Christopher M. Handley1, John H. Harding1 and Derek Sinclair1; 1University of Sheffield, Sheffield, United Kingdom; 2University of Warwick, Coventry, United Kingdom.

The functional ceramics community is increasingly exploring complex solid solutions containing multiple cations [1,2] to generate the desired properties and to avoid the need for rare or expensive dopants. These multi-component systems no longer possess regular, periodic lattices with occasional point
defects but show variable stoichiometry over nanometre scales, regions of disorder and cluster formation. These features are likely to be key to the properties. Because of the heterogeneous nature of these systems their characterisation can be very challenging as the bulk response must be an average of the different configurations present. Fabrication is also hindered as we move away from conventional processing where enthalpy is the dominant factor and must contend with entropic contributions.

We have performed a range of classical atomic scale simulations to study these systems. These are ideal tool as the atomic level detail explores the local relaxations that can occur around particular atomic configurations and identify issues of clustering. The relatively low cost of the simulations also means it is possible to look at multiple large cells providing the opportunity to actually sample the configurational variation that is present.

Our simulations examine the recently reported high entropy oxide system (Mg,Co,Ni,Cu,Zn)O [3]. We demonstrate that these phase is entropically stabilised over the enthalpy penalty of melting. By sampling an ensemble of configurations we are able to consider some the average structural and property features the material exhibits and comment on how mixing influences the local atomic behaviour. We also explore the formation of defects and how these might disrupt the material.

Chalcogenide phases, in particular tellurides, are of enormous technological importance nowadays because they serve as, for instance, phase-change [1] and thermoelectric materials [2]. The substitution of tellurium by selenium seems a promising pathway to obtain chalcogenide compounds with new electronic properties. Here we present the results of density-functional theory-based investigations regarding the structural, lattice-dynamical and thermodynamic properties of mixed chalcogenide materials in the Sb$_2$Se$_3$ – Sb$_2$Te$_3$ and GeSe – GeTe pseudo-binary systems compared with experimental measurements carried out by us.

Crystal structures in the system GeSe$_x$Te$_{3-x}$ have been studied up to pressures above 20 GPa using synchrotron radiation at DESY, Hamburg. The results are supported by theoretical investigations, including lattice dynamical and bonding properties [3]. We found an new orthorhombic structure type forming under pressure which has not yet been reported.

In the Sb$_2$Se$_x$Te$_{3-x}$ system we investigated the crystal structure as dependent from the selenium content $x$ [4]. We focused on the preferred incorporation of selenium into one of the possible chalcogenide sites of the Bi$_2$Te$_3$ structure type which is the ambient pressure structure up to a selenium content of $x = 1.8$. This incorporation was investigated additionally by DFT calculation as regards its energetic landscape and the bonding properties by making use of the COHP method as implemented in the LOBSTER code [5]. Additionally, low-temperature heat capacities were measured experimentally and compared to theoretically calculated data [6] using lattice dynamical calculations and the quasi-harmonic approximation [7].

References


9:15 AM CM01.10.05
Theoretical and Experimental Studies on the Mixed Chalcogenide Phases Sb$_2$Se$_x$Te$_{3-x}$ and GeSe$_x$Te$_{3-x}$ Ralf P. Stoffel and Richard Dronskowski; RWTH Aachen Univ, Aachen, Germany.

9:30 AM BREAK

10:00 AM CM01.10.06
Improving the Thermoelectric Efficiency of La$_{3-x}$Te$_4$ via F-Orbital Chemistry Sabah Bux1, Dean Cheikh1, Brea Hogan1, ’Trinh Vo1, Paul von Allmen1, Steven Gomez1, Bruce Dunn2 and Jean-Pierre Fleurial1; 1Jet Propulsion Laboratory, Pasadena, California, United States; 2University of California Los Angeles, Los Angeles, California, United States.

Since the 1960s, the National Aeronautics and Space Administration (NASA) has successfully utilized radioisotope thermoelectric generators (RTGs) as the primary power for many deep space probes, landers and orbiters for many missions including Voyagers 1 and 2, Cassini and Curiosity. RTGs are commonly used when other forms of on board power are not practical due to low solar flux, day/night cycles and settling of dust, or when they would significantly enable or enhance a mission’s ability to meet its objectives. RTGs are a proven technology and have been demonstrated to have high reliability, redundancy and long life. Historically, the thermoelectric (TE) materials used in the RTGs by NASA have either been based upon Si-Ge alloys or PbTe/TAGS (tellurium, silver, germanium, antimony), with system level conversion efficiencies of ~6.5%. The goal of the Advanced ThermOElectric Materials (ATOM) project in the Thermoelectrich Technology Development Project at the Jet Propulsion Laboratory (JPL) is to develop TE materials that can significantly enable or enhance a mission’s ability to meet its objectives. RTGs are a proven technology and have been demonstrated to have high reliability, redundancy and long life. Historically, the thermoelectric (TE) materials used in the RTGs by NASA have either been based upon Si-Ge alloys or PbTe/TAGS (tellurium, silver, germanium, antimony), with system level conversion efficiencies of ~6.5%. The goal of the Advanced ThermOElectric Materials (ATOM) project in the Thermoelectrich Technology Development Project at the Jet Propulsion Laboratory (JPL) is to develop TE materials that can significantly enable or enhance a mission’s ability to meet its objectives. RTGs are a proven technology and have been demonstrated to have high efficiency.

10:30 AM CM01.10.07
Design and Synthesis of Long-Term Heat-Storage Ceramics with a Low-Temperature Phase Transition Yoshitaka Nakamura; Panasonic Corporation, Osaka, Japan.

Long-term heat-storage materials can optimize heat utilization temporarily. Improved optimization requires the reuse of waste heat mainly below 473 K that is derived from vehicles, electronic devices, and industrial plants. Trititanium pentoxide (Ti$_3$O$_5$) has been reported recently as an external stimulation-controllable heat-storage ceramic [1]. Electron-localized β-Ti$_3$O$_5$ stores heat energy and transforms to delocalized λ-Ti$_3$O$_5$ by heating. λ-Ti$_3$O$_5$ releases energy and transforms to β-Ti$_3$O$_5$ by pressure. These properties are suitable for long-term storage, however, the phase-transition temperature of 470 K must be decreased for waste-heat reuse.
We have designed and synthesized Ti$_3$O$_5$ ceramics with a low-temperature phase transition by Ti-site substitution. The valence changes between Ti$^{3+}$ and Ti$^{4+}$ in Ti$_3$O$_5$ have been considered and the total electronic energy of Ti$_3$O$_5$ that is substituted by various trivalent or tetravalent elements from one of three Ti sites has been calculated by first-principles calculations using VASP code. Sc-substituted Ti$_3$O$_5$ showed a stable electronic energy, compared with Ti$_3$O$_5$ that is substituted by other elements. To predict the phase-transition temperature, the Gibbs free energies of Sc-substituted λ-Ti$_3$O$_5$ and β-Ti$_3$O$_5$ with optimized supercell structures (1 × 3 × 1) were calculated using Phonopy code. At a 2.8 at% Sc substitution, the crossover temperature of the calculated free energies that corresponds to the phase-transition temperature decreases by ~30% from the calculated temperature of the non-doped structures. Polycrystalline Sc-substituted Ti$_3$O$_5$ samples have been synthesized by arc melting with a mixture Ti metal, TiO$_2$, and Sc$_2$O$_3$ powder in an Ar atmosphere. The crystal phase in the Ti$_3$O$_5$ samples measured by X-ray diffraction changes from β-Ti$_3$O$_5$ to λ-Ti$_3$O$_5$ as the Sc substitution increased. The Sc-substituted Ti$_3$O$_5$ sample that consists of β-Ti$_3$O$_5$ and λ-Ti$_3$O$_5$ shows a pressure-induced phase transition from λ-Ti$_3$O$_5$ to β-Ti$_3$O$_5$ at 200 MPa or more, and transforms in reverse from β-Ti$_3$O$_5$ to λ-Ti$_3$O$_5$ by heating. During the heating, an endothermic reaction at 318–340 K with a Sc content of 3.0–3.5 at% was measured by differential scanning calorimetry. This reaction corresponds to the computationally predicted decrease in phase-transition temperature and this temperature range enables waste-heat reuse from vehicles, electronic devices, and plants.


10:45 AM CM01.10.08
Antisite Pairs Suppress the Thermal Conductivity of Boron Arsenide (BAs) (111:15 AM)
Qiang Zheng1, Carlos A. Polanco1, Mao-hua Du1, Lucas R. Lindsay1, Miaofang Chi2, Jiaqiang Yan1,3 and Brian C. Sales1; 1Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3Department of Materials Science and Engineering, University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

As microelectronic devices become faster and smaller, materials with ultrahigh thermal conductivities ($\kappa$) are becoming important for next-generation electronic devices. Recently, based on first-principles calculations, boron arsenide (BAs) with a zinc blende cubic structure was predicted to possess a uniaxially high $\kappa$ at room temperature of over 2000 Wm$^{-1}$ K$^{-1}$, comparable to that of diamond [1]. However, the experimentally measured $\kappa$ of BAs single crystals was only 200–350 Wm$^{-1}$ K$^{-1}$, an order of magnitude lower than the predicted value [2–4]. While theoretical calculations revealed that As vacancies even with very low concentration could significantly suppress $\kappa$ [5] and X-ray photoelectron spectroscopy (XPS) studies suggested possible As-deficiency in BAs single crystals [2,3], there has been no direct observation of As vacancies ($V_{\text{As}}$) in BAs crystals. Therefore, direct observation and identification of the defect types in BAs that suppress $\kappa$ become quite urgent for growth of high-quality BAs crystals or films with significantly improved $\kappa$.

In this work, we use aberration-corrected scanning transmission electron microscopy (STEM) to investigate the lattice structure and possible defects in BAs single crystals at atomic scale [6]. Rather than finding $V_{\text{As}}$, as widely thought to suppress $\kappa$ of BAs crystals, STEM results showed the enhanced intensity of some B columns and reduced intensity of their neighboring As columns, suggesting the presence of $\text{As}_x\text{B}_{1-x}$ antisite pairs with significant concentrations. Additional calculations on formation energies confirm that such antisite pair is preferred energetically among the different types of point defects investigated. Using a concentration of 1.8(8)% (6.6±3.0×10$^{-10}$ cm$^{-3}$ in density) for the antisite pairs estimated from STEM images, we estimated $\kappa$ to be 65–100 Wm$^{-1}$ K$^{-1}$, in reasonable agreement with the measured value. Finally, we also propose possible approaches, such as flux growth out of alkali metals-based or Ni-based melts and MBE, to achieve high-quality BAs single crystals or films with high thermal conductivity.


11:00 AM CM01.10.09
Synthesis, Crystal Growth and Ultrahigh Thermal Conductivity in Cubic BP and BAs Crystals (11:15 AM)
Sheng Li1, Qiye Zheng2, Yinchuan Lv2, Chunhua Li3, Xiaoyuan Liu1, Pinshane Huang2, David Broido3, David G. Cahill2 and Lv Bing1; 1University of Texas at Dallas, Richardson, Texas, United States; 2University of California at Berkeley, Berkeley, California, United States; 3National Renewable Energy Laboratory, Golden, Colorado, United States.

The zinc blende cubic BAs and BP, due to their potential ultra-high thermal conductivity calculated through first principle approach, have attracted significant research efforts in the past few years. The crystal growth of these materials, on the other hand, remains a challenge due to incongruent melting/peritectic decomposition nature of BAs/BP, and the low solubility of B in the common metal fluxes. Here, we report our synthetic efforts to grow the high quality of BAs/BP crystals through chemical vapor transport/metal flux method. We obtained the single domain, and defect-free crystals of BAs and BP up to mm size, evidenced by both single crystal diffraction and scanning transmission electron microscopy (STEM) studies. More importantly, ultrahigh thermal conductivities, ~1000W/mK for BAs and ~500W/mK for BP respectively, have been achieved through time-domain thermoreflectance (TDR) measurement. The measured experimental thermal conductivity values are also compared with theoretical calculations based on both three phonon (3ph) scattering and three+four phonon (3ph+4ph) scattering process.

11:15 AM CM01.10.10
Understanding Crystalization Pathways Leading to Manganese Oxide Polymorph Formation (11:20 AM)
Bor-Rong Chen1, Wenhao Sun2, Danil Kitchaev7, John Mangum3, Vivek Thampy1, Lauren Garten1, David Ginley1, Brian P. Gorman1, Kevin H. Stone2, Gerbrand Ceder2,5, Michael F. Toney3,6 and Laura Schluesener3,5; 1Stanford Synchrotron Radiation Lightsource, Menlo Park, California, United States; 2University of California, Berkeley, California, United States; 3Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, California, United States; 4Colorado School of Mines, Golden, Colorado, United States; 5National Renewable Energy Laboratory, Golden, Colorado, United States; 6Lawrence Berkeley National Laboratory, Berkeley, California, United States; 7Applied Energy Programs, SLAC National Accelerator Laboratory, Menlo Park, California, United States; 8Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, California, United States.

