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APS POSTER ABSTRACTS



Biology

A-1

SONICC Implementation at GM/CA-beamline 23IDB at the APS

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Second order nonlinear optical imaging of chiral crystals (SONICC), based on femtosecond laser scanning microscopy, has been implemented at GM/CA@APS undulator beamline 23ID-B for rapid protein crystal localization and centering [1]. The technique is based on infrared laser light impinging on non-centrosymmetric crystals of proteins, which may selectively yield a frequency-doubled, visible signal generated by the anharmonic response of the electron cloud of the protein in response to the laser field. One aim of this method is to locate small crystals grown in opaque crystallization media for centering in x-ray beams of only a few microns or less in cross-section, such as for membrane-protein crystals grown in mesophase. The optical system implemented for generation and detection of Second Harmonic Generation (SHG) signals at beamline 23IDB has been described. Recent efforts towards providing user-friendly capabilities include: increasing rates of data acquisition, providing bright-field laser imaging capabilities, and incorporation of laser-safety interlocks suitable for a user program. SHG imaging has also enabled direct experimental visualization of electric fields generated by photoelectrons that are produced as a result of x-ray absorption, which provides insight on x-ray damage in samples [2]. Recent advances will be presented.

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[1] J.T. Madden, S. Toth, C. Dettmar, J. Newman, R. Oglesbee, H. Hedderich, R. Everly, M. Becker, J. Ronau, S. Buchanan, V. Cherezov, M. Morrow, S. Xu, D. Ferguson, O. Makarov, C. Das, R. Fischetti, and G. Simpson. *J Synchrotron Rad.*, 2013, **20**, 531–540.

[2] C.M. Dettmar, J.A. Newman, S.J. Toth, M. Becker, R.F. Fischetti, and G.J. Simpson. *Proc. Nat. Acad. Sci.*, 2015, **112**, 696–701.

A-2

Cholesterol May Protect Mammalian Cells from Superwarfarins

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Warfarin is the most widely used anticoagulant used in the world, and prescribed for the prevention of heart attack, strokes, and blood clots. Superwarfarins are modified analogues of the commonly used anti-coagulant warfarin. In contrast to warfarin, superwarfarins typically have 100-fold or greater potency to inhibit vitamin K production, and have an extremely long biological half-lives. The precise biophysical properties underlying those increases are not fully known, however the presence of aromatic rings make them strongly lipophilic which may contribute to increased tissue retention or binding to vitamin K epoxide reductase. We tested the possibility that superwarfarins exhibit strong binding interactions with membranes that are not observed with warfarin. Lipid monolayers comprised of DPPC (diphosphatidyl phosphocholine) or cholesterol were generated in Langmuir troughs, to which was introduced varying concentrations of the superwarfarin brodifacoum (BDF), or difenacoum (DiF), the des-bromo form of BDF. Interactions with the monolayers were probed by specular x-ray reflectivity and grazing incidence x-ray diffraction,

and compared to results using warfarin. Reflectivity data reveals that both BDF and DiF interact with DPPC monolayers in dose-dependent manner at concentrations near their estimated lethal dose. In contrast, warfarin showed no interactions with DPPC. Grazing incidence x-ray diffraction shows a rearrangement of lateral crystalline order of the DPPC upon introduction of BDF and DiF. Neither BDF nor DiF showed significant interactions with cholesterol. Our *in vitro* studies show that BDF increases lactate production in rat glioma cells; however, following cholesterol depletion lactate production was significantly increased by BDF. These results demonstrate a preferential interaction of superwarfarins with zwitterionic phospholipids over cholesterol, suggesting a potential protective mechanism served by membrane cholesterol in mammalian cells.

Chemistry

A-3

Study of Pressure/Temperature Effects on Borate Cross-linked Hydraulic Fracturing Fluids by Small Angle X-ray Scattering

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Recently it was reported that borate cross-linked guar gums of the type that are commonly used in hydraulic fracturing fluids exhibit reversible pressure-induced changes in the viscosity that could potentially influence their application in the field under more adverse conditions, such as deeper wells. More recent work at SLB has demonstrated that the decrease in viscosity becomes evident at lower pressure as the temperature is increased. Similar effects were observed for polyvinyl alcohol (PVA) and a wide range of borate and polyborate cross-linking agents. We investigate these systems using *in situ* high-pressure/Temperature small angle x-ray scattering methods to obtain a better understanding of the underlying cause of the pressure effects on borate binding and polymer configuration under conditions of high temperature and pressure.

A-4

Exactly-doped Semiconductor Quantum Dots

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Progress on the synthesis of colloidal semiconductor quantum dots (QDs) has largely focused on simple binary systems such as ubiquitous CdSe QDs. Recently, the introduction of guest impurities into such binary quantum confined systems has become topical. This is due to the fact that the incorporation of such impurities imparts a novel method for bandgap engineering beyond that achievable with size control. Unfortunately, present methods to synthesize doped QDs, such as the well-established rapid injection process, create samples with a dispersion of properties as the number of dopants per dot is dictated by Poissonian statistics. Lately, our group developed a strategy to synthesize QDs that contain an exact number of copper guest ions into CdSe [1], and recently into CdS and InP QDs matrixes controllably. This breakthrough has enabled us to fully characterize the structural, photophysical, and chemical properties of those exactly-doped QDs systems. In this regard we have used Small Angle X-ray Scattering and X-ray Absorption Spectroscopy technologies. Specifically, we have demonstrated that the photophysics of copper dopants is strongly dependent on the host material in the case of Cu(I)-doped CdSe vs. CdS QDs. Another exciting result using time-resolved x-ray transient absorption spectroscopy has revealed the Cu(I) dopants embedded in CdS



QDs matrixes capture electrons after QD excitation, while the hole remains delocalized in the host. To the best of our knowledge, this is the first direct observation of Cu(I) dopants' role in the relaxation of excitation within a semiconductor host.

[1] A. Jawaid et al., *ACS Nano*, 2013, 7, 3190–3197.

A-5

Time Resolved X-ray Absorption Spectroscopy of a Highly Stable Nickel Catalyst for Artificial Photosynthesis

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Production of cost-effective hydrogen gas through solar power is an important challenge of the Department of Energy among other global industry initiatives. In natural photosynthesis, the oxygen evolving complex (OEC) can carry out four-electron water splitting to hydrogen with an efficiency of around 60%. Although, much progress has been carried out in determining mechanistic pathways of the OEC, biomimetic approaches have not duplicated Nature's efficiency in function. Over the past years, we have witnessed progress in developments of light harvesting modules, so called chromophore/catalytic assemblies. In spite of reportedly high catalytic activity of these systems, quantum yields of hydrogen production are below 40% when using monochromatic light. Proper understanding of kinetics and bond making/breaking steps has to be achieved to improve efficiency of hydrogen evolution systems. This project shows the timing implementation of ultrafast x-ray absorption spectroscopy to visualize in “real time” the photo-induced kinetics accompanying a sequence of redox reactions in a nickel-based molecular photocatalytic system. Time-resolved XANES supplemented by Density Functional theory calculations illustrate formation of a Ni(I) species.

A-6

In situ Pair Distribution Function Studies of Homogeneous Iridium Catalysts under Reaction Conditions

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Homogeneous metal catalysis is a very common tool in organic synthesis. However, mechanistic aspects concerning many of these processes remain poorly understood. Knowledge of the metal local structure in solution and under catalytic conditions would allow the development of more efficient catalysts.

Iridium-based catalysts are versatile and very selective in a wide range of chemical transformations. We have reported a new Ir(III) complex containing an N-heterocyclic carbene ligand functionalized with an alcohol group (complex 1) that catalyzes the formation of carbon-nitrogen bonds with high efficiency [1]. The mechanism has been investigated experimentally (e.g., isotopic labeling and kinetic investigations) and with computational studies [2]. We have recently expanded this family of Ir-carbene catalysts by modifying the ligand (complexes 2 and 3), observing different catalytic activities depending on the metal coordination environments.

In situ Pair Distribution Function (PDF) analyses have been performed at 11-ID-B in solution. These measurements have provided critical insights the local structural changes of Ir-complexes under catalytic conditions.

[1] Bartoszewicz, A., Marcos, R., Sahoo, S., Inge, A.K., Zou, X., Martín-Matute, B., *Chemistry: A European Journal*, 2012, 18, 14510.

[2] Bartoszewicz, A., Gonzalez Miera, G., Marcos, R., Norrby, P.-O., Martín-Matute, B., 2015, submitted.

A-7

***In situ* XAS Study of Oxygen-evolving Ruthenium Complex under Water Oxidation Conditions**

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Today there is a strong need in using and storing energy from alternative sources. One of such possible sources is artificial photosynthesis (i.e., a process similar to the water oxidation that occurs during natural photosynthesis). Though several devices based on water splitting were created, their efficiency has to be improved. So far, ruthenium-based molecular catalysts are most stable and well studied. However, the behavior of ruthenium complexes during the process of water oxidation is not yet very clear. *In situ* studies under catalytic conditions may provide answers to the questions about process of water oxidation by ruthenium molecular catalysts and involved intermediates.

In this work, single site Ru complex $[\text{RuII}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$ (tpy = 2,2';6',2"-terpyridine, bpy = 2,2'-bipyridine) [1] was studied using *in situ* x-ray analysis under electrochemical conditions of water oxidation. Solution of Ru complex at different pH (pH=1 and pH=7) were electrolyzed at different voltages (1.6 and 1.8 V relative to normal hydrogen electrode) and x-ray absorption spectra were recorded during electrolysis. XAS measurements were done at beamlines 20-ID and 20-BM at Advanced Photon Source.

Applying 1.6 or 1.8 V potential to initiate water oxidation we quickly achieved sample oxidation and catalytic current. In spite of the claims that RuV=O species should be dominant at 1.8 V oxidizing potential [2], measured Ru oxidation state does not increase above RuIV while ligand environment of $[\text{Ru}(\text{tpy})(\text{bpy})\text{H}_2\text{O}]^{2+}$ catalyst undergoes significant modification. After up to 18 hours of electrolysis, XANES comparison indicates that only Ru(IV) is presented in all solutions. Also, by comparing EXAFS spectra at different times during electrolysis, it was found that at pH=7 structure of Ru complex matches that of $[\text{Ru}=\text{O}(\text{tpy})(\text{bpy})]^{2+}$ and does not change with time. However, this is not the case at pH=1: there changes in first and second coordination spheres happen quickly after start of electrolysis. EXAFS and DFT modeling is ongoing to assign structure of new Ru(IV) intermediate. During electrolysis no new Ru-O-Ru bridge signatures were observed in EXAFS. Sample remains catalytically active. Clear solutions show no signs of sample degradation. X-ray damage analysis at Ru K-edge shown that inside electrochemical cell solutions of Ru complexes can be exposed for extended periods of time to 22–23 keV x-ray beam without causing changes to Ru oxidation state or ligand environment. This stability is due to low absorption of Ru K-edge x-rays by water and sufficient sample volume (5–10 ml) of the cell.

