The Pittsburgh Diffraction Society

Established 1943

Thursday 19 Oct 2017

Morning Session

"Neutron powder diffraction studies of magnetic materials"

Session Chair: Stuart Calder, HFIR-ORNL

A1: Multiferroic h-$LuFeO_3$—adventures in neutron scattering

William Ratcliff

National Institute of Standards, Neutron-Condensed Matter Science Group

It was initially reported that h-$LuFeO_3$ films are ferroelectric and magnetically ordered above room temperature [1]. During this talk, we discuss our results [2] on well characterized molecular beam epitaxy grown films. While we find the films are ferroelectric at room temperature, we find that films grown on both YSZ (111) and Al_2O_3 (0001) substrates are magnetically ordered well below room temperature. The magnetic order is the standard 120 degree structure found in these materials, with a canted moment out of the a-b plane. We find that the magnetic structure of these films is consistent with the possibility of switching this small canted moment with an electric field [3]. I will also speak on our recent results on the bulk realization (in the form of powders and single crystals) of this system and our exciting results in thin film heterostructures. Along the way, I will provide a gentle introduction to magnetic neutron diffraction, symmetry analysis, etc.

[1] W. Wang et al, Phys. Rev. Lett. 100, 237601 (2013).
[2] Steven M. Disseler et al, Physical Review Letters, 114, 217602 (2015); Steven M. Disseler et al, Phys. Rev. B 92, 054435 (2015).
[3] H. Das et al, Nat. Commun. 5, 2998 (2014).
[4] Julia Mundy et al, Nature 537, 523 (2016).

A2: Using neutron diffraction to study competing orders in unconventional superconductors

Keith Taddie

Oak Ridge National Laboratory, Oak Ridge · Quantum Condensed Matter Division

Superconductivity remains a vibrant field – despite nearly a century of study – due to the still ill-understood pairing mechanism of unconventional superconductors. These materials which tend to be chemically complex, low-dimensional and strongly correlated typically exhibit a bevy of competing tunable ground states and, consequently, diverse competing orders out of which superconductivity arises. Understanding how superconducting electron Cooper pairs form out of these numerous interactions and which is playing the role of the pairing 'glue' is vital to achieving usable materials. In this talk, I will discuss a particularly rich family of unconventional superconductors – $A\mathrm{Fe}_2\mathrm{As}_2$ (with A = Ca, Sr, Ba) – which show competing magnetic, structural and superconducting order and how neutron diffraction has been an invaluable tool in the determination of the primary of these orders.

A3: Powder Neutron Diffraction and Magnetic Structures of Intermetallics and Oxides: Advantages and Limitations

John.E. Greedan[a,c], Fang Yuan[a], Yurij Mozharivskyj[a,c], T.J.S. Munsie[b], Anna Millington[b], Graeme M. Luke[b,c], Casey A. Marjerrison[b,c], Hanna Dabkowska[c], Chad Boyer[d], Adam Aczel[e] and Huibo Cao[e]

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Three recent case studies of magnetic structure determination in a series of intermetallic compounds, $\mathrm{RE}_3\mathrm{Co}_4\mathrm{Ga}_2$ (RE = Ho and Er) and two oxides, KRuO_4 and $\mathrm{NiNb}_2\mathrm{O}_6$, will be discussed. For the Ho and Er intermetallics, the advantages of the "heavy" rare earths for neutron diffraction, huge ordered moments (> 6 Bohr Magnetons) and extensive Q-range for the magnetic reflections, are highlighted. It is even possible to observe magnetic small angle scattering using a conventional diffractometer in such systems. KRuO_4 represents the opposite situation of very small moments (~ 0.5 BM) and limited Q-range for 4d series systems. Although only one magnetic reflection is observed, it is still possible to infer the magnetic structure. $\mathrm{NiNb}_2\mathrm{O}_6$ contains the 3d ion Ni^{2+} and is an intermediate case. The material in question is a high temperature polymorph with a structure closely related to tri-rutile. Here powder neutron data could be fitted to more than one magnetic structure model with more or less equivalent agreement indices. Single crystal data were needed to assign, unambiguously, a magnetic structure.

A4: Time of flight magnetic neutron powder diffraction on POWGEN

Simon Kimber

Chemical and Engineering Materials Division, Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, TN

Time of flight neutron powder diffraction offers a highly complementary view of magnetic materials. This is because very long d-spacings can be measured at high resolution using cold neutrons and back scattering detectors. Furthermore, the data is intrinsically low background and comparatively free from spurious signals. In this presentation, I shall describe the upgraded POWGEN diffractometer at the Spallation Neutron Source, ORNL. After giving brief details on the instruments performance, I will focus on several example materials. The first is the natural mineral Manganite (MnOOH), where an excellent signal can be measured on a small, hydrogenated natural sample. The reasonable incident flux and high resolution available on POWGEN enable the refinement of small shifts in the propagation vector of the incommensurate spiral magnetic structure. I will also describe the coupling of structure and magnetism in the distorted S=1/2 spinel $Ag_2Cu_2O_3$, whose small ordered moment is challenging to powder instrumentation.

A5: Spin fragmentation in Ising kagome magnets

Martin Mourigal

School of Physics, Georgia Institute of Technology, Atlanta, Georgia

The kagome lattice is at the forefront of the search for exotic states generated by magnetic frustration. Such states have been observed experimentally for Heisenberg and planar spins. In contrast, frustration of Ising spins on the kagome lattice has previously been restricted to nano-fabricated systems and spin-ice materials under applied magnetic field. In this talk, we will show that the layered Ising magnet $Dy_3Mg_2Sb_3O_{14}$ hosts an emergent order predicted theoretically for individual kagome layers of in-plane Ising spins. We present an analysis of experimental magnetic neutron diffraction and thermo-magnetic data, which reveal a phase transition at T=0.3 K from a disordered spin-ice like regime to an “emergent charge ordered” state. In the latter state, emergent degrees of freedom show long-range order while spins remain partially disordered. The coexistence of diffuse and Bragg scattering can be understood in terms of the recently proposed concept of spin-fragmentation. Part of this work is published in: Nature Communications 7, 13842 (2016).

Thursday 19 October 2017

Afternoon Session

"Powder diffraction from nanoparticles"

Session Chair: Cev. Noyan, Columbia University

B1: Determining Crystallite Size with GSAS-II: Improving a Classical Technique

Brian Toby

Senior Scientist, Group Leader and APS Chief Computational Scientist

It was understood nearly 100 years ago that crystallite size determined peak breadth in powder diffraction [Scherrer, P. (1918). "Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen," *Nachr. Ges. Wiss. Goettingen*, 98-100.] Since then, several different approaches have been used to determine this broadening from powder diffraction, but in the opinion of many, or at least this author, full pattern fitting (Rietveld analysis) with data over a wide Q-range provides the most precise measurement of size broadening within the accuracy of this classical model, particularly if any sample microstrain is present. The GSAS-II package provides a new approach to profile models, which further simplifies this analysis. The talk will also discuss progress towards application of the Fundamental Parameters approach within GSAS-II to establish the instrumental profile model.

B2: THE ANALYSIS OF NANOMATERIALS BY POWDER DIFFRACTION

T.G. Fawcett*, S. N. Kabbekodu, J. R. Blanton, T. N. Blanton

International Centre for Diffraction Data

The use of designed nanomaterials with tailored morphologies and properties is advancing many fields of science and is especially prevalent in energy materials, pharmaceutical design, and catalysis. Diffraction methods are well suited for studying nanomaterials due to the nanometer wavelengths that are of the same scale as the materials being studied. Diffraction methods are sensitive to the degrees of order and disorder in solid state materials and experts use both the coherent and incoherent scatter to understand nanomaterial structures. Modern advances in sources, improved optics, and energy selective detectors have improved our abilities to study atomistic level changes in nanomaterial composition.

The International Centre for Diffraction Data (ICDD) has worked with its international membership of scientists to develop a series of software tools and simulations to be able to study and characterize nanomaterials. Simultaneously the ICDD has developed reference data and editorial procedures for experimental nanomaterials as well as amorphous materials [1]. Methods have been developed that are generically grouped under the title of “Total Pattern Analyses” whereby the entire digital profile of a diffraction pattern is used to study degrees of order, domains sizes, and contributions from scatter and background in order to extract information about all the materials present in the solid state independent of their crystallinity. The use of digital patterns for both the material being analyzed and reference materials allows us to study crystallite size [2], molecular orientation and various instrumental and specimen contributions to the coherent and incoherent scatter [3], allowing for the analysis of crystallinity. Digital simulation tools are used to make the analyses radiation independent so that we can use experimental x-ray, neutron [4], electron [5] or synchrotron diffraction data for the analyses. Multiple examples of nanomaterial analyses using x-ray powder diffraction data will be shown.

[1] Fawcett, T.G., Kabekkodu, S.N., Blanton, J. R. and Blanton, T.N., (**2017**), “Chemical analysis by diffraction: the Powder Diffraction File™”, Powder Diffraction, Vol 32 (2), 63-71.
[2] Scardi, P., Leoni, M., and Faber, J., (**2006**), “Diffraction Line Profile from a Disperse System: A Simple Alternative to Voightian Profiles”, Powder Diffraction, Vol. 21 (4), 270-277.
[3] Fawcett, T.G., Kabekkodu, S.N., Blanton, J.R., Crowder, C.E., and Blanton, T.N., (**2015**), “Simulation tools and references for the analysis of nanomaterials”, Adv. in X-ray Analysis, 58, 108-120.
[4] Faber, J., Crowder, C., Blanton, J., Kabbekodu, S., Gourdon., S., Blanton, T., and Fawcett, T., (**2014**) “New neutron diffraction data capability in the PDF-4+ 2014 relational database”, Adv. in X-Ray Analysis 58, 77-89.
[5] Reid, J., Crane, D., Blanton, J., Crowder, C., Kabekkodu, S., and Fawcett, T., (**2011**), “Tools for Electron Diffraction Pattern Simulation for the Powder Diffraction File”, Microscopy Today, January, 38-42.