Computational driven design of materials has provided guidelines for designing novel materials with desired properties. However, the current computational approaches are not able to predict reaction pathways that pass through intermediate or metastable phases. As a consequence, repeated iteration is usually required to find the reaction conditions needed for realizing targeted materials with desired properties. To address this challenge, we combine theory, computation, and experiments to establish a theoretical framework that guides the synthesis of intermediate/metastable phases [1,2].

This framework has the ability to predict the multistage crystallization, as well as the influence of particle size and solution composition on polymorph
stability along reaction pathways. To validate this framework, hydrothermal synthesis of manganese oxide is utilized as a demonstration case. In the experiment, we track the evolution of manganese oxide polymorphs occurring during the synthesis by using in-situ X-ray wide-angle scattering and X-ray absorption spectroscopy. Three synthesis pathways with varying potassium ion concentrations ([K⁺] = 0, 0.2, and 0.33 M) in the solution were studied. By combining the experimental and computational results together, we find that our computed size-dependent phase diagrams capture which metastable/intermediate polymorphs appear, the order of their appearance, and their relative lifetimes [3]. Furthermore, we demonstrated that the intermediate phases can be isolated from reaction pathways by quenching the reaction to stabilize the phases at room temperature.

Overall, this combination of computational and experimental methodology offers a more rational and systematic paradigm for targeted synthesis of metal oxides. The future outlook for this “synthesis by design” approach is promising for other binary and ternary oxides with high polymorphism.

On heating, Cu2ZnGeS4 transforms at 1123 K, to a wurtzite-stannite-type structure with complete ordering of cations over the tetrahedral sites. The analogous selenide (Cu2ZnGeSe4) remains in I-4 at all temperatures to 973 K, despite the signature in thermal analysis data of a phase transition in the region 437 ≤ T/K ≤ 512. These observations are reconciled by Rietveld analysis, which reveals an order-disorder transition to a fully disordered kesterite structure at 450 K. Simultaneously, copper-ions become mobile, conferring phonon-liquid-electron-crystal characteristics, and copper-ion vacancies are created. This leads to marked changes in electron-transport properties: both ρ(T) and S(T) indicate the order-disorder transition is accompanied by a semiconductor to metal transition.

2:30 PM BREAK

3:00 PM *CM01.11.04
Improved Synthesis of Two-Dimensional Covalent Organic Frameworks
William Dichtel; Northwestern University, Evanston, Illinois, United States.

Polymerizing monomers into periodic two-dimensional (2D) networks provides structurally precise, layered macromolecular sheets that exhibit desirable mechanical, optoelectronic, and molecular transport properties. 2D covalent organic frameworks (COFs) offer broad monomer scope but are generally isolated as powders comprised of aggregated nanometer-scale crystallites. Here we control 2D COF formation using a two-step procedure, in which monomers are added slowly to pre-formed nanoparticle seeds. The resulting 2D COFs are isolated as single-crystalline, micron-sized particles. Transient absorption spectroscopy of the dispersed COF nanoparticles provides two to three orders of magnitude improvement in signal quality relative to polycrystalline powder samples and suggests exciton diffusion over longer length scales than those obtained through previous approaches. These findings will enable a broad exploration of synthetic 2D polymer structures and properties.

3:30 PM CM01.11.05
Microstructure—Properties Relationships in MOFs
Rifan Hardian, Marie-Vanessa Coulet and Philip Llewellyn; CNRS-Aix Marseille Univ, Marseille, France.

Metal-Organic Frameworks (MOFs) are a class of porous materials that combine metal oxide clusters with organic linkers. The wide variety of metal precursors and organic ligands allows tuning the properties of this class of materials to be used for gas storage and separation, catalysis, mechanical energy storage, etc. It has been recently proposed that the presence of defects and disorder in MOFs can have an impact on many of their properties [1,2]. In this contribution, the microstructure-properties relationships are studied in two kinds of defective MOFs.

The first example concerns the generation of defects by ball-milling in ZIF-8. It is shown that this kind of post-synthesis modification allows the control of the microstructure and the reactivity. Microstructure is analysed using X-ray diffraction while reactivity toward polar and non-polar molecules is studied using gas and vapour sorption experiments. Although the maximum uptake at high pressure is decreasing with increasing number of defects, the reactivity at low pressure is higher. This indicates that defects induced by ball-milling improve the reactivity which can be of interest for catalytic reactions.

The second example focuses on the influence of the microstructure on the structural flexibility in functionalized MIL-53(Cr) compounds. This MOF family presents the remarkable property of being flexible. This means that one compound exists in at least two crystalline states with distinct pore size and shape: a narrow pore (NP) structure and a large pore structure (LP). The NP-LP transition is reversible and can occur under gas adsorption and desorption or without any guest, that is to say under mechanical pressure or temperature. Functionalization of this compound allows tuning the NP-LP transition. Such a property, not always considered to date, could allow to fine-tune MOF flexibility and thus any potential application of these compliant materials.


3:45 PM CM01.11.06
Applications and Limitations of Nanocasting in Cluster-Based Metal-Organic Framework Materials
Andreas Stein, Camille Malonzo, Zhao Wang, Wenyang Zhao, Thomas Webber and R Lee Penn; Univ of Minnesota, Minneapolis, Minnesota, United States.

Metal-organic framework (MOF) materials containing oxometalate cluster-based nodes, such as oxozirconium or oxocerium nodes, can provide the basis for single-site heterogeneous catalysts, for example, if all nodes are uniformly modified with suitable metal species. However, the application of MOFs for catalysis at high temperatures, particularly in oxidizing environments, is limited, because the instability of the organic linkers under these conditions leads to loss of the MOF structure and aggregation/sintering of the catalytic clusters. Under those conditions, it may be necessary to stabilize the cluster sites. We will discuss methods of stabilizing MOF-derived functionalized and non-functionalized oxometalate clusters by nanocasting with silica, titania, or carbon scaffolds. A silica scaffold, for example, can prevent the oxozirconium clusters in the MOFs NU-1000 or UiO-66 or oxocerium clusters in related cerium-based MOFs from aggregating after the links are removed at temperatures between 500 and 600 degrees C. This is in contrast with bare NU-1000 or UiO-66, which shows sintering of the clusters after undergoing the same thermal treatment. The clusters in the nanocast material remain accessible to probe molecules and their Lewis acidity is maintained, keeping them active as catalysts in certain acid-catalyzed reactions. This nanocasting method can also be extended to other scaffolds to support cluster nodes in large-pore MOFs. We will consider synthesis parameters that permit uniform infiltration of the MOF with the scaffold precursors and correlate these to nanocast products that maintain discrete clusters after thermal treatment at 500 degrees C or higher, without formation of extended zirconia or ceria aggregates. Accessibility of the stabilized clusters in the scaffolds is probed by spectroscopic and catalytic reaction methods. Nanocasting, combined with the exceptional tunability of the composition and structure of MOFs, provides a starting point for designing a new generation of highly active and stable heterogeneous catalysts.

4:00 PM CM01.11.07
Growth and Characterization of an Sb-Based Ternary Nitride—A New Metastable Photoactive Material
Elisabetta Arcì, John D. Perkins, Stephan Lany, Wenhao Sun, Dylan Hamilton, Jonathan Partridge, Casey Haack, Aaron Holder, Gerbrand Ceder, William Tumas, Glenn Teeter, Adele Tamboli and Andriy Zakutayev; 1National Renewable Energy Laboratory, Golden, Colorado, United States; 2Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States; 3Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4Department of Materials Science and Engineering, University of California Berkeley, Berkeley, California, United States.
Wurtzite (WZ)-derived ternary nitrides are an interesting class of materials promising enhanced optoelectronic functionalities. Peculiar to this category of materials is their capability of accommodating large off-stoichiometries, as we recently demonstrated for the Zn$_3$MoN$_4$-ZnMoN$_2$ system. In the latter case, cation off-stoichiometry enables a continuous tuning of the composition between the two end points, while retaining the WZ structure, through a process that we defined as redox-mediated stabilization. Most of the cations in the periodic table have been reported to form nitrides as either a monometallic or bimetallic compound. To date, an exception to this rule is represented by antimony: M-Sb-N ternary compounds where Sb is acting as an anion are known, however crystalline nitrides where Sb is acting as a cation have not been reported to date. In this contribution, we theoretically predicted and experimentally realized the first ternary antimony nitride where antimony is a cation. A data-mined structure prediction (DMSP) algorithm was used to identify the compound and evaluated the stability of the candidate crystal structures by comparing their density functional theory (DFT) formation energies to the competing phases. Combinatorial RF magnetron sputtering was used as growth technique, to enable access to high nitrogen chemical potential (\(\Delta_{\text{N}}\)) and fast screening of deposition conditions. It was found that this metastable compound could be synthesized over a wide range of deposition conditions, showing tunable optical and electrical properties as a function of the Sb content in the cation sub-lattice and growth conditions. The low native n-type conductivity and moderate carrier concentration, coupled with an almost ideal direct band gap (1.7 eV theoretical, \(\approx 1.4\) eV experimental), make it a promising candidate as a photoactive material. Based on measured values of the ionization potential and the electron affinity, the applicability of this material as a photoactive absorber will be discussed.

1 Area et al., J. Am. Chem. Soc., 2018, 140, 4293

4:15 PM CM01.11.08
High-Resolution High-Sensitivity Characterization of Inorganic Materials Using Correlative Electron Microscopy and Secondary Ion Mass Spectrometry—Applications in Si Based Photovoltaics Santhana Eswara1, Ailsa Pshenova1, Mario Lehmann2, Gizem Nogay2, Andrea Ingento2, Quentin Jeangros2, Christophe Balilid2, 3, Franz-Iosef Haug2, Aicha Hessler-Wyser2 and Tom Wirtz4, 5; 1Advanced Instrumentation for Ion Nano-Analytics (AINA), MRT Department, Luxembourg Institute of Science and Technology, Belvaux, Luxembourg; 2Institute of Microengineering (IMT) Photovoltaics and Thin-Film Electronics Laboratory (PV-Lab), Ecole Polytechnique Fédérale de Lausanne (EPFL), Neuchâtel, Switzerland; 3PV-Center, Centre Suisse d’Electronique et de Microtechnique (CSEM) SA, Neuchâtel, Switzerland.

Development of advanced materials and processing methods often relies on the availability of suitable characterization techniques. To improve performance, modern materials are often designed with complex nanoscale structural and chemical (e.g. doping) features, thereby placing demanding requirements on the characterization techniques. Investigation of dopant distribution across nanoscale features requires a characterization technique with high resolution and high sensitivity [1]. It is well-known that high-resolution structural imaging can be routinely performed using Transmission Electron Microscopy (TEM) down to atomic resolution. However, the analytical techniques typically available in a TEM such as Energy Dispersive X-ray Spectroscopy or Electron Energy-Loss Spectroscopy do not have the sensitivity to detect or image dopant distributions. Secondary Ion Mass Spectrometry (SIMS), on the other hand, has excellent sensitivity (can be down to ppm range) but its lateral resolution is limited to around 50 nm. While a resolution < 20 nm was recently demonstrated [2], the SIMS image resolution is still a few orders of magnitude worse than the one of TEM. To combine the complementary strengths of TEM and SIMS, we have developed a new in-situ technique integrating both of them in a single instrument to enable selective passivating contacts used in c-Si solar cells. These contacts consist of doped nanometric layers, which are stacked in different configurations. The development and characterization of novel nanostructured inorganic materials in general and a special focus will be made on the analysis of carrier-selective passivating contacts used in c-Si solar cells. These contacts consist of doped nanometric layers, which are stacked in different configurations. The nanoscale materials characteristics retrieved from TEM and SIMS will then be correlated to process parameters and the overall device performances.


4:30 PM CM01.11.09
Exploring Reactivity in Complex Reaction Mixtures as a Route Toward Nanocrystals of Ternary Copper and Iron Chalcogenides for Applications in Photovoltaics Amy L. Prieto, Rebecca Miller, Jennifer Lee and Lily Moloney; Colorado State Univ, Fort Collins, Colorado, United States.

Colloidal inorganic nanocrystals offer many advantages for use in photovoltaic devices: controllable synthesis, processability, and tunable band gap energies. Ideal materials for photovoltaics would contain earth abundant, nontoxic elements and would possess ideal band gaps. Copper and iron chalcogenides exhibit these properties. However, many of these compounds are ternary compounds, with interesting bonding between transition metals, main group elements, and chalcogenides, so developing synthetic routes toward nanocrystals of these materials is a significant challenge. We are exploring how the interactions between precursors, surfactants, organic solvents, and temperature in injection-type reactions can effect the reaction pathways toward the ultimate products.

