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Preface: High-pressure studies with x-rays

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The study of matter at extreme conditions represents a forefront area of research activity across the sciences, including physics, chemistry, materials science, and even biology. Advancing the frontier of extreme conditions science requires powerful micro-sampling probes to access minute samples through the vessel walls and to separate weak sample signals from the background signals arising from the much more massive surrounding vessel materials. The development of synchrotron radiation sources has provided the essential breakthrough in extreme conditions field.

During the last decade, the High Pressure Collaborative Access Team (HPCAT), a consortium to advance compression science and technology using synchrotron radiation at the Advanced Photon Source (APS) of Argonne National Laboratory, has pioneered key developments in high-pressure technology for extreme conditions science using third-generation synchrotron radiation. A plethora of x-ray diffraction (XRD), x-ray spectroscopy, and x-ray imaging techniques has been developed and integrated with high pressure and high/low temperature capabilities at HPCAT. High-pressure x-ray diffraction, using energy or angular dispersive modes, provides comprehensive crystallographic, electron density topology, bonding, grain boundary, elastic, and deformation information from single-crystal, polycrystalline, nanocrystalline, and noncrystalline substances. High-pressure x-ray spectroscopy, using absorption, emission, inelastic, or nuclear resonant scattering techniques, yields phonon dynamics, charge dynamics, and electronic and spin states of materials under high pressure and high/low temperatures. High-pressure x-ray imaging, using full-field or position scanning, provides x-ray radiography, X-ray tomography, phase contrast, and coherent diffraction images for substance distributions in the sample, grain boundary, phase separation, and internal strain information. These new tools, integrated with hydrostatic or uniaxial compression, static or dynamic loading, laser heating or cryogenic cooling, and diamond anvil cells (DACs) or large volume presses, have enabled investigations of high-pressure structural, vibrational, electronic, and magnetic properties that were unimaginable only a few years ago.

The HPCAT facility has established nine experimental stations (hutches) on the two beamlines of Sector 16 at the APS, with five on the 16-ID line (sequentially downstream) 16-ID-A, -B, -C, -D, and -E, and four on the 16-BM line 16-BM-A, -B, -C, and -D. To increase the efficiency in utilization of precious beam time, the 16-ID and 16-BM beamlines are each split into two branches for the maximum of four

simultaneously operating experiments at hutches 16-ID-B, 16-ID-C or -D or -E, 16-BM-B, and 16-BM-C or -D. The beamline layout has been summarized in 2008.¹ Perhaps the most significant change in beamline layout since then was the installation of canted undulators in the 16-ID line in 2011. The canted undulators allow for establishing two independent ID beamlines: the 16ID-C-D branch for a range of high-pressure x-ray spectroscopy techniques and the 16ID-B branch for high-pressure XRD.

16-ID-B is a micro-XRD station mainly focusing on high-pressure powder and single crystal diffraction in DAC at high temperatures (double-sided laser heating and resistive heating) and low temperatures (various cryostats). The station is equipped with two experimental setups: one for general purposes with open space and heavy duty stages (Smith *et al.*, this volume) and the other is dedicated for a double sided laser heating system for *in situ* XRD measurements (Meng *et al.*, this volume). The established instrumentation allows high-quality XRD at megabar pressures from light element, fast experiments with modulated laser heating, and fast dynamic experiments with piezo and double-diaphragm drives.

16-ID-D station is dedicated to x-ray scattering and spectroscopy studies of materials under high pressure in DAC (Xiao *et al.*, this volume). The available techniques include nuclear forward scattering, nuclear resonant inelastic scattering for determining phonon density of state and Mössbauer effect, X-ray inelastic scattering (x-ray Raman) for the study of charge dynamics and chemical bonding, x-ray spectroscopy for the study of electronic excitations, and x-ray emission (including partial fluorescence yield, resonant emission). Many of these measurements can be done at low temperatures, with *in situ* pressure measurement, or at high temperatures with either resistive heating or portable laser heating.

16-BM-B is a white beam station, dedicated to Paris-Edinburgh (PE) large volume press experiments and white Laue XRD. The PE experiments address structures of amorphous and liquid materials using energy dispersive XRD, viscosity of high-pressure liquids, and elastic sound wave velocity of materials (Kono *et al.*, this volume). White Laue XRD, which is sensitive to subtle changes in crystal orientation, deformation, and strain, yields information of microstructural changes of materials under compression and decompression (Popov *et al.*, this volume).

16-BM-D station is used for micro-diffraction with monochromatic beam at high pressure and high (resistive heating)/low (cryostat) temperature. The beamline is also

equipped for x-ray absorption near edge structure (XANES) spectroscopy experiments. XRD and XANES measurements can be made interchangeably on the same sample at given pressure-temperature conditions (Park *et al.*, this volume).

In this volume, a collection of recent developments at HPCAT is presented as a snapshot of development projects. Among others, a few are highlighted below.