* emeritus

B3: Correlating Local Crystalline Structure with X-Ray Powder Diffraction Spectra of Nanocrystals

Shangmin Xiong,[a] Hande Öztürk,[b] Yan Li,[c] Hanfei Yan,[b] Seung-Yub Lee,[a] Ismail Cevdet Noyan[a]

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We present a rigorous modeling analysis of the correlation between real-space unit cell parameters (unit cell symmetry, lattice constants and interplanar angles) obtained from molecular dynamics computations for a powder ensemble consisting of pseudo-spherical Au nanoparticles 5 nm in diameter, and the average (reciprocal space) parameters obtained from Rietveld refinement of the X-ray powder diffraction spectra computed for such an ensemble using the Debye equation. We show that, while the

average symmetry of the simulated particles is adequately captured by the diffraction analysis, within the particles local regions with significant deviations from this average symmetry exist. In addition, our computations show that the unit cell parameters obtained from diffraction analysis are complicated averages of the local (real-space) values. These average values cannot be assigned directly to any real-space volume without significant assumptions. We conclude that, in general, the accuracy of structural parameters obtained from diffraction analysis is much worse than the precision reported by analysis codes.

B4 and B5: See Poster Session Abstracts

Friday 20 Oct 2017

Morning Session

"Monitoring changes in materials properties through diffraction methods"

Session Chair: Cora Lind-Kovacs, University of Toledo

C1: In-situ Structural Studies of Piezoelectric Materials

Michelle Dolgos

Department of Chemistry, Oregon State University, Corvallis, Oregon

Piezoelectric materials convert electrical to mechanical energy and vice-versa and are therefore used in both actuator and sensor applications. In situ structural studies of piezoelectric materials are the key to understanding the microscopic origin of their interesting properties. Our research uses in situ diffraction to gain fundamental knowledge of the piezoelectric response to external stimuli such as temperature or electric field. This presentation will summarize our work on in situ diffraction studies of $LiNbO_3$, a widely used piezoelectric material, and $(Ba,Ca)(Zr,Ti)O_3$, the highest performing lead-free piezoelectric material.

C2: Dynamic Disorder Activity of CH_3NH_3 Groups in Directing the Crystal Structure of $(CH_3NH_3)_2AgInBr_6$ Double Perovskite

T. Thao Tran,[a,b] Michael Quintero,[a,b] Xiaoping Wang,[d] and Tyrel M. McQueen[a,b,c*]

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The discovery of high efficiency photovoltaics in halide perovskites has revolutionized the field and stimulated substantial research efforts into solid–state materials. We discovered new double perovskites Cs_2AgMCl_6 (M = Sb, In) exhibiting soft phonon modes attributed to the Cs+ cations rattling within the perovskite structure that have a pronounced effect on the temperature-dependent photoconductivity. Motivated by the results, we have extended our synthetic design to methyl ammonium halide double perovskites. Our investigation has resulted in a new material, $(CH_3NH_3)_2AgInBr_6$, that exhibits a 1-D chain structure of face-sharing $[AgBr_6]$ and $[InBr_6]$ octahedra. $(CH_3NH_3)_2AgInBr_6$ undergoes a structural phase transition at 135 K, that was observed through heat capacity measurements and single crystal X-ray diffraction. The high temperature phase of $(CH_3NH_3)_2AgInBr_6$ crystallizes in trigonal crystal system, transitioning to the low temperature phase in triclinic symmetry. The structural phase transition of $(CH_3NH_3)_2AgInBr_6$ is thought to arise from disorder of the H atoms of $CH_3NH_3^+$ groups. Neutron scattering measurements have been performed to gain better insights into dynamic disorder activity of $CH_3NH_3^+$ groups in directing the crystal structures of $(CH_3NH_3)_2AgInBr_6$.

C3: In-situ powder diffraction studies of metal oxides under chemical looping conditions

Efrain E. Rodriguez

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In chemical-looping reactions (CLR), an oxygen storage material (OSM) is used in a closed loop to transport oxygen between two half reactions during either combustion of a fuel or steam reforming. By combusting a hydrocarbon fuel with oxygen from a solid source, the CLR process includes inherent separation of CO_2 from other gases in air and could therefore prove to be greener and more energy efficient than current carbon capture and sequestration technologies. We present some of our research activities aimed at further understanding the reactions between solid mixed-metal oxides at elevated temperatures with gaseous fuels such as methane. We focus on understanding how the chemical composition and crystal structure of the transition metal oxide affect product selectivity during CLR. We will present some in situ neutron and X-ray diffraction studies of several OSMs in order to answer some fundamental thermodynamic and kinetic parameters relevant to CLR.

C4: Following in situ synthesis using neutron powder diffraction

Ashfia Huq[1], Dileka Abeysinghe[2], Melanie Kirkham[3], Robert Schmidt[4], Gabriel Veith[4], Hanno zur Loye[2]

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Studying materials *in operando* has become the norm in most application oriented science endeavors. Neutrons have always had an advantage as a probe due to its high penetration. To date, discovery of new materials are often serendipitous, even though they are guided by centuries of knowledge gained in chemistry. However, a tremendous amount of information can be gathered for material synthesis in discovering new phases or finding ideal reaction conditions by following the reaction in-situ. In this presentation, I will talk about some examples of work done on sample synthesis at POWGEN diffractometer and the instrumentation challenges associated with it.

C5: *In situ* characterization of the phase behavior and thermoelastic properties of metal oxide systems at extreme conditions

Leighanne C. Gallington

X-ray Science Division, Argonne National Laboratory

In situ characterization of the non-ambient phase behavior of materials in the lab is complicated by both the difficulty of designing compatible sample environments and the long time scales required to acquire diffraction data with sufficient counting statistics for crystallographic analyses. The high energy x-rays available at synchrotron sources allow for penetration of most sample environments, while high flux allows for rapid acquisition of diffraction patterns, thereby allowing sampling of pressure-temperature space on reasonable time scales.

Low and negative thermal expansion (NTE) materials have been studied extensively, as they can potentially be used to create composites with finely controlled thermal expansion characteristics, improved resistance to thermal shock, and a broader range of operating temperatures. Cubic ZrW_2O_8 and HfW_2O_8 display isotropic negative thermal expansion between 3 and 1050K, even after undergoing a phase transition in which long-range orientational ordering of WO_4 tetrahedra is lost upon heating. While the thermal expansion behavior of these materials was well-described at ambient pressures, knowledge of the effects of stress on their thermal expansion was limited. *In situ* synchrotron powder diffraction was utilized to explore the role of orientational disorder in determining both the phase behavior and the thermoelastic properties of these materials. An especially designed pressure cell allowed for simultaneous sampling of temperatures up to 513 K and pressures up to 414 MPa. Reversible compression-induced orientational disordering of MO_4 tetrahedra occurred concomitantly with elastic softening on heating and enhanced negative thermal expansion upon compression in ZrW_2O_8 and HfW_2O_8, but only in the ordered phase. The order-disorder phase transition temperature of HfW_2O_8 was modestly reduced by compression.

In light of the comparatively recent nuclear disaster in Fukushima, understanding interactions and phase behavior in nuclear fuels under severe accident conditions is of paramount interest. While diffraction measurements have been performed on materials recovered from melts of corium (UO_2-ZrO_2), there is a lack of *in situ* characterization of this material at elevated temperatures. Achieving the extreme temperatures required for melting nuclear fuels in a controlled manner while minimizing potential contamination by the container can be accomplished by using a laser-heated aerodynamic levitator. The phase behavior of UO_2-ZrO_2 compositions was explored at temperatures up to 2850 K.

Friday 20 October 2017
Afternoon Session
"The Applications of Emerging Methods of Structural Biology"

Session Chairs: John Rose, University of Georgia-Athens and Aina Cohen, SSRL

D1: Novel Developments in Structural Biology

Guillermo Calero

University of Pittsburgh, Pittsburgh, PA

The field of structural biology is evolving fast. Development of X-ray free electron lasers, which provides X-rays ten times more brilliant than modern day synchrotrons, and electron crystallography or micro electron diffraction (microED) opens the possibility of solving three-dimensional structures of samples that can only crystallize as nano-crystals (NCs) or exhibit dose dependent- diffraction or -radiation damage. These developments are transforming the field of crystallography, however crystal structures are generally limited by the ability to obtain well diffracting crystals, *which remains as the most significant challenge in structure resolution*. In search for NC targets for XFEL experiments, my group developed the first comprehensive approach, using TEM, to discover NCs from highly relevant targets. In such work, we demonstrated that NCs are ubiquitous in crystallization drops and such studies paved the way towards the use of TEM as a tool to: *1) discover and optimize NC for XFEL and conventional X-ray diffraction experiments* and 2) characterize NCs for X-FEL and microED experiments. Application of this methodology to X-ray free electron laser (XFEL) and MicroED experiments has been highly successful and will be discussed.

D2: *Ab initio* electron density determination directly from solution scattering data

Thomas D. Grant

Hauptman Woodward Institute

Small angle scattering is an experimental technique used to analyze the molecular structures of a wide variety of biological and non-biological samples in solution. In contrast to X-ray crystallography and cryo-electron microscopy, where 3D electron density maps are calculated, available methods for generating 3D structural information from 1D solution scattering data rely exclusively on modeling. Many modeling algorithms rely on an implicit assumption that electron density is uniform inside the particle envelope. This assumption breaks down at resolutions better than approximately 10 Å where fluctuations in electron density contribute significantly to scattering and for particles with large scale conformational dynamics or containing mixed density species. Here we present a method for calculating electron density maps directly from solution scattering data. Using solvent flattening and positivity, this method avoids many of the assumptions limiting the resolution and accuracy of conventional modeling algorithms. We applied the algorithm to publicly available experimental scattering data from twelve different biological macromolecules. In each case the electron density maps closely match known atomic models, including complex shapes with multiple density components. These results demonstrate that accurate and complex electron density maps can be reconstructed from small angle scattering data and with significantly fewer restraints than imposed by existing modeling methods.