[1] Y. Pushkar, D. Moonshiram, V. Purohit, L. Yan, and I. Alperovich, *J. Am. Chem. Soc.* **136** (2014) 11938–11945.

[2] J.J. Concepcion, M.K. Tsai, J.T. Muckerman, and T.J. Meyer, *J. Am. Chem. Soc.* **132** (2010) 1545–1557.

A-61

Pressure and Temperature Effects on the Antiferrodistortive Phase Transition and Phonon Softening in SrTiO₃

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We report a study of the pressure-induced antiferrodistortive cubic-to-tetragonal phase transition in strontium titanate (SrTiO₃) at ambient temperature. High-resolution inelastic x-ray scattering measurements reveal the softening of a phonon mode (R_{25}) at the Brillouin zone boundary; a lattice distortion sets in at a critical pressure of 9.5 GPa, which corresponds to a critical volume reduction of 5.3%. Distortion can be induced under ambient pressure by lowering the sample temperature through a critical temperature of 105 K. The relationship between the two phase transitions is clarified by comparing the power laws of the pressure and temperature dependences of the softening behavior and by first-principles calculations of the energetics of the system.



Condensed Matter Physics

A-8

Strong Lattice Correlation and the Hopping of Non-equilibrium Hubbard Excitons in a Pseudospin-1/2 Mott Insulator Sr_2IrO_4

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In correlated oxides the coupling of quasiparticles to other degrees of freedom such as spin and lattice plays critical roles in the emergence of symmetry-breaking quantum ordered states such as high temperature superconductivity. Here we report a strong lattice coupling of excitonic quasiparticles in spin-orbital coupling Mott insulator Sr_2IrO_4 probed via optical photon excitation. Combining time-resolved x-ray diffraction and optical spectroscopy techniques, we further reconstructed spatiotemporal map of the diffusion of quasiparticles. In comparison with superconductor parent compound La_2CuO_4 , the strong lattice correlation is unexpected due to the different electronic structure. The observation extends the similarity between Sr_2IrO_4 and cuprates to the strong coupling between lattice and quasiparticles which persists to highly non-equilibrium conditions.

A-9

Magnetic Exchange Interaction between Fe^{3+} and Ho^{3+} Ions in Hexagonal HoFeO_3 Thin Films

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Multiferroic materials have been of great interest because the multiple ferroic orders simultaneously existing in these materials may lead to diversified applications in information technology, sensing, and actuation. However, multiferroic materials with room-temperature spin order are rare in nature. Engineered hexagonal HoFeO_3 (*b*-HFO) thin film is a promising candidate for a multiferroic material with room temperature ferromagnetism because of the expected exchange interaction between the Ho^{3+} ions and Fe^{3+} ions. Here we report the study of magnetic ordering and interactions in epitaxial *b*-HFO thin films by x-ray magnetic circular dichroism (XMCD) measurements. Epitaxial (0001) *b*-HFO thin films were deposited on (111) yttria-stabilized zirconia substrates via pulsed laser deposition. XMCD spectra were measured at the Fe $L_{2,3}$ edges and Ho $M_{4,5}$ edges at beamline 4ID-C of the Advanced Photon Source at Argonne National Laboratory. During the XMCD experiments, the magnetic field was applied parallel in the x-ray propagation direction and 60° away from the film normal (*c*-axis). Temperature dependence of the XMCD results show ferromagnetic ordering of Fe^{3+} ions up to 200 K and paramagnetic behavior for Ho^{3+} ions above 10 K. The saturation magnetic moment per Fe^{3+} ion, calculated from the XMCD spectra using the sum rules, is $0.26 \mu_B$, which is about 10 times larger than that in *b*- LuFeO_3 [1]. Magnetic moment per Ho^{3+} is $3.02 \mu_B$ measured at 10 K and 6 T magnetic field. The comparison of the XMCD polarities of the Fe L_2 peak and the Ho M_5 peak suggests that the average magnetic moments of Fe^{3+} and Ho^{3+} are aligned in the same direction. The observed enhancement of Fe^{3+} moment can be attributed to the exchange interaction between the Fe^{3+} and Ho^{3+} ions.

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[1] Jarrett A. Moyer et al., *APL Materials* **2**, 012106 (2014).

Energy and Geology

A-10

Iron Sulfide Particle Size Effects in a Maya Vacuum Resid and an Illinois #6 Argonne Premium Coal

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Coal is, and will remain for the foreseeable future, a major source of energy worldwide. Despite advances in renewable and gas resources, the U.S. Energy Information Administration predicts that coal will provide the majority of fuel for the generation of electricity continuing up to at least 2035. An understanding of sulfur-based mineral behavior in coals is still needed for coal processing and mining.

The FeS₂ polymorph pyrite and marcasite were mixed together with a Maya Vacuum Resid coal model in known ratios, and a scheme was devised to deduce particle size. The behavior of these samples was then tracked with increasing pyrolysis. The results show that marcasite is much less structurally stable if the initial particle size is large. This will result in a sudden generation of H₂S and generation of pyrrhotite, Fe_(1-x)S, which is a coal gasification catalyst.

A large-particled and a small-particled Illinois #6 coal Argonne Premium Coal was also pyrolyzed to various degrees. The iron sulfide behavior in this sample showed that there was a difference in transformations from pyrite to pyrrhotite and then to troilite dependent on the particle size. One explanation is the shrinking-core model, in which escaping sulfur gas eventually weakens the particles' outer sulfur-poor matrix, which breaks away, exposing the inner pyrite core.

A-11

Hydration at Yttrium-stabilized Zirconia (110)-water Interface

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Interfacial structure of yttrium-stabilized zirconia or YSZ (110) in contact with de-ionized water under ambient condition has been investigated by high resolution specular x-ray reflectivity (HRXR). The interfacial electron density profile with atomic resolution is derived from a model structure factor analysis which reproduces the measured HRXR data. The derived interfacial structure indicates that a possibly re-adsorbed Y³⁺ ion layer is sandwiched between surface oxygen layer and adsorbed water layer. The selective depletion among Y³⁺ and Zr⁴⁺ species is inferred based on their solubility in water. The re-adsorbed Y³⁺ ions are suggested to be constrained from further propagating into the bulk aqueous phase by forming Y-O bonds with surface O atoms (i.e., forming an inner-sphere complex) and water molecules as well as by electrostatic interaction between the Y³⁺ and the negatively charged vacancy sites of Y near the surface. The vacancy sites by Y³⁺ depletion and inherent O vacancies on the surface are likely occupied by adsorbed water underneath the Y³⁺ layer which overlaps with the surface oxygen layer. These results show characteristic interfacial hydration structure that compensates the depletion-induced surface charges by partially-hydrated species of the depleted ion itself. There is no indication of subsequent depletion of Y³⁺ ions from deeper substrate within the experimental time scale (~8 hrs). While the majority of surface Zr atoms, exposed to water, seem to stay stable due to its intrinsically low solubility, the depletion of Y³⁺ and its re-adsorption mechanism appears favorable in minimizing the interfacial energy.



A-12

Uranium Immobilization by Plant Roots in Acidic Wetlands: Microcosms and XAFS Study

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Uranium mobility and biogeochemistry is profoundly different in wetlands compared with upland sediments due to sharp geochemical gradients, elevated organic carbon concentrations and microbial activity, and the transient nature of hydraulic regimes. However, chemical speciation and biogeochemical behaviors of U in such systems are not well understood. At Savannah River Site (SRS), there were several former U processing facilities that released ~45,000 kg of depleted U into seepage ponds between 1958 and 1980. Approximate 70% of the depleted U still remains in the Tims Branch and associated wetlands, and becomes a sink of U contaminant to the environment. In this study, we investigated U chemical speciation and retention mechanisms by living plant roots in the acidic SRS wetlands using microcosms, U L₃-edge x-ray absorption fine structure (XAFS), and x-ray fluorescence (XRF) mapping.

The microcosm experiments were set up to mimic the biogeochemical conditions of the SRS wetlands. American bur-reeds (*Sparganium americanum*) transplanted from a noncontaminated SRS creek were grown in Ottawa sand pots under controlled temperature (25–30°C) and lighting (14 h/day). Several different nutrient solutions were supplied in sequence to keep the plants healthy while promoting Fe plaque formation on the roots and to allow the spiked U species to interact with plant roots under reducing conditions. The plant roots were then harvested, and together with the associated sand samples, examined using U L₃-edge XAFS and XRF mapping. Our findings were: 1) The U concentrations in the roots were qualitatively several hundred times higher than the U concentration in the Ottawa sands. 2) The chemical species of U on the Ottawa sands were U(VI). However, on 15 days after the root harvest, U chemical species on the plant roots were both U(IV) (up to 40%) and U(VI), and bound to carbon as a bidentate species and phosphorus as a monodentate species. 3) On 140 days after the root harvest, all U species became U(VI), but remained to bond with carbon as a bidentate species and phosphorus as a monodentate species. (4) XRF mappings indicated that there were hot spots for Fe and U, but they were not correlated in the distribution. The μ -XANES of Fe hot spots indicated the presence of Fe oxides and pyrite; while the chemical species of the U hot spots were U(VI), likely uranyl phosphate minerals as observed in electron scanning microscope (SEM) and the backscattering electron images of the roots. Together, these findings indicated that in the acidic SRS wetlands where U species is less likely to be immobilized by sediment minerals like goethite, they could be highly retained by plant roots that become a major source of high natural organic matters in the acidic SRS wetlands, even under oxidizing conditions.

