

American Conference on Neutron Scattering

Materials Chemistry and Energy

* Invited Paper

SESSION E02.01: Materials Chemistry and Energy I

PM E02.01.02

Improving Phonon Predictions in Organic Semiconductors with Classical Molecular Dynamics and Force-Matching

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The most important challenge in the development of organic electronics is the limited charge mobility of organic small-molecule semiconductors. The mobility is limited in these materials due to long-range, low-energy molecular vibrations which localize charge transiently across a small number of molecules. We can measure the low-energy vibrational spectrum using inelastic neutron scattering (INS), but the peaks cannot be assigned without accurate simulations of every molecular configuration. Previously we showed that density functional theory (DFT) could be used to simulate the INS spectrum. However, these simulations are confined to infinite crystals with a small unit cell. In contrast, molecular dynamics (MD) simulations are much less expensive and can consequently be used to simulate more complex materials. In this study, a MD forcefield is parametrized using DFT calculations of the small molecule semiconductor rubrene in both crystalline and amorphous samples. After parametrization, the INS spectrum, predicted from MD, more closely resembles the experimental spectrum than the DFT predictions in the low-energy region. This is likely because MD can probe a variety of molecular arrangements simultaneously whereas DFT can probe only one. Our study indicates that MD simulations are a viable tool to study the molecular motions in materials too complex for DFT alone if the force fields are properly parameterized.

E02.01.03

Incoherent Dynamics of Hybrid Halide Semiconductors and a Photovoltaic Revolution

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Hybrid inorganic-organic halide perovskite crystals, such as $\text{CH}_3\text{NH}_3\text{PbI}_3$, have garnered significant attention for their use as the light-absorbing semiconductor layer in low-cost photovoltaic devices with high power conversion efficiencies (>20%) as well as in efficient broad-band light emission. This talk focuses on neutron spectroscopy and x-ray scattering of these materials to elaborate on the relationship between the dynamics of organic molecules in the crystal structures and the relationships of those dynamics to the functional electronic properties. Our results provide a platform from which to understand structure-dynamics-property relationships in functional perovskite halides, which have the potential for transformative applications in photovoltaics.

E02.01.04

The Role of Nuclear Quantum Effects and Chemical Bonding on the Thermal Expansion in Cuprous Oxide

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Nuclear quantum effects (NQEs) are usually ignored in favor of a simpler classical interpretation, but they are beginning to enter the mainstream [1]. Even at room temperature, many phonon modes may be active only with their zero point contribution, but these modes can interact with other modes in anharmonic crystals. We recently showed that for the

thermal expansion of silicon, nuclear quantum effects and anharmonicity were needed to obtain the correct experimental trend [2]. Our current study of cuprite (Cu_2O) shows the importance of nuclear quantum effects, along with chemical bonding, for predicting the anomalous negative thermal expansion and large phonon broadening at modest temperatures.

An inelastic neutron scattering (INS) study was performed on a single crystal of Cu_2O using ARCS at the SNS. These datasets were post-processed using Mantid and binned once. The multiphonon background was removed with a new algorithm for polyatomic crystals, and the data were folded back into a single irreducible wedge in the first Brillouin zone to improve the statistical quality of the 4D scattering function $S(\mathbf{Q}, E)$ [3][4]. These INS data show large broadenings of phonon energies which cannot be explained through harmonic or quasiharmonic interpretations alone. Anharmonic calculations were performed using VASP with s-TDEP [5][6]. Anharmonic theory calculations with quantum effects included and experimental dispersions are largely in agreement, but fail to completely predict the total broadening seen in experiment, even at modest temperatures of 300K. Results show that nuclear quantum effects and chemical bonding are both largely responsible for the anomalous thermal expansion behavior seen in cuprite.

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E02.01.05

Water Interactions and Dynamics in Porous Metal Organic Polyhedra

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Recent work on Metal Organic Frameworks (MOFs) have shown that when these materials are stable in the presence of water, they are quite remarkable for

the storage of water, allowing for better understand of H-binding environments. One such material, Co-BTDD, can adsorb as many as 12 equivalents of water per Co in its large 1-D pores, with remarkable stability and reversibility. In addition, the adsorbed water has several binding environments, from ice-like to liquid-like, including some longer-range translation. Utilizing a combination of the High-Resolution Powder Diffractometer, BT1, and the Disc Chopper Spectrometer, we conducted both neutron diffraction and quasi-elastic neutron scattering to characterize the binding environments and dynamics of water bound in these materials. The stability of these materials for water adsorption may also be discussed.

SESSION E03.01: Materials Chemistry and Energy II

E03.01.01

Crystal Structures and Rotational Dynamics of a Two-Dimensional Metal Halide Perovskite $(\text{OA})_2\text{PbI}_4$

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The extended charge carrier lifetime in metal halide perovskites is responsible for their excellent optoelectronic properties. Recent studies indicate that the superb device performance in these materials is intimately related to the organic cation dynamics. Here, we focus on the investigation of the two-dimensional hybrid perovskite, $(\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{PbI}_4$ (henceforth, $\text{OA}^+=\text{C}_8\text{H}_{17}\text{NH}_3^+$). Using elastic and quasielastic neutron scattering techniques and group theoretical analysis, we studied the structural phase transitions and rotational modes of the $\text{C}_8\text{H}_{17}\text{NH}_3^+$ cation in $(\text{OA})_2\text{PbI}_4$. Our results show that in the high-temperature orthorhombic ($T > 310$ K) phase, the OA^+ cation exhibits a combination of a twofold rotation of the $\text{NH}_3\text{-CH}_2$ head group about the crystal c-axis with a characteristic relaxation time of ~ 6.2 picoseconds, threefold rotations (C_3) of NH_3 and CH_3 terminal groups, and slow librations of the other atoms. Contrastingly, only the C_3 rotation is present in the intermediate-temperature orthorhombic ($238 \text{ K} < T < 310 \text{ K}$) and low-temperature monoclinic ($T < 238 \text{ K}$) phases.

