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A scanning angle energy-dispersive X-ray diffraction technique for high-pressure structure studies in diamond anvil cells

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A scanning angle diffraction technique with an energy-dispersive solid-state detector (SSD) and white synchrotron radiation has been developed for high-pressure structure studies in diamond anvil cells (DACs). This technique is similar to the CAESAR technique [Y. Wang, T. Uchida, R. Von Dreele, M.L. Rivers, N. Nishiyama, K. Funakoshi, A. Nozawa, and H. Kaneko, *A new technique for angle-dispersive powder diffraction using an energy-dispersive setup and synchrotron radiation*, J. Appl. Cryst. 37 (2004), p. 947] developed for large-volume presses, but extended to DAC applications with high spatial resolution. The main feature of the technique is the well-defined collimation in the beam path to the detector, which improves the signal-to-noise ratio significantly, compared to routine monochromatic angle-dispersive powder diffraction with area detectors. This is particularly useful and essential for low-scattering materials and for amorphous and liquid diffraction/scattering studies using DACs. Data collected from crystalline and amorphous samples in DACs show that a coarse 2θ scan (0.1–0.2° for crystals and 0.5° for amorphous structure) is sufficient to obtain reasonable diffraction resolution. The scanning angle energy-dispersive X-ray diffraction technique provides angle-dispersive X-ray diffraction (ADXD) data in multiple energies. Such multi-energy ADXD data carry much more information than regular single-energy ADXD, which could provide site-specific atomic structure information for full structure refinement.

Keywords: diamond anvil cell; energy-dispersive; structure refinement; amorphous; anomalous X-ray scattering

1. Introduction

The diamond anvil cell (DAC) is one of the most common devices for high-pressure structure studies. Due to the thin sample thickness in DACs at high pressure, the background from the surrounding material is often significant in angle-dispersive powder diffraction patterns collected with a two-dimensional area detector. The advantages of an area detector are the data collection speed and good average over all azimuth angles. A few seconds to minutes of exposure time is usually sufficient to collect diffraction data at third-generation synchrotron sources, such as the Advanced Photon Source (APS). With integration software, one can obtain one-dimensional

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profiles of the intensity *vs.* $Q(Q = 4\pi \sin(\theta)/\lambda$, where θ and λ are the diffraction angle and X-ray wavelength, respectively) for structure refinement and new structure analysis. However, background subtraction from the integrated intensity profile remains a challenge, especially for amorphous and liquid studies [1]. A well-collimated point detector can significantly reduce background signal levels, but at the cost of longer data collection time [2]. For a point detector without energy-dispersive capability, this method can only be applied with monochromatic X-rays, which have relative weak intensities. Typically, it takes hours or days to complete one scan.

Another approach is combining an energy-dispersive detector with white synchrotron radiation. Incident and diffracted beam paths can be well collimated to prevent or reduce the scattering from the surrounding environment. The energy-dispersive X-ray diffraction (EDXD) method has been widely used for phase identification and unit cell parameter determination in high-pressure studies. Typically, the diffraction peak positions can be obtained rather accurately in EDXD, but the diffraction resolution is limited to intrinsic detector energy resolution. A Ge solid-state detector (SSD) with multichannel analyzer (MCA) is usually used to collect the diffraction intensity with an energy range 1–120 keV. With the Ge SSD at a fixed angle, different d-spacing diffraction lines will be collected at corresponding energy channels following Bragg's law. Data collections at several different 2θ angles were used to cover a larger Q-range [3,4]. In order to use the intensity information for structure refinement, one needs to know the overall incident beam spectrum over the entire energy range and to correct the absorption effect from the diamond anvils and seats for each channel.