Rapid compression and decompression. Pressures in the DAC are often controlled manually or mechanically by turning screws, and the DAC is usually considered as a type of static high-pressure device. By fast turning crews, however, pressures may be changed quickly, e.g., in obtaining metastable phases of Si and Ge when quickly decompressed from high-pressure phases.² Using electromechanical piezoelectric actuators to replace screws in DAC, time-dependent load-to-pressure cycles can be applied.³ Alternatively, pressure can be controlled remotely by the pneumatic (e.g., membrane or double-diaphragm) technique for fast compression and decompression coupled with fast x-ray detectors, such as Eiger and Pilatus. In this volume, Smith *et al.* describe the development of rapid compression and decompression at HPCAT. A compression rate of >35 TPa/s has been reached for a Mo sample in the megabar pressure region. Phase transformation pathways are strongly influenced by the time dependence of the driving mechanism (compression, thermal transfer, strain, irradiation, etc.). This fast (de)compression capability allows studies of the kinetics of phase transitions, phase growth, and metastable phases at various compression rates. In particular, this capability covers the regions of compression rates that are between static techniques (DACs and large volume presses) and dynamic shock-driven devices (gas guns, explosive, and laser shock), a region that has been sparsely studied.

Modulated laser heating. The transparency of diamond allows applications of near- and mid-infrared lasers (CO₂, Nd:YAG, Nd:YLF, and more recently fiber lasers) to heat samples between two diamond anvils at high pressure. HPCAT has established a stationary on-line laser heating system, based on two high power fiber lasers (>200 W), that has been routinely used for user operation,⁴ with the recent developments described by Meng *et al.* in this volume. One important feature of the HPCAT laser heating system is the capability of adjusting the heating spot; the focus size of the heating area can be defocused to achieve large heating areas (>100 μm in diameter) on the sample. A larger heating area means smaller temperature gradient and more accurate x-ray and temperature measurements at extremely high pressure-temperature conditions. Another development area is the modulated heating. As described by Meng *et al.* in this volume, modulated laser heating in a DAC can suppress thermally activated diffusion, suppress possible chemical reactions of the sample and environment and can generate even higher temperatures. The timing structure of synchrotron radiation suits well for developing *in situ* x-ray measurements of samples heated by modulated lasers in the DAC. The modulated laser heating holds great potential for accurate measurement of melting curves, phase transition relations, thermal diffusivity, and pressure-volume-temperature equations of state.

Background discrimination in x-ray inelastic scattering. While maximizing signal-to-background ratio is important in all types of experiments, it is particularly critical in high-pressure studies, because the volume ratio between sample and surrounding materials can be as small as 10^{-5} – 10^{-9} . Proper collimation in detection side is critical to reduce the background from surrounding materials. In x-ray inelastic scattering measurements, however, the collimation requirement is in conflict with the need of large solid angle for collecting weakly scattered signals. This problem has been partially solved by using an x-ray focusing optic (e.g., x-ray polycapillary) for signal collection, reported in this volume by Chow *et al.* A focusing optic provides desired depth resolution, significantly discriminating sample signals from those arising from surrounding materials, but can still be used for scattering collection with a sizable solid angle of ~ 0.007 sr.

Multiple element analyzers for x-ray emission spectroscopy (XES). High pressure XES data are typically obtained by a Rowland circle spectrometer with synchronized θ - 2θ scan of the analyzer and the detector. Multiple analyzers can be used to increase solid angle coverage that matches to the opening access of the DAC. Xiao *et al.* reported in this volume a design of 7-element analyzers to be used in 2015. The increased efficiency is particularly beneficial to both the resonant XES (RXES) and the partial fluorescence yield (PFY), when emission spectra are measured at each step as the incident beam energy is changed or scanned across an absorption edge. The increased efficiency due to the use of the 7-element analyzer system will be particularly beneficial in megabar RXES or PFY experiments.

Comprehensive studies of high pressure liquids with a Paris-Edinburgh cell. Techniques for measuring liquid structure (by x-ray diffraction), elastic wave velocity (by ultrasonic interferometry), and viscosity (by radiographic imaging) under high pressure have been integrated using a Paris–Edinburgh cell at 16-BM-B.⁵ The Paris–Edinburgh press allows to compress large volume samples (up to 2 mm in both diameter and length) up to 7 GPa and 2300 K. Multi-angle energy dispersive XRD provides structure factors of liquid to a large Q of more than 20 \AA^{-1} . Ultrasonic techniques have been developed to measure sound wave velocity of liquids combined with the X-ray imaging. Falling sphere viscometry with high speed X-ray radiography (>1000 frames/s) enables us to examine not only high viscosity silicate and oxides melts but also low viscosity (<1 mPa s) liquids and fluids such as liquid metals or salts. The integration of these multiple techniques has made it possible to study correlations between structure and physical properties of liquids at various pressure-temperature conditions. In this volume, Kono *et al.* report the development of x-ray imaging techniques for studying behavior of liquids at high pressures and high temperatures using a Paris-Edinburgh cell. In x-ray radiography or tomography, imaging relies on absorption (or density) contrast. Alternatively, phase contrast imaging (PCI) depends on variations of the phase of the radiation. At grain boundaries, the sharp variations in refractive index can lead to strong phase contrast even with polychromatic radiation. PCI is especially useful in imaging light materials, where the density contrast

may be weak. PCI has been used to study immiscibility of two or more liquids in systems under pressure.