E03.01.02

Correlating White Light Emission and Structural Dynamics in Layered Hybrid Perovskites

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Efficient, single material white light emitters are rare and of interest for solid-state lighting applications. Intrinsic broadband white light emission has been observed in layered hybrid organic-inorganic perovskites (HOIPs) with the formula $(R\text{-H}_3^+)\text{PbBr}_4$ and has been correlated to static lattice distortions. The white light emission is thought to arise from the recombination of self-trapped excitons in the inorganic sublayer. The structure and relevant electronic states of the inorganic sublattice are impacted by the choice of organic spacer cation ($R\text{-H}_3^+$). The emission and structural dependence on the organic cation suggest the movement of the organic moieties within the crystal may play a role in octahedral tilt angles and magnitude of exciton self-trapping, and, therefore, affect broadband emission. To understand the role of the organic spacer cation in layered hybrid perovskites we have prepared a series of lead bromide HOIPs with varying white light emission; $(n\text{BA})_2\text{PbBr}_4$, $(\text{ODA})\text{PbBr}_4$, $(\text{GABA})_2\text{PbBr}_4$ ($n\text{BA} = n\text{-butylammonium}$, $\text{ODA} = 1,8\text{-diaminooctammonium}$, $\text{GABA} = 4\text{-aminobutyric acid}$). Using quasielastic neutron scattering and photoluminescence, we have shown more intense broadband emission is observed in materials with slower cation dynamics and larger octahedral distortions. In $(\text{ODA})\text{PbBr}_4$ and $(\text{GABA})_2\text{PbBr}_4$, slower cation dynamics compared to $(n\text{BA})_2\text{PbBr}_4$ were observed concurrently with an increase in broadband emission. This work shows the intensity of the observed excitonic emission is dependent on the lattice dynamics and the organic cation, suggesting these dynamics are coupled.

E03.01.03

Giant Low-Temperature Anharmonicity in Silicon Nanocrystals

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The phonon density of states of silicon nanocrystals with size between 4 and 7.5 nm was measured by inelastic neutron scattering for the first time in the 5~600 K temperature range. The narrow particle size distributions enable the unprecedented study of size effects on phonon dynamics. Giant softening of phonon features below 30 meV, universal broadening of phonon features, and the disappearance of intermediate-energy phonons were observed with decreasing nanocrystals size. Such size effects are

mostly attributed to the structure variations within the nanocrystals. The phonons below 30 meV in silicon nanocrystals show temperature dependence opposite to the bulk silicon, explained by the large anharmonicity of the under-constrained near-surface phonons. This is supported by the abnormal atomic mean-square-displacement, and low energy phonon population in small silicon nanocrystals. This work provides crucial information on the phonon dynamics in spatially confined materials.

E03.01.04

Lattice Thermal Conductivity Evaluation of Burnup Degradation on Heterogeneous Mixed Oxide Fuel

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A study on Mixed Oxide was performed to assess the effect of radiation damage by heavy ions at burnup temperatures. Analysis of Lattice thermal conductivity of (irradiated) MOX to its microstructure are of practical importance to enhance the understanding of how (high burnup) fuel properties can be affected including its pellet-cladding interaction. These structures were used to fit a specified ZBL interatomic potential, which was used to generate molecular dynamics (MD) configurations at temperature ranging from 500 - 2600 K. Our results shows a number of defects remaining after cascade events in PuO_2 which is higher than that in UO_2 at all temperatures. Defect concentration in $(\text{U, Pu, Np})\text{O}_2$ is observed to be in between that of the pure oxides. A number of residual defects decreases as the temperature increases and finally tends to approach a plateau at elevated temperatures. It is reported that both pure and mixed oxide fuels form defect clusters in the residual damage. The modern MOX fuel show fission gas releases comparable to that of UO_2 fuel at moderate burnups and heat ratings. The fraction of interstitials is higher than the vacancies; however, the size of these clusters are smaller than that of voids. Results are consistent with experimental and theoretically-determined values.