SESSION CM01.12: Poster Session IV: Solid-State Chemistry of Inorganic Materials
Session Chairs: Ashafia Huq and Kirill Kovnir
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

CM01.12.01
Lattice Dynamics of Layered AMg$_2$Pn$_n$: Zintl Compounds Wanyue Peng1, Guido Petretto2, Gian-Marc Riganese3, Geoffrey Hautier2 and Alexandra Zevalkink4; 1Michigan State University, East Lansing, Michigan, United States; 2Université catholique de Louvain, Louvain-la-Neuve, Belgium. AMg$_2$Pn$_n$; compounds with the layered CaAl$_2$S$_2$ structure type have received a great deal of attention recently due to their excellent thermoelectric properties. The binary member of this structure type, Mg$_2$Sb$_2$, exhibits the highest peak \(zT\) of 1.6, due in part to its surprisingly low lattice thermal conductivity. Here, we explore trends in the thermal properties of AMg$_2$Pn$_n$-compounds (Pn = Sb or Bi and A = Mg, Ca, Sr, Ba, Yb, Eu, Sm) to elucidate the role of the cation radius and cation electronegativity in determining the elastic moduli and anharmonicity in this structure type. Temperature-dependent
Oxidation-Resistive Two-Dimensional Dihafnium Sulfide Electride with Efficient Electrocatalytic Activities in Water-Based Solution

SeHyung Kang, Ye Ji Kim and Sung Wng Kim; Sungkyunkwan Univ, Suwon, Korea (the Republic of).

Electrides are exotic ionic crystals where excess electrons are located in cavities as anions. Because of the loosely bound anionic electrons, electrides have been received much attention, exhibiting intrinsic physical and chemical phenomena, such as low work function, high electron mobility and excellent catalytic reactivity. However, the electro-active functionalities of electrides have been degraded once oxygen and/or moisture is absorbed, preventing the novel applications for an industry. It is thus highly demanded to discover a thermally or chemically stable electrode in ambient or moisture condition. Here, we report the highly oxidation-resistive dihafnium sulfide ([(HfS)]2−2e−) electride with efficient hydrogen evolution electrolysis (HEE) activities over 5,000 cycles in water. We have grown single-crystalline [(HfS)]2−2e− electride by floating zone melting method. X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) combined with density functional theory (DFT) calculations clarify that [(HfS)]2−2e− electride has two excess electrons per formula unit, which are confined in the Hf-Hf interlayer with dumbbell-like shape. [(HfS)]2−2e− electride shows a state-of-the-art durability against air and water among the existing electrides, retaining the crystal structure and physical/chemical properties over 1 month. Furthermore, Cu-loaded [(HfS)]2−2e− electride shows highly effective HEE performances comparable to the defect-rich MoS2, which is one of the most effective catalyst except Pt for water splitting. Transmission electron microscopy (TEM) observation indicates that the formation of thin native amorphous HfO2 layer, known as oxidation-resistive passivation layer, is responsible for the electro-catalytic activity in water. It is verified that the anionic electrides of [(HfS)]2−2e− can migrate to the Cu nanoparticle through the amorphous HfO2. Our findings provide an important insight into the design strategy of new oxidation-resistant electrides and their active functionality through electrocatalysis.


Effect of Crystal Structure on Hole Carrier Generation in Wide-Gap P-Type Tin-Niobate

Akane Samizo1, 2, Naoto Kikuchi2, Yoshihiko Aiura2 and Keishi Nishio1; 1Tokyo University of Science, Tokyo, Japan; 2National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Transparent conducting oxides are widely used as transparent electrodes in displays and solar cells. However, most of existing TCOs are n-type semiconductors such as ITO (In2O3:Sb) and ZnO. In order to fabricate transparent devices based on p-n junctions, the development of p-type TCOs are required. The reason of the difficulty in development of p-type TCOs is low hole mobility. Since the wide band-gap of TCOs comes from significant contribution of ionic character to chemical bonds between metal cations and oxygen anions, positive holes at valence band maximum (VBM) are strongly localized around O 2p orbitals. Thus, delocalization of VBM is essential for material design for realizing p-type TCOs. The oxides of metal cations with ns electronic configurations (n: the principal quantum number) such as Pb2+, Sn4+ (hereafter s-orbital-based oxides) have been recently attracted as new candidates for p-type TCOs. The large spatial spreading and isotropic nature of metal s orbitals delocalize the VBM, then low effective mass of holes is expected. However, only a few reports on electrical properties of these oxides exist because of difficulties in hole carrier generation. The s-orbital-based oxides require to anneal in reduced atmosphere in order to prevent oxidative decomposition (eg. SnO changes to SnO2), which results in a charge compensation of holes by electrons generated by the formation of oxygen vacancies (Vo**). Therefore, controlling of structural defects including oxygen vacancies is indispensable for introduction of hole carriers. We focus on Sn4+ oxides, which is more environmental-friendly compared to Pb2+, and succeeded in preparation of p-type SnNb2O6 and SnNbO3 by sample annealing. The crystal structure of both oxides has a substructure of NbO6 octahedral, and there are considerable three kinds of native point defects, V0**, Sn4+ on Nb5+ substitutional defects (Sn'Nb), and tin vacancies (VSn''). We found that the hole carriers were generated by Sn'Nb in Nb5+ octahedra in both p-type tin-niobates. Although same hole carrier source was found, the carrier generation efficiency of SnNbO2 was in two orders higher than that of SnNb2O6. In this paper, the amount of each defects and distortion of the crystal structure was discussed by the Rietveld analysis in order to clarify the origin of difference in the carrier generation efficiency. We summarize characteristics of hole carrier generation related to structural defects of two tin-niobates. The findings obtained in this study may bring us detailed mechanisms of carrier generation in Sn4+ oxides, leading to future transparent device applications.

Grain Boundary and Discontinuous Precipitation Phenomena in a Multicomponent Alloy

Julio C. Spadotto1, 2, Grace Burke1 and Guillermo Solórzano3; 1University of Manchester, Manchester, United Kingdom; 2PUC-Rio, Rio de Janeiro, Brazil.

Discontinuous precipitation (DP) reaction is a grain-boundary (GB) diffusion-controlled phenomenon driven by migrating GB, acting as fast reaction path under the action of chemical and capillary forces, leaving behind a regularly-spaced array of lamellar precipitates growing cooperatively from the supersaturated matrix. In multicomponent alloy systems containing both substitutional and interstitial solutes normally the DP colonies are constituted of either Cr-rich M23C6 or Cr2N lamellae. However, DP colonies in superaustenitic stainless steel have been observed in which the lamellar Σ phase has precipitated at the migrating GB and the additional precipitation of CrN has occurred within the colony with increasing ageing time [1]. The present investigation deals with the DP reaction in Alloy 33, with nominal composition (wt.%) 33Cr-32Fe-31Ni-1.6Mo-0.6Cu-0.4N, upon aging at 800 °C. In order to understand the complex DP phenomenon in this alloy, both analytical scanning (SEM) and analytical transmission electron microscopy (TEM) have been used extensively for detailed microstructural characterization. The DP reaction in Alloy 33 displays different characteristics from those reported in the literature. After aging at 800 °C for 1 hour heterogeneous precipitation occurred at the GBs, where, in some cases, the initial stages of development of DP colonies were observed. At this stage, dislocations walls marking the original grain boundary position had been observed. Upon aging for 2 hours its verified in some regions of DP colony that the precipitates are connected to migrating GB, but in other regions of the same GB the boundary appears disconnected from the precipitate in a similar fashion as diffusion-induced grain boundary migration (DIGM) topologies. The intergranular precipitates were identified using selected area electron diffraction (SAED) and EDX microanalysis as Cr-rich M23C6 carbide with FCC structure. Based on DP theory, it is expected that the precipitate initially formed at GB grows together with the GB migration.

After aging at 800 °C for 5 hours, energy dispersive X-ray spectrum imaging and SAED analyses confirmed that the original GB position is M23C6 in the DP colony, as expected. However, in the same DP colony, a platelet-type precipitate, identified as α-Cr phase with BCC structure, was also observed at the
GB. Similar behavior was also observed in a different DP colony; Mn,Cr precipitation did not occur at the original GB position. In this DP colony, α-Cr phase was also observed along with a phase rich in Cr, Mo, and Fe at reaction front. These results showing different types of precipitates occurring at the early stages of the DP reaction show the complexity of this phenomenon in Alloy 33, and suggest a high entropy system behavior [2].

References
[2] The authors are grateful to CNPq. Thanks are due to Dr Octav Ciucu for the help with the electron microscopes.

CM01.12.06
Unveiling the Nature and Structure of ZnO-Bi2O3 Grain Boundaries

Marcelo A. Martinho, Gabriel D. Rocha, Marco A. Cordeiro and Edson R. Leite; UFSCar, São Carlos, Brazil.

Owing to the structural and chemical nature of polycrystalline materials, grain and phase boundaries play a fundamental role in these materials properties by tailoring desired material features. For example, grain boundaries have a tremendous implication in plastic deformation in materials, especially in failure mechanisms such as fatigue, fracture and creep, which are fundamental for the development of new materials, as superplastic ceramics. In spite of the evident importance, the basic understanding of interfaces is still in its beginning, and lacks an essential correlation of its structure and materials properties. In order to provide fundamental insights into the structure and chemical nature of the grain boundary in oxides, Bi2O3-doped ZnO system was used. Due to its unique physical and chemical properties (e.g., chemical stability, broad range of radiation absorption and high photostability), ZnO2 materials find place in a myriad of applications (e.g., varistors, photocatalysts, solar cells.). Besides, Bi2O3-doped ZnO2 has been studied as a model for liquid-phase/activated sintering due to the lower temperature in the eutectic (~740 °C). Despite the important studies over the years, the knowledge of the sintering and grain boundary development is based on ex situ studies, which approach could hide fundamental aspects of sintering and grain boundary formation phenomena. Then, in this study, ex situ and in situ studies of sintering and grain boundary formation were performed. Ex situ studies were carried out by using samples produced by oxide mixture (Bi2O3 and ZnO) followed by conventional sintering. The resulted pellets were polished and the grains revealed by temperature, and then studied by scanning electron microscopy (SEM). On the other hand, in situ studies were carried out by using ZnO2 and Bi2O3 nanoparticles (NP) (10-20 nm), both synthesized by non-hydrolytic route (thermodecomposition of the acetate precursors) under the action of organic ligands (oleylamine and/or oleyl alcohol). Self-organization of ZnO2 and Bi2O3 NPs on amorphous carbon film supported on nickel grids were submitted to in situ heating experiments in a Gatan 628 single-tie heating holder (with an Inconel-based furnace) in a FEI Tecnai F20 field emission TEM operating at 200 kV. By real-time tracking the NPs sintering and grain boundary formation, it was possible to analyze the structure formation and further grain restructuration and correlation with the ex situ experiments. Moreover, the evolution of grain boundary formation and the final structure were correlated to the complex structures, providing a promising avenue toward the construction of grain boundary phase diagrams.

CM01.12.07
Control of Size Distribution of Surface Nanoparticle Formed by Selective Phase Transition in Sr0.98Ti0.95Me0.05O3-δ (Me = Mn, Fe, Co, Ni, and Cu)

Jun Kyu Kim, Bonjoo Koo and WooChul Jung; Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejon, Korea (the Republic of).

Supported metal nanoparticles (NPs) are of significant importance in heterogeneous catalysis owing to their excellent dispersion and many undercoordinated surface sites. Recently, the in-situ growth phenomenon of metal NPs directly from an oxide support, known as ‘ex-solution,’ has been reported as a new method of decorating oxide surfaces with uniformly dispersed metal NPs. Here, a catalytically active metal is embedded in the crystal lattice of a backbone in oxidizing conditions, forming a solid solution, and then is released (ex-solved) on the surface of the structure as metallic nanoparticles upon exposure to a reducing atmosphere. Compared to conventional nanoparticle synthesis and dispersion techniques, this process is faster, more cost-effective and allows finer and better particle distribution. Furthermore, the sintering of nanoparticles can be prevented by re-oxidation, enhancing the life-time of the supported nanoparticles. Despite extensive research efforts, however, the fundamental mechanisms of the processes remain largely unknown. Accordingly, how to control particle size and distribution precisely are also unknown, despite the fact that these processes are crucial to render this phenomenon technologically attractive.