A-13

Structural Study of Surface Complexation of Pb(II) on a High-temperature Annealed Hematite (1-102) Surface

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Structural study of Pb(II) adsorption at a high temperature-annealed hematite (1-102) surface was undertaken using crystal truncation rod (CTR) x-ray diffraction technique. The best fit CTR model suggests that Pb(II) adsorption at an annealed hematite (1-102) surface occurs under an inner-sphere mode with a bidentate edge-sharing binding configuration. The local structure of Pb surface complex species is a distorted trigonal pyramid with an average Pb-O

bond length of 2.27 Å in good agreement with that reported in previous XAFS studies. Pb adsorption at three different bidentate sites (i.e., edge-sharing site of type 1, edge-sharing site of type 2 and corner-sharing site) was testified separately in the surface modeling. It was found that the edge-sharing site of type 2, which is the only site showing affinity for Pb(II) observed in the present study, is the preferable binding site mainly due to the existence of an O-Fe-O angle in this binding site structure more appropriate in producing a stable Pb surface complex species. In addition, it was also found that the Pb surface complex species bound at this site could be further stabilized via the formation of an extra weak Pb-O bond as well as a strong hydrogen bond between the distal oxygen and one surface oxygen. The bond valence rule was employed as an extra constraint in the process of CTR modeling to assure the steric feasibility in the optimized surface complexation structure. The post-model bond valence analysis suggests that both surface atoms and sorbate atoms in the best fit model structure could achieve a bond valence saturation state after a proper assignment of protonation schemes to under-coordinated oxygen groups. An unique stoichiometry of Pb(II) adsorption on the hematite (1-102) surface was proposed based on the best fit surface complexation structure as well as the protonation schemes obtained in the bond valence analysis, and the proposed stoichiometry indicates that the source of proton releasing is solely through the deprotonation of surface functional groups, which are chemically bound to Pb atom in the process of surface complexation. The molecular-scale structural information derived from this study is a great advance in the understanding of the Pb adsorption on a hematite (1-102) surface, which can be applied for a better modeling of the environmental behavior of Pb(II).

A-14

Sorption Mechanisms of Metals to Graphene Oxide

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Environmental toxic metal contamination remediation and prevention is an ongoing issue. Graphene oxide is a promising material that adsorbs significant quantities of a wide variety of heavy metals under different pH and ionic strength conditions. We present x-ray absorption fine structure (XAFS) spectroscopy results investigating the binding environment of Pb(II), Cd(II), and U(VI) ions onto multi-layered graphene oxide (MLGO). Analysis indicates that the dominant sorption mechanism of Pb and U to MLGO changes as a function of pH. In contrast, the sorption mechanism of Cd to MLGO remains electrostatic across a wide range of pH values for a variety of pH values and ionic strength conditions. Determination of the sorption mechanism of various metals to MLGO will guide remediation strategies and prevention methods for toxic metal removal from aqueous environments.

A-15

X-ray Micro-computed Tomography for the Durability Characterization of Aggregate

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A novel method, x-ray computed tomography, has recently emerged as a powerful, non-destructive methodology for material characterization, including geomaterials. This method produces 3D images of the object that can be analyzed in various ways based on the purpose of the scan. The objective of this research is to use x-ray CT technology to



investigate the internal structure and porosity of various types of aggregates such as limestone, granite, and quartzite. In addition, this research used x-ray CT technology to investigate the influence of harsh environments such as freezing and thawing on the durability of the aggregate. Virgin and treated aggregate specimens were subjected to x-ray CT to obtain high-resolution 3D images. Aggregate treatments (wetting/drying and freeze-thaw cycles) were conducted using the sodium sulfate soundness test and the actual free-thaw test. The CT scans were carried out using a sector 13-BMD synchrotron microtomography beamline at the Advanced Photon Source of the Argonne National Laboratory, Illinois. Analysis was conducted on the acquired 3D high-resolution images to investigate the pore structure and micro-cracks of these aggregates types. The x-ray CT technology was useful for visualizing the internal structure of aggregate particles with high resolution. This visual inspection provided information on pore space characteristics such as pore shape, connectivity, and distribution. In addition, volumetric quantities such as the volume of aggregate particles and the volume of pore space were identified and measured. These measured quantities were used to calculate porosities of the investigated aggregates, which provided properties of these aggregates using the constructed 3D CT images (non-conventional method). Sodium sulfate soundness test effects on the treated aggregates (degradation, disintegration, and weathering) were significant, as observed in the 3D CT images of treated aggregate particles. Pore space volume increased as the aggregate particles were treated with wetting/drying cycles of sodium sulfate solution. The sodium sulfate soundness test significantly affected the permeable (connected) pore space and induced degradation/disintegration, which increased the volume of connected pore space with the increase of the number of wetting/drying test cycles. Isolated pore space remained unchanged with the number of sodium sulfate test cycles, since the salt could not penetrate these pores to induce internal force of expansion, which degraded and disintegrated the aggregate structure. The freeze-thaw test induced changes to the pore space of the treated aggregates with a noticeable impact on the connected pore space of the aggregate particle.

High Pressure

A-16

Technical Developments on High-pressure Melting of Metals Using Laser Pulse Heating and Synchrotron X-ray Diffraction

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We discuss several important experimental developments relevant to carrying out careful structural measurements on pure metals close to and above their melting temperature with pulse laser heated diamond anvil cell (DAC) and synchronized *in situ* x-ray diffraction. Precise high temperature generation and measurement for many metals close to their melting temperatures is not feasible with continuous laser heating in a diamond anvil cell approach due to the chaotic nature of the temperature response of the sample as well as chemical reactions which can take place in a DAC over even a relatively short time scale. However, provided that a number of important experimental considerations have been met, metal samples in a diamond anvil cell can now be controllably laser heated to 6000 K for relatively long pulse periods of 10–30 milliseconds, which is enough time to simultaneously collect x-ray diffraction in a single pulse with the currently available x-ray photon flux at the beamline 16-IDB of Advanced Photon Source. Time-scale dependent temperature response of the sample during the laser pulse duration is one of the most critical experimental variables and several key strategies for running successful experiments are presented. Several developments in areas such as sample preparation, sample chemistry during laser heating, laser pulse time-structure, alignment and synchronization of laser pulse, the temperature measurement and the x-ray beam will be discussed. We also present an example of an experiment involving controlled heating and measurement of x-ray diffraction of molybdenum metal samples under high pressure to temperatures thousands degrees above the melting point.

A-17

X-ray Imaging for Studying Behavior of Liquids at High Pressures in Paris-Edinburgh Press

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Several x-ray techniques for studying structure, elastic properties, viscosity and immiscibility of liquids at high pressures have been integrated using a Paris-Edinburgh press at the 16-BM-B beamline of the Advanced Photon Source [1]. Here we report the development of x-ray imaging techniques suitable for studying behavior of liquids at high pressures and high temperatures. White x-ray radiography allows for imaging phase separation and immiscibility of melts at high pressures, identified not only by density contrast but also by phase contrast imaging in particular for low density contrast liquids such as silicate and carbonate melts. In addition, ultrafast x-ray imaging, at frame rates up to $\sim 10^5$ frames/second (fps) in air and up to $\sim 10^4$ fps in Paris-Edinburgh press, enables us to investigate dynamics of liquids at high pressures. Very low viscosities of melts similar to that of water can be reliably measured [2–4]. These high-pressure x-ray imaging techniques provide useful tools for understanding behavior of liquids or melts at high pressures and high temperatures.

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A-18

Kinetics of the B1-B2 Phase Transition in KCl under Rapid Compression and Decompression

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Kinetics of the B1-B2 phase transition in KCl has been investigated at different (de)compression rates in a dynamic diamond anvil cell using time-resolved x-ray diffraction. The pressure (time)-dependent x-ray diffraction images show that the grain size of the product phase in the B1-B2 phase transition is (de)compression-rate dependent, *viz.*, slow (de)compression may result in large grains and rapid (de)compression may result in small grains. The over-(de)pressurization increases with (de)compression rates. There are two stages for the increase of over-(de)pressurization: one is a rapid increase at low compression rate and the other is slow increase at high compression rate. The logarithm of the transition time, defined by the coexistence of B1 and B2 phases, has a linear relationship with the logarithm of the compression rates which, when extrapolated this linear relationship to high compression rates, is in agreement with shock-wave data. The volume fraction as a function of pressure shows sigmoidal curves against pressure at different (de)compression rates. Based upon classical nucleation and growth theories (Johnson-Mehl-Avrami-Kolmogorov theories), we propose a model to fit the experimental data of the volume fraction as a function of pressure. Analogous to temperature-induced phase transitions at isothermal heating or non-isothermal heating conditions, we define an effective activation energy (Q_{eff}) that can be experimentally determined by fitting the (de)compression-rate dependent volume fraction. It is found that the change of the nucleation mechanism, transition time, nucleation rate, and grain growth rates are related to compression-rate dependent effective activation energy. Our dynamic (de)compression experiments on KCl may bridge a gap between static compression and shock-induced phase transition.



A-19

Study of Phase Transition Pathways, Metastable Phases, Melting and Crystallization Using Time-resolved X-ray Diffraction and Dynamic (de)compression Techniques

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High-pressure Diamond Anvil Cell-based time-resolved x-ray diffraction and dynamic (de)compression techniques at High Pressure Collaborative Access Team (HPCAT) provide the possibility to observe (de)compression-rate dependence of phase transition pathways, pressure-quenching of metastable phases, as well as kinetics of phase transformations, melting and crystallization. Here we present some examples of our recent experimental results of dynamic (de)compression in common elements and compounds — water, silicon and gallium.

For water, we observed compression-rate dependence of phase transition pathways directly using time-resolved x-ray diffraction. We found that at large compression rates water transformed to ice VII directly without going through ice VI, while at slower compression rates it crystallizes to ice VI phase first and only then to ice VII.

It is well known that silicon has several metastable at low pressures. We consistently observed different metastable phases (crystalline and amorphous) or mixture of them at different controlled decompression rates, and these metastable phases can be kept for a long time at ambient conditions.

In pure metal gallium we studied the process of cyclic melting and crystallization under cyclic decompression and compression. We found that the compression rate has a remarkable effect on the phase transition/crystallization (over-pressurization), while during decompression the rate has a negligible effect on transition/melting pressure (over-depressurization).

In summary, the combination of time-resolved XRD and dynamic (de)compression techniques is a powerful tool for studying the rate dependence of phase transition pathways, metastable phases, and process of melting and crystallization in the high-pressure field. These techniques are currently available at HPCAT.

A-20

Integration of Micro-x-ray Diffraction and X-ray Absorption Spectroscopy for High-pressure Research Using Diamond Anvil Cells with Beryllium Gaskets

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X-ray absorption spectroscopy (XAS) measurements using diamond anvil cells suffer from “diamond glitches,” when the absorption spectra are measured with transmitted x-rays through the anvils. Efforts have been made to remove glitches in recent years (e.g., using nano-diamond anvils, by rotating the sample, or using focused beam with a polycapillary). Here we introduce a method for bypassing the problem by utilizing an x-ray transparent beryllium gasket in radial transmission geometry (i.e., x-rays pass through the beryllium gasket perpendicular to the loading axis). The beryllium gasket technique is well-used in high-pressure radial diffraction experiments. The versatile setup of the HPCAT 16-BM-D beamline at the Advanced Photon Source, which can adapt 90-degree rotation of sample stage with less than 1 μm precision, allows a combined transmission XAS measurement, utilizing a diamond anvil cell with beryllium gasket, with a typical micro-XRD experiment. The fixed exit feature of the monochromator together with achromatic KB focusing mirrors facilitates a wide range of energy change for both XRD and XAS without significant changes in beam profile and intensity. This further allows back-to-back switching between XRD and XAS measurements at an identical sample condition. A study of phase transition behavior in an isostructural volume collapse system, PrH_2 , has been performed with the combined XRD-XAS. The XRD was measured at 36.000 keV

and the XAS was measured at the K-edge of Pr around 42 keV for each studied pressure point. The experimental results are demonstrated and discussed in terms of direction toward future development for the broader application.