E03.01.05

Quantification and Observation of the Carbon-Nafion Interface for PEM Fuel Cells Using Neutron Reflectometry

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The Nafion ionomer is widely deployed as an ion exchange membrane in proton exchange membrane fuel cells (PEMFCs). The structure and properties of

thin-film Nafion at interfaces with gas, platinum, and carbon phases in the PEMFC catalyst layer (CL) plays a key role in determining cell performance and durability. Observations of the interfacial interactions between membrane and electrode materials assist in understanding previously unexplained performance and degradation issues. Neutron reflectometry (NR) is a particularly useful technique in the study of these interactions due to its chemical and spatial sensitivity being consistent with those of the PEMFC CL. Previous NR studies on silicon and platinum substrates show complex layered structures near the interface in humidified environments [1-4]. In our previous work, these structures have been correlated to material properties and used in modeling efforts to predict ways to improve designs for the membrane electrode assembly [5]. While critical electrochemical reactions occur at the platinum and Nafion interface, carbon acts as a substrate for most of the Nafion in the CL. To date, these Interfacial interactions have not sufficiently been characterized in literature. This work presents some of the first NR results from four carbon-based substrates spin-coated with thin-film Nafion. Studies completed in both dry and humidified environments suggest that the layered structures previously observed near hydrophilic substrates are not present to the same degree on carbon. Despite the lack of water-rich layers near the carbon substrates, results show that the overall water absorption into Nafion is comparable to what has been reported with hydrophilic substrates. As water heavily influences the conductivity of Nafion, this suggests that carbon-Nafion interactions have negligible impacts on performance. We will present NR results for the carbon-Nafion interface as well as a discuss the impact these results have on PEMFC performance and durability. Performance is investigated using a physically based model of the cathode CL. This model incorporates structure-property relationships derived from NR experiments.

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SESSION E04.01: Materials Chemistry and Energy III

E04.01.01*

A Combined Neutron Scattering and First-Principles Study of Novel Materials—From 2D Weyl Superconductor MoTe₂ to Hybrid Halide Perovskite Solar Cells

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We will discuss phonons and their role in phase transition and superconductivity in various novel materials such as 2D Weyl semimetal MoTe₂ and hybrid halide perovskite solar cells. Layered transition metal chalcogenides have received much recent attention as potential hosts of electronic Weyl nodes and topological superconductivity. MoTe₂ is a striking example that harbors both noncentrosymmetric T_d and centrosymmetric T' phases, both of which have been identified as topologically nontrivial. In this work, we discuss the mechanical control of crystal symmetry and superconductivity between these two phases by combined neutron scattering measurements and first-principles calculations. Our calculations reveal that by controlling non-hydrostatic components of stress, it is possible to mechanically control the ground state crystal structure. This allows for the tuning of crystal symmetry in the superconducting phase from centrosymmetric to non-centrosymmetric. This mechanical control of crystal symmetry gives a route to tuning the band topology of MoTe₂ and possibly the topology of the superconducting state. In the second part of our talk, we will discuss dynamics of methylammonium (MA) ions (CH₃NH₃) as local probe of ferroelectric ordering in hybrid perovskites MAPbI₃. Despite tremendous work on these systems, it is still not clear what role the CH₃NH₃⁺ (methylammonium, MA) cations play in enhancing solar cell performance. To shed some light on the influence of the MA cations, we present a combined neutron scattering and first-principles computation study of the structure and dynamics of MAPbI₃. Our study has revealed the role of organic CH₃NH₃⁺ ions in determining the structural and dynamical properties of the hybrid halide perovskites. The ground state is non-polar but ferroelectric states where the dipole moments are ordered in parallel are very close in energy, with small barriers of ~0.3 eV. The spontaneous dipole moment is found to be dominated by the off-centering of the MA ions with respect to PbI₃ framework rather than due to dipole moment of the MA ions itself. We find that the CH₃NH₃ twisting mode energy is especially sensitive to the ordering of the CH₃NH₃⁺ ions with dipole

moments, and that it shifts and split significantly depending on the surrounding molecule orientations. We therefore propose using the vibrational dynamics of MA ions as a local probe of the dipole ordering. Under an electric field, one may stabilize different ferroelectric domains that can be monitored via the vibrational spectrum of MA. Such ferroelectric ordering, and its impact on the performance of the hybrid halide perovskite solar cells, could then be accurately quantified and understood.

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E04.01.02

Molecular Structure and Dynamics of Multicomponent Molten Salts by Neutron Scattering and *Ab Initio* Molecular Dynamic Simulations

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Multicomponent molten salt mixtures are fascinating materials that also play a very important role in many energy-related and chemical industries. In the last decade, there has been a sustained resurgence of the Molten-Salt Nuclear Reactor (MSR) concept. International R&D programs and many start-up companies have propelled MSR into the forefront of the next-generation reactor concepts. The design of fully functional MSR's requires detailed knowledge of the molten salt properties at the molecular scale. Fundamental properties of interest include molecular structure and speciation of salt components that determine thermophysical properties such as viscosity, heat capacity, etc. We are conducting elastic and inelastic neutron-scattering measurements to determine Pair-Distribution Functions (PDF) and the dynamic structure factors in Chloride salts containing Chromium ions. The measurements are compared with *ab initio* molecular dynamics simulations. Simulations are necessary for predicting physical and chemical properties especially in the presence of more than 10 chemical species in the melt. However, large-scale atomistic modeling of technologically important molten salts is significantly hindered due to a lack of realistic interatomic potentials. We are applying machine learning algorithms to regress from the simulation and experimental data to develop a fast-acting model that can handle molten salts with an arbitrary number of chemical elements and be able to predict chemical potential as a function of composition and temperature since measuring all these mixtures is an