D3: XFEL structures of the influenza M2 proton channel at 1.4 Å: room temperature water networks and insights into proton conduction

Jessica L. Thomaston,[1] Rahel A. Woldeyes,[2] Takanori Nakane,[3] Kotaro Koiwai,[4] Ayumi Yamashita,[5] Tomoyuki Tanaka,[5] Toshi Arima,[5] Jun Kobayashi,[5] Tetsuya Masuda,[6] Mamoru Suzuki,[7] Michihiro Sugahara,[5] Rie Tanaka,[5] Eriko Nango,[5] So Iwata,[5] Fumiaki Yumoto,[4] James S. Fraser,[2] William F. DeGrado[1]

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The M2 proton channel of influenza A is a drug target that is essential for the reproduction of the flu virus. It is also a model system for the study of selective, unidirectional proton transport across a membrane. The channel is a homotetramer whose gate consists of four histidines and four tryptophans. When the channel is at near-neutral pH, the gating His tetrad has a charge of +2 [1]. Proton transport is thought to occur as the channel cycles from a +2 to a +3 charge state on its His gate. Water wires inside the channel pore have been proposed to play a role in both the conduction of protons to the gating His tetrad and the stabilization of multiple positive charges within the channel. In previous studies[2], lipidic cubic phase crystallization techniques were used to solve high resolution (1.10 Å) structures of M2 under cryogenic data collection conditions at a synchrotron source; in these structures, continuous water wires span the channel pore from the N-terminus of the channel to the gating His residues. Room temperature data collection techniques at a synchrotron source revealed a water network that was more mobile. However, it was not clear if this loss of solvent ordering at room temperature was a result of the increased amount of radiation damage during data collection. Room temperature data were collected to a resolution of 1.4 Å using an X-ray free electron laser (XFEL) to visualize the solvent in the pore of the channel while minimizing the effects of radiation damage. Three different pH conditions were examined: pH 8.0, pH 6.5, and pH 5.5. At pH 5.5, which is the pH condition at which the M2 channel has maximal proton conductance[3], the solvent network within the pore of the channel has a hydrogen bonding network that continuously spans the vertical length of the channel. This is consistent with a Grotthuss mechanism for proton transport. An increasing volume of ordered solvent density, and correspondingly a larger number of pore waters, is observed with decreasing pH. This ordered solvent could act to stabilize the multiple positive charges that build up on the gating His tetrad during the proton transport cycle.

References:
[1] Hu, et al. JACS 2012. 134(8):3703-13.
[2] Thomaston, et al. PNAS 2015. 112(46):14260–14265
[3] Pielak and Chou. JACS 2010. 132:17695–17697.

D4: New Opportunities for Structural Biology Research at LCLS and SSRL

Aina E. Cohen, representing the entire SSRL-SMB group

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Femtosecond crystallography (FX) is an emerging method that expands the structural information accessible from very small or very radiation sensitive macromolecular crystals. Utilizing extremely bright, short-time-scale X-ray pulses produced by X-ray free electron lasers (XFELs), this method exploits a 'diffraction before destruction' phenomenon where a still diffraction image is produced by a single X-ray pulse before significant radiation induced electronic and atomic rearrangements occur within the crystal. FX confronts a major challenge impeding progress in structural enzymology by providing a means to determine catalytically accurate structures of acutely radiation sensitive metalloenzymes which may be significantly photo-reduced during a single X-ray exposure at the synchrotron, even at very small doses.

A diffractometer-based experimental setup for FX experimentation is available to general users at the new Macromolecular Femtosecond Crystallography (MFX) instrument of the LCLS XFEL. LCLS-MFX began experiments on July 1, 2016. This instrument is based on developments at SSRL and LCLS-XPP to provide an efficient framework to carry out goniometer-based FX experiments using automated strategies tailored to handle a variety of sample requirements, crystal sizes and experimental goals. Various sample delivery and data acquisition systems are currently being implemented including injectors and in-situ spectroscopic monitoring. Also supported is a new sample delivery device developed by SSRL-SMB, the Sample-Extractor, that uses a mesh to mount crystals directly from a vial of mother liquor. These developments coupled with improvements in data processing algorithms make it possible to derive high resolution crystal structures using only 100 to 1000 still diffraction images. The MFX project and recent results using radiation sensitive crystals in limited supply and a variety of crystal delivery methods for serial diffraction data collection will be described.

New methods originally developed for serial diffraction experiments at XFELs, are proving valuable at synchrotron sources to study protein dynamics. Recent results using the MESH injector at the SSRL undulator micro-focus station BL12-2 will be described. Building on experiences at BL12-2, a next-generation undulator microfocus beam line, BL12-1, which will provide a preeminent capability for serial diffraction in the US, is under development. BL12-1 will be outfitted with a broad bandpass capability which will provide exceptional brightness, smaller microbeams and a high number of reflections when rastering crystals on the fly or using crystal injectors. It will be equipped with a high speed EIGER PAD detector and a high speed multi-axis goniometer, enabling new approaches for data collection and phasing. Similarities in instrumentation, existing and new sample delivery systems, and software environments will form the foundation of a synergistic relationship between the SSRL BL12-1 and a new Macromolecular Femtosecond crystallography instrument (MFX) at LCLS, through a Gateway approach.

D5: Neutrons: Complementary Probes for Protein Crystallography

Leighton Coates

Biology and Soft Matter Division, Oak Ridge National Laboratory, 1 Bethel Valley Rd, Oak Ridge, TN 37831.

This lecture will focus on the role of neutrons in protein crystallography which offer complementary data to X-rays enabling us to understand evermore complex systems. Understanding how the structure and dynamics of an enzyme system governs function through the catalytic steps of an enzyme and binding of ligand remain a major challenge in molecular biophysics. For example, many biologically important reactions depend on the transfer of protons, and a complete understanding of the catalytic power of enzymes requires knowledge of the protonation status of residues throughout the reaction pathway. The uniqueness of neutrons is in their fundamental physical properties, which result in the strong scattering from the lightest atoms in the Periodic Table, and in the neutrons’ benignity towards biological samples. Thus, whilst X-ray crystallography has unrivalled ability to determine the ‘heavy’ atom structure of biological systems, locating hydrogen atoms in proteins is challenging using X-ray techniques, and is complicated by radiation damage effects. The state-of-the-art in neutron macromolecular crystallography beamlines and protein perdeuteration techniques for challenging crystal systems will be discussed.

"Sidhu Award Presentation and Lecture"

Session Chairs: Ashfi Huq, Oak Ridge National Lab, Charles Lake, Indiana University of Pennsylvania, and Mary Pittman

S1: Sampling and Intensity Statistics of Diffraction Experiments with Nanocrystalline Powders

Hande Öztürk[1] and I. Cevdet Noyan[2]

Brookhaven National Laboratory

[1] National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973 USA
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In this talk, I will introduce a modelling algorithm that simulates an ideal diffraction experiment from a monodispersed ensemble of nanocrystalline particles. Based on this algorithm, the expected diffraction signature from an irradiated sample of identical nanoparticles can be generated and a direct connection between the scattering material and the diffracted intensity can be established. This introduction will be followed by a thorough statistical analysis of the proportion of irradiated particles contributing to the diffraction signal (real space), as well as that of the resulting diffraction data (reciprocal space). Finally, our findings from the statistical analyses will be compared with the predictions of the classical analysis developed by Alexander, Klug and Kummer (AKK) in 1948 (J. Appl. Phys. 19, 742 (1948); doi: 10.1063/1.1698200). This comparison will demonstrate that the validity of the classical (AKK) analysis is limited to powder samples with particle sizes above a certain threshold and that our generalized methodology can reveal the statistical processes behind particle selection and intensity measurement in a diffraction experiment, irrespective of the individual particle size within the powder sample.

Saturday 21 Oct 2017

Morning Session

"Structural analysis using atomic pair distribution functions"

Session Chair: Pavol Juhas, BNL

E1: Atomic pair distribution function methods: Introduction and Applications

Simon J. L. Billinge

Materials Science and Engineering and Applied Physics and Applied Mathematics, Columbia University in the City of New York

Over the past 25 years, the atomic pair distribution function analysis of total scattering x-ray and neutron diffraction data has grown in importance and impact. This is due to the confluence of three factors. First sources of x-rays and neutrons suitable for PDF work have become increasingly powerful. Second, computing, software and algorithms for PDF data analysis and modeling have grown in power and capability. Finally, the world has realized that not all materials are perfect crystals, and if we can make them nano-sized, or incorporate and engineer non-periodic defects, or work with even highly disordered materials, that we can engineer super-materials that can do way more things, better than crystals. It is precisely these materials that are ideal for study with total-scattering and PDF methods.

In this talk, I will introduce total scattering and PDF methods, highlighting recent methodological developments that we believe can have significant impacts in research and in industry. I will illustrate these developments with concrete examples from the fields of pharmaceuticals, energy materials such as batteries and photovoltaics and catalysts.

E2: Balancing freedom and constraints in large-box PDF modeling

Daniel P. Shoemaker

Materials Science and Engineering Department and Materials Research Laboratory, University of Illinois at Urbana-Champaign

One of the key advantages of local structure analysis is its ability to describe disorder beyond traditional unit-cell models of crystals. Large-box models are common tools used to fit experimental pair distribution function data, so they describe a nontraditional structure. Such models have many degrees of freedom, so the uniqueness of the solution must be evaluated alongside its fit to the data. This check is a key practical distinction between large- and small-box modeling such as Rietveld refinement. I will discuss examples from our studies on inorganic materials (functional oxides and sulfides) where the evaluation of multiple models produces descriptions of the structures and of the constraints imposed by the data themselves.