A-21

Combination of Laser Ultrasonics and Raman Spectroscopy in the Laser Heated Diamond Anvil Cell

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Understanding of the elastic behavior of minerals under high pressure is a crucial factor for developing a model of the Earth structure since the information about Earth interior comes mainly from seismological data. Laboratory measurements of velocities and other elastic properties of minerals are the key for understanding observed seismic information, allowing us to translate it into quantities such as chemical composition, mineralogy, temperature, and preferred orientation of minerals. Laser ultrasonics (LU) combined with diamond anvil cell (DAC) demonstrated to be an appropriate technique for direct determination of the acoustical properties of solids under high pressure. The use of lasers generating subnanosecond acoustical pulses in solids allows measurements of the velocities of shear and longitudinal waves propagated in opaque materials *in situ* at high pressure and temperature [1–4]. Absorption of the incident laser pulse energy and the associated temperature gradients induces a rapidly changing strain field. This strain field, in turn, radiates energy as elastic (ultrasonic) waves. At low pulse power, this is an entirely thermoelastic process resulting in no damage to the sample. The acoustic echo arriving at the probed surface causes both the displacement of the surface (a few nanometers) and the strain in the subsurface material, which might be detected through its influence on the optical reflectivity of the material (i.e., through the acousto-optic effect).

The details of the advanced system including laser ultrasonics in a point-source-point-receiver configuration coupled with Raman spectroscopy and laser heating techniques in the DAC for studying elastic properties of materials *in situ* at high pressure and temperature will be demonstrated. Future combination of this innovative system with high-resolution synchrotron x-ray micro-diffraction technique at GSECARS (Sector 13, APS) for full characterization of materials at extreme conditions will be discussed.

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A-22

Fast Compression/Decompression of Materials in Diamond Anvil Cells

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Fast compression/decompression constitutes one of the fundamental technical approaches to time-resolved high pressure research in the diamond anvil cell. Through careful choice of pressure generating apparatus and relevant time scale, a number of important scientific challenges can be address including, for example, non-equilibrium transformations and phase boundaries, unusual thermodynamic pathways to metastable phases, and compression-dependent nucleation rates and crystal growth. In this work we show preliminary results from a number of different scientific studies, each taking advantage of a particular apparatus and compression rate to measure, for example, equations of state at ambient and elevated temperatures, high sample compression and strain rates in materials, and compression-rate dependent sample stress and subsequent relaxation.



A-23

16ID-D: High Pressure Spectroscopy Beamline at HPCAT

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As part of a third generation synchrotron radiation beamline dedicated to high pressure research, 16-ID-D of HPCAT at the Advanced Photon Source engages in x-ray spectroscopy research of samples under high pressures, typically in diamond anvil cells (DAC) [1].

The spectroscopy line consists of IDA with a liquid nitrogen cooled Si (1 1 1) double crystal monochromator with 4.5–37 keV energy range, transport lines; IDC with an interchangeable high-resolution monochromator at ~2 meV energy resolution and two 1-meter K-B mirrors; and IDD, the experiment station, with a 2.7 meter 0–90 degree horizontal inelastic x-ray scattering spectrometer and a dedicated x-ray emission spectroscopy setup. Typical beam size at sample position is ~25 (V) × 50 (H) μm² at FWHM when using meter-long KB mirrors, smaller beam size (4 × 5 μm²) can be achieved by using a pair of 200 mm KB mirrors.

Current techniques include x-ray emission spectroscopy, inelastic x-ray scattering and nuclear resonant scattering. Examples of high pressure studies using these techniques and recent developments such as 7-element analyzer array for XES will be discussed in details in the meeting.

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A-24

A Paris-Edinburgh Cell for Liquid Silicate Structural Studies Using Monochromatic Diffraction and Multi-channel Collimator

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A Paris-Edinburgh Press (PEP) has been commissioned at the GSECARS beamline 13-ID-C, with a Si (311) high-energy monochromator and a multi-channel collimator (MC) assembly, which consists of two arrays of fine slits (WC blades) arranged in two concentric circular arcs. Both arrays consist of 75 slits with 0.8° separation and are located 50 and 200 mm, respectively, from the center. Slit widths of the inner and outer arrays are 0.05 and 0.20 mm, respectively. By oscillating the slits during data collection, background scattering can be effectively removed. Similar MC assemblies have been used extensively with PEP at ESRF for studying metallic liquids and low-Z materials [1]. The PEP is mounted on a general purpose diffractometer [2], with an area detector (MAR CCD) mounted on the two-theta arm. With unfocused incident monochromatic beam (65 keV) collimated at 0.2 mm, 30 min is sufficient to collect weak signals of a 2 mm diameter amorphous silicate sample, with minimal background due to the surrounding solid pressure medium. An analysis shows that with a fine incident beam of 50 μm, a collimation depth of 0.5 mm can be achieved at 2θ angles above 10°. To increase pressure and temperature range, we have developed a cupped-toroidal Drickamer (CTD) anvil [3]. The anvil design, with a central depression, a toroidal groove and a small tapered angle, combines features of modified Drickamer anvil and the traditional PE anvil. By optimizing the parameters for the CTD anvil design, pressures corresponding to the mantle transition zone can be generated. Cell assemblies with thermally insulating materials have been developed and temperatures up to 2000°C have been maintained steadily over hours. In the future, the large horizontally focusing Kirkpatrick-Baez mirror will be applied to focus the incident beam, thus allowing samples with diameters below 0.5 mm in diameter to be studied. The excellent spatial selectivity provides an exciting opportunity for liquid structure studies in the PEP.

We thank Mohamed Mezouar of ESRF for the design of the MC and advice during the setup.

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Instrumentation

A-25

Checking Intensity Corrections on a CCD Detector with a Fiber-optic Taper

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CCD detectors employing phosphors and fiber-optic tapers have been in use for more than 20 years. Thousands of structures have been solved and continue to be solved to this day. However, there is a lot of leeway in structure solution going from intensity to structure factor. Detector manufacturers attempt to account for any non-uniformity in the phosphor and light losses in fiber-optic tapers by measuring the response of the assembly to an isotropic flood field of x-rays, usually using some kind of fluorescence radiation. In this study, the same Si (3 1 1) reflection was imaged and integrated at various fiber-optic taper positions on an Area Detector Systems Corporation Quantum 210r CCD detector. Results indicate that corrections made for intensity losses in the fiber-optic taper/phosphor assembly are not adequately accounted for by the current flat-field correction, with uncorrected losses in excess of 30% near the corners of the fiber-optic taper. These results will also show that by using a simple radial fall-off correction term in addition to the flat-field correction, losses not accounted for by the current flat-field correction can be limited to less than 5%. All work was performed at beamline 19BM, at the Structural Biology Center located at the Advanced Photon Source.

This work was supported by the U.S. Department of Energy, Office of Biological and Environmental Research, under contract DE-AC02-06CH11357.

A-26

FASPAX: A Fast, Integrating Detector for the APS-upgrade

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FASPAX (Fermi-Argonne Semiconducting Pixel Array X-ray detector) has been planned as a fast integrating area detector with wide dynamic range for time resolved applications at the upgraded APS. The detector will achieve a burst image rate of 13 MHz, matching the bunch rate of the proposed storage ring timing mode. A unique integration circuit will permit wide dynamic range — from single photon sensitivity to 10^5 photons/pixel in a single exposure. Incorporation of a novel interposer layer in the hybrid stack will permit large area sensors without the usual coverage gaps associated with hybrid pixel devices. The detector will provide access to the full temporal resolution of the APS, and enable novel science, such as pump-probe studies of irreversible systems.

The APS Upgrade is currently funding development of small prototypes that will be tested in the next few years. This poster will present an overview of the detector, and give some details about the ongoing development of the major detector systems, including the sensor and readout chip, mechanical design, back end readout electronics, and software.



A-27

Elemental Sensitivity near the Atomic Scale

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Variants of the scanning probe microscope have proven tremendously valuable for extracting detailed information about the nature of a sample's surface (atomic, electronic, magnetic); however, it has proven difficult to yield direct chemical information utilizing scanning probe techniques alone. At Argonne National Laboratory's Advanced Photon Source, a new *in situ* high-resolution microscopy technique, the synchrotron x-ray scanning tunneling microscope (SXSTM), combines synchrotron x-rays as a chemical probe and the nanofabricated metal-insulator-metal tips of a tunneling microscope as a detector. The SXSTM technique takes full advantage of 1) the chemical, electronic, magnetic and structural sensitivities that synchrotron x-ray radiation offers and 2) the sub-nanometer spatial resolution offered by the scanning tunneling microscope.

Utilizing SXSTM, chemical fingerprinting of individual nickel clusters on the Cu(111) surface has been achieved with a 2 nm lateral resolution and a chemical sensitivity confined to the first atomic surface layer. The surface sensitivity demonstrated by the SXSTM technique will enable exciting new areas of opportunity and discovery in the chemical and materials sciences.

This work was funded by the Office of Science Early Career Research Program through the Division of Scientific User Facilities, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant SC70705. Work at the Advanced Photon Source, the Center for Nanoscale Materials, and the Electron Microscopy Center was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.

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[2] U.S. Patent Application 13/791,157.

A-28

Minimizing Thermal Drift in a Dual Crystal Monochromator

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Undulators on 3rd generation synchrotron sources such as the APS can produce high heat loads on downstream optics. User requests for different x-ray energy (undulator gap) can significantly change the power loading and induce thermal drifts in optics. A channel-cut monochromator (CCM) tends to be less sensitive to the varying thermal load, but all downstream components must track the vertical beam movement as a function of energy. A double crystal monochromator (DCM) offers an operational advantage over the CCM due to the ability to maintain constant exit-height over a wide range of energies. However, the DCM is more sensitive to varying power loads which may result in thermal fluctuations that distort the mechanics and cause intensity loss and beam position drift. Here we report a thermally stabilized DCM that incorporates PID control of the temperature of key points in the DCM. The DCM exhibits negligible thermally induced drift as the undulator gap varies from fully open to fully closed and the power load on the 1st crystal varies from less than 100 W to in excess of 1000 W, respectively.