unrealistic task. Chloride salts were measured extensively by neutron scattering, using isotope substitution of ³⁵Cl and ³⁷Cl. These earlier measurements reached Q values of only about 10 Å⁻¹ and so resulted in a much lower resolution than is possible at modern neutron and X-ray facilities. Importantly, earlier measurements mostly covered single or binary mixtures. Here, we report on initial studies of NaCl-CrCl₃ and NaCl-CrCl₂ eutectics that were chosen because Cr is one the most important corrosion product that is dissolved from metal alloys in contact with molten salts. For neutron diffraction, the samples were enriched with ⁵³Cr, which has negative scattering length, in contrast to positive in natural Cr. The isotopic substitution allows for high-resolution measurements of partial PDFs for Cr-containing pairs of ions. We also report on inelastic neutron scattering measurements of the same isotopically-substituted melts. These measurements are compared with ab-initio computer simulations with a high degree of fidelity.

E04.01.03

Phase Transitions and Framework Stability Predicted from Lattice Dynamics

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Porous materials such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and hydrogen-bonded organic frameworks (HOFs) have been shown to have promising electronic and dielectric properties that can be linked to and controlled by the porosity of the framework structure. However, high levels of porosity often couple with low structural stability, and hence new approaches to understanding and predicting the origin of structural instability and response properties are desirable. In this talk, I will highlight how collective lattice dynamics can provide unique insight and reveal a diversity of valuable information relating to the structural flexibility and the mechanistic origins of anomalous mechanical phenomena. Spectroscopic techniques such as inelastic neutron scattering (INS), in conjunction with density functional theory (DFT), are used to study the phonon mode dynamics, including those related to gate opening and breathing, trampoline-like mechanisms and hindered rotations reminiscent of negative thermal expansion (NTE), and buckling of 2D layers. The approach can also reveal the effect of external pressure and temperature and aid in the prediction of stimuli-induced phase transitions and amorphization.

E04.01.04

Frequency Dependent Data Filtering of Stroboscopic Pumping of Hydrogen Movement in Potassium Dihydrogen Phosphate

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The structure of potassium dihydrogen phosphate (KDP) exhibits a short OH...O bond below the paraelectric-ferroelectric phase transition. The hydrogen can switch between two phosphate oxygens by applying an alternating high voltage electric field along the c-axis. Driving the hydrogen switching through an alternating applied electric field was used to gain insight in the dynamics of the switching behavior. An alternating voltage with approximately triangular wave function was applied with frequencies between 0.1Hz and 10Hz. The hydrogen position cycled between one end position to the other. Data were collected continuously in a stroboscopic mode, where statistically significant intensities are accumulated by repeated electric field cycling. Using the single crystal time-of-flight Laue neutron TOPAZ diffractometer and collecting data in event mode allowed to filter the individual events according to experienced voltage and recombine events with the same voltage into a narrow voltage bin. A full structure refinement of each bin or in fine steps across the voltage cycle was accomplished. Here we will present the preliminary results of event filtering of stroboscopic data and structure analysis.

E04.01.05

Investigation of Kerogen Structures through Simulation and Scattering Approaches

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Shale gas becomes an emerging alternative energy resource, having relatively less carbon emission than coal and petroleum, which is because of the shale gas revolution in the United States. Shale, as a source rock, has heterogeneous and anisotropic pore structures with low porosity and ultralow permeability. Typically, shale rock has a variety of mineral matters and organic matter (kerogen). Kerogen is an intrinsically complex and heterogeneous material that serves as a gas generation source as well as diffusion pathways because of a large population of interconnected nanopores inside its matrix. Despite extensive studies in kerogen molecular structure and fluid adsorption

and transport in kerogen have been investigated, limited studies have been devoted to reconstructing complete molecular structure and characterizing *in situ* fluid injection. In this study, Marcellus shale outcrop was used for kerogen isolation. 2D kerogen macromolecule was analyzed by ¹³C NMR, XPS, and FTIR. 3D kerogen molecular structure was reconstructed using 2D kerogen macromolecules through molecular dynamics simulation. The theoretical physical properties are comparable with measured helium density, micropore volume from CO₂ adsorption, and X-ray pair distribution function. Moreover, unified fitting was conducted on the USAXS profile, where three levels of structures may be revealed in the kerogen sample. The maximum particle size is comparable with the result of laser diffraction. Furthermore, *in situ* SANS was conducted under D-methane injection condition up to 700 bar. Three levels of structures may also be revealed. Porod invariant was determined for each structure under each pressure condition. The invariant value has a clear lowest point around 400 bar for low-Q level. Whereas, the invariant value decreases for middle-Q level and increases for high-Q level with increasing pressure and remained nearly constant after 300 bar. In addition, *in situ* X-ray total scattering was conducted under methane injection condition up to 140 bar. It was found the peak intensities (mostly in positions within 3 Å) of PDF profile reduced with increasing pressure.