In this study, we prepared dense thin-films of 3d-transition metal (Mn, Fe, Co, Ni and Cu) doped and A-site deficient SrTiO3 with highly flat surfaces and observed the ex-solved particles on their surfaces depending on the annealing temperature, oxygen partial pressure, and kind of dopants. SrTiO3 was selected as a model perovskite host due to its superior phase stability in a wide range of temperatures and gas atmospheres, and the thin-film samples were used for reliable and reproducible surface analysis. We found that the nucleation and growth of ex-solved particles took place extremely fast, and their rate gradually increased as the pO2 decreases. Significantly, the lower the pO2 at the same temperature, or the higher the temperature at the same pO2, the greater the number of nuclei, which forms metal NPs with higher density and smaller size. These observations were explained through the classic nucleation theory, suggesting a novel technique to control the size and dispersion of supported metal NPs, which can be readily applied to various applications.

CM01.12.08
Rapid Discovery of Ternary Transition Metal Chalcogenides

Ankita Bhutani1, Julia Zuo2, Thiruvengadam Rangarajan1, Pishu Behera1, Awadhesh Narayan1, Joshua Schiller1, James N. Eckstein1, Santanu Chaudhuri4, Lucas K. Wagner1 and Daniel Shoemaker1; 1University of Illinois at Urbana-Champaign, Illinois, United States; 2Chalmers University of Technology, Sweden; 3University of California, Santa Barbara, California, United States; 4Illinois Applied Research Institute, Urbana, Illinois, United States.

In order to capitalize on computational modeling and predictions, fast and accurate experimental synthesis and characterization techniques must evolve. In this study, we investigate transition metal chalcogenides using high-throughput experimental techniques, such as temperature and time-resolved in-situ x-ray diffraction, powered by computational predictions. High-temperature in-situ x-ray diffraction accelerates materials discovery by allowing us to watch a chemical reaction in real time and identify new stable/metastable phases. It provides useful insights into the thermodynamics and kinetics of reactions. Transition metal chalcogenides are particularly interesting because of their understudied d-electron correlations which lead to various interesting properties including superconductivity, meta-magnetic behavior, and quantum phase transitions.

I applied such a tandem approach to explore the Ba–Ru–S phase space using a combination of evolutionary algorithms and density functional theory (DFT) to inform traditional and in situ diffraction methods. My work identified a high-temperature polymorph of BaS2, that would have been otherwise missed in ex-situ reactions and did not reveal formation of the predicted candidates BaRuS4 or BaRuS3 (Bhutani, A. et al. Chem. Mater. 29 (14), 5841–5849 (2017)). I then used this methodology to study several other ternary systems to screen for novel phases. I screened 31 ternary chalcogenide phase diagrams of the form XYZ (X = K, Na, Ba, Ca, Sr, La, K, Bi, Pb; Y is a 3d transition metal; and Z = S or Se), where DFT predicted new compositions (Wagner Research Group, Physics, UIUC). I discovered 9 new phases belonging to the K/Na-Zn-S/Se systems with potential uses as wide band gap semiconductors and found 27 phase diagrams to be “empty” in the case of bulk synthesis (Narayan, A., Bhutani, A. et al. Phys. Rev. B. 94, 045105 (2016)). I complete my study with detailed characterization of new phases using XRD, UV-Vis Spectroscopy, SEM and magnetic and transport measurements.
We show that an electrochemically-driven oxide overcoating substantially improves the performance of metal electrodes in high-temperature electrochemical applications. As a case study, we overcoat Pt thin films with (Pr,Ce)O$_2$. (PCO) by means of cathodic electrochemical deposition process that produced nanostructured oxide layers with a high specific surface area and uniform metal coverage and then examine the coated films as an O$_{2}$ electrode for thin-film-based solid oxide fuel cells (TF-SOFCs). The resulting structures were examined by SEM, XRF and ICP-MS. The electrode activity of symmetric cells (cathode|electrolyte|cathode) was analyzed by the AC impedance spectroscopy (ACIS) measurements. The combination of excellent conductivity, reactivity and durability of PCO dramatically improves the oxygen reduction reaction rate while maintaining the nanoscale architecture of PCO layers and thus the performance of the PCO-coated Pt thin-film electrodes at high temperatures. As a result, with an oxide coating step lasting only 5 min, the electrode resistance is successfully reduced by more than 1000 times at 500 °C in air. Based on these observations, furthermore, we successfully deposited nano-columar ACO films on an enhanced specific surface area and succeeded in achieving high electrode performances. These findings provide useful guidance for design and fabrication of high-performance TF-SOFCs.

**CM01.12.09**

Exceptionally Enhanced Electrode Activity of (Pr,Ce)O$_2$-Based Cathodes for Thin-Film Solid Oxide Fuel Cells Han Gil Seo, Yoonseok Choi and WooChul Jun; Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

**CM01.12.10**

Oxygen Interstitial Migration in Solids from First Principles—Apatites and Melilites Steffen P. Griesshammer$^{1, 2}$; 1Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany; 2Helmholtz-Institut Münster, Forschungszentrum Jülich GmbH, Münster, Germany.

Solid state oxygen ion conductors play a crucial role as electrolytes in solid oxide fuel cells (SOFC), solid oxide electrolyzer cells (SOEC) and rechargeable oxide batteries (ROB). In common oxygen ion conductors, like yttria-stabilized zirconia, oxygen transport is enabled by oxygen vacancies, while in recent years oxygen ion conductors where transport is enabled by ionic charges have gained increasing attention. In the present study, two examples of oxygen ion conductors with an interstitial mechanism are investigated using density functional theory. Lanthanum apatites with the general formula La$_{10-x}$X$_{6}$Si$_{6}$O$_{24}$ form a hexagonal structure with oxygen ion channels enabling transport along the crystallographic c-direction. Melilites with the composition Y$_{3}$Ga$_{2}$O$_{12}$ crystalize in a tetragonal layered structure with oxygen interstitials migrating in a layer composed of GaO$_{6}$-units. The energies of defect formation of oxygen ions via vacancy and interstitial mechanism are calculated for different compositions. In both types of materials the transport of oxygen ions by a cooperative interstitialcy mechanism is favorable compared to vacancy migration. However, the migration energies clearly depend on the ordering of the cations around the migration oxygen ion.

**CM01.12.12**

Light Absorption Coefficient of CsPbBr$_3$ Perovskite Nanocrystals Jong-Min Kang$^{1, 2}$, Lieve Balcaen$^{1}$, Emilie Drijvers$^{3, 2}$, Qiang Zhao$^{3}$, Jonathan De Roo$^{4, 1}$, André Vertommen$^{1}$, Frank Vanhecke$^{1}$, Pieter Getereg$^{4, 1}$ and Zeger Hens$^{2, 3}$; 1Department of Chemistry, Ghent University, Ghent, Belgium; 2Center for Nano and Biophotonics, Ghent University, Ghent, Belgium; 3Instituut voor Kern- en Stralingsfysica, KU Leuven, Leuven, Belgium; 4Department of Chemistry, Columbia University, New York, Belgium.

The concentration of colloidal nanocrystals (NCs) is a key characteristic for any quantitative study on nanocrystals. At present, the concentration of CsPbBr$_3$ NCs is typically quantified by means of an absorption coefficient or cross section obtained from photoluminescence saturation or by thermogravimetric analysis; two methods that are not accurate and need benchmarking by direct quantification methods. We combined inductively coupled plasma mass spectrometry (ICP-MS), UV–vis absorption spectroscopy and transmission electron microscopy to determine the size, composition, and intrinsic absorption coefficient $\mu_0$ of 4 to 11 nm sized colloidal CsPbBr$_3$ NCs. The ICP-MS measurements demonstrate the nonstoichiometric nature of the NCs, with a systematic excess of lead for all samples studied. Rutherford backscattering measurements indicate that this enrichment in lead concurs with a relative increase in the bromide content. At high photon energies, $\mu_0$ is independent of the nanocrystal size. This allows the nanocrystal concentration in CsPbBr$_3$ nanocollod to be readily obtained by a combination of absorption spectroscopy and the CsPbBr$_3$ sizing curve.

**CM01.12.13**

Control of Transition Metal—Oxygen Bond Length Boosts the Redox Ex-Solution in Perovskite Oxide Surface Bonjoo Koo$^{1}$, Kyeoungghak Kim$^{2}$, Yong-Ryun Jo$^{1}$, Siwon Lee$^{1}$, Jun Kyu Kim$^{1}$, Min Ji Seo$^{1}$, Bong-Joong Kim$^{1}$, Jeong Woo Han$^{1}$ and WooChul Jung$^{1}$; 1Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea (the Republic of); 2Pohang University of Science and Technology (POSTECH), Pohang, Korea (the Republic of); 3Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of).

Nano-sized metal particles have been widely used as heterogeneous catalysts for various reactions due to their high surface-to-volume ratios and possibly unique catalytic properties. Particularly when dispersed on oxide supports, their catalytic activities are often greatly enhanced compared to those in pure metal particles. Recently, $in-situ$ growth phenomenon of metal nanoparticles (NPs) directly from an oxide support, known as 'ex-solution', has been reported by multiple researchers in the fields of high-temperature catalysis and renewable energy. When perovskite oxides (ABO$_3$) are used as a hosting matrix, A-cations and oxygen ions determines the outcome of ex-solution. To the best of our knowledge, however, there is no atomic-level consideration of the intrinsic stability of a reducible cation surrounded by six oxygen ions in a lattice, and thus a solution that effectively controls the amount or distribution of the exsolved phases is not yet known.

Here, we investigate the influence of the bond length between the B-site transition metal and the neighboring oxygen in a perovskite lattice on surface transition metal ex-solution. Considering dense epitaxial thin films of Sr$_{0.5}$La$_{0.5}$O$_{1.9}$ (STC) as a model system, we control the average Co-O bond length through the misfit strain of STC films, and monitor how the surface composition and catalytic reactivity for CO oxidation changes accordingly. Combined theoretical and experimental analyses show that the relatively weak bond strength induced by the elongated Co-O bond in STC drives the Co ex-solution significantly and thus activates the CO oxidation. Based on the observations, we conclusively demonstrated that the tensile strain could be sufficiently increased by introducing a large-sized oxidant dopant, offering a new strategy for activating the ex-solution phenomenon.
Despite the wide applicability of oxynitrides from photocatalysis to refractory coatings, our understanding of the materials has been limited in terms of their thermodynamics. The configurational entropy via randomly mixed O/N or via cation vacancies are known to stabilize oxynitrides, despite the positive formation enthalpies. Here, using tin oxynitrides as a model system, we show by ab initio computations and experimental characterization that oxynitrides in seemingly charge-unbalanced composition stabilize by forming nitrogen dimers among metal-(O,N)₆ octahedra. The nitrogen dimer, -(N=N)-, reduces the effective charge of nitrogen to -2, facilitating the formation of nitrogen-rich oxynitrides. We rationalize that the dimer forms only in structures with corner-sharing octahedra, since the N-N bond formation requires sufficient rotational degrees of freedom among the octahedra. X-ray photoemission spectra of the synthesized tin oxynitride films reveal two distinct nitrogen bonding environments, confirming the computation results. This work opens the search space for a novel kind of oxynitrides stabilized by N dimer formation, with specific structural selection rules.

CM01.12.15
Magnetic Heating Monitoring with Quantum Dots Nanothermometers Celine Navral, Gaelle Muraille, Robert Swain, Benjamin McVey, Bruno Chaudret and Fabien Delpech; Univ of Toulouse, Toulouse, France.

The use of magnetic nanoparticles (NPs) to convert electromagnetic energy into heat is known to be a key strategy for numerous biomedical applications but is also an approach of growing interest in the field of catalysis. We have shown that, associated to catalytic metals (Ni, Ru), iron carbide NPs submitted to magnetic excitation very efficiently catalyze CO₂ hydrogenation in a dedicated continuous-flow reactor. Since a huge gradient of temperature between the self-heated particles and the “cold” environment is expected, nanoscale measurements need developments to correlate the result of catalysis reaction to NPs temperatures, but also to control the process to keep constant the heating power or the NP surface temperature. Thermometric probes have been described at low temperatures with different luminescent species. However, using phosphors to determine high temperatures under harsh experimental conditions remains largely unexplored and highly challenging. At the nanoscale, QDs optical properties offer a rare opportunity to build an innovative complex nano-object integrating heating capacities, catalytic ability and thermal reporting property. The temperature-dependent emission of different QDs (InP@ZnS and CdSe@ CdS) have been investigated in this purpose. Peak emission wavelength, intensity, and full width at half maximum were completely characterized as a function of temperature. We will present here the use of QDs as local temperature probes during the magnetic heating of iron carbides NPs in catalysis conditions. We evidence that the global temperature (measured by a thermal camera) of the catalytic solid is drastically lower than the local temperature measured by the QDs at the nanoscale.