High pressure multi-grain crystallography. Polycrystalline structural refinement for ultrahigh-pressure samples becomes increasingly challenging and the results could be ambiguous. Single-crystal structural refinement is necessary, but successful examples of growth and preservation of μm -size single crystals above 100 GPa are extremely rare. With the developments in micro-beam technology in synchrotron radiation, many traditional powder samples may be treated as multiple grains of tens or hundreds, often resulting in “spotty” patterns in diffraction images, which were previously viewed as poor XRD images. A new tool of “multigrain crystallography” has been recently developed with the quality of the resulting refinements comparable to single crystal work.⁶ In such multigrain approach at HPCAT, the same data collection procedures are used as those in the single crystal XRD. Diffraction signals of a few to hundreds of single crystals are simultaneously collected. Apparently, the multigrain approach is an effective way to increase redundancy and completeness in data collection, thus significantly improving the single crystal data quality.

High pressure white Laue diffraction. Laue XRD is sensitive to subtle changes in crystal orientation, deformation, and strain and can be used for studying pressure induced microstructural changes in single crystals under pressure. A clear and important advantage of white Laue diffraction compared to monochromatic diffraction is that there is no need to rotate the sample, eliminating the problem of rotational stage eccentricity and significantly improving spatial resolution. Because the microstructural heterogeneity of most samples makes it necessary to collect spatially resolved, as well as time resolved, diffraction data, white Laue diffraction technique has advantages in resolution and efficiency in getting spatially resolved information by translational scans with tightly focused beam. In this volume, Popov *et al.* report a study of spatially resolved Laue diffraction from Si across the α - β phase transition. A series of consequential 2D Laue images have been collected on a Si single-crystal at the onset of the α - β phase transition. These data provide information on the nucleation of the high pressure phase and the phase transition mechanism.

Support equipment. High-pressure technology has undergone rapid development in areas such as maximizing pressure, precise pressure control and measurement, control of hydrostaticity, strain rate, stress fields, as well as integrating with high/low temperature techniques and other extreme conditions (magnetic fields, electric fields, etc.). Support equipment is an important part of the HPCAT program. Various supporting facilities are described in different papers in this volume. Sinogeikin *et al.* report the development of sample environment instrumentation which allows remote and automatic pressure control in DACs during synchrotron experiments. These devices (mechanical gearboxes, single and dual double-diaphragm setups, and piezo drives) can be used for automated data collection along predefined pressure-temperature paths at high and low (cryogenic) temperatures for static and time-resolved measurements. Every experimental station at HPCAT is equipped with a portable online optical systems

for ruby fluorescence pressure measurements and/or *in situ* Raman sample characterization. Temperature in high pressure devices is another extremely important variable and can be controlled by a variety of means. HPCAT has established laser heating systems for heating samples from 600 K to several thousands of degrees (>6000 K) (e.g., Meng *et al.*, this volume). Resistive heating techniques are used for relatively modest temperatures at up to 1200 K for DAC (e.g., Smith *et al.*, this volume) and 2500 K for Paris-Edinburgh cell (Kono *et al.*, this volume). A number of specially designed cryostats, suitable for various x-ray diffraction and spectroscopic measurements, are used for cooling DACs to temperatures of 4 K. The results from x-ray measurements are often combined with those from complementary techniques at HPCAT, including a micro-Raman spectroscopy, electrical resistivity, and magnetic measurements which can often be performed at *in situ* high pressure conditions. For efficient use of synchrotron beamtime, high-pressure samples and sample assemblies should be always prepared before the allocated beamtime. However, samples and/or pressure devices may be subject to unpredicted changes or even failures during the experiments. Therefore, it is essential to have advanced facilities for sample preparation on site. At HPCAT, we have established state-of-the-art facilities for sample preparation. In addition to standard sample lab equipment (e.g., microscopes, micro-EDM machine), HPCAT sample preparation lab is equipped with a glove box with ultra-high purity argon atmosphere and a micro-manipulator, a stand-alone computer controlled micromanipulator for precise sample loading with special configurations, and a HPCAT-designed laser micro-machining system (reported in this volume by Hrubak *et al.*). With pressure being an experimental variable, high-pressure experiments are often dynamic in a sense that users continuously need to make decisions for the next steps based on the collected data. Thus, it is essential to have software for immediate data evaluation. Therefore, HPCAT is putting significant effort into development of software routines for determinations of pressure, temperature, unit cell parameters, and other sample features. All these supporting facilities significantly increase experimental capabilities, quality of data, and productivity of beamlines during high-pressure experiments.

With the APS Upgrade program on the horizon, the future brighter and more coherent source will enable submicrometer probes to be developed, higher energy resolution in inelastic x-ray scattering, new imaging techniques using coherent beams, and finer time resolution in time-resolved experiments. Ever more complex samples at increasingly broader pressures and more extreme temperatures will be studied with higher-accuracy x-ray probes for characterization of structural, electron, and phonon properties.

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