With the advanced developments of X-ray optics and highly brilliant and stable synchrotron radiation sources, both data collection speed and incident beam stability have been improved. Thus, instead of measuring the EDXD pattern at a fixed angle, one can scan the diffraction angle over a certain range. A combined angle and energy-dispersive method (CAESAR) has been developed with a large-volume press for powder diffraction structure refinement [5], and a new phase has been determined. This method adopts a normal EDXD geometry, with diffraction angle scanning in fine steps over a certain range. We have extended this scanning angle EDXD (SA-EDXD) method, making it suitable for DAC experiments by employing high-precision stages with a sphere-of-confusion less than 5 μm at the high-pressure collaborative access team (HPCAT) bending magnet beamline, 16BM-B, at the APS. The incident X-ray beam is typically focused to $5 \times 5\mu m^2$ at full width at half maximum (FWHM). The eccentricity of rotation stages is built within 5 μm. Taking the advantage of the smooth and broad X-ray spectrum from a bending magnet source, we are able to use energies up to 100 keV. In this paper, we describe and demonstrate the SA-EDXD technique for high-pressure structure studies in DACs with super signal-to-noise ratio. In particular, the technique provides multi-energy (ME) angle-dispersive X-ray diffraction (ADXD) data, which could be used for element and/or site-specific crystal structure refinement and amorphous partial structure factor determination.

2. Experimental setup

The experimental setup is located at the HPCAT 16BM-B station, APS, Argonne National Laboratory. The schematic of SA-EDXD technique is shown in Figure 1. A pair of K–B mirrors is used to focus the white beam from the bending magnet. The mirrors are made of 200 mm long trapezoid shaped ultra-flat silicon blanks with a thin layer of Rh coating [6]. The focal lengths are 450 and 650 mm for horizontal and vertical mirrors, respectively. With the mirrors set at about 30 m from the source, the demagnifications for the horizontal and vertical directions are 67 and 46, respectively. Usually, both mirrors are tilted to 0.65 mrad with 130 μm incident beam acceptance. With proper adjustment of the bender's moments, a 5 μm diameter FWHM beam is routinely maintained at the sample location with energy up to 100 keV. An incident beam collimation

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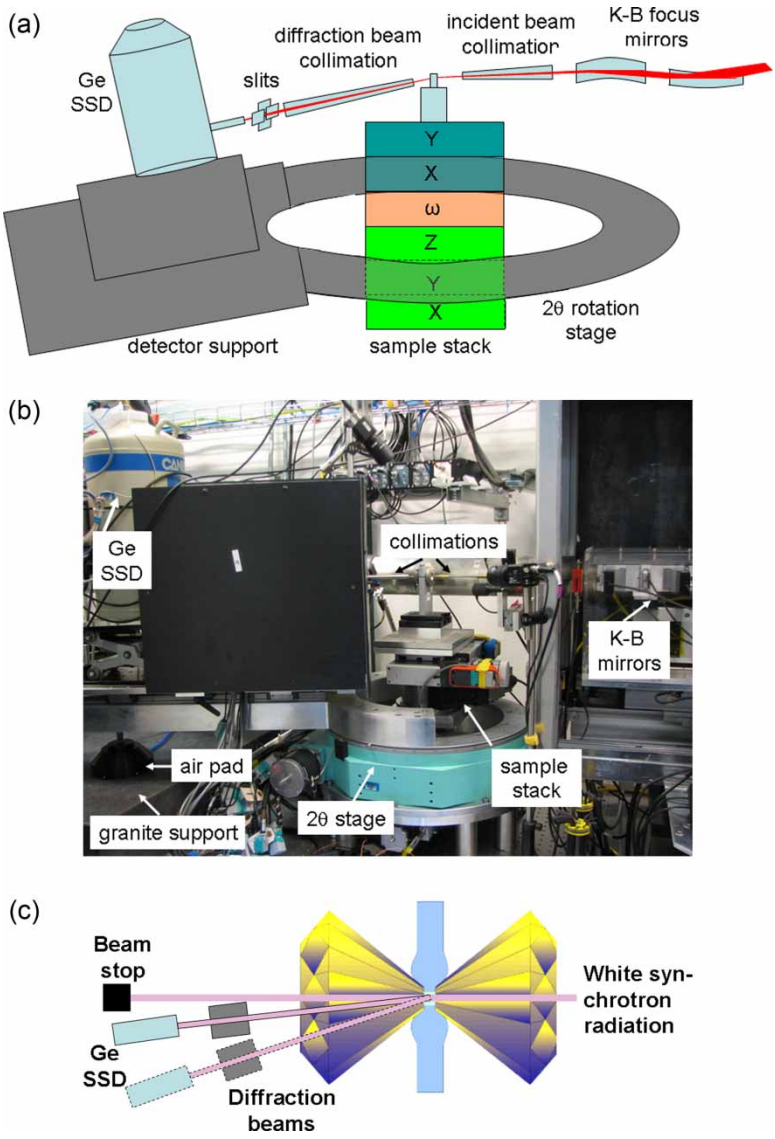