E3: Trends in the lone pair-induced local off-centering of tin and lead atoms in halide perovskites

Geneva Laurita[1,2], Douglas H. Fabini[2,3], Constantinos C. Stoumpos[4], Mercouri G. Kanatzidis[4], and Ram Seshadri[2,3,5]

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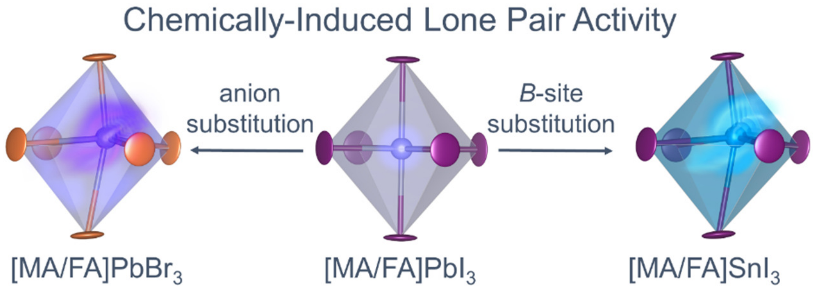
Hybrid halide perovskites have attracted significant recent attention due to their excellent photovoltaic performance, ease of preparation, and abundant constituent elements. However, a full description of the chemical and structural drivers of their remarkable functionality remains incomplete. While much attention has focused on dynamic disorder of the *A*-site molecular cations, this talk will discuss a key aspect of the inorganic framework that impacts electronic, thermal, and dielectric properties, revealed through the use of local structure techniques. The pair distribution functions of various AMX_3 (A = Cs^+, $CH_3NH_3^+$, $CH(NH_2)_2^+$; B = Sn^{2+}, Pb^{2+}, X=Br^-, I^-) halide perovskites at and above 300 K reveal temperature-activated, dynamic displacements of the divalent group IV cations from their nominal sites, a phenomenon previously referred to as *emphanisis* in rock-salt group IV chalcogenides.[1-3] This anharmonicity arises as a consequence of lone pair stereochemistry, and the chemical trends describing the magnitude of the effect are in agreement with existing theory. The work herein offers new design principles in the search for defect-tolerant semiconductors.



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E4: Direct structural evidence of phase separation in the phase diagram of $Ir_{1-x}Rh_xTe_2$

Emil S. Božin

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Exploring the details of competition and cooperation in electronic, orbital, spin, and lattice sectors of complex electronic systems is a challenging task in condensed matter. Materials with structures containing corner sharing triangular and tetrahedral motifs often exhibit complexity and compelling ground states, providing fruitful playground for studying the interplay of these entangled degrees of freedom. Iridates featuring such topological motifs on iridium sublattice are no exception. $IrTe_2$ has been in focus over the past several years not only because it displays an unusual first-order metal-metal (M-M) transition and a dimerized lattice at low temperature, topology and origin of which have been heavily debated, but also due to the emergence of superconductivity upon chemical substitution and intercalation. Results of X-ray total scattering based atomic pair distribution function (xPDF) analysis carried across the (x, T) phase diagram of $Ir_{1-x}Rh_xTe_2$ ($0 \leq x \leq 0.3$, $10\ K \leq T \leq 300\ K$) will be presented. Observed hysteretic structural transition from high temperature trigonal (P-3m1) to low temperature triclinic (P-1) dimer phase for low Rh content evidences close tie between the lattice and electronic properties. Results of PDF analysis across the M-M transition are inconsistent with a scenario where local Ir-Ir dimers survive into the high temperature metallic regime, in contrast to previous local structural reports based on EXAFS. In superconducting concentration regime away from the dimer/superconductor phase boundary structural transition is absent and the system remains trigonal down to at least 10 K on all length-scales. In the narrow range of compositions close to the boundary PDF analysis reveals structural phase separation on a nanometer lengthscale, suggestive of weak first order character of the dimer/superconductor transition at a constant low temperature. Phase separated compositions show anomalies in electronic transport and magnetization, hallmarks of the dimer phase, as well as superconductivity albeit with incomplete diamagnetic screening. There is no evidence from xPDF for persisting fluctuating dimers deep into the superconducting regime, ruling out a possibility of significance of such fluctuations for observed superconducting properties. The two competing electronic instabilities likely do not coexist within the same sample volume.

E5: RMCProfile: Moving closer to complex modelling

Matt Tucker

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The importance of local structure and disorder in crystalline materials is being recognized more and more as a key property of many functional materials. From negative thermal expansion to solid state amorphisation and the 'nanoscale' problem to improved fuel cell technology, a clear picture of the local atomic structure is essential to understanding these phenomena and solving the associated problems. Total scattering, an extension of the powder diffraction method, is increasingly being used to study crystalline materials. The unique combination of Bragg and diffuse scattering can be used to determine both the average structure and the short-range fluctuations from this average within a single experiment. To maximize the structural information from such data, three-dimensional atomistic models consistent with all aspects of the data are required. RMCProfile[1] expands the reverse Monte Carlo (RMC) modelling technique[2] to take explicit account of the Bragg intensity profile from crystalline materials. Analysis of the RMCProfile-generated atomistic models gives more detailed information than is available directly from the data alone. As the systems being studied become more complex, the information from many experimental techniques and any prior chemical knowledge needs to be combined into one consistent atomic model. The continued development of RMCProfile and its new capabilities are moving us closer to the complex modelling paradigm[3] required to drive the discovery of new functional materials.

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Saturday 21 October 2017

Special Morning Session

"Symposium in memory of Bryan M. Craven, Crystallography Department of the University of Pittsburgh"

Session Chairs: John Rose, University of Georgia-Athens and Aina Cohen, SSRL

F1: In memory of Bryan Craven: My Postdoctoral Work with Him and Continuing

Bi-Cheng Wang

Biochemistry and Molecular Biology, University of Georgia, Athens, GA

I met Bryan for the first time in May 1970 at the ACA meeting in New Orleans and he offered me a postdoctoral position in his lab at the Department of Crystallography starting July 1, 1970. Eleven months later Martin Sax offered me a more permanent position at the VA Medical Center next to Pitt. Sixteen years later (1986) Bryan recruited me to join the Department of Crystallography as a faculty of protein crystallography. Bryan's offer in 1970 essentially shaped my career in Pittsburgh.

When I was in Bryan's lab I was assigned to work on his NIH projects of metal (Co, Ni, Cu and Zn) complexes of barbiturates. The Ni-complexes surprisingly gave crystals in three different colors (green, orange and pale blue) under the same crystallization conditions. I only had enough time to solve the structure of the pale blue complex before relocating to Martin's lab to start working on protein structures an area where I had no previous experience. I always wanted to solve the structures of the other two (green and orange) complexes when I had spare time. The spare time never came and soon I forgot those complexes.

The news of Bryan's passing brought back many fond memories of the Department of Crystallography and those forgotten colored Ni-complex crystals that I left behind. I mentioned these color Ni-Complexes to my colleagues at one of our recent lab meetings. In two days they reproduced those color crystals and I was happy to see them after 46 years. Soon after they solved the structures. These new structures will be presented. In addition, we will use these crystals as additional test samples of small molecules in our current UGA-APS Pilot Program that will be presented as a poster at the 2017 PDC, titled "… extending the concept of visible-light color photography to synchrotron crystallography".

F2: Some personal recollections of Bryan Maxwell Craven

Robert H. Blessing

Hauptman-Woodward Biomedical Research Institute and Department of Structural Biology, University at Buffalo, The State University of New York

I was a postdoc in the Crystallography Department at the University of Pittsburgh for just over two years, from spring 1970 to summer 1972. Those were years in which the Pitt Lab was in its heyday. The Lab was one of the best places in the world to learn and to do X-ray crystallography, and Bryan Craven was a leading light in the Lab's teaching and research. Some thirty years after my postdoctoral sojourn in Pittsburgh, Bryan asked me to become one of the instructors in the ACA Summer Course in Small Molecule Crystallography, which Bryan and Charles Lake had re-organized in the course's new "Camp X-ray" homestead at Indiana University of Pennsylvania in Indiana, PA. Thus my learning and doing of crystallography under Bryan's tutelage resumed.

F3: DNA: Not Merely the Secret of Life

Nadrian C. Seeman

Department of Chemistry, New York University, New York, NY 10003, USA

We build branched DNA species that can be joined using Watson-Crick base pairing to produce N-connected objects and lattices. We have used ligation to construct DNA topological targets, such as knots, polyhedral catenanes, Borromean rings and a Solomon's knot.

Nanorobotics is a key area of application. We have made robust 2-state and 3-state sequence-dependent programmable devices and bipedal walkers. We have constructed 2-dimensional DNA arrays with designed patterns from many different motifs. We have used DNA scaffolding to organize active DNA components. We have used pairs of 2-state devices to capture a variety of different DNA targets. We have constructed a molecular assembly line using a DNA origami layer and three 2-state devices, so that there are eight different states represented by their arrangements. We have demonstrated that all eight products can be built from this system.

We have self-assembled a 3D crystalline array and reported its crystal structure to 4 Å resolution. We can use crystals with two molecules in the crystallographic repeat to control the color of the crystals.

Rational design of intermolecular contacts has enabled us to improve crystal resolution to better than 3 Å. We can now do strand displacement in the crystals to change their color, thereby making a 3D-based molecular machine; we can visualize the presence of the machine by X-ray diffraction.
The use of DNA to organize other molecules is central to its utility. Earlier, we made 2D checkerboard arrays of metallic nanoparticles, and have now organized gold particles in 3D. Most recently, we have ordered triplex components and a semiconductor within the same lattice. Thus, structural DNA nanotechnology has fulfilled its initial goal of controlling the internal structure of macroscopic constructs in three dimensions. A new era in nanoscale control awaits us.