E04.01.06

Understanding the Structure-Property Relationships of the Ferroelectric to Relaxor Transition of the (1-x)BaTiO₃-(x)BiInO₃ Lead-Free Piezoelectric System

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Lead zirconate titanate, PbZr_{1-x}Ti_xO₃ (PZT), is a ceramic perovskite material that has exceptional striking piezoelectric properties at the morphotropic phase boundary (MPB). This compound plays an important role in industry and has many commercial applications. However, the toxicity of lead has spurred considerable interest in the discovery of Pb-free ferroelectric materials. Bismuth based perovskites are established as good ferroelectric materials, but it is still necessary to improve the piezoelectric properties of Bi-based perovskites in order to compete with the exceptional ferroelectric properties of PZT. Here, we study the electromechanical properties and the structure of the solid solution between the Bi-based material BiInO₃ (BI) with orthorhombic space group *Pna2*₁ and the classical piezoelectric material BaTiO₃ (BT) with tetragonal structure, *P4mm*, and a

piezoelectric coefficient (d_{33}) of 190 pC/N, (1-x)BT – (x)BI, in the region $0.03 \leq x \leq 0.12$. Based on a structural analysis study previously carried out by Datta et al. (Appl. Phys. Lett. 96, 221902 (2010)), it was predicted that there is an MPB created by a polarization extension mechanism for the system (1-x)BT – (x)BI at $x = 0.1$. In this work, based on Rietveld analysis performed on neutron and synchrotron radiation X-ray diffraction data, we have found that a gradual structural phase transition takes place from a polar tetragonal structure ($P4mm$) and passes through two regions of coexisting phases: 1) $P4mm + R3m$ in the range $0.03 \leq x \leq 0.075$, and 2) $Pm-3m + R3m$ for $0.10 \leq x \leq 0.12$. The properties also transition from ferroelectric ($x \leq 0.03$) to relaxor ferroelectric ($x \geq 0.05$) as the dielectric permittivity maximum becomes temperature and frequency dependent. This transition was also confirmed via polarization-electric field measurements as well as strain-electric field measurements. At the critical composition of $x = 0.065$, a moderate strain of $\sim 0.104\%$, and an effective piezoelectric coefficient (d_{33}^*) of 260 pm/V were observed. The original purpose of this study was to demonstrate the polarization extension mechanism as predicted in the literature, but due to the ferroelectric to relaxor transition, this mechanism was not found to be present in this system. However, this demonstrates that BaTiO₃-based lead-free ceramics could be modified to obtain enhanced electromechanical properties for actuator applications.

Poster Session: Materials Chemistry and Energy

PE.01.01

Quasi-Elastic Neutron Scattering Investigation of Proton Diffusion in SrHPO₄

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As a class of materials, phosphates are employed across a diverse range of applications such as catalysts, ion-exchange materials, solid electrolytes for batteries, chelating agents, bone cement, phosphors, detergents, and linear and non-linear

optical components. Our interest in these materials has been focused on understanding the dynamics and diffusive behavior of protons in rare-earth and alkaline-earth members of the phosphate family, which are candidate solid electrolytes for proton-conducting solid oxide fuel cells (SOFC). The development of SOFC alternatives to fossil-based energy calls for suitable membranes and electrolytes capable of high proton transport at temperatures below 773K. SrHPO₄ is of interest for these roles, although its proton mobility has not previously been reported. Here, we use quasi-elastic neutron scattering (QENS) to investigate the temperature dependence of the proton diffusive motion in SrHPO₄ from 20K to 523K and compare the behavior to Monetite (CaHPO₄). We complement our analysis with a study of the crystal structure and structural phase transitions of SrHPO₄ using Neutron Powder Diffraction (NPD) at temperatures ranging from 6K to 300K, and X-ray Diffraction (XRD) at 150K and 300K. Morphology of the crystals was investigated with Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Overall, our findings provide a preliminary understanding of the effectiveness of SrHPO₄ as a proton conductor and unveil a constraint imposed by the stability of proton diffusion at high temperatures.

PE.01.02

Improving Charge Mobility through Molecular Design Based Mode Damping in Organic Semiconductors

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The use of organic semiconducting materials in optoelectronic devices is limited by poor charge mobility (μ). The prior assumption of a band model for organic semiconductors led synthetic groups to optimize nearest neighbor wave function overlap (J) to increase μ , often with disappointing results. The new model paradigm, transient localization theory, shows that free charges are localized by instantaneous fluctuations in the wave function overlap (ΔJ). Transient localization theory thus posits that the magnitude of the coupling with respect to the fluctuation ($J/\Delta J$) controls μ . This would mean that synthetic chemists seeking to increase μ need to minimize $J/\Delta J$. Here we compare a series of substituted pentacenes designed to reduce $J/\Delta J$ by damping long axis intermolecular motions. We show that in fact, the highest mobility molecule also has

the largest long axis motion, which shows that the full motion spectrum must be considered, not just a single phonon. We also compared fluorinated and non-fluorinated benzodithiophene (BDT) Trimers, which were specifically designed to quench long axis molecular motions and thereby reduce $J/\Delta J$. Since the fluorinated BDT-trimer has a higher μ than the non-fluorinated, we expect to see reduced phonon amplitude at relevant energies 10-100 meV. Our preliminary data shows that the fluorinated BDT-trimer has a reduced dihedral angle range, which explains the reduced disorder and increased μ . This study shows that INS is the most important tool to understanding the link between molecular structure and charge mobility in organic semiconductors.