Figure 1. Schematic of SA-EDXD setup. (a) The sample stack, detector, focused beam and incident/diffraction beam collimation drawing, (b) instruments in the experimental station and (c) experimental geometry.

element with a 30 μm diameter Pt pinhole is used to remove the tail of the double-focused beam and to block the direct and two single-focus beams. A Ge SSD sitting on a 2θ rotation arm is used to collect the diffraction intensity with energy range 1–120 keV. The sample stack is separated from 2θ rotation stage to isolate the sample from the detector and rotation arm (see Figure 1 for setup). In the sample stack, the bottom X, Y stages are used to align the ω rotation axis co-axis to the 2θ rotation axis. This is a one time alignment performed by optical checking with a thin crosshair. To facilitate smooth rotation, the detector arm is supported by an air pad on a flat granite surface. The top X, Y stages are used to align the sample to the omega rotation center by checking the sample absorption feature with respect to X-ray micro-beam at different omega angles. The eccentricities for both rotation stages are better than 5 μm. Typically, the incident beam clean-up pinhole and diffraction beam tip are set as close to the DAC as possible to reduce the background.

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The schematic drawing and a photograph of the actual setup are shown in Figure 1a and 1b. The data collection procedure is shown in Figure 1c. After aligning the sample and the focused beams to the rotation center, one can start to collect EDXD data at any 2θ angle. The Ge SSD with an MCA is calibrated with several characteristic lines, including Ag Kα (22.104 keV), Ag Kβ1 (24.942 keV), Ag Kβ2 (25.454 keV), and ^{109}Cd γ1 (88.034 keV), ^{57}Co γ2 (122.100 keV) from radioactive isotopes ^{57}Co and ^{109}Cd. A linear fitting of channel numbers to the above energies is used with typical uncertainties of 5–10 eV at Ag lines (22–24 keV) and 10–20 eV at 122 keV. An amplifier with a shaping time of 4 μs was used. Typically we use 0.1° and 0.5° 2θ scan step size for crystalline and amorphous materials, respectively. The counting time at each measurement point varies from 30 s to 20 min.

3. Data analysis

Statistically well-determined scattering data from crystalline or amorphous materials in a DAC allows one to determine the structure factors from these materials. The quality of the data largely depends on the intensity correction and background reduction. The observed X-ray scattering intensity, $I^{\mathrm{obs}}(Q)$, may be expressed by [7,8].

$$I^{\mathrm{obs}}(Q) = PAG[I^{\mathrm{coh}}(Q) + I^{\mathrm{inc}}(Q) + I^{\mathrm{mul}}(Q) + I^{\mathrm{back}}(Q)]. \tag{1}$$

Here $Q = 4\pi \sin(\theta)/\lambda$, P is the polarization factor, A the absorption factor, G the so-called geometric factor and I^{coh}, I^{inc} and I^{mul} are the coherent, incoherent and multiple scattering intensities, respectively. I^{back} is the background scattering from the surrounding materials (diamond anvils and pressure-transmitting medium). I^{mul} is usually weak and neglected in X-ray scattering. The incoherent scattering contribution can be calculated following Smith et al.'s method [9]. I^{coh} can be expressed as $f^2 \cdot S(Q)$, where f is the atomic scattering factor and $S(Q)$ the structure factor. To obtain $S(Q)$, incoherent scattering and background have to be subtracted from the observed intensity.