Poison’s ratio (PR) is a measure of a material change along its transversal dimensions under the application of an axial strain. Most materials present positive PR, i.e., they laterally shrink (expand) under the application of a tensile (compression) strain. Other materials and structures present, on the other hand, negative PR and are called “auxetic”. Re-entrant polymeric crystals and/or foams are examples of auxetic materials [1]. Even more rare are the materials and structures presenting zero Poison’s ratio (ZPR) [2], i.e., materials that neither contract nor expand laterally under the application of an axial strain. Gases and semi-re-entrant honeycomb structures are known examples of ZPR materials [2,3]. Motivated by recent attempts to produce new ZPR structures [4,5], we propose a new type of ZPR structure that is not based on re-entrant honeycomb or hexagonal structures. The proposed structural model is composed of planar structures formed by the junctions/fusions, side by side, of several blocks in the shape of letters “Z” or “N”, which are two parallel bars connected by a diagonal bar, so the name “ZN” model. These diagonal bars are formed by soft, low bending stiffness materials, while rigid, high stiffness materials form the other two parallel bars. We show that such a kind of structure presents ZPR along both orthogonal directions. We discuss the challenges involving the production of these models, how to build a tri-dimensional ZPR structure from our two-dimensional “ZN” model, and the feasibility of having such a ZPR structure at nanoscale.


CM01.12.21
Thermal Properties of 2:1 Bismuth Borate Ceramics—Microscopic Contribution of Lone Electron Pairs for Lattice Expansion Tensors Mangir Murshed1, 2, Hillek Petersen1, Michael Fischer2, Mariano Curti3, Cecilia B. Mendive2, Volodymyr Baran2, Anatoly Senshyn5 and Thorsten M. Gesing1, 2; 1 Institute of Inorganic Chemistry and Crystallography, University of Bremen, Bremen, Germany; 2 MAPEX Center for Materials and Processes, University of Bremen, Bremen, Germany; 3 Crystallography, University of Bremen, Bremen, Germany; 4 Departamento de Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Mar del Plata, Argentina; 5 Research neutron reactor ZWE FRM-II, Munich University of Technology, Munich, Germany.

The applications of bismuth-borates require knowledge of thermal expansion coefficients for optical, mechanical and electronic properties. However, to understand the microscopic features leading to macroscopic thermal expansion of bismuth borates is not straightforward as borates mostly show high anisotropic thermal expansion even with negative expansion tensors. Herein we report the thermal expansion of Bi2B2O7 between 4 K and 900 K using temperature-dependent neutron and X-ray powder diffractions and Raman spectroscopy. Thermal expansion was modeled using the Debye-Einstein-Antiharmonicity [1,2]. The calculated phonon density of states (PDOS) shows two broad continua with a sharp feature at 890(1) cm\textsuperscript{-1}. Comparing the highest frequency of the PDOS the model simulation results in a Debye frequency that represents only the acoustic lower frequency parabolic spectrum. The model also follows six independent thermal expansion tensors of the monoclinic system. The Bi\textsuperscript{11} Bond distance of 138(1) pm within the whole investigated temperature range. Due to stereochemical activity of the 6s\textsuperscript{2} lone electron pair (LEP) of Bi\textsuperscript{3+}, four distinctive BiO\textsubscript{6} polyhedra showed different distortion. The Wang-Liebau eccentricity (WLE) parameter [3] for each Bi-atom decreases with increasing temperature, indicating the electron deformation density associated with LEP is a function of temperature as well as the thermal expansion tensors. These phenomena are of fundamental interest to understand temperature-dependent non-linear optical and ferroelectric behaviors of relevant centrosymmetric systems.


CM01.12.20
Temperature-Dependent Structural and Spectroscopic Investigations of (Bi1-xFe\textsubscript{x})FeO\textsubscript{3} (x = 0.17 and 0.33) Using Neutron Elastic and Light Inelastic Scattering Andrea Kirsch1, Mangir Murshed1, Ashfaq Huq4 and Thorsten M. Gesing1, 2; 1 Institute of Inorganic Chemistry and Crystallography, Bremen, Germany; 2 Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3 University of Bremen; MAPEX Center for Materials and Processes, Bremen, Germany.

BiFeO\textsubscript{3} is one of the widely studied multiferric materials for interesting properties [1] depending on crystal chemistry [2] and crystallite/particle dimensionality [3]. Recently, a Bi-3+ Mössbauer spectroscopy and X-ray powder diffraction (XRPD) study revealed a series of (Bi1-xFe\textsubscript{x})FeO\textsubscript{3}, perovskite-type structures, where the Bi-site is partially shared by Fe [4]. To further tune the multiferric property either from electric or magnetic approaches, or simultaneously both directions, the present study reports two compositions (Bi0.83Fe0.17)FeO\textsubscript{3} and (Bi0.67Fe0.33)FeO\textsubscript{3}. Samples were synthesized by a sol-gel route at 873 K. Starting from X-ray amorphous nano-crystallites heating time and temperature exclusively determine the iron occupancy on the perovskite A-site [4]. The materials were investigated by temperature-dependent neutron time-of-flight powder diffraction at P0WGEN (SNS, Oak Ridge, USA) from 10 K to 650 K. A deep minimum has been observed at about 240 K for the change of z-coordinates of Fe-site and O-sites in the (Bi\textsubscript{0.83}Fe\textsubscript{0.17})FeO\textsubscript{3} system, which has been shifted to 260 K for (Bi0.67Fe0.33)FeO\textsubscript{3}. Any anomaly was not observed for the temperature-dependent atomic displacement parameters (ADPs) and thermal expansion. Fitting the ADPs using Debye approach, all three-atom sites showed usual harmonic behavior, leading to a Debye temperature of 288(10) K and 368(13) K for (Bi0.83Fe0.17)FeO\textsubscript{3} and (Bi0.67Fe0.33)FeO\textsubscript{3}, respectively. Notably, the Bi/Fe and O-sites show higher static disorder in (Bi0.83Fe0.17)FeO\textsubscript{3} than those in (Bi0.67Fe0.33)FeO\textsubscript{3}. The thermal expansion of the metric parameters were modeled using DEA approach [5,6]. The intrinsic optical phonon anharmonicity has been extracted from the temperature-dependent Raman spectra. Both samples showed significantly a higher frequency shift of two selective modes than those of the stoichiometric BiFeO\textsubscript{3} perovskite. The damping factors obtained from the simplified Klemens phonon decay model distinguishes between the phonon and magnon contributions to the microscopic heat capacity of the modes.

Investigation of Structural and Magnetic Properties of RT$_2$Ga Compounds

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Ternary RT$_2$X compounds (R = rare earth, T = transition metal, X = Al, Ga, Si, Ge) and their derivatives have been the subject of intense research during recent years. These compounds crystallize in three structure-types, cubic MnCu$_2$Al, orthorhombic YPd$_2$Si, and hexagonal GdP$_2$Sn. In this system, the silicides, germanides, and aluminides are the most studied and little is known about their gallium congeners. RPt$_4$Ga (R = La – Dy) is the only gallium compounds that have been studied thus far. These compounds exhibit both ferromagnetic (R = Tb) and antiferromagnetic (R = La – Gd, Dy) properties with an ordering temperature ranging from 2 to 24 K. We have synthesized several new RT$_2$Ga phases (T = Fe, Co, R = Gd, Tb, Dy), with ferromagnetic transitions greater than those exhibited by the Pd-analogs. The structural and physical properties of these new ternary compounds will be highlighted in this talk.

CM01.12.22 Structural Transitions, Jahn-Teller Distortion, Cyclability and Specific Energy in P2-Type Na$_2$MO$_2$ (M=Transition Metals) Materials as Candidates for Sodium-Ion Cathode Applications

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Development of reliable, high-performance solid state materials for advanced energy conversion and storage is of technological importance for the US economy as well as for a secure, sustainable energy future for humankind. The design of present-day Li and Li-ion batteries have relied on previous studies of composition, crystal structure, property characterization, and device performance. Na-ion cathode materials are potential alternatives to Li-ion materials due to the natural abundance, and low cost, of sodium resources. Recent developments in suitable electrolyte and anode materials have revived interests in the use of newer Na-based compositions and structures as potential battery electrode materials.

Here, we report our results on different compositions of layered oxides of the type Na$_2$MO$_2$ (where M is a transition element, or a combination of transition elements) as cathodes in coin cells built using a Na anode, NaClO$_4$ electrolyte and Celgard separator in a CR 2032 coin cell assembly. Specifically, we discuss the effect of in-situ battery voltage cycling on crystal structure, and on structural transitions, in P2-type Na$_2$M$_3$S$_4$Fe$_2$O$_9$ (NMFO). We find NMFO to have a reversible capacity of 185 mAh/g, but relatively low cyclability. Our results confirm that NMFO undergoes a structural transition from P6/mmc (P2) to P6$_3$ (OP4) at 4.3 V while charging, and to a Cmcm (P2$^1$) phase at 1.5V while discharging. It is currently believed that the presence of Mn(II), a Jahn-Teller active ion leads to a cooperative distortion and structural instability, resulting in a transition from hexagonal P2 to orthorhombic P2 during cycling. We have studied the effect of substitution of additional transition metals in NMFO in an effort to suppress this distortion and structural instability and to increase cyclability. We performed crystal structure refinement on ex-situ x-ray diffraction under controlled atmospheric conditions, as well as studies of battery capacity, specific energy, and cyclability at different battery voltage values during cycling. The substitution of additional transition metals is found to lead to an absence of structural transitions during charging and discharging to 4.3 V and 1.5 V respectively. However, charging at 4.3 V affects the crystallinity of the material as observed by the broadening of x-ray diffraction (XRD) peaks. The cyclability and capacity was found to improve when the cells are cycled in the voltage range 1.5-4.0 V and 2.0 – 4.0 V, with an increase in specific energy from 325 Wh/g to 375 Wh/g when cycled in the 1.5 – 4 V range. Specific energy remains steady up to 100 cycles, pointing to the possibility of higher cyclability. We believe that additional detailed work on the effect of the Mn(III) Jahn-Teller distortion on properties of Na-ion cathode phases can lead to battery materials with improved capacity and cyclability.

CM01.12.23 Epitaxial Growth and Characterization of Multifunctional CrFe$_2$O$_4$ on MgAl$_2$O$_4$

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CrFe$_2$O$_4$ is a spinel/inverse spinel structured crystal with potentially interesting magnetic, electronic, and photophysical properties. The parent materials Fe$_2$O$_3$ (magnetite) and FeCr$_2$O$_4$ (chromite) are naturally occurring minerals each with their own interesting and industrially useful properties. Despite the general interest in the parent compounds, CrFe$_2$O$_4$ is among the least studied of the transition metal spinels. Part of this gap in research lies in the lack of availability of high quality single crystals to study on top of being an unnatural compound. To get around the latter part we can use molecular beam epitaxial (MBE) growth techniques to control the precise stoichiometry and orientation to allow for synthesis of meta-stable or unnaturally layered materials. However, there still remains a lack of suitable single crystal substrates for epitaxial growth of CrFe$_2$O$_4$. MgO (magnesia) has a favorable lattice mismatch of just ~0.34% compressive, but Mg diffusion from the substrate into the overlying film can become significant at deposition temperatures as low as 230°C, creating a tradeoff between crystallization kinetics and intermixing. MgAl$_2$O$_4$ (spinel) is isostructural with CrFe$_2$O$_4$ and more stable against intermixing, but it also has a much smaller lattice constant, and lattice mismatch >5% compressive. Here we report on novel MBE synthesis of CrFe$_2$O$_4$ on spinel and compare with a variety of similar systems, previously studied. A novel method for estimating cation concentration is presented and scrutinized. Transmission electron microscopy (TEM) has been used to analyze the material structure in detail and correlated to bulk techniques like x-ray diffraction. We have investigated the effect of additional Mn(III) Jahn-Teller distortion on properties of Na-ion cathode phases can lead to battery materials with improved capacity and cyclability.