PE.01.03

Elucidating the Role of Hydride for Ammonia Synthesis over Ru-Loaded Electrides

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Catalytic ammonia synthesis is crucial for producing synthetic fertilizer and active nitrogen source for important chemicals. The conventional large-scale Harber-Bosch process is usually operated under high pressure (10~30 MPa) and high temperature (400~500°C), which results in high energy consumption. Giving that NH_3 synthesis is thermodynamically favorable under ambient condition, new catalysts based on electrides which have low work function have been developed. Recently, a Ru-loaded electride catalyst was reported to reduce the apparent activation energy of ammonia synthesis by promoting N_2 dissociation on Ru. In this study, we synthesized Ru loaded 3D electride which is a mixture of calcium oxide and aluminum oxide that is consist of cages and it was confirmed that ruthenium particles supported on the electride catalyzed ammonia synthesis from mixtures of N_2 and H_2 at turnover frequencies 5 times faster than other basic-metal-promoted Ru nanocatalysts reported in the literature. From the neutron scattering studies, we directly confirmed that hydride species engaged in the framework of the C12A7 electride modified by Ru, which demonstrated that these species are stable inside the framework cages. Temperature-programmed desorption and surface reaction studies indicated that removal or exchange of the surface cage hydride species from the electride took place more readily under ammonia synthesis conditions than under inert atmospheres such as Ar. Further study of 2D electride – CaN_2 – supported Ru

for ammonia synthesis is also underway to reveal the impact of electride structure, 3D vs. 2D, on the reactivity of included hydride species during ammonia synthesis. Acknowledgments: This research is supported by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy. The neutron studies used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. Part of the synthesis work was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

PE.01.05

Local Structure Origin of the Relaxor Behavior in Tetragonal Tungsten Bronzes (TTBs)

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Tetragonal tungsten bronze (TTB), with the general formula $(A1)_4(A2)_2B_{10}O_{30}$, is a family of lead-free relaxor with great piezoelectric and electrochemical properties. Despite its wide-range application, the atomic origin of the relaxor behavior remains elusive. In this contribution, we establish the link between the local structure and the dielectric/relaxor behavior in TTB phases, using a combination of Rietveld analysis, PDF analysis, RMC modelling and DFT calculation. We have focused on two compositions, namely the archetype $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN) and the $\text{K}_4\text{La}_2\text{Nb}_{10}\text{O}_{30}$ (KLN). For the $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ phases, we have investigated temperature dependent structural evolution of $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ ($x = 0.33$ and 0.67) and for the first time, provided comprehensive information relating the local atomic ordering. We have revealed an abnormal change of the oxygen ADPs, which gradual *decreases* over *increasing* temperature and thus indicate a disordered anion network. Furthermore, we have demonstrated local polarization well above the Curie temperature, while the average structure has transferred to the ferroelectric state. The crossover from ferroelectric to the relaxor behavior is ascribed to local cation ordering. $\text{K}_4\text{La}_2\text{Nb}_{10}\text{O}_{30}$ (KLN) is another very interesting composition: conventionally site-mixing is a prerequisite for relaxor behavior in both TTB and the related compounds (perovskite relaxor for instance). However, neither our neutron scattering nor DFT

calculation indicates mix occupancy between K and La, while a standard relaxor behavior was captured by dielectric measurement. Indeed, our results indicate very similar local structure, composed of distorted coordination Nb-O polyhedra, at 20 K and 300 K respectively, while the latter is well above its Curie temperature. Overall, our results pointed to a new mechanism based on local oxygen static disorder, which is responsible for the observed relaxor behavior in KLN.

PE.01.06

Structure and Dynamics Investigation of Barium Hydrogen Phosphate BaHPO₄

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From a materials design perspective, phosphates offer nearly limitless possibilities for various applications, including ion-exchange materials, solid electrolytes for batteries, linear and non-linear optical components, chelating agents, synthetic replacements for bone and teeth, phosphors, detergents, and fertilizers. As a consequence of its thermal and chemical properties, Barium Hydrogen Phosphate (BaHPO₄) plays an important role in catalytic chemistry, industrial paint manufacturing, and ink-related charge direction. Because hydrogen and hydrogen bonds significantly affect these properties, studying proton mechanisms such as proton diffusive motions and jumps is critical to developing a comprehensive understanding of the compound, allowing further determination of potential applications. Here, we utilize incoherent quasi-elastic neutron scattering (QENS). QENS is a useful technique to determine diffusive motions in the 10⁻¹² to 10⁻⁹ second time range at length scales from 3 Å to 60 Å, which apply to hydrogen ion diffusion and hydrogenous species. Protons have a substantial neutron cross section, which subsequently enhances the associated QENS signal, and permits studies of low-proton systems such as BaHPO₄. The QENS investigation was conducted using 7 discrete temperatures ranging from 293 to 573 Kelvin, while subsequent fitting and analysis revealed the diffusion coefficient as a function of temperature. Obtained results for BaHPO₄ were compared to Monelite (CaHPO₄). In addition to QENS, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) provided support by giving insight to the surface topography of the sample. Structural and

topographic results were compared with similar studies of other relevant phosphates.