Since the X-ray beam from a synchrotron source is fully polarized, the polarization effect $P = \cos^2(2\theta)$ can be applied to the intensity of each channel. The absorption factor depends on the energy of each channel, the absorption materials, and path length for each material. The geometric factor is connected to the diffraction volume as a function of detector angle, slit size and sample thickness. It could be calculated from the following equation [5]:

$$G = \begin{cases} \dfrac{\sin(2\theta)}{w_{\mathrm{i}} w_{\mathrm{d}}}, & \text{when } L \le D \\ \dfrac{1}{[w_{\mathrm{i}} w_{\mathrm{d}}/\sin(2\theta) - (L-D)^2 \tan(2\theta)/4]}, & \text{when } L > D. \end{cases} \tag{2}$$

Here w_{i} and w_{d} are the width of incident beam and slit size in front of the SSD, respectively; D the sample thickness along the incident beam; L the length of the diffracting volume along the incident beam calculated by $L = w_{\mathrm{i}}/\tan(2\theta) + w_{\mathrm{d}}/\sin(2\theta)$. The sample thickness ($D$) for a DAC under high pressure is usually shorter than the length (L) of diffraction volume. Since the measurement sometimes covers a long period of time, the incident beam flux needs to be normalized. The fluorescence from the sample element does not have any angular dependence except the absorption length change for diffraction beam, and so it is often used for intensity normalization.

The experimental setup uses a bending magnet beamline to take advantage of the wide and smooth spectrum of incident beam and wide energy-dispersive capability of the SSD. A diffraction pattern at each 2θ step is collected and sorted to 4000 channels by energy. For a certain $2\theta_0$ angle, the intensity near an energy E_0 by ΔE can be considered as the diffraction intensity as energy E_0

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at an angle $\theta_0 + \Delta\theta$ following Bragg's law in the form:

$$\frac{\Delta E}{E_0} = -\mathrm{ctg}(\theta_0)\Delta\theta. \tag{3}$$

For getting the comparable angular resolution from ADXD, only a coarse 2θ scan is needed.

Based on the above consideration, we have compiled an analysis program using interactive data language. The diffraction angle, calibration parameters for SSD (offset and slope of the energy *vs.* channel number) are stored in the file header. The options for intensity correction are built into the graphical user interface (GUI) to choose, and w_i and w_d can be specified. A fluorescence-based correction function is built in for the user to specify the characteristic energy for normalization. The escape lines from the Ge SSD are often seen in the diffraction profiles and the option for removing these is also built in the package based on the constant offset from Bragg's peaks [10]. Different two-dimensional maps of E–2θ, E–d and d–2θ are built in for data visualization. The output ADXD profiles can be saved to standard Q–I or 2θ–I format for structure refinement