F4: Archiving Structural Models Derived using Integrative/Hybrid Methods

Helen M. Berman

Department of Chemistry and Chemical Biology, Center for Integrative Proteomics Research, Rutgers University, Piscataway NJ 08854

Since its inception each entry in the Protein Data Bank contains an atomic structural model derived from a single structure determination method such as X-ray crystallography, NMR spectroscopy and 3D electron microscopy. Recently, integrative/hybrid (I/H) methods have been developed that use a combination of two or more experimental techniques together with complex computational algorithms to determine structures of large macromolecular complexes. The ways in which the wwPDB is meeting the challenges involved in validating and archiving these models will be presented.

F5: Application of structural biology in biologic drug discovery

Jinquan Luo

Janssen R&D, LLC, Johnson & Johnson

Antibodies and other biologics are a fastest growing class of therapeutics. Structures of biologics and their complexes with disease targets provide very useful information for their engineering and understanding of their mechanism of action. We describe several examples of use of X-ray crystallography, electron microscopy (EM) and small angle X-ray scattering (SAXS) in biologics discovery.

F6: Memories

John Ruble

Department of Crystallography, University of Pittsburgh and New Century Pharmaceuticals, Huntsville AL (retired)

Remembering Bryan and the Department of Crystallography over my 23 years there.

21 October 2017

Afternoon Session

"Powder Diffraction Studies of Metal Organic Frameworks"

Session Chair: Winnie Wong-Ng, NIST

G1: Combined DSC-XRD for rapid simultaneous screening of phase evolution and thermal properties.

John B. Parise

Department of Geosciences and Chemistry Department, Stony Brook University, Stony Brook, NY 11794

The use of combined X-ray diffraction – differential scanning calorimetry (XRD-DSC) is an excellent means to rapidly survey phase maps and enthalpies as a function of temperature, humidity and time. The technique has proven powerful, especially in combination with theoretical predictions, to rank order the likely effectiveness of targets for processes that involve significant heat signatures and structural distortion, such as gas separation by molecular sieves. Molecular simulations now quantify and rapidly test known compounds (for example see [1,2]). Simultaneously, and quickly, the joint techniques provide information on a compound's 1) novelty, 2) structural changes upon change in temperature/RH 3) and 3) thermal response (enthalpy, gas binding energy, etc.) and structural changes accompanying and gas sorption. Commercially available set-ups were modified for these purposes and interfaced to lab-based and synchrotron x-ray sources.

We used the *in situ* XRD-DSC technique initially at synchrotron sources to study the dehydration behavior of the ubiquitous nano-mineral ferrihydrite to constrain its water content and structure modifications [3]. We find the technique to be especially useful for evaluating the effect of humidity on CO_2 adsorption performance of metal-organic frameworks (MOFs) and zeolites. The strategies developed over the past few years are applicable to a wide range of materials being considered for separations applications.

Modification of commercial equipment with a custom-built humidity swing chamber and buffer allow rapid evaluation of heats of absorption and overall stability of many cycles or gas sorption/desorption, at different gas pressures and with variable humidity. Atmospheres can be set to any pressure between 0 – 1 atm at any relative humidity (RH) between 0 – 80%, while simultaneously recording the heat flow and XRD pattern of the sample. Typical adsorption experiments are carried out using either vacuum to atmosphere swings or with different gas atmosphere swings. Examples of studies and applications include evaluations of separations potentials for light hydrocarbons in Ca-based, porous, metal organic frameworks, indicating that these have high potential to selectively adsorb ethane, ethylene and acetylene over methane.

DSC-XRD techniques were useful in discovering the absorption mechanism in a new MOF, suggesting design criteria for increased selectivity important for treatment of radioactive waste. The cryogenic separation of noble gases is energy-intensive. Novel frameworks containing polarizing groups within their pore spaces are selective toward Xe over Kr at ambient conditions, with Xe/Kr selectivity of about 10 and Xe capacity of 37.1 wt% at 298 K, confirming their practical potential for separating Xe from Kr. Once identified, more complex. Costly and time-consuming gas breakthrough experiments confirm the potential first identified in screening experiments using theory and XRD-DSC [2].

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G2: *In situ* Powder Diffraction Measurements of Metal Organic Frameworks at 17-BM: Modern Techniques and Methods of Structural Analysis

Andrey A. Yakovenko

Advanced Photon Source (APS), Argonne National Laboratory

17-BM is a rapid acquisition powder diffraction beamline at Advanced Photon Source, Argonne National Laboratory. The beamline uses monochromatic beam and a 2-D detector for fast data collection up to 10 images per second. 17-BM is equipped with an extensive array of sample environments including high temperature (furnace), low temperature (cryostream), controlled-atmosphere (flow cell), electrochemistry, high pressure (diamond anvil cell), and high throughput (sample changer). This beamline serves the powder diffraction community who need fast and reliable data collection in various in situ processes, such as energy storage, catalysis, gas sorption and separations, ion exchange, solid state synthesis, etc.

Recently, scientists at 17BM introduced several more sample environment setups for general users. First, users can perform powder diffraction measurements at different gas pressures. The sample environment was built by combining the follow cell together with syringe pump. In this type of experiment, users can create gas or gas mixture atmosphere around the sample and then seal the system and pressurize it using syringe pump. The setup has been tested and is operational in the pressure range of 0-600 bar. Another unique part of the gas high-pressure set up is that it can be combined with our furnace or cryostream equipment which allows change of pressure and temperature at the same time. Such combination allowed to track positions and occupancies of hard to detect, low electron density atoms, such as neon in the pores of MOFs.

In addition, to ease the structural investigations of porous materials (MOFs and zeolites), methods which apply the analysis of Structure Envelope and Difference Envelope Densities can be used. These densities can be easily generated from the structure factors of a few (1 to 10) most intense low index reflections. This allows us to study guest related issues of MOFs such as, location of guest molecules in the pores, tracking activation of MOFs and catalysis and gas loading without need of performing full structural determination.

G3: Application of Powder Diffraction in MOF Research: Rigid and Flexible Frameworks

Tomče Runčevski

University of California at Berkeley, Berkeley

Metal-organic frameworks (MOFs) are porous materials with promising applications in gas sorption, capture, storage and purification. *In situ* X-ray powder diffraction (XRPD) is proven to be very useful technique to follow and explain the interactions of MOFs and incoming gas molecules, as well as diverse structural transformations under variable temperature, gas pressure, photoirradiation and other external stimuli. Here, we focus on two classes of MOFs and we show how XRPD help their developments.

First, we talk about MOFs with open metal sites. Recent work has shown that the presence of highly polarizing, unsaturated metal coordination centers (Lewis acid open metal sites) on the internal surface of framework pores increases the surface packing density of adsorbates, induces selectivity and provides a mechanism to achieve charge transfer on the internal surface. *In situ* diffraction studies were performed with different probe molecules, including CO2, H2, D2, Xe, and Kr, in metal-organic frameworks with single[1] or double exposed metal sites.[2] Furthermore, we show that complementary structural information for the gas-framework interactions can be obtained by neutron diffraction, but also by *in situ* IR spectroscopy, which is particularly useful for probing specific sites at poorly crystalline materials.[3]

Second, we focus on flexible metal-organic frameworks. These materials collapse under reduced gas pressure and step-vise expand under increasing pressure. In the collapsed form they are virtually nonporous, whereas when expanded they exhibit high porosity. Accordingly, these materials exhibit very high working capacities. XRPD was successfully applied to explain the framework flexibility and to inform the design of better preforming materials.[4]

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G4: Neutron Powder Diffraction studies of small molecules adsorbed in MOFs

Craig M. Brown

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and
Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716

Adsorption of molecules in functionalized and high surface area microporous materials is of technological importance in a multitude of areas ranging from chemical separations to energy storage. Over the past several years we have focused our research efforts on understanding the properties of metal-organic frameworks (MOFs) and zeolites for storage and separations of industrially important small molecules such as hydrogen,[1] oxygen,[2] carbon dioxide,[3,4] noble gases,[5] and short chain organics.[6] Besides the geometrical and porosity control in either class of materials, the properties of metal-organic frameworks can be tuned to optimize electrostatic interactions by exposing open metal cation sites. Here, we discuss the different requirements for performing these experiments at X-ray compared to neutron sources and reflect on the information potentially obtainable in both cases. The results illustrate the power, and limitations, of diffraction in elucidating many of the governing characteristics of these material properties and the interactions with the guest molecules.

(1) Adsorption of Two Gas Molecules at a Single Metal Site in a Metal-Organic Framework, T. Runcevski, M.T. Kapelewski, R.M. Torres-Gavosto, J.D. Tarver, C.M. Brown, J.R. Long, *Chem. Commun.* (2016) **52**, 8251.
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G5: Linking Microstructure and Structure to Sorption Properties During Selective Gas Adsorption in Metal Organic Framework (MOF) Materials

Andrew J. Allen

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To be effective, advanced gas sorbent materials must adsorb large quantities of the target gas, selectively, in the presence of multiple gases. The capacity to adsorb CO_2, for example, under different pressure and/or temperature conditions can frequently be linked to changes in sorbent structure, which must be understood if sorbents are to be improved and optimized by material development. In this connection, metal-organic frameworks (MOFs) and MOF-like materials show considerable promise and potential for future development. Obviously, a lack of selectivity to adsorb only the target gas will result in other gases or water molecules being adsorbed and occupying sites within the sorbent that cannot then be occupied by the target gas. Selective adsorption cannot simply be established by measuring the sorption isotherms for different gases; it is necessary to determine whether one gas being adsorbed (e.g., CO_2), also lets in a second gas by some collective gate-opening effect. Such sorption selectivity (or lack of it) can frequently be related to sorbent structure and microstructural or structural changes during the adsorption/desorption cycle. Building on previous work to elucidate these issues [1-4], we have carried out a range of *in situ* small-angle X-ray and neutron scattering (SAXS and SANS), X-ray and neutron diffraction studies on different MOF-like sorbent systems during adsorption and desorption of CO_2 and CO_2 gas mixtures under realistic pressure conditions. Pressure conditions include both static and flowing gas environments, and also supercritical CO_2 conditions. With these results, we seek new insights that connect features in the isotherm curves and underlying changes in sorbent microstructure or structure.