Keywords: Molecular beam epitaxy (MBE), ellipsometry, reflected high energy electron diffraction (RHEED), low energy electron diffraction (LEED), x-ray photoemission (XPS), thin film, stoichiometry, magnetite, Fe3O4, chromium, iron, oxygen, Fe$_2$CrO$_4$, maghemite, hematite, semiconductor, optical, x-ray diffraction (XRD), extended x-ray absorption fine structure (EXAFS), x-ray absorption near edge spectroscopy (XANES), Rutherford backscattering spectrometry (RBS)

CM01.12.24 Heterointerface Effects on the Peculiar Growth Characteristics of Brownmillerite SrFeO$_2.5$ Thin Film Grown on Perovskite SrRuO$_3$ and SrTiO$_3$

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The rich properties and broad utilities of transition metal oxides are enabled by the strong hybridization between transition metal d and oxygen 2p orbitals.[1,2] Engineering such complex correlations has thus been recognized as a route for tailoring functional properties of transition metal oxides. In recent years, unprecedented physical phenomena further emerged by manipulating the heterointerface of transition metal oxides, such as two-dimensional free electron gases, which have never
been accessed in their bulk equilibrium phases.[3] These new phenomena were born through the interface controls which essentially modify the degree of the orbital hybridization. Basically, such interface structure and/or chemistry could also exert a profound influence on the growth dynamics of oxide thin films on foreign substrates. In addition to controlling the growth process of the thin films by a conventional method, i.e. imposing an epitaxial strain, various interface effects can extend the range of choice for manipulating the growth behavior of oxide thin films. The resulting growth behavior significantly affect the microstructures and physical properties of the thin films correspondingly. Therefore, accurate determination of oxide heterointerface structure is essential for understanding the growth characteristics of oxide thin films and for fabricating the functional devices having desired physical properties. Here, we demonstrated that the interface effect can play a crucial role in controlling the growth behavior of oxide thin films by overcoming the simple epitaxial strain energy. For that purpose, brownmillerite SrFeO2.5 (BM-SFO) thin films were grown on SrTiO3(STO)(001) and SrRuO3(SRO)/STO(001) substrates as a model system, and their microstructures were investigated using first principles calculations and transmission electron microscopy. The BM-SFO thin films grown on both the STO(001) and SRO/STO(001) substrates showed b-axis oriented growth at the interface, as opposed to the a-axis oriented growth predicted simply by the epitaxial strain effect from lattice mismatch with the substrates. They even revealed distinct heterointerface structures and growth processes on the two substrates having the same in-plane lattice parameters, which indicates the presence of additional key factors controlling growth characteristics of the thin films. We found that these discrepancies in the growth processes of the thin films originated from the interface effects governed by the heterointerface structures such as the ‘peculiar transition layer’ as well as the different chemical species and ‘octahedral connectivity’.


CM01.12.25

Diamond-Clad Semiconductor Optical Fibers

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Optical fibers are a cornerstone of modern communications and research. The simplest of these fibers, made of silica, guide light with exceptionally low losses, while more complex microstructured or doped silica fibers are capable of advanced photonics. Such structures are immensely useful but have one clear limitation: optical fiber technology has historically been limited to glass. Materials such as semiconductor materials can expand the optical and electronic functionality of fiber technology, but have proven difficult to manufacture because their properties are not compatible with conventional glass drawing processes1.

High pressure chemical vapor deposition (HPCVD) circumvents this issue by enabling the direct deposition of semiconductor materials into glass capillaries via the thermal decomposition of gaseous precursors. With HPCVD, optical fibers composed of highly pure semiconductor cores, including silicon and zinc selenide, have been synthesized. These fibers possess low optical losses due to their atomically smooth surfaces and infrared transparency and exhibit a range of tunable material properties, opening the way for new functional fibers2. Despite broadening the materials base for optical fibers, HPCVD continues to operate with the constraint that materials are deposited into glass templates. Current efforts are underway to replace this glass cladding with materials such as diamond. Diamond possesses a range of extraordinary properties, including high thermal conductivity and wide optical transparency in the IR, making it an ideal cladding for materials such as silicon or zinc selenide fiber3.

To synthesize diamond claddings, silicon wires are first deposited using HPCVD4. Following deposition, the silica glass is removed by etching in hydrofluoric acid, leaving a bare silicon wire that may be used as a substrate for microwave plasma CVD. Dip-coating and sonication are then used to seed such fibers and enable the deposition of diamond claddings tens of microns thick around the entire fiber structure. Scanning electron microscopy and Raman spectroscopy are used to characterize the diamond, revealing excellent crystallinity. In addition, waveguiding of infrared light has been demonstrated in such fibers.

References

CM01.12.26

Synthesis and Structural Characterization of Non-Stoichiometric Ferrite Nanopowders

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Sol-gel processes, followed by an auto-combustion reactions to synthesize ferrites with tailorable stoichiometry have been investigated. Different compositions were produced by this method, substituting the iron in some sites of the crystal structure with other metals, including nickel, zinc, copper, manganese, and cobalt. A parametric study was conducted on the different compositions to determine the effects of calcining and leaching on the structure of the material. The as-synthesized, calcined, and leached nanopowders were characterized by x-ray diffraction and transmission electron microscopy.

CM01.12.27

Visible Absorbance Variation in Bismuth-Containing Dion-Jacobson Perovskites

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Dion-Jacobson perovskites with the general formula A’A2B5O15 are of interest due to their photocatalytic, piezoelectric, ferroelectric properties as well as their ability to exfoliate into nanosheets and restack into new heterogeneous materials. Insertion of lead or bismuth into the interstitial sites of the layered niobates can shift the band gap of the material from the UV into the visible region. Incorporation of bismuth is desired to produce an alternative to the known A’Pb5NbO15 (A’ = Cs, Rb) due to toxicity concerns with lead containing materials. However, the band gap energies of the double and triple perovskite layer version appear to depend on the A’ cation and A cation identities and the synthesis and ion exchange pathways when bismuth is part of A interstitial site population. The double-perovskite layer version, RbBiNbO5, is reported to display ferroelectric and piezoelectric properties as well as possess a moderate indirect band gap (2.5 eV). However, when RbBiNbO5 is acid-exchanged to remove rubidium under typical conditions (6M HNO3 at
60 °C) in preparation for the exfoliation process, the observed band gap of the material is no longer in the visible region, yet acid-exchange at low temperatures preserves the visible region band gap. A new Dion-Jacobson perovskite RbBiKbO₃ has been synthesized via high-temperature solid state methods using RbBiNbO₄ and KNbO₃. The triple-perovskite layer version, RbBiKbO₃₆, maintains an indirect band gap in the visible region (2.5 eV) before and after acid-exchange over a wide temperature range. However, replacement of the interstitial site potassium atoms with sodium results in a band gap in the ultra-violet region even in the rubidium-containing parent form. Results from x-ray diffraction, diffuse reflectance spectroscopy, and ⁹³Nb solid-state NMR spectroscopy will be presented to discuss the evident changes in local structure due the site population variations that drive the band gap changes.

CM01.12.28
Comparative Study on Structural and Optical Properties of InGaN/GaN MQWs Grown by Pulsed MOVPE

InGaN alloys continue to experience problems of incorporating indium (In) when grown by metalorganic vapor phase epitaxy (MOVPE) [1]. On a theoretical level it should be possible to incorporate higher In concentrations into InGaN alloys, however, current attempts to do so lead to In clustering or even segregation into metallic In, ultimately leading to the deterioration of crystal quality. One of the possible solutions to overcome In segregation is to use growth with metalorganic (MO) flow interruptions [2]. This method gives extra time for adsorbed atoms to migrate on the surface and either be incorporated to crystal or to desorb.

In this work we present a detailed analysis of InGaN multiple quantum wells (MQWs) grown by MOVPE using interruptions of MO flow into the reactor chamber. All samples were grown using Aixtron CCS 3+2 reactor keeping all growth parameters constant except timing of MO flow interruptions from 0s (conventional growth) up to 15s. X-ray diffraction (XRD) measurements were conducted to evaluate the In mole fraction, composition, homogeneity and crystalline structure of the InGaN QWs. Structure morphology and layers thicknesses of MQWs were studied using transmission electron microscopy (TEM). XRD measurements revealed that In concentration in InGaN MQWs was 9.5 ± 0.5% for all samples and so the desorption of In during the interruptions was found to be minor. TEM measurements showed, that the QW, barriers, as well as super-lattice (SL) structure are easily distinguishable by the In fluctuation, which confirms a well-formed crystalline structure.

A systematic study of the photoluminescence (PL) intensity on interruption duration was carried out at different temperatures from 10 K up to 300 K. PL intensity increases up to 2 times with blue shift of 54 meV at room temperature with interruption time increase. The FWHM value increase is minor and can be neglected. To determine the extent of the carrier localization effect in MQWs the Gaussian broadening parameter of carrier localization states s was evaluated from s-shape temperature dependence of the PL peak. Though, the value of s parameter does not change significantly (21-24 meV) with increase of interruption duration.

To get a better understanding of MO flow interruption influence on In fluctuation in InGaN layers spatially-resolved sub-micrometer scale PL (µPL) measurements were carried out. Extracted areas (grains) having the average values of PL peak position with ± 3 nm deviation represent the carrier localization centers. It was found that increasing duration of interruption resulted in reduction of the average grain area. Meanwhile, the number of individual grains increased and resulted in a total grain area increase. This leads to a higher density of states and an increase in PL intensity.


CM01.12.29
Atomistic Origins of Shear Strength in 2D Materials

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The low-friction behavior of two-dimensional lamellar materials has been reported in dry, inert environments and is known to depend upon the diffusive motion of the lamella and their relative degree of commensurate stacking, as well as temperature. However, no encompassing theoretical framework presently exists to predict macroscopic friction-related properties such as shear strength. We present a simplified, yet unifying model where the thermolubricity of lamellar materials is described entirely in terms of rotational and translational energy barriers, whose values are determined directly from chemically reactive molecular dynamics (MD) calculations. In the specific case of molybdenum disulfide (MoS₂), the barrier heights are shown to converge with increasing lamellar flake size, and reveal the most probable activation mechanisms to interlamellar sliding. We evaluate the model's prediction of interfacial shear strength by comparing to related MD shear simulations and thin-film sliding experiments of MoS₂, and find strong agreement over a wide range of temperatures.

CM01.12.30
Defect Architecture for Decoupling Carrier Mobility and Lattice Thermal Conductivity in N-Type PbSe Thermoelectric Materials

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Structural defects including vacancies, nanoprecipitates, and dislocations can reduce lattice thermal conductivity. However, they also tend to be deleterious to carrier mobility. As a result, the overall effects for improving ZT are often compromised. In fact, developing strategies allowing for strong phonon scattering and high carrier mobility at the same time is a primary task in thermoelectrics. In this presentation, we report a high performance thermoelectric system of PbₓPbSeₓSe₄₋ₓTeₓ (0-0.4) embedded with unique defect architecture. Considering the mean free paths of phonons and electrons, we integrate multiple defects that include point defects, vacancy-driven dense dislocations, and Te-induced nanoprecipitates with different sizes and mass fluctuations. They scatter thermal phonons collectively in a wide range of frequency to give ultralow lattice thermal conductivity of ~0.4 W m⁻¹ K⁻¹, which approaches to the theoretical lower limit. Remarkably, Te alloying increases a density of nanoprecipitates that affect mobility negligibly and disrupt phonons significantly, and it also reduces a density of dislocations that scatter both electrons and phonons heavily. As y is raised to 0.4, electron mobility is increased and lattice thermal conductivity is decreased concurrently. As a consequence, Pb₀.₄Se₀.₄Te₀.₄ exhibits the highest ZT ~1.5 at 823 K, which is attributed to the significantly enhanced power factor and depressed lattice thermal conductivity, compared with a ZT ~0.9 for Pb₀.₃Se₀.₃Te₀.₄ that contains heavy dislocations only. These results highlight the potential of defect engineering to control electrical and thermal transport properties independently.

CM01.12.31
Enhanced Energy Storage Properties of Ba(Zn₁₋ₓTiₓ)₂O₃-0.15(Ba₅₋₋₀.₃Caₓ)₃TiO₇ Ceramics with BaO-SrO-TiO₂-Al₂O₃-SiO₂-BaF₂ Glass

Addition Weiwei Ping1, Wenfeng Liu2 and Shengtao Li2; 1Electrical Engineering, Xi’an Jiaotong University, Xi’an, China; 2Department of Electrical Engineering, Xi’an Jiaotong University, Xi’an, China.
Glass addition BaO-SrO-TiO2-Al2O3-SiO2-BaF2 was employed to improve the microstructures and energy storage properties of the Ba(Zr0.2Ti0.8)O3-0.15(Ba0.7Ca0.3)TiO3 ceramics, which exhibited a large dielectric constant of 3458 at 25 °C under 1kHz, slim hysteresis loop with the maximum polarization of 12.53 μC/cm² and a remnant polarization of 4.05 μC/cm². Microstructural observation indicated that the average grain size reduced significantly with increasing the glass concentration. Macroscopically the glasses exhibited diffusion phase transition with reduced peak dielectric constant but broad peak with relatively large dielectric constant of around 1000 within the room temperature region. Meanwhile the electrical breakdown strength (BDS) of the glass modified ceramics was nearly quadruple to the pure ceramics form. Energy storage performance of the glass modified ceramics, both 419.4 J/m³ calculated from the product of dielectric constant and square of BDS and 192.8 kJ/m³ from the integration of the hysteresis loop under the electric field of 9.6 kV/mm, showed significant superiority to that of the pure ceramic form.