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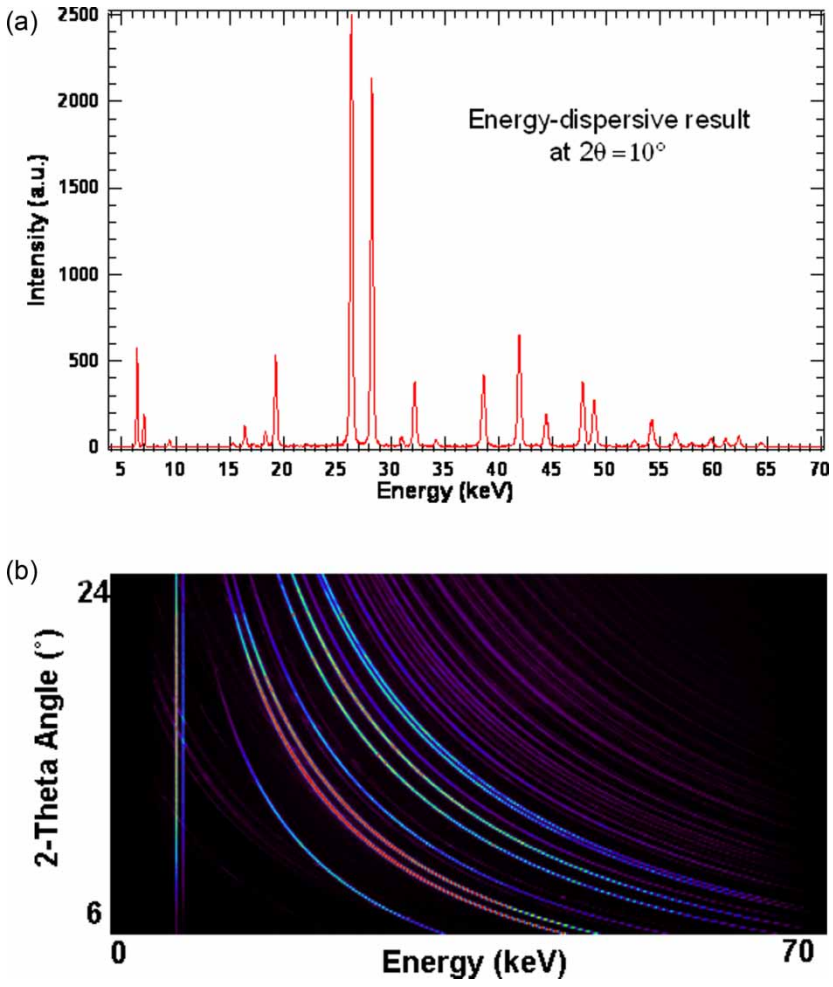

Figure 2. (a) A typical energy-dispersive diffraction pattern from a Fe_2O_3 sample in a DAC. (b) A two-dimensional map of intensity *vs.* energy and 2θ. The Fe fluorescence lines can be seen at the constant channel, which is used for incident beam normalization after the absorption correction.

with user-defined parameters including ADXD energy, binning energy width used in Equation (3), output range and resolution.

4. Experimental results

To demonstrate the capabilities of the SA-EDXD method, we present here preliminary experimental results from a crystalline material and a metallic glass. Fine polycrystalline hematite (Fe_2O_3) powder was compressed to a thin plate (~20 μm thick) and loaded in a symmetrical DAC with slotted tungsten carbide (WC) seats at both sides and argon as the pressure medium. Pressure was measured from the fluorescence wavelength of a ruby ball in the sample chamber. The typical