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Thursday 19 Oct 2017

Poster Session

Session Chair: Colin Ashe, IUP

B4: In-situ and high-resolution x-ray diffraction study of pyrite (FeS_2) stoichiometry

Rebecca D. McAuliffe and Daniel P. Shoemaker

Materials Science and Engineering Department, University of Illinois at Urbana-Champaign,

Iron pyrite, FeS2, is a low-cost, non-toxic alternative to many In-, Ga-, and Cd-containing compounds as a photovoltaic absorber material [1]. FeS2 exhibits many properties, including high absorption coefficient and high quantum efficiency, that make it a promising material for solar cell applications [2, 3]. However, several limitations have prevented pyrite from being a successful solar cell material [4]. One potential explanation for these limitations is that intrinsic defects, such as sulfur vacancies, effect the transport behavior of FeS2. While recent density functional theory studies have put the limit of intrinsic defects at a defect concentration of 1020 cm-3, we aim to experimentally resolve the temperature dependent sulfur stoichiometry in pyrite and set an upper bound on sulfur vacancies observed within the lattice [5]. This study utilizes high-resolution synchrotron and in-situ x-ray diffraction in non-ambient conditions to understand the anion concentration in the Fe-S system. By studying FeS2 in reducing conditions, we can fully investigate the transition from FeS2 to other sulfur deficient compounds, resolving the debate of whether FeS2 has a fixed stoichiometry or a potential sulfur deficiency of up to 12.5% [6, 7]. By understanding the stoichiometry of FeS2 we can provide further information to better control the synthesis of FeS2 and potentially increase the efficacy of pyrite as a photovoltaic absorber material.

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B5: Tunable Negative Thermal Expansion found in ReO$_3$-type fluoride solid solutions

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Most materials expand when they are heated, but an increasing number contract on heating. This negative thermal expansion (NTE) is associated with a variety of structure types and mechanisms.[1] NTE is potentially advantageous for compensation of thermal expansion in industrial materials. The thermal population of vibrational modes involving the rocking of "rigid units" (example shown in figure 1) in, for example, ScF$_3$ and MgZrF$_6$ leads to NTE over specific temperature regions.[2] For maximal utility the temperature range and magnitude of NTE should be tunable in a rational fashion. In the present study, we explore the control of thermal expansion by introducing additional anions into the cation ordered ReO$_3$-type material MgZrF$_6$. Solid solutions of the type Mg$_{2-x}$Zr$_x$F$_{4+2x}$ have been prepared and investigated using variable temperature/pressure synchrotron X-ray diffraction. The incorporation of extra fluoride provides a means of tuning the temperature at which these materials show zero thermal expansion. This work has been complemented by density measurement.

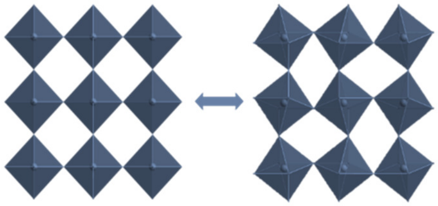

Figure 1: Distortion of corner shared cubic system via rigid unit mode rotations

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P1: Developing metal organic frameworks for catalysis applications

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Metal organic frameworks (MOFs) have potential for use in energy storage, catalysis, and waste water treatment. Our work aspires to access catalysis using sensitive functionality introduced by post synthetic modification of the prepared MOF. 9,10-disubstituted anthracene derivatives are used in conjunction with zinc intending self-assembly of a robust framework in the IR MOF family. Sensitive MOF functionality is to be introduced using Diels-Alder chemistry. Along the way, more favorable, stable architectures such as a DMF-carboxylate adduct and 1D-coordination polymers prevailed.

P2: Unlocking the structure of mixed amorphous-crystalline ceramic oxide thin films synthesized under low temperature electromagnetic excitation

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The promise of using electromagnetic (EM) fields for low temperature materials synthesis is limited by our ability to structurally characterize these materials, which are often nanocrystalline or amorphous. Here we demonstrate that synchrotron x-ray radiation coupled with the recently developed thin film pair distribution function (tfPDF) analysis yields quantitative information about mixtures of crystalline and non-crystalline materials synthesized under EM excitation, which represents a new direction to study the chemical reactions and lattice ordering induced by EM fields. Our experiments demonstrate for the first time that ceramic oxide films of titanium dioxide (TiO_2) grown under microwave radiation (MWR) exposure contain a different phase composition and increased crystallinity compared to TiO_2 grown at similar temperatures without EM fields. Specifically, the field-assisted TiO_2 is composed of a mixed-phase structure consisting of long-range anatase TiO_2 phase with short-range amorphous components, while furnace-grown materials are amorphous with local ordering most resembling the brookite phase of TiO_2. Further analysis reveals that the amorphous components form differently with and without the presence of MWR, indicating an effect of EM fields on phase formation mechanisms. The disordered component of MWR-grown TiO_2 also results in a slightly narrower energy band gap relative to fully crystalline anatase, indicating enhanced light absorption in the visible spectrum. The impact of EM field-influenced atomic structure on resultant material properties creates the opportunity to utilize MWR-assisted synthesis as a novel method for rapid, single-step, low temperature synthesis of mixed ordered-disordered materials for potential use in photocatalysis, thermoelectrics, or lithium ion batteries.

P3: Effect of Indium and Antimony doping on the electrical transport properties of direct vapour transport (DVT) grown SnSe single crystals

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Keywords: Single crystals, SnSe, thermoelectric power, d.c. electrical conductivity, power factor.

Pure SnSe, 5% In doped SnSe and 5% Sb doped SnSe single crystals were grown by direct vapour transport (DVT) technique. The energy dispersive analysis of X-ray (EDAX) showed that all the samples are near stoichiometric but slightly Sn deficient. The X-ray diffraction (XRD) study of all the three as-grown single crystal samples showed that they possess orthorhombic structure and the lattice parameters are in good agreement with the reported parameters. The thermoelectric power S and d.c. electrical conductivity σ variation with temperature from ambient to 573K substantiated the semiconducting nature of the all the three samples. The sign of S was positive for all three samples for all the temperature range stating the sample to be p-type semiconducting. The power factor S2⍰ variation with temperature showed pure SnSe having highest value compared to doped samples. Thus doping by indium (In) and antimony (Sb) does not improve the thermoelectric efficiency of the SnSe.

P4: Reversible oxygen intercalation of RFe_2O_4 (R= Lu, Yb, Y, In) as studied by *in situ* powder diffraction.

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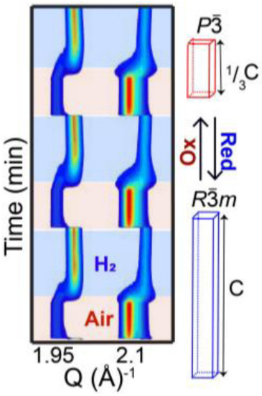
Chemical looping combustion and chemical looping reforming are widely studied processes due to their many advantages in numerous industrial applications.[1] These processes utilize a metal oxide system as an oxygen storage material (OSM) that exhibits reversible oxygen intercalation in the crystal lattice as a function of temperature and atmosphere. Among many such metal oxides, ternary metal oxides have proven to retain long term chemical stability over binary metal oxides.[2] The ternary metal oxide, $LuFe_2O_4$ was proposed as a potential OSM for the first time in 2014.[3] It was found that $LuFe_2O_4$ can be successfully cycled at 500°C under a dynamic vacuum and hydrogen due to its reversible transition between two crystalline phases. However, no conclusive studies have been conducted yet to explore the optimum reaction conditions for fast oxygen uptake/release, thermal and mechanical cycling stability, the impact of elemental substitution on the kinetics of redox reactivity and the oxygen storage capacity (OSC). In this work four RFe_2O_4 analogues (R=Lu, Yb, Y and In) were synthesized. To extend the understanding of their suitability as OSMs, *in situ* X-ray and neutron powder diffraction experiments combined with thermogravimetric analysis were carried out. Cycling experiments with *in situ* diffraction were done in oxidizing and reducing atmospheres emulating a chemical looping reactor. Sequential Rietveld refinements[4,5] and Lebail fits were done to calculate the unit cell volume change as a function of time and temperature.



Reversible oxygen intercalation of LuFe2O4 in alternating atmospheres at 600 °C.

In this study, *in situ* powder diffraction experiments were conducted on the 17BM at the Advanced Photon Source (APS) at the Argonne National Laboratory and on POWGEN and NOMAD beam lines at the Spallation Neutron Source (SNS) at the Oak Ridge National Laboratory.

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P5: Switching Thermal Conductivity in Mn-Doped NiMn$_x$Ge

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The technological utility of materials exhibiting a metal insulator transition (MIT) has, in general, been limited to applications taking advantage of their change in resistivity. A material able to switch from thermally insulating to thermally conducting is desirable for multiple applications and is a new capability of MIT materials. This project seeks to identify systems with a thermally conducting high temperature phase and measure the thermal conductivity across its structural transition. NiMnGe possesses an antiferromagnetic to paramagnetic magnetic transition at 81°C and an orthorhombic (Pnma) to hexagonal (P63/mmc) structural transition at 220°C [1]. These transition temperatures are tunable through doping and varying the Mn content [1, 2].