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A-29

Spherically Bent Quartz Analyzer Characterization at 1-BMAlbert Macrander¹, Naresh Kujala^{1*}, Stan Stoupin¹, and Nino Pereira²¹Argonne National Laboratory, Argonne, IL 60439²Ecopulse, Inc., Springfield, VA 22152

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The bending magnet beam line 1-BM at the Advanced Photon Source was reconfigured recently, in part, as a test bed for hard x-ray optics. The beamline has a Si(111) × Si(111) double crystal monochromator and covers the energy range from 6 to 28 keV. The beam size available is 100 mm horizontally and 5 mm vertically. This paper reports on a study of a spherically bent crystal analyzer typical of those used for plasma spectroscopy or x-ray imaging. The crystal is alpha-quartz, 60 mm by 40 mm, which is bent by optical (direct) contact to a glass substrate that has been polished and ground to a 672 mm radius of curvature. The crystal had been ground and polished down to 0.1 mm thickness with the surface parallel to the (1 0 -1 1) crystal plane. Bragg case rocking curves and x-ray topographs were obtained at 12.75 keV for the (3 0 -3 3) reflection at a Bragg angle of 25.86 deg. A rocking curve with a very small vertical beam was relatively narrow, but a rocking curve obtained with a large vertical beam was very wide corresponding to the range of spherical curvature sensed in the vertical diffraction plane. For this large vertical beam, a continuous-exposure topograph obtained by rocking slowly across the full rocking curve with the same film in place showed a surprising amount of structure and revealed a strain pattern corresponding to several round features of roughly 0.3 mm diameter. These features are interpreted presently as due to gas bubbles formed and trapped at the interface between the bent crystal wafer and the spherical form during the bonding process.

We acknowledge E.O. Baronova for the fabrication of the analyzer. The beamline development work at the APS was supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC-02-06CH11357.

A-30

Failure Modes of OFE and GlidCop® Copper Absorber Materials under X-ray Induced High Heat Load Thermal Fatigue Conditions

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Water cooled, high thermal conductivity, oxygen free copper and dispersion strengthened copper composites (GlidCop®) are workhorse absorber materials as strike surfaces for synchrotron x-ray masks, shutters and stops around the world. Although conservative design criteria keep these materials from ever approaching failure, a knowledge of the material's failure modes allows for more informed discussions of the safety factors inherent in using established design limits.

Thermomechanical fatigue tests were conducted under normal incidence x-ray thermal loading from low power, up to limit power levels of 4,800 W at peak power density of 430 W/mm². The materials respond to these increasing power loads in a progressive and logical fashion. In oxygen free copper (UNS C10100) increased thermal loading induces surface twinning, recrystallization, grain pop-out and surface rumpling leading to a roughened strike surface. In dispersion strengthened copper (UNS C15715) failure modes progress through stages from surface fiber drop-out or "cat scratching," crack generation, surface heaving, crack growth, surface folding and eventual melting.

This poster presents metallurgical and microstructural, observations and measurements on these materials over the scope of thermal loading conditions that can be tolerated in synchrotron x-ray components.



A-31

Vibrations, Spot Size, and Flux Measurements at XSD Beamlines

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The proposed Multi-Bend Achromat lattice replacing the existing Double Bend lattice at the APS will reduce the beam emittance by two orders of magnitude. Several new beamlines are being considered to take full advantage of the brightness increase and others should be upgraded to increase their capabilities.

To this end, we have started measuring the performance of the XSD beamlines to identify issues that could limit their performance in the new lattice. We have measured the spot size, flux, and vibrations of several beamlines.

The results of the measurements are interpreted using ray tracings and wave propagations using the SHADOW1 and the Hybrid2 code. In general, the measured flux and the calculated flux are in good agreement. The measured source sizes are usually larger than the calculated ones, but can be explained by assuming larger figure errors than those measured over 10 years ago. We have identified several vibration frequencies common in several beamlines, some of which are present in the electron beam.

The Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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A-32

Vortex® SDD X-ray Spectrometers with Improved Counting Rate Performance

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Silicon Drift Detectors (SDD) are most often used the Energy Dispersive Spectrometer (EDS) for x-ray microanalysis, x-ray fluorescence (XRF), total reflection XRF (TXRF), XRF imaging and x-ray absorption spectroscopy (XAS). Also the SDD spectrometers are very popular in synchrotron based experiments such as XAFS (x-ray absorption fine-structure) and XANES (x-ray absorption near-edge structure) because of their high-count rate capability and high energy resolution.

We will present several aspects of our design efforts toward the development of the SDD XRF spectrometers with an extremely high counting rate performance. Our spectrometers are based on the Vortex® SDD with the sensitive area of 50 mm² and the thickness of 0.5 mm and 1 mm. A new advanced front-end ASIC preamplifier integrated with the Vortex® SDD enables to increase the output count rate up to 850 Kcps at about 50% DT with the energy resolution (FWHM at 5.9 keV) better than 250 eV when it is used with conventional pulse processing electronics. With the latest adaptive pulse processing electronics achievable output count rate is even higher than 1 Mcps at relatively low DT and with the energy resolution better than 200 eV. However, despite the high count rate capability of the Vortex® SDD, the performance of the spectrometer is limited by a signal processing electronics. Therefore, to get a further increase in count rate capability we have developed multi-element SDD spectrometers with several design configurations including options for ultra high vacuum applications. A detailed data concerning the total solid angle of different Vortex multi-element detectors, their energy resolution and output count rate performance will be presented.

A-33

Low Temperature Synchrotron X-ray Scanning Tunneling Microscopy (LT-SXSTM)

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Low temperature scanning tunneling microscopy (LT-STM) combined with synchrotron based x-rays provides a new tool to capture chemical interactions and magnetic spin states on surfaces at high spatial resolution. The technique will drastically increase the spatial resolution, and it measures chemical and magnetic information along with surface topography. Here, we will present the current status of the ongoing development of a LT-SXSTM. The system is equipped with, high stability 4 axis stages, a half focusing polycapillary and positioners, a vacuum suitcase for sample and tip exchanges, custom designed STM head and a liquid Helium flow cryostat.

A-34

Mechanical Design of Multiple Fresnel Zone Plates Precision Alignment Apparatus for Hard X-ray Focusing in Twenty-nanometer Scale

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To overcome the limitations in today's fabrication techniques for high-efficiency Fresnel zone plates (FZPs) capable for hard x-ray focusing in the twenty-nanometer scale, a new approach of stacking FZPs in an intermediate-field was published by Vila-Comamala et al. in 2012 [1]. With this approach, a precision alignment apparatus for multiple FZPs handling and aligning must be designed to meet the following challenging design requirements: 1) Each of the stacking FZPs need to be manipulated in three dimensions with nanometer-scale resolution and travel range of several millimeters. 2) The relative three-dimensional stabilities between all of the stacking FZPs (especially in the x-ray beam transverse plane) are required to be kept within few nanometers for more than eight hours, the duration of the hard x-ray focusing for nanoprobe operation. 3) Compatible with the operation of multiple optics configurations, such as switchable optics between FZPs and K-B mirrors, for the APS future x-ray nanoprobe design.

Several prototypes have been designed and tested at the APS [2,3]. In this poster we present the precision mechanical design of the apparatus prototypes for two, three, and six FZPs alignment in an intermediate-field, as well as the test results of their hard x-ray focusing performances.

Work supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

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A-35

Rocking Curve Imaging at 1-BM X-ray Optics Test Beamline

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We report progress on implementation and commissioning of rocking curve imaging capability [1] at 1-BM Optics Test Beamline of the Advanced Photon Source. Si collimator crystals of various crystallographic orientations were designed and fabricated using in-house capabilities to accommodate growing needs of strain characterization in diffractive crystal optics and other semiconductor single crystals (e.g., crystal wafers). Quality of the Si collimator crystals was characterized using monochromatic beam topography across the entire working crystal surfaces. The initial design features evaluation of strain in single crystals in the nearly-nondispersive Bragg double-crystal geometry. Preliminary monochromatization of the x-rays is performed using a double-crystal Si 111 monochromator (DCM). An area detector (CCD) imaging the double-reflected beam permits sequential acquisition of x-ray topographs at different angular positions on the rocking curve of the crystal under investigation. Results on sensitivity and spatial resolution in imaging crystal strain are presented. The new setup complements laboratory-based x-ray topography capabilities [2–4] of the Optics group at the Advanced Photon Source.

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A-36

The APS Detector Pool

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The APS Detector Pool provides users with access to many different types of x-ray detectors and related equipment. The most popular devices include: Area Detectors (Pilatus 100K, PixiRad, Mar 165 CCD), Microscopy Cameras (Andor Neo, Prosilica), Spectroscopic Detectors (Vortex ME4, Oxford Ge, Amptek CZT), Point Detectors (Oxford Cyberstar, Mythen silicon strip, PIN Diodes), and Temperature Control Stages (Linkam, CryoStream). It also coordinates equipment loans between beamlines, provides hardware and EPICS troubleshooting, and works with vendors to circulate demo units of next generation detectors.

A-37

New Mini-beam Collimator Provides Lower Background

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The GM/CA-developed, quad-mini-beam collimator, and advanced rastering and vector data-collection software tools, have enabled successful data collection on some of the most challenging problems in structural biology. This is especially true for membrane-protein crystals grown in lipidic cubic phase, where crystals are typically small, fragile, and “invisible” when cryo-cooled.

The current quad mini-beam collimators have 5-, 10-, and 20- μm beam-defining apertures with 250 μm exit apertures, and a 300 μm aperture (ScatterGuard) for the full beam with a 600 μm exit aperture. Due to tolerances in the alignment of each beam defining aperture/exit aperture pair, two motorized translations and two manual angle adjustments are required for optimal alignment.

Tests with a new prototype mini-beam collimator with 5 μm beam defining aperture and a 150 μm exit aperture in combination with a 0.5 mm diameter beam stop have shown that the background can be further reduced. The design and test results of the new and upgraded mini-beam collimator will be presented.

A-38

Rapid *in situ* X-ray Position Stabilization via Extremum Seeking Feedback

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The Double Crystal Monochromator (DCM) 2nd crystal is one of the primary sources of intensity and position instabilities. While efforts to provide the 2nd crystal with thermal stabilization, vibration isolation, and strain relieved cables have substantially attenuated externally driven instabilities, long term drift remains a tedious problem requiring occasional intervention. Here, we address this problem using simultaneous Extremum Seeking Feedback Control (ESFC) for monochromator x-ray flux and *in situ* vertical beam position stabilization. Monochromator flux intensity stabilization is achieved using previously demonstrated extremum seeking feedback [1–5]. Intensity gradient detection for position ESFC is achieved by exploiting pre-existing vertical oscillations used for monochromator flux stabilization. Flux recovery at the sample after a 2 keV energy move is < 6 seconds and intensity stability through a 5 μm aperture is 1.5% FWHM over a period of 8 hours.