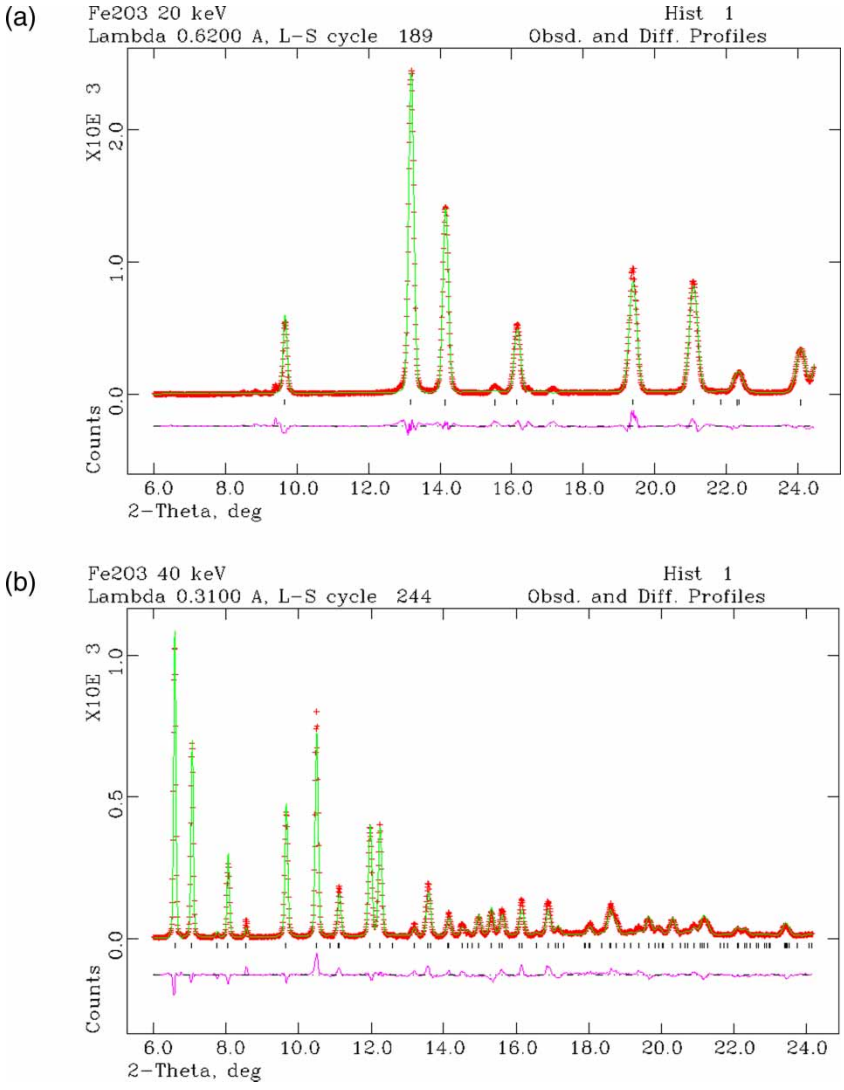

Figure 3. ME-ADXD profiles can be generated by binning the intensity from neighboring energy to the diffraction angle. ADXD profiles at 20, 40 and 60 keV are extracted from SA-EDXD measurement and applied to Rietveld refinement with GSAS as shown in (a), (b) and (c), respectively. (d) The monochromatic ADXD pattern from the same sample for comparison.

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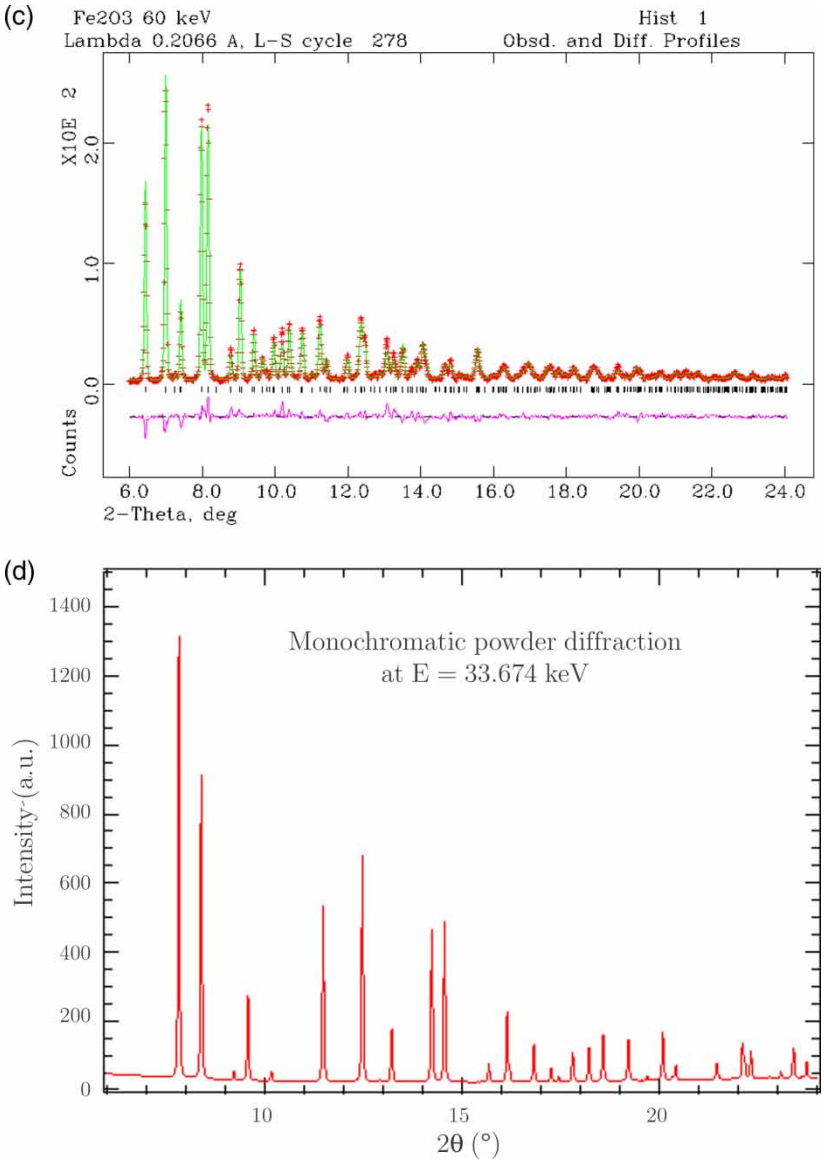