Using solid state methods, samples with varying amounts of Mn (x = 0.98 to 1.02) were synthesized and X-ray fluorescence was applied to determine their composition. The structural transition temperature is extremely sensitive to the Mn content. For x = 0.98 and 1.006 the transition temperature was found to be 106°C and 306°C, respectively. Using *in-situ* XRD, we verified NiMnxGe transforms from the orthorhombic to hexagonal phase. This is in agreement with previous reports [1]. Additionally, room temperature *ex-situ* XRD was used to determine the compositional dependence of the lattice parameters. The lattice parameters are directly related to x up to approximately x = 1.01, after which the lattice parameters plateau. This trend implies a limit to the Mn-doping of NiMnxGe. The same trend is seen with the structural transition temperature with respect to x. This similarity demonstrates the direct relationship between the crystal structure and structural transition temperature.

Time-domain thermal reflectance (TDTR) was used to determine the change in thermal conductivity as the samples experienced the temperature-induced phase transition. With increasing amounts of Mn, both the magnitude of change in thermal conductivity across the transition and the maximum thermal conductivity increase. Across its structural transition (approximately 550K), NiMn1.018Ge exhibits a 40% increase in thermal conductivity.

The thermal conductivity anomaly can be attributed, in part, to the large decrease in the unit cell volume as the system transforms from orthorhombic to hexagonal. It is known that a large primitive unit cell volume results in a lower lattice thermal conductivity [3, 4]. This relationship has been demonstrated previously by Zintl antimonides [4]. Therefore, the change in unit cell volume should be considered when selecting candidates to study in search of an increase in thermal conductivity across a structural transition.

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P6: SER-CAT Staff Research and UGA-APS Pilot Program: Extending the Concept of Visible Light Color Photography to Synchrotron Crystallography

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Diffraction from the soft X-ray region (wavelength > 1.5Å) has played an important role in recent success for macromolecular structure determinations by Native-SAD phasing (reviewed by Rose, Wang & Weiss, 2015; Rose & Wang, 2016). Other unique applications of soft X-rays for structural biology research, which may not be well recognized, are also becoming possible due to recent advances in both experimental design and data collection technology.

In this presentation, we are focusing on Phase II of an UGA-APS Pilot Program (http://uga-aps.pilot.uga.edu) – the use of wavelength-dependent data for polychromatic X-ray analyses. In layman's terms, the concept is equivalent to that of using color photography (recording the components of light according to wavelength) to aid in the positive identification & differentiation of visible objects. Polychromatic X-ray analysis can improve the accuracy in the identification & differentiation of atoms in both macromolecules and small molecules by combining atomic spectra with structural coordinates, similar to the power of color photography for visible objects.

Examples will be given for the exploration of biophysical/biochemical aspects of metals/ions in protein crystals, including the positive identification of atoms (e.g. Fe vs. Zn) and the valence states (and redox-states) of individual atoms in a molecule containing more than one atom of the same metal. The theoretical basis and test results, as well as the procedures for accessing the Pilot Program through the General User portal will be presented.

P7: Low temperature synthesis of molybdenum oxide for future use in composites

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Molybdenum oxide (MoO_3) is a potential filler material for conducting polymer composites to improve their stability and conductivity. For one-pot in-situ methods, the oxide must be prepared at low temperatures compatible with the oxidative polymerization reaction. Samples are synthesized in aqueous medium using ammonium molybdate tetrahydrate as the precursor. This is a desirable precursor since molybdenum is in its highest oxidation state of 6, so it cannot be oxidized any further during the oxidative polymerization process. MoO_3 can become crystalline at low temperatures under certain synthetic conditions. These samples are characterized using PXRD, SEM, and EDS. PXRD is the main method used to analyze the MoO_3 samples because the scans provide information such as whether the sample is crystalline or in an amorphous state, if it is hydrated, and if it still contains ammonia based on the crystal structure it forms. It was found that the synthesis of MoO_3 is compatible with the polypyrrole synthesis, as it can be crystallized at low temperatures, which is necessary to prevent the polypyrrole from decomposing

P8: *In situ* X-ray powder diffraction study on iron oxide for ammonia decomposition reaction

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Ammonia decomposition reaction is recently raised its interest because it is regarded as one of the hydrogen production processes where ammonia contains about 17 wt.% hydrogen and thermally decomposes above 200 °C. The hydrogens obtained by decomposition of ammonia are carbon-free source, which can be benefited for fuel cell application. An efficient decomposition of ammonia can be driven with either the application of high temperature (> 700 °C) or the use of active catalysts during the reaction at rather low temperature. Ru-based catalysts have been reported as an active component for ammonia decomposition reaction. However, it is limited in used and the cost of such catalysts is high. An alternative catalyst can be conducted to iron oxide since it has been used as an active catalyst for industrial ammonia synthesis process. Therefore, low cost iron-based phases such as iron oxide spinel, binary iron-cobalt oxides are popularly studying. Interestingly, researchers found that while iron oxide catalyzing the ammonia decomposition reaction the phase has changed to iron nitrides after the catalytic tests.[1][2] However, detail crystallographic information of phases and microstructure changes upon ammonization of iron oxide and their correlation with the catalytic behaviors is not yet clear. Therefore, this study made the effort on investigating the dynamic phase changing of iron oxide with high resolution XRD under a continuous flow of 100% NH_3 from room temperature to about 700 °C and further understanding the relationship of crystal chemistry with the catalytic behaviors.

Nitridation of iron oxide was also found in this study where iron nitride with hexagonal structure (Fe_3N_x) is formed after the first heating cycle of ammonization reaction. After cooling, stoichiometric Fe_3N is identified. During the second and the subsequent cycles, iron nitride instead of iron oxide remains as an active phase for ammonia decomposition reaction. It is thus the first cycle can be only regarded as an activation cycle and the iron oxide is not the essential active phase for ammonia decomposition reaction. In addition, below 500 °C iron nitride is thermally expanded without the structural changing. Starting above 500 °C, the structure of iron nitride is shrinkage with the release of nitrogen atoms. Such iron nitride structure with the mobility of nitrogen seems to be the promising active catalysts for ammonia decomposition shown in the catalytic test with higher conversion rate of ammonia. At high temperature range (> 700 °C), the phase of iron-rich nitride (gamma-FeN_x) is found and the formation of such phase is getting earlier while cycling the iron nitrides under ammonia decomposition reaction condition. However, the presence of iron-rich nitride seems to degrade the catalytic activities at high temperature range. The results in combination with crystallography and catalysis will be presented in more detail on the poster.

P9: Bence-Jones Protein Pav: the first ISIR structure

John P. Rose, Chung Soo Yoo, William Furey, Chong-Hwan Chang, Martin Sax, Bi-Cheng Wang

Work carried out in the Biocrystallography Laboratory, Veterans Administration Hospital, Pittsburgh, Pa and the Department of Crystallography, University of Pittsburgh

This amazing story begins with a need. In the early 1980's macromolecular crystals structures were determined by the technique of Multiple Isomorphous Replacement. The technique required the

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[1] Chem. Eur. J. 2011, 17, 598-605

[2] ACS Catal. 2015, 5, 4167-4174

collection of a minimum of three data sets: a native data set plus two or more data sets collected on crystals of isomorphous heavy atom derivatives.
The 45 kD Bence-Jones Protein Pav had been crystallized and 4.5Å data sets were collected on crystals of both the native protein and a $K_2Pt(CNS)_4$ heavy atom derivative. Unfortunately, obtaining a second isomorphous derivative needed for phasing proved to be problematic. This need for a means of solving a protein structure based only on one derivative is what prompted B.C. Wang to develop what we now know as solvent flattening and opened the door for SIR and SAD structure determination that we use today.
The presentation will describe the non-routine (even by 1980's standards) structure determination of Pav by Wang's ISIR technique including the (1) generation of a 2.8 Å native data set based on film and diffractometer data, (2) phase extension from 4.5 to 2.8Å (3) the use of a wire model and a 2D Richards Box to carry out the initial real space alignment of the model with the ED map and (4) the resulting 2.8Å refined structure.

P10: Polycrystalline XRD data from a single crystal instrument with CMOS detector

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Large size of contemporary are detectors (>10 cm) allow relatively quick XRD data collection for small polycrystalline samples (<0.1 mg) without any sample pre-treatment. Reliable data could be obtained in 1-20 min. Quality of resulting datasets is sufficient for unambiguous identification of various inorganic and organic solids. Peculiarities of data processing and analysis will be displayed.
In this presentation, we show several application examples: Identification of Schachnerite and Paraschachnerite at the surface of daguerreotype images. Identification of inorganic pigments in various artifacts. Identification of polymorphs of polycrystalline organic compounds (pharmaceuticals, alkaloid drugs, etc.).

P11: Synthesis and characterization of $Al_xSc_{2-x}Mo_3O_{12}$ using non-hydrolytic sol-gel methods

La'Nese Lovings, Cora Lind-Kovacs

Department of Chemistry and Biochemistry, The University of Toledo

Materials that possess positive thermal expansion (PTE) have been highly studied. However, some materials possess negative thermal expansion (NTE). When the thermal expansion properties of two materials that are in intimate contact in a device are mismatched, the outcome can be detrimental and lead to stresses or device failure. NTE materials can be utilized to counteract the undesirable PTE of a material by forming a controlled expansion composite. Here we study NTE materials in the $A_2M_3O_{12}$ family (A= trivalent cation, M= Mo, W). Within this family some materials undergo a phase transition from an orthorhombic NTE phase at high temperatures to a monoclinic PTE phase at low temperatures. A suppression of this phase transition could be beneficial if one phase is desired, for example the NTE phase as a component for composites. In this family, some trends have been proposed but not all materials can be described by these trends. For example, $AlScMo_3O_{12}$ shows a much lower transition temperature than either $Al_2Mo_3O_{12}$ or $Sc_2Mo_3O_{12}$. The goal of this research is to synthesize mixed A-site occupancy materials and probe their phase transition behavior as a function of composition. Various $Al_xSc_{2-x}Mo_3O_{12}$ compounds have been synthesized using non-hydrolytic sol-gel methods, and their variable temperature behavior characterized.