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Materials Science

A-39

ALD-grown Pd Nanoparticles Supported on TiO₂- and SrO- terminated SrTiO₃ Nanocuboids

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We report the application of SrTiO₃ (STO) nanocuboids with well-defined {001} facets as the support for Pd nanoparticles deposited by atomic layer deposition (ALD). The advantage of using a support with well-defined surfaces is that the surface resembles a model catalyst but retains a high surface area enabling catalytic reaction studies. This approach bridges the materials gap between single crystal models and catalysts with more complex structures. We demonstrate how the surface termination (TiO₂- or SrO) influences the growth mode, morphology and the chemical properties of the supported Pd nanoparticles. The morphology and chemical nature of the Pd particles were studied by transmission electron microscopy (TEM), x-ray scattering, and x-ray absorption fine structure



(XAFS) measurements. We also report that the effective coverage, chemical state, and the size of Pd nanoparticles can be controlled by the number of ALD cycles. CO oxidation reaction was used as a probe to determine and compare the catalytic performance of the Pd nanoparticles supported on TiO₂- or SrO- terminated STO nanocuboids. The study helps demonstrate how to prepare supported catalysts on mixed metal oxide supports.

A-40

Understanding the Complex Structure of Composite, Lithium-ion Cathode Materials

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Composite electrode materials, as indicated in the notation $y[x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2] \cdot (1-y)\text{LiM}_2\text{O}_4$ (M=Mn, Ni, Co), are ideally comprised of several structural motifs. One is the prototypical, layered $R\text{-}3m$ (LiMO_2) structure, one is that of the layered, monoclinic ($C2/m$) Li_2MnO_3 , and the third is the spinel ($Fd3m$) LiM_2O_4 . Such compositions have shown promising electrochemical performance as lithium-ion cathode materials and are currently being studied as such. In order to fully ascertain the actual promise of these materials a better understanding of their structural and elemental compositions is necessary. However, the nanoscale integration of the different components, along with local, chemical inhomogeneity, gives rise to extremely complex overall structures. Furthermore, once cycled in real cells, these structures change in ways that are not yet understood.

This project focuses on advanced characterization of pristine, end-member and composite structures in order to build a “baseline” understanding that can be used for future studies on working, composite electrode structures of all types.

A-41

Ferroelectric Domain Engineered Strain Investigated Using Diffuse Multiple Scattering

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The physical properties and functional efficiency in many real systems are intimately related to their internal stresses and strains. Thus, it is possible to control and tailor the functional properties of a material through modification of its structure. Different effects are observed in bulk crystals, polycrystalline thin films or in epitaxial nanostructures due to the differences in the dimensionality of any long-range order. Recently, there has been considerable research effort on understanding the complex interplay between sample structure and the internal strain which gives rise to the ferroic orders that can be observed in a wide range of materials including the important $(1-x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3] - x[\text{PbTiO}_3]$ (PMN-PT or $\text{PbZn}_{(1-x)}\text{Ti}_x\text{O}_3$ (PZT)). Of particular technological relevance is the correlation between strain and electric polarisation in these systems which we are exploiting, through the European Metrology Research Programme's Nanostrain project, to develop a new Piezoelectric-Effect-Transistor (PET). Suitably patterned architectures of these materials may offer a new route to replace aging CMOS technology with increased speed (x10) and, critically, significantly lower power consumption (~x100 less energy). To address this transformative technology the Nanostrain project brings together several European national laboratories in a consortium including nine commercial companies.

In this poster, we describe the first application of a new diffraction metrology similar to Rutherford, Kikuchi and Kossel lines and named Diffuse Multiple Scattering lines (DMS) [1]. As the DMS features arise from the crystal truncation rods they act as divergent secondary sources within the sample and hence have the crystallographic information encoded. Following a Laue description, the DMS appear as cones/circles on a 2D detector [1]. The newly developed experimental metrology, supported by robust modelling has several noteworthy implications: 1) the strain (and its dispersion) can be determined without moving the sample and in a single exposure. This allows a much wider range of sample environments (*in situ* application of electric/magnetic fields, temperature, etc.) to be used with significantly reduced errors than more conventional strain measurements, 2) where two, or more, features intersect the lattice parameter determination is very precise [2], 3) unlike Kossel lines [3,4], the sampling volume can be tuned through the x-ray energy. We report the application of DMS to domain engineered single crystal PMN-PT samples whilst under the application of an external electric field. We will show how DMS can extract the subtle evolution in both the lattice parameters and the strain state with E-field in real time. These measurements form a critical step in exploiting ferroelectric materials in general, and are crucial in our continuing efforts to develop a PET device.

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A-42

Probing the Role of Ga in Amorphous Conducting Oxides through Local Structure Studies

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The study of amorphous (a-) conducting oxides is an emerging field. The lack of grain boundaries, smooth surfaces, and low temperature deposition position these materials as ideal candidates for large area applications and flexible electronics. Most impressively, these materials maintain high electron mobility in the amorphous state. These benefits have led the recent commercialization of a-IGZO (Ga and Zn doped indium oxide) as a replacement for a-Si as the channel layer of thin film transistors in display technology. Despite this success, fundamental understanding of structure-property relationships is still lacking and must be improved to guide further development of amorphous conducting oxides. X-ray absorption spectroscopy (XAS) is one of the few tools that can be used to probe the structure of amorphous materials. Amorphous indium oxide doped with Ga (a-IGO) is a model system to help develop the role of dopants in amorphous oxides. An in depth XAS study was carried out to determine inter-atomic distances, coordination numbers, and structural disorder parameters as a function of Ga doping level. The correlation between XAS-derived structural features and the dopant-dependent evolution of both electrical properties and thermal stability of a-IGO will be discussed.

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A-43

High-energy X-ray Techniques for Studying Nuclear Energy Relevant Materials

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High performance materials that can withstand intense radiation fields, elevated temperatures, multi-axial stresses, and corrosive environment and nuclear fuel technologies that minimize waste and fully-utilize the fuel's stored energy are necessary for the deployment of advanced nuclear energy systems and the expansion of nuclear energy as a reliable, affordable, and clean energy source.

High energy x-ray techniques at the Advanced Photon Source (APS) are a unique set of nondestructive tools that can be used to understand the structure-processing-property relationship, characterize the thermos-mechanical state, and investigate failure mechanisms in polycrystalline nuclear materials *in situ*. In this poster, we illustrate the use of these high energy x-ray techniques to better understand polycrystalline materials employed in nuclear engineering applications.

A-44

In situ XAS Investigation of an Iron Oxide Battery Anode in Aqueous Electrolytes: Effect of Surface Modification on Rheology and Electrochemistry

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Iron oxides have been demonstrated to be anode materials in aqueous environments and multiple literature reports [1] exist proposing possible redox events that can occur in the system such as Fe(3+)/Fe(2+), Fe₂O₃/FeO and accompanying lithiation. However, the nature of the redox event varies with several factors such as repeated electrochemical cycling, nature of electrolyte used, concentration of electrolyte used and rate of charge/discharge. In order to optimize the system to a certain capacity and operational conditions, it is important to understand the nature of the redox transition occurring during electrochemical cycling and how to control it. Furthermore, performance in aqueous environments have been found to be heavily dependent on the lithium ion content of the electrolytes; [1] higher concentrations facilitating the reduction process and improving coulombic efficiency. However, a satisfactory explanation currently does not exist and further analysis is required to fully establish the nature of redox events.

This study reports on the use of XAS as an investigative tool to study the reversible redox chemistry of Iron (III) oxide nanoparticles, establish the role of Li⁺ and correlate redox events with coulombic input. SEM and XRD data in conjunction with *in situ* XAS analysis reveals that the Iron oxide nanoparticles can be fully reduced to metal in aq. 5M LiOH electrolytes, but leads to growth of large micron sized crystals. A simple surface modification procedure has also been developed for the nanoparticles to facilitate preparation of low viscosity nanofluids and prevent growth of crystallites due to repeated electrochemical cycling as observed in the pristine material. SEM, XRD and *in situ* XAS data are collectively used to understand these phenomena in both pristine and modified nanoparticles. This study forms the basis for electrochemical and rheological testing of the same system as a suspension type nanoelectrofuel electrode. [2]

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A-45

Micro CT Microscopy and Ultra Small-angle Neutron Scattering Characterization of Alkali-Silica Reaction (ASR) Gel Development in Mortar Specimens with Recycled Glass Particles

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The alkali-silica reaction (ASR) (or alkali-aggregate reaction) is a major distress in cementitious concrete and structures due to the expansion damage initiated from reactive siliceous aggregates. The ASR takes place between the reactive silica contained in aggregates and the alkalis in pore solutions of cement paste. The alkali-silica reaction is initiated by a reaction between the hydroxyl ions in the pore solution and certain types of silica in the aggregate. Once the ASR gel is formed, the gel will expand by imbibing water. The driving force for expansion and cracking is the osmotically-derived imbibition of water into the insoluble reaction gel. This study aims to characterize the microstructure of alkali-silica reaction gels formed from alkali solutions and to capture the ASR damage development with different reaction conditions by utilizing the X-ray Micro-tomography and Ultra Small Angle Neutron Scattering (USANS).

To better understand this process, an accelerated chemical reaction between glass particles and strong alkali solution was conducted to simulate the ASR reaction in reality. The cement mortar samples were prepared using recycled glass particles (mesh size 20–40) as fine aggregates with a volume percentage of 30% and a water to cement ratio (w/c) of 0.5. Cement mortar samples were molded in plastic tubes with an inner diameter of 2 mm. After hardening for 24 hours, the samples were merged into different concentration NaOH solution for curing. The ASR gel (with lower density) and microcracks can be identified from the x-ray CT images. The damage development in glass particles were also observed. To further investigate the microstructure of ASR gel, the 3D porous gel microstructure was reconstructed and the average averaged size of ASR gel particle was determined as 2.88~2.92 μm . With USANS data, the microstructural properties such as surface area and porosity at micron scales were obtained by analyzing the I-Q data with the Porod scattering theory [1]. An Guinier-Porod model [2,3] was used to determine the size and dimensionality of the reacted Alkali-silica gel scattering data. The analyzed ASR gel size dimensions from USANS match well with CT image data.