PE.01.08

High-Pressure Neutron Diffraction on WAND² in a Paris-Edinburgh Cell

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Pressure is a useful tool for the increase in reactivity of materials and can thus aid and even enable synthesis of novel materials. However, this higher reactivity can also be a hinderance to experiments as samples interact with the apparatus generating the pressure. For example, the diamonds used to generate pressure in one of the most common high pressure cells – the diamond anvil cell – interact with samples at the extremes of pressure. One such system where this phenomenon is a hinderance are high-pressure studies of lithium. Li is often used as a prototype system for the nearly-free electron model. With the application of pressure this simple metal displays a wealth of complex phase behavior as a result of the increased interplay between the core and valence electrons; however, despite decades of theoretical and experimental research dedicated to understanding the complex nature of lithium at high pressure, many conflicting results exist and large regions of pressure-temperature conditions remain unexplored. This is in part due to a lack of high-quality data as a result of lithium's low atomic number, making x-ray diffraction structural investigations difficult. It is however also due to lithium's propensity to break the diamond anvils used in high pressure experiments. The exact mechanism behind this lithium-induced anvil failure at high pressure is unclear and no experimental evidence on the lithium-diamond has been reported. This current work addresses this shortcoming. Here, we present diffraction data from a diamond-lithium mixture pressurized to above 15 GPa to understand this phenomenon. Data were collected in a Paris-Edinburgh cell with double toroid anvils on WAND² at the High Flux Isotope Reactor at Oak Ridge National Laboratory. These double toroidal anvils are made from sintered polycrystalline diamond in order to reach 20 GPa but often interfere with the sample signal. The diamond-lithium sample was loaded into encapsulated gaskets to avoid breakage of the diamond anvils. The high flux combined with the small monochromatic beam yield the ability to collect diffraction data from samples with minimal contamination from the diamond anvils

which allows for the study of samples with diffraction signals overlapping with diamond at high pressure such as our diamond-lithium mixture here. This study thus represents unique new insight into the failure mechanism of diamond when exposed to Li under pressure. It also represents the first use of the double-toroidal Paris-Edinburgh cell on WAND² and thus the first studies above 10 GPa the High Flux Isotope Reactor.

PE.01.11

***In Situ* Redox Dynamics of Sr_{1-x}Ba_xMn_{1-y}Ti_yO₃ Investigated by Neutron Powder Diffraction**

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Multiferroic perovskite materials, Sr_{0.4}Ba_{0.6}Mn_{0.94}Ti_{0.06}O_{2+d} (with d= 0.41 – 1), were studied by in-situ neutron diffraction under various oxidizing and reducing atmospheres. A precursor hexagonal phase of the same composition was subjected to several redox annealing cycles from which we observe a reproducible sequence of phase transformations. Preliminary data analysis suggests the possible stabilization of a previously unknown phase under mild hydrogen reduction conditions. The exact details of the new phase are being investigated. We further demonstrate the reversibility of the process with the parent hexagonal phase fully recovered when annealing the reduced sample in pure oxygen. Annealing an oxygen deficient sample (d= 0.41), on the other hand, in low oxygen partial pressure conditions revealed the possible presence of a miscibility gap with phase separation consisting of two coexisting d= 0.41 and d= 3.0 phases. The miscibility gap could explain the suppression of intermediate oxygen ordered states previously observed with the parent SrMnO_{2+d} material. Detailed synthesis and structural investigations will be discussed in this presentation. Funding

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PE.01.12

Visualization and Quantification of Spatial Distribution of Dendrites in Polymer Electrolytes for Lithium Metal Batteries

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The integration of Li metal anodes with polymer electrolytes is a necessity for next-generation high-capacity batteries, but dendrites tend to form during cycling, causing short-circuit risk, by mechanisms that remain elusive. Identifying the three-dimensional (3D) microstructure of dendrites in the polymer electrolyte is critical to understanding their formation mechanisms, but up to now 3D quantification and visualization of dendrites, especially those with low Li contents, remain a high challenge to the battery community. Here, we visualize and quantify the spatial distribution of Li dendrites grown in PEO-LiTFSI polymer electrolyte using 3D tomographic neutron depth profiling (NDP). 3D mapping of Li dendrites in polymer electrolyte reveals rather heterogeneous lateral distribution over wide length scales from below a millimeter to centimeters. While most dendrites grow from the plating electrode toward the cathode with the overall Li concentration decreasing gradually from the electrode interface to the bulk of the electrolyte, dendrites that are not grown from the plating electrode are also observed. This study reveals new insights in dendrite formation in polymer electrolytes and help refine design principles to improve the safety and operation capacity of lithium metal batteries.

PE.01.13

The Impact of Li Doping on the Structure and Phase Stability in AgNbO₃.

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The impact of Li doping on the temperature induced phase transitions in silver niobates Ag_{1-x}Li_xNbO₃ has been investigated using a combination of high resolution powder neutron diffraction and synchrotron X-ray diffraction. Considering both the cell metric and distortions of the NbO₆ octahedra, estimated by Rietveld refinements, it is shown that the sequence of temperature induced phases in AgNbO₃ is P2₁am → Pcam → Cmcm → P4/mbm

→Pm-3m. This sequence is simpler than that proposed in earlier studies. Evidence is presented from a second order Jahn-Teller distortion in the *Pcam* phase. At $x > 0.05$ Li doping favors the formation of a rhombohedral phase in space group *R3c* and such samples display the temperature induced sequence *R3c* → *Pbnm* → *Cmcm* → *P4/mbm* → *Pm-3m*. Unusual volume changes associated with the phase transitions point to the potential importance of lattice matching in optimizing the properties of thin films of doped AgNbO_3 .