CM01.12.32

Building Optical Anisotropy via Polarizability Engineering in Quasi-1D Crystal Structures Shan-yuan Niu1, Huan Zhao2, Graham Joe3, Yucheng Zhou2, Thomas Orvis4, Huixuan Han5, Jal Salaman6, Krishnamurthy Mahalinga7, Brittany Urwin4, Jiangbin Wu2, Yang Liu1, Tom E. Tiwald1, Stephen B. Cronin1, Brandon M. Howe1, Matthew Mecklenburg1, Ralf Haiges1, David Singh1, Han Wang1,2, Mikhail A. Kats1 and Jayakanth Ravichandran1,2,3,4,5

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Rational design or discovery of new materials or innovative functionalities in underexplored materials, has been a key contributor to several electronic, photonic, and energy technologies. We report the realization of strong optical anisotropy via chemically tuning the polarizability tensor in quasi-one-dimensional (quasi-1D) crystal structures. Optically anisotropic materials are of great scientific and technological importance in photonic and optoelectronic applications. Quasi-1D structures feature long parallel chains with strong intra-chain bonding and weak inter-chain interaction. In contrast to other low-dimensional materials, they offer robust cleavage planes with easily accessible in-plane anisotropy, which is critical for practical application of optical crystals. The optical anisotropy is enhanced by considering the constituent ions' polarizability to maximize the polarizability difference along different axes in the system. We demonstrate two model systems, BaTiS3 and Sr1+,2TiS3+,2, both with hexagonally aligned chains of face sharing TiS6 octahedra. Large single crystals were grown using chemical vapor transport method with iodine as a transporting agent, allowing extensive spectroscopic studies of their inherent anisotropic properties. We report the observation of strong and broadband infrared birefringence, as well as linear dichroism with distinct polarization-dependent optical absorption edges in the mid-infrared spectrum. Notably, the unprecedented birefringence of up to 0.76 in the transparent region of BaTiS3 more than doubles that in any other bulk crystal.
MnO₂ abundantly exists in the earth’s crust and marine sediment. Based on how its structural units ([MnO₆] octahedra) are linked, polymorphic MnO₂ is categorized into two types: two-dimensional (2D) layered and one-dimensional (1D) tunnel phases. In general, layered MnO₂ can transform into tunnel phases sintered at hundreds degree centigrade and for YIG (yttrium iron garnet, original), the sintering temperature should be 1450 °C. The high level of sintering conditions limits the applications of ferrite for instance of co-sintering with silver. In decades, many researchers launched the research in ions doping, conductivities and machinability. These features lead to diverse applications such as structural, microelectromechanical, protective coatings, sensors, and ceramic characteristics exhibiting oxidation/ corrosion resistance, elastic stiffness and low friction coefficient together with high thermal and electrical behaviors of the layered precursors. The lack of fundamental and atomic level understanding of this phase transition leads to poorly controlled synthesis of Mn-rich marine sediment on the Earth. Current mechanisms explaining the L-T transition are debating, particularly in the critical role of Jahn-Teller distortion of [Mn³⁺O₆] in guiding the behavior of the layered precursors. The lack of fundamental and atomic level understanding of this phase transition leads to poorly controlled synthesis of polycrystalline SnSe samples. Therefore, it is highly desirable to design a new synthesis process that allows us to improve it. Here, we study doped Bi-YIG simples synthesized by multi-steps including sintering at hundreds degree centigrade and for YIG (yttrium iron garnet, original), the sintering temperature should be 1450 °C. The high level of sintering conditions limits the applications of ferrite for instance of co-sintering with silver. In decades, many researchers launched the research in ions doping, conductivities and machinability. These features lead to diverse applications such as structural, microelectromechanical, protective coatings, sensors, and electrical contacts. Although very large volume of outstanding work has been done on these systems in bulk by Gogotsi and coworkers as well as others, there is hardly any work on high quality Mn₃₋₁AXₙ and MXene films. Here we report oriented growth of films (~100 nm thickness) of Ti₃AlC₂, a well-recognized Mnₓ₋₁AXₙ phase comprising earth-abundant elements, on substrates such as sapphire, silicon and quartz by pulsed laser deposition (PLD) at moderate temperatures (550–600°C) under vacuum (~10⁻⁶ mbar). These depositions were carried out by ablating a Ti₃AlC₂ target using the 248 nm radiation from a Kr⁺* excimer laser (10 Hz frequency and fluence ~2 J/cm²). PLD technique was chosen for depositing the films because its hyperthermal particle energies enable low-temperature processing which is advantageous over conventional techniques such as chemical vapor deposition. Deposition of...
Ti$_3$AlC$_2$ films were confirmed by X-ray diffraction, Raman and energy dispersive X-ray spectroscopy (EDS). Preferred orientation of hexagonal Ti$_3$AlC$_2$ film grown on c-cut (006) sapphire was found to be along (103) plane while that on p-type (100) Si and quartz substrates was along (105) plane. Most intense Raman band ~270 cm$^{-1}$ exhibited by the deposited films corresponds to longitudinal displacements of Ti and Al atoms of A$_g$ symmetry. High energy band around 680 cm$^{-1}$ corresponds to vibrations in C sublattice. Observed atomic % of Ti, Al and C were 30.8, 20.1 and 49.1, respectively, as per EDS elemental analysis (on films deposited on Si), fairly in accordance with 3:1:2 atomic ratio of Ti:Al:C in Ti$_3$AlC$_2$. Scanning electron microscopic images of the films showed homogeneous deposition. Thickness of films was tuned by varying the number of laser shots in optimizing the electrical conductivity for pertinent device applications.

**CM01.12.40**

**Highly Ordered and Nanostructured Hexagonal Boron Nitride Synthesized through Molten Salt Synthesis Method**

Kaitlin Wang$^1$, Metin Örnek$^1$, Sisi Xiang$^2$, Chawon Hwang$^1$, Kelvin Xie$^1$ and Richard A. Haber$^1$; 1Materials Science and Engineering, Rutgers, The State University Of New Jersey, Piscataway, New Jersey, United States; 2Materials Science and Engineering, Texas A&M University, College Station, Texas, United States.

Hexagonal boron nitride (h-BN) is one of the materials of choice for applications such as electronic insulators, heat sinks, and coatings due to its unique properties of high thermal conductivity, low thermal expansion, high thermal shock resistance, high electrical resistance, and a low dielectric constant. These properties, along with chemical inertness and resistance to wetting by metallic or non-metallic melts, make h-BN a viable material for metallurgical applications as a solid lubricant as well. However, commercial highly ordered h-BN is synthesized at temperatures of 1800°C or higher, while lower synthesis temperatures through conventional methods result in unstable and less ordered (turbostatic) BN. Molten salt synthesis (MSS) allows precursor reactions to occur in a liquid media, allowing for improved diffusion and reaction kinetics, and therefore reduces synthesis temperatures. Through MSS, highly ordered h-BN was formed at 1000°C, and confirmed through X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and high-resolution transmission electron microscopy (HR-TEM). In this presentation, we will address the effect of synthesis conditions including heating temperature, dwelling time, and precursor composition on the formation of BN and its structural ordering. We will also propose a possible reaction mechanism to describe BN formation in molten salt based on thermodynamic considerations.

**CM01.12.41**

**Precursor Dependent Synthesis of Aluminum Oxide Thin Films**

Yvonne Affrifie; Washington Univ-St. Louis, Saint Louis, Missouri, United States.

**Abstract**

Aluminum is an ideal metal for solution-processed oxide dielectrics because it can form polymerized hydroxo networks in aqueous solution and dense amorphous oxide dielectrics by vacuum methods. Atomic layer deposition (ALD) is the traditional vacuum method for thin film deposition, however, ALD is not the most economically feasible method for fabrication due to the higher operational cost and limitations in large surface-area applications. Solution deposition is a more economical deposition method which is more cost-saving and ideal for large surface area thin film fabrication. The behavior of the solution-solid conversion remains an enigma thus the project seeks to understand the thin film transformation from solution to solid in order to fabricate films with optimal properties.

Aluminum oxide (Al$_2$O$_3$) thin films prepared from aqueous solution-deposited cluster precursors have been proposed for use in devices such as high-k dielectrics in solar cell materials. The films are fabricated with different Al precursors, spin-coated on a substrate and annealed to high temperatures. The low-temperature range of these films are amorphous and lack long-range order which complicates the analysis by traditional means; however, solid-state nuclear magnetic resonance (ssNMR) can be used to determine the structure of these materials. Herein, a combination of x-ray diffraction (XRD), and NMR techniques are used to elucidate the phase transformation of these thin films as they are annealed to high temperatures.

**References.**


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**CM01.13.01**

**Innovations in Indium Phosphide Chemistry and Characterization for Emissive Applications**

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Indium phosphide is the leading Cd-free quantum dot material for application in photoluminescence downconversion display and lighting technologies. To date the performance of InP quantum dots has lagged behind cadmium selenide in terms of both luminescence line width and quantum yield. Extensive studies in our lab have implicated kinetically persistent magic-sized cluster intermediates as a leading contributor to polydispersity in these samples, providing new opportunities for achieving high color purity. Now, using a combination of X-ray emission and solid-state NMR spectroscopy we have studied the evolution of oxidized phosphorus species during both synthesis and shell growth. Correlations of this data with observed ensemble and single particle luminescence will be used to reveal the role of interfacial oxidation on the luminescence properties of InP QDs.

**CM01.13.02**

**Ultrasmall Inorganic Cages Directed by Surfactant Micelles**

Tangi Aubert$^1$, Kai Ma$^1$, Yunye Gong$^2$, Melik Z. Turker$^1$, Teresa Kao$^1$, Peter C. Doerschuk$^3$ and Ulrich Wiesner$^1$; 1Department of Materials Science and Engineering, Cornell University, Ithaca, New York, United States; 2School of Electrical and Computer Engineering, Cornell University, Ithaca, New York, United States; 3Nancy E. and Peter C. Meinig School of Biomedical Engineering, Cornell University, Ithaca, New York, United States; 4Department of Chemistry, Queen's University, Belfast, United Kingdom.

Functional silica nanoparticles have become highly relevant materials in the fields of biology and medicine. Ultrasmall fluorescent silica nanoparticles developed in our group (Cdots) have now reached phase 2 of clinical trials for cancer diagnostics. Nevertheless, modern nanomedicine techniques and their increasing complexity today are still in demand for more efficient and multifunctional tools for advanced applications such as theranostics. To this end, important developments have been made in order for these nanoparticles to achieve their full potential, including chemical modification of their matrix to improve their optical properties, and new synthetic strategies for multifunctional nanoparticles via a surface modification approach with various functional groups. In parallel, new alternative particle geometries have been investigated for targeted drug delivery applications.
In this contribution, we will review some of the recent progress made in our group that ultimately led to the discovery of highly symmetrical dodecahedral silica nanocages, or ‘silicages’ [1]. Ultrasound (< 10 nm) silica nanoparticles with tunable geometries can be obtained through their templating with surfactant micelles. The self-assembly of silica clusters on these micelles gives rise to unique and well defined structures. The dodecahedral cage structure in particular is of great fundamental importance. It is the simplest of a set of Voronoi polyhedra suggested to form the smallest structural units of multiple forms of mesoporous silica, yet such highly symmetrical silica cages had never been isolated before. In order to resolve the actual structure of these ultrasmall objects, single-particle 3D reconstruction from tens of thousands of cryo-electron microscopy images was performed using a custom-built ‘Hetero’ machine learning algorithm. We will finally show that cage formation is not limited to silica, but has been observed for other materials including metals and transition metal oxides.

The chemical and practical value of this polyhedral structure may prove immense. Given the versatility of silica surface chemistry one can readily conceive of cage derivatives of many kinds, which may exhibit unusual properties and be useful in applications ranging from catalysis to drug delivery. For example, given recent success in the clinical translation of ultrasmall fluorescent silica nanoparticles with similar particle sizes and surface properties to these cages, one can envisage a range of new diagnostic and therapeutic probes with drugs hidden inside the cages.

Reference:
follow first-order unimolecular reaction kinetics. We anticipate that our findings on structural isomerism should stimulate attention towards solid-solid transformations and advanced design and synthesis of functional nanomaterials for a diversity of applications enabled by structural transformations.

9:45 AM BREAK

10:00 AM CM01.13.07
Solution-Grown Sodium Bismuth Dichalcogenides—Toward Earth-Abundant, Biocompatible Semiconductors Javier Vela, Bryan Rosales and Miles White; Iowa State University of Science and Technology, Ames, Iowa, United States.

Many technologically relevant semiconductors contain toxic, heavily regulated (Cd, Pb, As), or relatively scarce (Li, In) elements and often require high manufacturing costs. We report a facile, general, low-temperature, and size tunable (4–28 nm) solution phase synthesis of ternary APhE₂ semiconductors based on Earth-abundant and biocompatible elements (A = Na, Pn = Bi, E = S or Se). The observed experimental band gaps (1.20–1.45 eV) fall within the ideal range for solar cells. Computational investigation of the lowest energy superstructures that result from “coloring”, caused by mixed cation sites present in their rock salt lattice, agrees with other better-known members of this family of materials. Our synthesis unlocks a new class of low cost and environmentally friendly ternary semiconductors that show properties of interest for applications in energy conversion.