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A-46

Atomic Layer Deposition of Doped Films Studied by *in situ* Synchrotron Techniques with a Mobile and Modular Reactor

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Progress for understanding growth of thin films by atomic layer deposition (ALD) has been aided by application of synchrotron studies over the past ten years. ALD is a vapor phase deposition technique, similar to chemical vapor deposition, where precursors are introduced subsequently, in two complementary half-cycles, to grow thin films. In ALD, film growth is controlled by chemically self-limiting reactions at the gas/surface interface, which produces conformal films blind to aspect ratio of trenches and intricate nano-structures. While significant advancements have been made by other *in situ* techniques, such as quartz-crystal microbalance, infrared spectroscopy and ellipsometry,



the power of *in situ* synchrotron studies will provide wealth unique information. To take advantage of this an ALD apparatus was designed to integrate with the APS.

The ALD apparatus consists of common process hardware (precursor delivery, temperature and pressure control, and heater supply) and a set of reactor chambers which are specifically tailored for compatibility with individual x-ray techniques (or groups of techniques) and incorporated into the portable ALD system in a plug-and-play fashion. X-ray scattering studies are enabled by an open-top reactor cell which can be fitted with either a hemispherical graphite dome or a kapton/mica/sapphire window assembly. X-ray absorption spectroscopy (XAS) is performed on flat substrates in a grazing incidence mode using a closed reactor cell with removable kapton windows. Both reactor cells are compatible with a standard Huber threaded goniometer mount.

To demonstrate the capabilities of the *in situ* ALD tool, initial results from three separate experiments will be presented. 1) *In situ* crystal truncation rod (CTR) and reflectivity (XRR) measurements of epitaxial ALD growth of ZnO on c-plane sapphire at 150°C were performed at 33-BM-C. 2) *In situ* grazing incidence small angle x-ray scattering (GISAXS) at 12-ID-B was employed to study island nucleation and coalescence of ALD MnO and ZnO at 150°C. 3) The coordination environment of low dopant levels of Er₂O₃ and the half-cycle ALD chemistry of erbium incorporation into amorphous Al₂O₃ and crystalline MgO, both grown by ALD on c-sapphire, were examined at 300°C with *in situ* XANES/XAFS at 20-ID-B.

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A-47

A Novel Phase in Li-Si System

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Li₁₅Si₄, the only crystalline phase that forms during lithiation of the Si anode in lithium-ion batteries, was found to undergo a structural transition to a new phase at approximately 7 GPa. Despite the large unit cell of Li₁₅Si₄ (152 atoms in the unit cell), *ab initio* evolutionary metadynamics (using the USPEX code) successfully predicted the atomic structure of this new phase (beta-Li₁₅Si₄), which has an orthorhombic structure with a Fdd2 space group. In the new beta-Li₁₅Si₄ phase the atomic packing is more efficient owing to the higher Si-Li coordination number and shorter Si-Li, Li-Li bonds. Beta-Li₁₅Si₄ has substantially larger elastic moduli compared with alpha-Li₁₅Si₄, and has good electrical conductivity. As a result, beta-Li₁₅Si₄ has superior resistance to deformation and fracture under stress. The theoretical volume expansion of Si would decrease 25% if it transformed to beta-Li₁₅Si₄, instead of alpha-Li₁₅Si₄, during lithiation. Moreover, beta-Li₁₅Si₄ can be recovered back to ambient pressure, providing opportunities to further investigate its properties and potential applications.

In addition, bulk modulus of Li₁₅Si₄ was obtained experimentally for the first time (B=28.4±0.6 GPa), and shear modulus and Poisson's ratio were calculated as well. We found that the bulk modulus of Li₁₅Si₄ follows a linear

interpolation relationship between the bulk moduli for pure Li and Si. These results provide valuable experimental data to validate the theoretical calculation and are also important inputs for modeling the Li-Si system.

Nanoscience and Nanotechnology

A-48

Metrology of Positioning Systems at the Nanometer Level

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Verifying claims of performance or even simply characterizing performance in a positioning system at the sub-micrometer to nm-level is a non-trivial problem. To do this requires specific equipment and software as well as specialized knowledge about the tools, techniques and best practices. In this paper, we show performance data obtained on various stages and how both the system-design and metrology methods affect the quality of the results.

A-49

Enhancing Solar Cell Performance through the Use of Plasmon Generating Nanocomposite Materials

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Over the last ten years Mantis Deposition has developed an ultra-high vacuum compatible nanoparticle source capable of producing a wide range of nanoparticle structures with exquisite control over their composition and size. In collaboration with our customers we have demonstrated the capability of this technology in several sectors including energy, surface science, catalysis, biotechnology, and information technology. In this presentation we will describe how the properties of particles on the nanometer scale are being harnessed to enhance the performance of solar cells. We will show how plasmon generating nanocomposite materials can be tuned to optimise the absorption wavelength by controlling the diameter of silver nanoparticles in various thin film structures. We will also outline some of the outstanding challenges and potential strategies on the road to exploitation of this technique.

A-50

Operando Investigation of the Hydriding Phase Transformation in Single Palladium Nanocubes

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Phase transitions in reactive environments are crucially important in energy and information storage, catalysis, and sensors. Nanostructuring materials used in these systems can cause a host of desirable properties, including faster charging/discharging kinetics, increased lifespan, and record activities. However, establishing the causal link between structure and function is challenging for nanoparticles as ensemble measurements convolve intrinsic single particle properties with sample size and shape diversity. Here we study the hydriding phase transformation in individual palladium nanocubes under operando conditions using coherent x-ray diffractive imaging. We directly observe two-phase coexistence in the single particle diffraction data. The phase transformation initiates at the corner of the cube, penetrates further into the particle, and eventually violently rearranges the crystal structure. The strain distributions of the α and β phases are markedly different, indicating more than a simple Wulff geometric construction is required. A phase field model is constructed to interpret the phase transformation. Our results provide



a general framework for understanding phase transformations in individual nanocrystals under operating conditions in reactive environments while highlighting the utility and importance of single particle investigations to truly understand important systems.

A-51

X-ray Absorption Spectroscopy (XAS) Study of Sorption Mechanisms of Cd(II) to Hematite (α -Fe₂O₃) Nano Particles with Varying Size and pH Environment

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Natural mineral nanoparticles have gained attention due to their wide occurrence in soil and high sorption capacities for cationic and anionic contaminants influencing the mobility and transport of contaminants in the environment. This is a consequence of their small size and non-optimal surface coordination environment compared to the bulk. Hematite (α -Fe₂O₃) is a mineral whose particles are found in the nano-sized region. This study involves investigating the sorption mechanisms of the highly toxic heavy metal cadmium to hematite. Experiments were normalized to total hematite nanoparticle surface area within reaction vessels. The sorption mechanisms were investigated under different hematite particle sizes (8 nm and 40 nm surface area/mass normalized (SAN/MN)) and different pH environments (pH 7.5 and pH 9).

The adsorption edge experimental results suggested particles sorbed more Cd(II) as the pH environment was increased and the particle size was decreased. For the larger particles, the sorption edge was shifted to the right approximately by 1 pH unit. X-ray absorption near edge structure (XANES) results on 8 nm nanoparticles and the 40 nm SAN at pH 7.5 indicated the presence of similar coordination environment around the absorbing Cd atom. Cd was adsorbed to 8nm particles at pH 7.5 but did not form a precipitate whereas at pH 9, minor amounts of CdCO₃ and CdO were present. When experiments were normalized to hematite surface area, particle size did not substantially affect the sorption mechanism at pH 7.5. However, at pH 9 a combination of CdCO₃ precipitate and adsorption complex(es) were formed of which contribution from the precipitate was larger. When experiments were normalized to hematite mass, more Cd precipitation was observed in larger nano particles at both pH values. This is most likely due to the presence of fewer surface adsorption sites on the particles. Extended x-ray absorption fine structure (EXAFS) results revealed binding site details as a function of pH and particle size and will be presented.

Application of XAS technique for the purpose of gaining insights into the mechanisms of interaction between hematite nano particles and heavy metal cadmium suggests a first step towards alleviating nano particle related environmental and health hazards.

Other

A-52

Globus Data Publication Services and Their Application at the Advanced Photon Source

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Globus is software-as-a-service for research data management, used at dozens of institutions and national facilities for moving, sharing, and publishing big data. Recent additions to Globus include services for robust data publication, cataloging, and discovery to support researchers with a unified set of data tools that spans the entire data lifecycle, from data capture, to active phase collaboration and sharing, to final dataset publication. These services allow users and institutions to: 1) enable publication of large research datasets with flexible policies; 2) grant the ability to publish data directly from local storage, institutional data stores, or from self-managed cloud storage, without third party publishers; 3) build extensible domain-specific metadata that describe the specific research attributes; 4) develop publication workflows and automate experiment workflows to meet institutional and researcher requirements; 5) deploy public and restricted collections that define control over who may access published data; and 6) access a rich discovery model that allows others to search, interrogate, and build upon published data.

In this poster, we will discuss Globus [1] services for data publication, cataloging, and discovery and their application at the Advanced Photon Source to high-energy diffraction microscopy, tomography, and diffuse scattering. Specifically, we will discuss how these services are being utilized to develop automated workflows that leverage high-performance compute and storage resources to stage and synthesize results from experiments and simulation; to enable near real-time visualization and inspection of complex datasets; to catalog experiment and simulation parameters, in conjunction with other dataset provenance, in an intuitively searchable form; and to present simple web interfaces for users to interact with as well as robust API and CLI to facilitate incorporation into existing data capture workflows.

[1] I. Foster. *IEEE Internet Computing* 15 (2011): 70.

A-53

Using Focused X-ray Pulses to Probe Microelectronic Devices for Single Event Effect Susceptibility

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Integrated circuits (ICs) scheduled for use in satellite electronic systems need to withstand the harsh radiation environment of space [1]. Energetic particle strikes on an integrated circuit can generate a conduction band carrier track along their trajectory that results in current or voltage transients which can disrupt the normal operation of the IC, and potentially debilitate entire electronic systems. It is of the utmost importance that all ICs under consideration or scheduled for on-orbit deployment are tested beforehand so that their susceptibilities to these single event effects (SEEs) are documented, characterized, and if possible mitigated [2].

In order to fully understand SEE susceptibilities, it is important to develop methods that can simulate the effect of charged particle strikes (i.e., a method that can deposit charge in a highly localized area around individual circuit



elements such as transistors, and measure the IC's response to the impulsive charge deposition). In principle, using a beam of relativistic particles with low flux, such that a single particle would be incident on a transistor at any given time, would be the ideal method. In practice, however, no known sources allow for the regular placement of incident ions with high spatial resolution and accuracy. Lasers can be used to generate conduction band carriers and inject current into a circuit, but most wavelengths are too long to be focused to a spot size corresponding to an individual circuit element in sub-100 nm fabrication technologies. Furthermore, lasers will not penetrate metallization layers which can cover virtually all of the functional area on newer ICs. In contrast to heavy ion or pulsed laser techniques, x-rays have properties that are advantageous for characterizing individual circuit elements on microelectronic circuits — they can be focused to extremely tight spots and they can penetrate metallization. We have previously used the Advanced Photon Source to show that focused x-ray pulses can generate charge transients in microelectronic devices. These measurements were highly successful and a paper on the technique has been recently published [3]. We will present data from our recent APS measurement campaigns that compare x-ray induced transients with those produced by both lasers and heavy ions. We will show that having the capability of focusing high energy radiation provided by synchrotrons like the APS on localized spots on microelectronic circuits of high value for SEE susceptibility testing.