P12: Structure and Dynamics of Main-Group Halide Perovskite Photovoltaics

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Inorganic and hybrid organic–inorganic main-group halides that adopt the perovskite structure combine excellent performance in photovoltaic applications, ease of preparation, and abundant constituent elements, but the origins of their remarkable properties are a matter of debate.[1] Here, we address two unusual aspects of these materials which have significant implications for functionality.

First, X-ray scattering studies reveal local, temperature-activated off-centering of the group 14 cations within their coordination octahedra across the materials class reflecting a preference for lower symmetry coordination than that implied by crystallographic approaches.[2,3] Ab initio calculations, optical measurements, and analogies to existing theory implicate the ns^2 lone pair electrons (and the corresponding second-order Jahn-Teller effect) as the origin of this phenomenon, which we propose leads to enhanced defect screening, reduced thermal conductivity, and unusual temperature dependence of the electronic bandgap.[2] We further demonstrate tuning of this phenomenon by homovalent chemical substitution on all sites of the perovskite structure.[3]

Second, the size, shape, and polarity of the molecular cations are shown to have a profound effect on the temperature evolution of structure and dynamics in the lead iodides.[4,5] In contrast to the well-studied $MAPbI_3$ (MA = CH_3NH_3), $FAPbI_3$ (FA = $HC(NH_2)_2$) exhibits an unusual reëntrant pseudosymmetry on cooling which is reflected in the optical properties, as well as persistent molecular motion below 100 K which indicates a markedly different molecule–cage interaction in the two compounds.[5] Despite markedly different barriers for molecular rotation, solid state nuclear magnetic resonance reveals similar dynamics at ambient temperatures for these high-performance compounds. Lastly, comparisons of the structure evolution of $FAPbBr_3$ and $FASnI_3$ from that of $FAPbI_3$ suggest that the nature of the metal—halogen bond has an inductive effect on the strength of hydrogen bonding to the halogens. This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under award number DE-SC-0012541.

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P13. Synthesis and structural characterization two new I_4-II-IV_2-VI_7 diamond-like semiconductors

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Diamond-like semiconductors (DLSs) are of interest for their potential applications in nonlinear optics, photovoltaics, and thermoelectrics. Named for their structural resemblance to diamond, DLSs are crystalline materials in which the anions are tetrahedrally coordinated in a cubic or hexagonal closest packed arrangement, while the cations occupy half the tetrahedral holes. The compositional flexibility available in quaternary DLSs offers a great opportunity for fine-tuning physicochemical properties that could lead to improvements over present commercial materials. I_4-II-IV_2-VI_7 compounds violate Pauling’s second rule of local electroneutrality and therefore, are predicted to possess crystal structures deviating from that of perfect diamond. We feel that because of this, few I_4-II-IV_2-VI_7 compounds have been targeted and reported; yet we believe that compounds of this stoichiometry constitute an entire class of materials. In this work, single crystals of two new I_4-II-IV_2-VI_7 compounds have been synthesized via high-temperature, solid-state synthesis and characterized with single crystal X-ray diffraction.

P14: Synthesis and Characterization of New Diamond-like Semiconductors with Potential as Nonlinear Optimal Materials

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Diamond-like semiconductors (DLSs) are compounds of increasing interest in the materials science community due to their attractive physicochemical properties, which can be controlled by tailoring their composition. Currently, ternary DLSs such as AgGaS2 and AgGaSe2 are commercially available for applications in nonlinear optical (NLO) devices. Although ternary DLSs are benchmark materials, they suffer from narrow phase matching ranges, multiphoton absorption and low laser-induced damage thresholds. Due to these pitfalls and the important applications of IR-NLO materials (including military and medical applications), improved materials must be developed. Quaternary DLSs of the formula I2-II-IV-VI4 and I4-II-IV2-VI7 are an attractive replacement for the ternary phases. Recently several compounds of these quaternary formulas have been discovered and characterized, which have the potential to possess impressive properties that could overcome the deficiencies of the commercially available DLSs. This poster will present the crystal structure and characterization of these new promising materials.

P15: Neutron diffraction study of the temperature-dependent magnetic ordering of $LiMn_xFe_{1-x}PO_4$

Stephanie Gnewuch

University of Maryland

Our group is studying magneto-electric materials which are predicted to exhibit a theorized form of primary ferroic ordering called ferrotoroidicity. Analogous to ferroelectrics exhibiting a net electronic polarization and ferromagnets exhibiting a net magnetic polarization, ferrotoroidics would exhibit a net spontaneous toroidal moment upon breaking both spatial and time inversion symmetry.[1] To begin searching for materials which would display this type of ordering, we have synthesized the olivine Li*M*PO4 (*M* = Mn, Fe, Co, Ni) series of materials. While the iron, cobalt, and nickel analogs are predicted to exhibit a toroidal moment in one direction, the manganese analog is not. [2] Thus the purpose of this study is to explore how iron doping impacts the magnetic structure above and below their ordering temperature. Neutron diffraction data was collected on three solid solutions of $LiMn_xFe_{1-x}PO_4$ at room temperature, base temperature, and in five-degree increments around the ordering temperatures of the samples. We will present the magnetic structures for these compounds as a function of temperature

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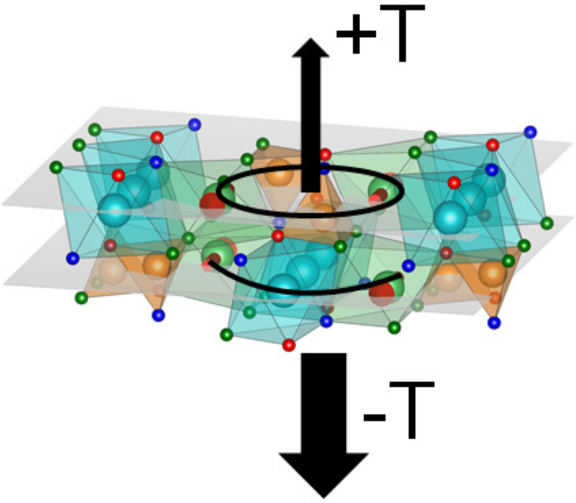


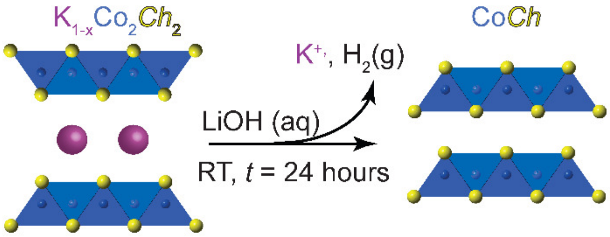
P16: Metastable layered metal chalcogenides: from Superconductivity to ferromagnetism

Wilfong, Zhou, Vivanco, and Rodriguez E.E.

University of Maryland

FeSe has attracted significant attentions for its unconventional superconductivity since its discovery in 2008. It exhibits a critical temperature (T_c) of 8 K, and can be further increased to 37 K by applying pressure and 43 K by inserting layers of ions or neutral molecules. Its interesting properties is related to its two-dimensional (2D) anti-PbO type structure, the $FeSe_4$ tetrahedra edge-share to form 2D layers held by weak van der Waals interactions. An interesting question arises: what new properties will emerge to replace Fe with other transition metals? Until now, iron has been found to be the only transition metal to form stable binary chalcogenides with the anti-PbO type structure (*P4/nmm*). To answer this question, we targeted cobalt first due to its proximity to Fe on the periodic table.

Here, we present a general strategy to synthesize metastable layered materials via topochemical de-intercalation of thermodynamically stable phases. Through kinetic control of a de-intercalation reaction, we have prepared the two hypothesized metastable compounds, CoSe and CoS, with the anti-PbO type structure from the starting compounds $K_{1-x}Co_{2-y}Se_2$ and $K_{1-x}Co_{2-y}S_2$, respectively. Crystal structure from X-ray diffraction (XRD) and powder neutron diffraction (PND), magnetic susceptibility, magnetization, and electrical resistivity are studied for these new layered chalcogenides; both CoSe and CoS are found to be weak itinerant ferromagnets with Curie temperatures close to 10 K.



P17: Softchemical routes to new iron phosphates

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Efforts are underway to synthesize low-cost, efficient and environmentally benign cathode materials for Li ion batteries. Polyanionic compounds in the family of phosphates, sulfates and silicates have already shown promises as excellent cathode materials for lithium and sodium ion batteries. In quest for new phosphate materials we have been focusing on synthesizing new iron phosphates employing soft chemical routes. In this effort, we have synthesized a new iron phosphate, $NaFe(HPO_4)_2$, through a low-temperature hydrothermal route. The crystal structure of the compound has been solved using single-crystal X-ray diffraction technique, which revealed that the 3D structure is built up of corner sharing FeO_6 octahedra and PO_4 tetrahedra yielding channels along C-axis. The Na ions are located in those channels. Presence of protons and Na-ions in the channel provided further clues of creating new compositions by exchanging protons/sodium ions with lithium. The ion-exchange of sodium with lithium was successfully carried out in solution medium to form $Li_2Fe(HPO_4)(PO_4)$ and further proton-exchange of $Li_2Fe(HPO_4)(PO_4)$ by lithium at low temperature solid state method yielded fully lithiated compound, $Li_3Fe(PO_4)_2$. The structure of $Li_3Fe(PO_4)_2$ has been solved from synchrotron powder X-ray diffraction data by employing ab initio techniques and finally refined using the Rietveld method resulting in a good convergence. All these iron phosphate phases are electrochemically active with respect to lithium and sodium ion batteries. The presentation will include the syntheses, structure determination and the electrochemical properties of the new iron-phosphate phases.