PE.01.14

No (...But Maybe Slow?) Dynamic Tetragonal Domains in Cubic Methylammonium Lead Triiodide

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Hybrid organic-inorganic metal-halide perovskites (HOIPs) are a novel class of semiconductor with unusual and promising optoelectronic properties for high-efficiency, solution-processable solar cells. The HOIP family exhibits significant dynamical disorder due to weak bonding, and in hybrid variants, additional rotational degrees of freedom of organic cations. The dynamical disorder is linked to phase transitions in the prototypical HOIP, $\text{CH}_3\text{NH}_3\text{PbI}_3$ (herein MAPI), which transitions between orthorhombic, tetragonal, and cubic phases at 162 K and 327.5 K, respectively. The cubic-tetragonal transition in MAPI proceeds as a condensation of the soft, transverse acoustic, cubic *R*-point phonon. X-ray inelastic scattering studies have observed *R*-point scattering up to 350 K in cubic MAPI, leading to predictions of critical scattering from dynamic tetragonal domains.^{1,2} We investigated the *R*-point scattering with high-resolution neutron inelastic scattering from a deuterated MAPI single crystal. Constant-energy and constant-wavevector scans were measured at several temperatures on cold and thermal neutron triple-axis spectrometers, and fit to models corresponding to dynamic-domains and the famous neutron “central peak” first observed in SrTiO_3 .³⁻⁵ The energy linewidth is resolution-limited, whereas the wavevector linewidth is not, consistent with the “central peak” phenomenon. Furthermore, the scattering only has a weak temperature dependence, inconsistent with the dynamic-domain hypothesis. The origin of the “central peak” is still debated; our data indicates that the scattering from

MAPI likely originates from small, static, tetragonal domains nucleating about crystal defects.

Discontinuities in the temperature dependence of the fitted parameters indicate the transition is first-order.

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PE.01.15

Size, Structure and Luminescence of $\text{Nd}_2\text{Zr}_2\text{O}_7$ Nanoparticles by Molten-Salt Synthesis

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Pyrochlore materials with $\text{A}_2\text{B}_2\text{O}_7$ composition are in high demand for various applications such as optoelectronics, scintillator materials, and thermosensors due to their novel properties. Some reports have already indicated the importance of synthesis techniques for $\text{Nd}_2\text{Zr}_2\text{O}_7$ (NZO) nanoparticles (NPs), however no explanation has been provided for the reasons behind the nature of its phase selectivity. Here, we have explored the structural and optical properties of the NZO NPs synthesized by a facile and scalable molten salt synthesis (MSS) method. We have synthesized size-tunable NZO NPs and correlated the particle size with their structural behaviour and optical performance. All NZO NPs are stabilized in defect fluorite phase. Collected neutron diffraction data provide insight on the behaviour of oxygen in the presence of heavy atoms. We have collected bright amalgam of blue and green emissions from these NPs

upon UV irradiation due to the presence of oxygen vacancies. We have carried out in-situ x-ray diffraction (XRD) and Raman investigations to observe the temperature-induced phase transformation in a controlled argon atmosphere. Interestingly, we have not observed phase change for the molten salt synthesized fluorite NZO NPs, however, we observed phase transformation from a precursor stage to pyrochlore phase by in-situ XRD directly. These observations provide a new strategy to synthesize nanomaterials phase-selectively for a variety of applications in materials science.

PE.01.16

Solvent-in-Salt Electrolyte with Eutectic Solvent— Consequences to the Microscopic Dynamics in Bulk and Confinement

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In this work, we focus on the solvent-in-salt electrolytes (SISEs), which are a promising alternative to the electrolytes presently used in commercial devices. On one hand the SISEs' have interesting advantages, such as expansion of electrochemical voltage window, non-flammability, non-volatility and high charge density. On the other hand, their applications are still not consolidated due to some limiting chemical and physical properties related to the poor mobility of their chemical species. As an option to lift these restrictions, we explore the inclusion of a stable and soluble species whose interactions with the solvent and ions in the electrolyte are weak enough to reduce the viscosity of the solution and increase the self-diffusion of all molecular species. Namely, we had added chloroform to a SISE formed by acetonitrile and a Li-salt - LiTFSI. Initially, with preliminary cycling experiments, we have been able to highlight the potential of this approach. In the sequence, we focused on describing the microscopic dynamics of the electrolytes and revealed the relevant aspects to be considered in the pursue of achieving their ideal performance. Interestingly, while the conductivity at low temperatures is improved by the addition of chloroform, a divergent outcome occurs at room temperature, i.e. chloroform suppresses the SISE's conductivity. As investigated by molecular dynamics simulations and quasielastic neutron scattering (QENS) experiments, this effect is related to a

reduction in the screening effect of ions caused by the addition of chloroform, which occurs despite the observation of an increase in the mobility of the chemical species. The dynamics of the electrolytes while confined in porous carbon was also investigated using QENS. Under this condition, low concentrations of chloroform lead to diffusivities of the molecular species higher than those observed for the bulk electrolytes. Nevertheless, no further increase in the diffusivities is observed as chloroform's concentration increases. Overall, chloroform is immobilized on the carbon surfaces and this behavior may intensify at compositions closer to the eutectic mixture.