Figure 3. Continued.

energy-dispersive pattern is shown in Figure 2a, where the diffraction intensity is plotted as a function of energy at $2\theta = 10°$. With scanning 2θ from 6° to 24° at a step size of 0.1°, a total of 180 diffraction patterns were collected in 4 h from 16BM-B station with white beam size of about 5 μm FWHM in diameter. The intensity as a function of 2θ angle and energy is plotted in Figure 2b from all 180 measurements.

With the binning process, we could gain much denser data points in the monochromatic ADXD profiles. Since the spectrum of the bending magnet is smooth and the flux variation is small for a narrow energy range, we apply Equation (3) to convert the energy dimension data to 2θ angle data. The ADXD data at different energies from the same data set collected by SA-EDXD are shown in Figure 3. Rietveld refinements using GSAS have been applied to the ADXD data extracted at 20, 40 and 60 keV separately and the results are displayed in Figure 3 a–c, respectively. All the data fit the

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hematite structure very well. For comparing the angular resolution with monochromatic beams, a monochromatic powder diffraction with energy at 33.674 keV was collected with a mar345 imaging plate and displayed in Figure 3d. The angular resolution $\Delta 2\theta/2\theta$ from SA-EDXD with a 0.1° step size scan is around 0.008, which is a little worse than that from the monochromatic ADXD pattern ($\Delta 2\theta/2\theta \sim 0.005$). Since ME data are obtained simultaneously, one can use all the diffraction data for structure refinement. This will be especially useful to determine the atomic positions of different elements from energy-dependent atomic scattering factors, which have been largely used for anomalous scattering in biological materials.

Recently, amorphous and liquid structure studies under extreme conditions have attracted much interest. 'Polyamorphism' has been introduced to describe different amorphous phases at high pressure for a decade [11]. Coordination number change, compressibility change and thermal densification have been reported [12–14]. Detailed atomic structure determination is very important for characterizing amorphous phase transitions and for design and fabrication of new functional amorphous materials. The well-defined collimation and intensity correction procedure of the SA-EDXD technique ensures the necessary signal-to-noise ratio for weak signals from sample materials in DACs. Figure 4 is an example of a binary amorphous $Ni_{60}Nb_{40}$ sample made by a fast-quenched ribbon measured in a DAC under 20 GPa. A two-dimensional plot of intensity as a function of d-spacing and 2θ is shown in Figure 4a, where one can clearly see several broad peaks with very low background. Several different energy ADXD profiles are shown in Figure 4b. The major oscillation features have been reproducibly present at all energy profiles, but a broad bump marked by an arrow in Figure 4b is enhanced when the corresponding energy decreases. As the diffraction energy decreases towards the Nb K-edge (18.986 keV), the diffraction intensity