10:30 AM CM01.13.08
A New Perovskite-Type Sulfide Semiconductor, SrHfS₃, Exhibiting Intense Green Emission at Room Temperature Kota Hanzawa⁴, Soshi limura¹,², Hidenori Hiramatsu¹,² and Hideo Hosono¹,²; ¹Laboratory for Materials and Structures, Tokyo Institute of Technology, Yokohama, Japan; ²Materials Research Center for element Strategy, Tokyo Institute of Technology, Yokohama, Japan.

Semiconductors that are capable to dope into both of p- and n-types are key components in practical devices such as light-emitting diodes and CMOS transistors. Currently we have critical issues on next-generation device applications such as higher resolution display. To overcome such issues, the most difficult challenge is to develop blight green-emitting sources (λ ≈ 550 nm), which has not been realized even in GaN-based systems. Thus it has strongly been required to explore novel semiconductors with a bandgap of ~2.3 eV exhibiting efficient green emission at room temperature (RT). We focus on exciton in semiconductors due to its highly efficient emission. High ionicity of the chemical bonding is a key factor to obtain high exciton binding energy (BE); for SrF₂ with high ionicity, the exciton has a large BE (0.9 eV), while for covalent compounds such as Ge and GaAs the BE is quite small (4 m eV for Ge and GaAs).

On the other hand, deep CBM and shallow VBM are also required to achieve n- and p-type dopings, respectively. However, the d-orbitals of low electron-negativity elements such as alkaline earth (AE) and early transition metals (eTM) usually form a shallow CBM level, while energy level of oxygen or halogen-p-orbital is too deep to dope hole. Hence, ionic compounds composed of AE and eTM have not attracted interest as a constituent of semiconductors so far.

Recently, our research group proposed a design concept for eTM-based semiconductors [1]. Our idea is to create non-bonding state at a specific k-point in high symmetry crystal structure. Since the non-bonding d-orbitals of cation form a deeper energy level than that of anti-bonding state between cation d- and anion p-orbitals, the deep CBM is realized in high symmetry crystals. In the same manner, shallow VBM is also obtained due to the formation of the non-bonding p-orbital of anion. Based on the above consideration, we selected SrHfS₃ with a high symmetry perovskite-type structure. The DFT calculations indicate that the CBM and VBM consist of nearly non-bonding state of Hf 5d and S 3p orbitals, respectively. As a result, the deep CBM and shallow VBM as well as the resultant bandgap of 2.2 eV meet our research target.

We successfully synthesized polycrystalline SrHfS₃ by a solid-state reaction. The optical bandgap was 2.3 eV and photoluminescence (PL) exhibited intense green emission peaking at ~521 nm, which are all consistent with the DFT results and meet our all requirements. It should be noted that the emitting light can be seen by human eyes even at RT. PL arising from defects was not observed, suggesting that concentration of deep defects is quite low. The PL blue shift and shorter lifetime than 4 ns suggest that the intense green emission comes from the exciton. These results indicate that SrHfS₃ is a promising candidate for a new green-emitting semiconductor with large BE. We will also discuss thin-film growth and electronic properties.


10:45 AM CM01.13.09
Controlling the Surface Chemistry of Metal Phosphide Quantum Dots Celine Nayral, Robert Swain, Benjamin McVey, Edwin Baquero, Bruno Chaudret and Fabien Delpech; Univ of Toulouse, Toulouse, France.

Metal phosphides, Zn₃P₂, Cd₃P₂, InP, are an important class of semiconductor quantum dots (QDs) with applications ranging from light emitting diodes to biomedical imaging. [1] The extreme sensitivity of metal phosphate quantum dots to air and moisture require the development of robust surface passivation strategies to truly harness their potential in the above applications. To create such robust surface passivation strategies, a thorough understanding of metal phosphide surface chemistry and interfaces is required.[2]

In particular, we have previously demonstrated that the use of classical high-temperature procedures with indium carbonate precursors induces an indium oxide surface layer that readily forms as a result of decarboxylation processes leading to water-based, in-situ – formed impurities.[3] We present here a comprehensive study that elucidates this oxidation mechanism utilizing a novel indium precursor, [In(aminidate)], more reactive than traditional carbonate or halide indium sources.[4] Indeed, while several reports utilizing different phosphorus sources can be found,[5] the variation of the indium source has been much less described. Our research has granted insight into the mechanism of oxide formation, including the sources of oxidants arising from previously unconsidered side-reactions. This increased knowledge of ligand and surfactant chemistry is valuable to the further efforts of precise surface control. The possibility to avoid oxidation of the QD surface under the correct conditions will be exposed and we demonstrate the ability to successively grow multiple layers of oxide-free InP nanocrystals, allowing us to study surface passivation strategies via a clean, native interface. [6] The role of Zn²⁺ and Zn precursors played in i) producing robust surface passivation, ii) enhancing key optical properties (emission linewidth, quantum yield) for InP QDs will also be discussed, highlighting the importance that surface chemistry and interfaces play in unlocking the true potential of these emerging materials.


11:00 AM CM01.13.10
Titanium dioxide (TiO₂) is a material, whose many well-known properties make it appealing in a wide and diverse range of fields, both in its amorphous and polycrystalline phases. Then, a complete understanding of the parameters that control its amorphous-to-crystalline transition upon different conditions and on the possible polymorphs formed represents an intriguing field of study that embraces implications for both fundamental and applicative sciences. In this framework, anodically grown TiO₂ amorphous nanotubes (TANs) are a good example of the multiple application of titanium dioxide, but so far their thermally-driven crystallization has been mainly studied under ambient pressure and by techniques that require very large populations of nanotubes, thus unavoidably providing averaged collective responses. On the other hand, High Resolution Transmission Electron Microscopy (HRTEM) provides a most local and sensitive technique to study these transitions at a single nanotube level. Thus, the crystallization of TANs was studied upon different conditions according to ex situ and in situ approaches. Besides, different electron beam energies were used for the in situ investigations. The ex situ approach enabled us to study with unprecedented detail the early stages of crystallization for TANs heated in air at ambient pressure, showing the formation of small-sized nanocrystalline seeds and their subsequent development. [1] Conversely, the results obtained by the in situ approach highlighted how the combination of high vacuum and different beam energies can trigger the crystallization at different temperatures, while also providing novel insights on the structural evolution of nanosized TiO₂ polymorphs in this relatively uncommon high-vacuum regime. [2] The first approach pointed out the crystallization temperatures of different TiO₂ phases; the latter provided a direct local observation of the in situ crystallization process and of its evolution, and was again applied heating the TANs upon both inert (N₂), oxidizing (O₂) and reducing (H₂) atmosphere. In such a case also the fine stoichiometry of the TANs was studied pre- and post-crystallization by Electron Energy Loss Spectroscopy (EELS), together with their structural evolution by HRTEM. Thus, the comparison of these diverse processes showed the influence of pressure, electron beam energy and chemical environment on the formation and evolution of different polymorphs. This combination of ex situ and different in situ approaches provides a broader framework to develop novel and different ways to study nanostructured TiO₂ in fundamental and applicative fields.

References

11:15 AM CM01.13.11
Inorganic Cluster-Molecules—Molecular Assembly and Reversible Isomerization
Curvis Williamson1, Richard Robinson2, Douglas Nevers3, Uri Bannì4, Tobias Hanrath5, Ido Hadar6, Lena Fitting Kourkoutis7 and Benjamin H. Savitzky8; Cornell University, Ithaca, New York, United States; 2Chemistry, Northwestern University, Evanston, Illinois, United States; 3The Hebrew University of Jerusalem, Jerusalem, Israel.

Magic-size clusters (MSCs) are renowned for their identical size and precise composition, existing at an intermediate length scale between a small molecule and a conventional nanocrystal. Traditionally, the origin of the MSC stability was thought to derive from the “closed-shell” arrangement of atoms; this inhibits the continuous growth that is typically seen with nanocrystals. However, in semiconductor MSCs, we report that the MSC stability is strongly coupled to an organic-inorganic mesophase: a fibrous self-assembly of inorganic clusters passivated with organic ligands that form during high concentration (1000 mM) synthesis. This mesophase behaves as a large suspended network (>100 nm grains) that stabilizes and promotes a well-defined isomerization. At the length scale between small molecules and nanocrystals, the transformation of MSCs presents an interesting bridge between molecular isomerization and solid-solid transformation that typify structural transformation in chemistry.

11:30 AM CM01.13.12
Designed Single-Source Precursors for Iron Germanide Nanoparticles—Colloidal Synthesis and Magnetic Properties
Alexandre Sodreau1,3, Lise-Marie Lacroux1, Karine Miqueu1, Jean-Marc Sotiropoulos2, David Madec3, Celine Nayar1 and Fabien Delpech1; 1Laboratory of Physics and Chemistry of France; 3Laboratoire Heterochimie Fondamentale et Appliquee, Toulouse, France.

Iron germanides (Fe₅Ge₃) is a fascinating class of material that provides several phases with attractive and, in some cases, exotic properties including ferromagnetism (Fe₅Ge₃), antiferromagnetism (Fe₅Ge₇), or helimagnetism (B20–FeGe). This latter phase has become the focus of intense interest due to the chiral magnetic ordering at RT which makes them highly relevant for the next generation of magnetic information storage.[1] Despite the attractiveness of nanoscale Fe₅Ge₃ structures, there exist only two synthetic approaches for their preparation: chemical vapor transport process to Fe₅Ge₃ at 650°C,[2] and solution phase thermolysis of precursors at high T (>260°C).[3] This latter example provides a proof-of-concept of the relevancy of solution-based strategies. However, the size, the shape or the phase purity are poorly controlled.

We will present herein a novel approach for the preparation of iron-germanium nanocrystals, which relies on the design of single source organometallic precursors that display special features: i) a preformed iron germanium bond, ii) labile substituents to facilitate their removal and iii) low coordinate metal to provide an easy access to Fe₅Ge₃ NCs. We will show i) how the design of novel organometallic single source precursors allows the synthesis of nanocrystals at the lower temperature ever reported using thermolytic approach, ii) the dramatic influence of the substitution on the germanium atom to control the NCs formation and their magnetic properties.


11:45 AM CM01.13.13
Nano-Grained Hexagonal LaMgAl11O19 Doped with Ce for Optical Applications
Ladislav Nadherny, Vaclav Dolezal, Vit Jakes and Katerina Rubesova; University of Chemistry and Technology, Prague, Prague, Czechia.
Due to their isotropic properties, high chemical stability and radiation resistance, aluminates (such as Y₃Al₅O₁₂, MgAl₂O₄, LaAlO₃, LaMgAl₁₁O₁₉) are suitable for use in optical applications for the detection of high-energy sources. One of the main advantages of lanthanum-magnesium hexaaluminate (LMA) is its ability to be doped with high concentrations of transition metals or rare-earth elements (REE) without the need for quenching. Hence, LaMgAl₁₁O₁₉ doped with REE has been investigated for many applications such as solid-state lasers, thermal barriers, w-LEDs, solar panels and non-contact thermometers.

Cerium is frequently used as an optical activator; for example, in mixed oxides, halides or glasses [1]. However, it has rarely been studied as a dopant for LMA, largely because of technological demands involved in preparing such a material by a solid-state method at 1600 °C [2, 3]. Recently, though, sol-gel methods have emerged as a new approach for preparing perfectly homogenous materials at a lower sintering temperature and in a shorter reaction time. We prepared LaₓCe₁–ₓMgAl₁₁O₁₉ with four different non-hydrolytic sol-gel methods La³⁺, Ce³⁺, Mg²⁺ and Al³⁺ cations in the form of oxides, carbonates, chlorides and acetates. Two of the methods were based on active polymerization while water-soluble polymers were applied in the others. All these sol-gel methods produced stable solutions, from which white-to-brown fine amorphous and nanocrystalline precursor powders were prepared. These precursors were then pressed into pellets and annealed for 0.1–16 h at 1150–1300 °C in an Ar–H₂ flow. The annealing temperature was several hundred degrees lower than that of a solid-state method.

The phase compositions of the precursor powders and final polycrystalline materials were analyzed by RT-XRD, using Cu-Kα₁,₂ radiations in the range of 5–120° 2θ. The XRD data were matched with the PDF-4 reference database and refined by Pawley and Rietveld analysis. XRD full profile, TEM image analysis and dynamic light scattering were used to describe the relationships between precursor properties (particle size, morphology, crystallinity) and the final phase composition. In addition, we outline the mechanism of LMA phase formation. Finally, the optical activity of cerium in the prepared LMA matrices is shown in UV-Vis photoluminescence excitation and emission spectra.