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- [2] R.A. Reed, et al., "Single-event effects ground testing and on-orbit rate prediction methods: the past, present, and future," *IEEE Trans. Nucl. Sci.*, vol. **50**, pp. 622–634, 2003.
- [3] D. Cardoza, et al., "Single Event Transients Induced by Picosecond Pulsed X-ray Absorption in III-V Heterojunction Transistors," *IEEE Trans. Nucl. Sci.*, vol. **59**, pp. 2729–2738, 2012.

A-54

Swift Parallel Scripting for Fast, Productive Beamline Data Analysis

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The Swift parallel scripting language (<http://swift-lang.org>) allows APS users to perform large-scale concurrent execution of data analyses and simulation more efficiently and with less effort. At the APS, Swift is used to express and run analysis workflows for high energy diffraction microscopy (HEDM), diffuse scattering, and powder diffraction, as well as more general post-processing scripts of area-detector data. Recent use of Swift leveraged the ALCF Mira supercomputer for real-time analysis of a sample during an APS near-field HEDM experiment, allowing the detection and resolution of an apparatus error that would have otherwise gone undetected until much later. In such HEDM analyses, over 100,000 CPUs can be used concurrently. For *in situ* experiments where temperature and or strain is varied, fully automated Swift workflows can guide the experimental variables and eliminate manual errors, by analyzing in minutes what previously took months to perform without parallel processing. Furthermore, this allows users to leave the APS facility with most of their bulk data processing already completed.

The beamline user writes (or runs) what looks like ordinary serial scripts; Swift automatically spreads the work expressed in those scripts over parallel desktop, cluster, cloud or supercomputer resources. Swift efficiently automates functions which are hard, costly, and unproductive to do manually: 1) parallelization, using "data flow" techniques; 2) distribution of work and data across diverse systems; 3) failure/error handling; and 4) provenance recording for auditing, validation, and reproduction of results. As computing systems from laptops to supercomputers become increasingly parallel, Swift enables users to leverage this parallel power implicitly and largely automatically, with little or no experience in parallel programming.

Polymers

A-55

High Molecular Weight Insulating Polymers Can Improve the Performance of Molecular Solar Cells

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Solution-processed molecular semiconductors for the fabrication of solar cells have emerged as a competitive alternative to their conjugated polymer counterparts, primarily because such materials systems exhibit no batch-to-batch variability, can be purified to a greater extent and offer precisely defined chemical structures. Highest power conversion efficiencies (PCEs) have been achieved through a combination of molecular design and the application of processing methods that optimize the bulk heterojunction (BHJ) morphology. However, one finds that the methods used for controlling structural order, for example the use of high boiling point solvent additives, have been inspired by examination of the conjugated polymer literature. It stands to reason that a different class of morphology modifiers should be sought that address challenges unique to molecular films, including difficulties in obtaining thicker films and avoiding the dewetting of active photovoltaic layers. Here we show that the addition of small quantities of high molecular weight polystyrene (PS) is a very simple to use and economically viable additive that improves PCE. PS could give rise to film thickness and uniformity without sacrificing desirable phase separation and structural order. Remarkably, the PS spontaneously accumulates away from the electrodes as separate domains that do not interfere with charge extraction and collection or with the arrangement of the donor and acceptor domains in the BHJ blend.

A-56

Dynamics of Nanoparticles within Gum Arabic Solutions

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Gum Arabic is a polysaccharide-protein complex widely used in food, pharmaceutical and cosmetic industries due to its good emulsifying, stabilizing and encapsulation properties. These technologically important features are related to the structural characteristics, conformation in solution and molecular composition of the biopolymer.

Herein we report x-ray photon correlation spectroscopy (XPCS) analysis using silica nanoparticles as a probe within dispersions of gum arabic from two different species. We found distinct intensity autocorrelation functions for each gum demonstrating that dynamics reflects proper characteristics of gum internal structure.



Technique

A-57

Tracking Molecular Dynamics from Picoseconds to Microseconds Using High-fidelity, Laser-pump, X-ray-probe Techniques

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Laser-pump, x-ray-probe techniques are powerful tools for exploring molecular structural changes that occur during a photo-initiated reaction. We are developing such methods at 7-ID-D of the Advanced Photon Source to study dynamics of molecules in solutions, combining x-ray emission spectroscopy and x-ray absorption spectroscopy as probes of electronic and geometric structure and using high-power, MHz lasers as pumps. The high-duty-cycle pump-probe measurements efficiently utilize the synchrotron x-ray flux and enable high-fidelity measurements of the structures of transient intermediates. Time scales from the ~80 picosecond x-ray pulse duration out to the microsecond regime can be explored. Recent measurements on solvated transition metal coordination complexes excited with 532 nm, 355 nm, and 266 nm laser light will be presented.

A-58

Dioplas and T-Rax: New Python-based Programs for On-the-fly 2D X-ray Diffraction and Optical Spectroscopy Data Analysis

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Dioplas and T-Rax are open source Python programs with user-friendly graphical interface, designed for providing fast feedback during synchrotron and in-house experiments at ambient and extreme conditions.

Dioplas is intended to be a modern improvement of the widely used FIT2D software for analysis of x-ray powder diffraction data [1]. It uses the pyFAI library [2] as its basis for integration of 2D x-ray diffraction images and provides uniquely designed and easy to use interface for image auto-processing, browsing, detector geometry calibration and mask creation. It exhibits an optimized calibration algorithm with tunable parameters, which enables the calibration of even complex experimental geometries (high detector angle, off detector beam center position, etc.) [3]. The core of the application is a coordinated view where the image data and the integrated patterns can be explored simultaneously. Due to the fast integration time (~100 ms for a 2048 × 2048 pixels) collected data files can be investigated on-the-fly in almost real time. Integrated diffraction patterns can be compared by using scalable overlays and the positions of individual diffraction lines of selected (editable) phases can be displayed using the jcpds format. The line positions can be adjusted to pressure and temperature conditions if the equation of state parameters are provided. Dioplas includes a number of additional features for on-line or off-line data processing (e.g., algorithms for automatic background subtraction, and absorption correction for diamond and cBN seats typically used in diamond anvil cell experiments).

T-Rax is a graphical toolbox for the analysis of spectroscopic data frequently collected during high pressure diamond anvil cell experiments. It handles wide range of spectroscopic data measured with Princeton Instr. detectors (WinSpec or LighField file format) including thermal radiation, fluorescence and Raman spectroscopy. Temperature of laser or externally heated samples is calculated by fitting grey-body radiation curve to collected spectra with optional correction of the known system response. Unique features are automatic new file processing, fast switching between different system response calibrations and options, graphical selectable regions of interest, time-series analysis and

communication with EPICS. Furthermore, T-Rax can calculate pressure at various temperatures using Ruby spectra, with optional peak fitting, and diamond anvil Raman spectra showing the derivative of the spectrum.

Dioplas has started being used for user operation at GSECARS/APS in June 2014 and is now frequently used/requested at other high-pressure beamlines, and T-Rax has been employed since September 2013.

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A-59

Pink Beam Tomography at 13-BM-D

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Conventional monochromatic tomography at 13-BM-D covers the energy range from 6 to 60 keV with excellent energy resolution from a Si (111) monochromator. However, it is rather slow, requiring .25–5 seconds per projection, and hence 3 to 30 minutes per 3-D dataset. It allows performing above and below edge imaging, typically for elements like I, Cs, and Xe which are used as contrast agents for fluids in porous media.

We have now performed the first pink beam tomography measurements at 13-BM-D. Using pink beam reduces the exposure time to 1–5 ms, and the total time to collect a 3-D dataset to 7–12 seconds. This allows performing measurements on dynamic systems, albeit only rather slow ones.

The camera being used for both the monochromatic and pink beam measurements is a new CMOS camera from Point Grey that can collect up to 162 frames/s and costs less than \$1,400.

A-60

Probing Optically Dense, Flowing Systems with X-ray Absorption and Fluorescence of Argon and Krypton at Beamline 7BM

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The non-invasive study of the internal structure of optically dense, flowing systems is challenging and requires techniques that can fully penetrate the system with high spatial resolution. Recently, two separate experiments were performed at Beamline 7BM using x-ray fluorescence to image and characterize flowing systems relevant to combustion research: a sooting flame and a resistively heated SiC micro-reactor. In both of these experiments, a 5 μm by 5 μm beam of x-rays was focused on the flowing system, and simultaneous x-ray fluorescence and absorption measurements were taken, with the fluorescence signal collected orthogonal to the incident x-rays. A 2D image was created by raster scanning across the flame or micro-reactor surface. The magnitude of the fluorescence signal is directly proportional to the density of fluorescing species and thus provides a way of measuring gas density in these systems. These measurements represent the first attempts to the authors' knowledge to probe gas density in high temperature, optically dense environments.

In the first experiment, an argon jet within a sooting atmospheric pressure flame on a modified McKenna burner was imaged with 8 keV x-rays. Flow rates of argon were varied to examine mixing of the argon jet with the flame gases and to estimate the sensitivity of the observation technique. The absorption and fluorescence measurements



gave excellent agreement and the fluorescence technique gave better sensitivity. These experiments demonstrated that gaseous structures can be resolved with x-ray fluorescence and absorption with high spatial resolution within dynamic environments such as sooting flames. A second set of experiments were run after recent upgrades to Beamline 7BM which allowed absorption and fluorescence measurements with krypton. In these experiments, 15 keV x-rays were focused onto a resistively heated SiC micro-reactor, through which a few percent Kr in He was flowing. The x-rays penetrated the micro-reactor and were absorbed by Kr, and the resulting 12.6 keV fluorescence was detected. A 2D image of the micro-reactor was taken at different temperatures to map the density of Kr within the micro-reactor. Images of the free jet expansion of gases from the end of the micro-reactor into a region of relatively high vacuum were also taken. These data will be compared with CFD calculations of the flow within the micro-reactor in order to validate these calculations and guide further development and refinement of the CFD models. From there, realistic reaction conditions can be calculated thereby allowing accurate kinetic and mechanistic data to be obtained for pyrolysis and oxidation studies with SiC micro-reactors.

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