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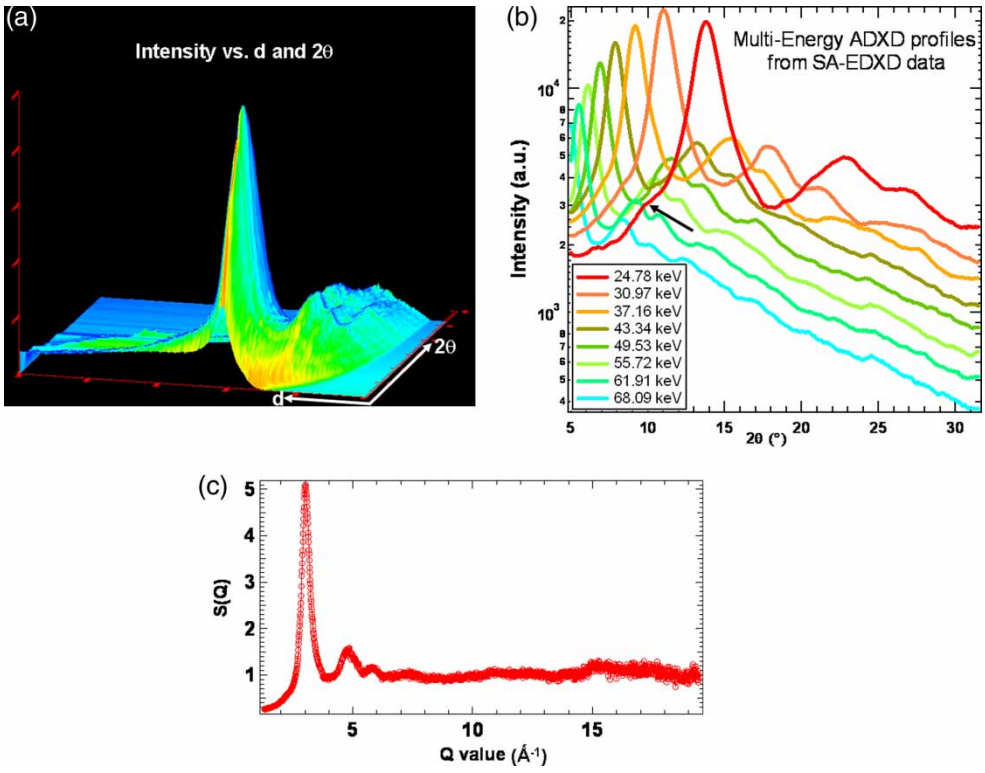

Figure 4. SA-EDXD results from a fast-quenched ribbon $Ni_{60}Nb_{40}$ metallic glass measured at 20 GPa in a DAC. (a) Two-dimensional map of intensity *vs.* d-spacing and 2θ angle, (b) ME-ADXD profiles from SA-EDXD data and (c) the full structure factor $S(Q)$.

contribution from Nb site is smaller, suggesting that the enhanced diffraction feature is mainly from Ni site. By fitting the intensities *vs.* Q with MEs, one can solve the partial structure and full structure factors. A processing software package for partial structure factors is under development and the results will be published elsewhere. Here we present the full structure factor as shown in Figure 4c. A systematic measurement of partial and full structure factor $S(Q)$ as a function of pressure is under further investigation.

5. Summary

A scanning angle energy-dispersive diffraction technique with white beam synchrotron radiation has been developed for high-pressure studies in DACs. The improvement of the signal-to-noise ratio with diffraction beam collimation is especially important for weakly scattering matter, such as low-Z materials, amorphous and liquid structure studies. For polycrystalline powder diffraction, because the diffraction intensity from only a small azimuth angle is accepted, fine powder samples without texture are required for good statistics. ME-ADXD profiles can be obtained simultaneously. The site-specific diffraction can be enhanced/reduced by choosing an energy with near-elemental absorption edges. The ME-ADXD profiles provide a new opportunity to extract partial and full structure factors.

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