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High-pressure pair distribution function (PDF) measurement using high-energy focused X-ray beam

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Abstract. In this paper, we report recent development of the high-pressure pair distribution function (HP-PDF) measurement technique using a focused high-energy X-ray beam coupled with a diamond anvil cell (DAC). The focusing optics consist of a sagittally bent Laue monochromator and Kirkpatrick-Baez (K-B) mirrors. This combination provides a clean high-energy X-ray beam suitable for HP-PDF research. Demonstration of the HP-PDF technique for nanocrystalline platinum under quasi-hydrostatic condition above 30 GPa is presented.

INTRODUCTION

It is well known that the atomic pair distribution function (PDF) method obtained using high-energy X-ray or neutron diffraction is a powerful tool for studying crystalline, disordered and nano materials¹⁻³. Although the pair distribution function, $g(r)$, is simply another representation of the diffraction data, real space exploration of the data has advantages especially in the case of materials with significant structural disorder². The total scattering, including Bragg peaks as well as diffuse scattering, contributes to the PDF, and is particularly useful for characterizing aperiodic distortions in crystals². Because of the potentially important role of liquids and disordered solids in the Earth's interior, it is of interest to use the PDF method to characterize the structural variation at short, intermediate and long range order under extreme conditions of high pressure and temperature^{4, 5}. However, acquiring PDFs using a large unfocused X-ray beam for high-pressure diamond anvil cell (DAC) experiments results in low signal intensity and long data acquiring time, with the data potentially adversely affected by parasitic scattering from upstream beamline slits and background contribution due to diamonds and gasket materials. As a result, PDF analysis is at present generally limited to pressures of <10 GPa. In this paper, we report recent development of high-energy X-ray focusing capabilities and HP-PDF determination under extreme conditions using a diamond anvil cell.

EXPERIMENT

Pt nanoparticles (99.5%, < 50 nm mean particle size) were purchased from Sigma-Aldrich Co., while nano Au (10–20 nm mean particle size) was obtained from Nanostructured & Amorphous Materials, Inc., USA. High-pressure X-ray total scattering experiments were carried out at beamline X17B3 of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. High-energy monochromatic X-rays with a beam size of 15 x 15 μm^2 was achieved by a combination of a sagittally bent double-Laue monochromator together with Pt-coated Kirkpatrick-Baez (K-B) mirrors. The X-ray wavelength was measured to be 0.1877 Å (66.054 keV) using CeO₂, Au and Si standards with a deviation of 1.9×10^{-4} using a diffraction-based calibration method⁶. Short piston-

cylinder diamond anvil cells with wide conical openings and 300- μm diameter culets were used for pressure generation. The accessible range of measured q -space is up to 22 \AA^{-1} . Data were collected with a Perkin-Elmer flat panel detector. For X-ray total scattering measurement, typically 50–100 datasets of data/dark current spectra were collected and then averaged for dark current reduction in order to improve the statistical accuracy at high Q range. The total scattering function, $S(Q)$, and the pair distribution function, $g(r)$, were obtained using the program PDFgetX2⁷, and then fitted in real space with the program PDFgui⁸.

RESULTS AND DISCUSSION

High energy X-ray diffraction, which can access a large range of scattering vectors, e.g. $> 20 \text{ \AA}^{-1}$, is becoming increasingly important in material and nano sciences. However, for high-pressure applications, there are some stringent requirements including high flux, clean, micro-focusing, and high energy beam ($> 60 \text{ keV}$).

Figure 1a shows the measurement of the focused X-ray spot obtained by scanning a cross-hair made of tungsten wire with a relatively large diameter ($15 \mu\text{m}$) (for better scanning contrast) across the beam. The K–B mirrors were bent to optimize the focal spot size. The focused beam size was achieved to $15 \mu\text{m}$ (full width at half maximum) both at the X-ray energies of 66 keV and 80 keV. Fig. 1b shows a diffraction image of nanocrystalline Pt compressed at 35.4 GPa in a Ne pressure medium with a high-energy X-ray beam (66.054 keV). Except a few spots from the diamond anvils, the diffraction pattern is clean and high quality.

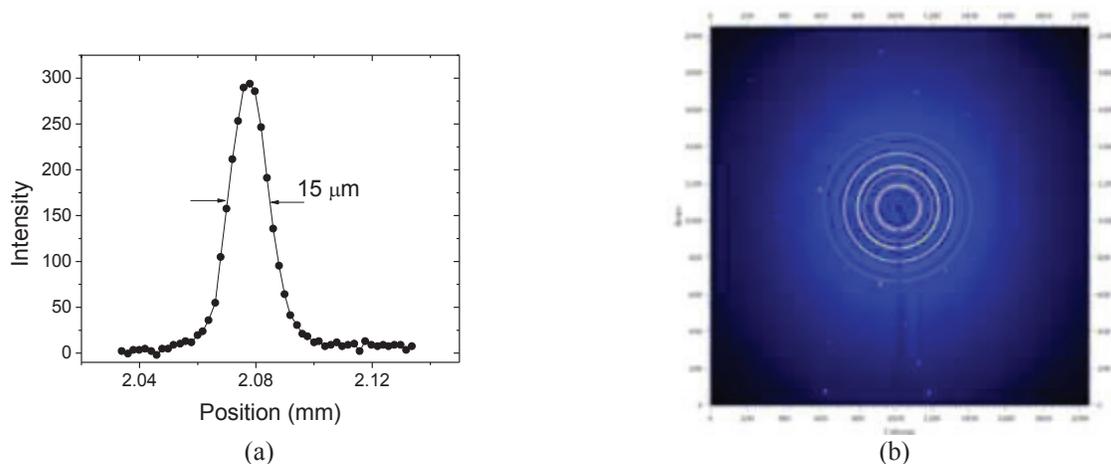


FIGURE 1. (a) X-ray intensity profile (the inverse scanning profile) obtained using a tungsten cross-hair. (b) X-ray diffraction pattern of nanocrystalline Pt (50 nm) at 35.4 GPa in a Ne pressure medium. The X-ray beam energy is 66.054 keV.

Figure 2 shows a typical high-pressure pair distribution function (PDF) measurement of nano Pt at 31.3 GPa in a quasi-hydrostatic Ne pressure medium. The PDF data are fit well using a simple face-centered cubic (FCC) Pt structure model with a fit residual, R_w , of 0.159 (lower panel, Fig. 2), confirming that the focused beam quality is suitable for HP-PDF measurement. The measured lattice parameter is $3.81668 (0.00026) \text{ \AA}$, showing a slightly lower stiffness than the bulk Pt material (3.8084 \AA at this pressure)⁹. This PDF fitting indicates there is only a small size-associated structural difference between nanocrystalline Pt and the bulk material. The good data quality also indicates that the combined focusing optics is promising for high-pressure research using PDF techniques.

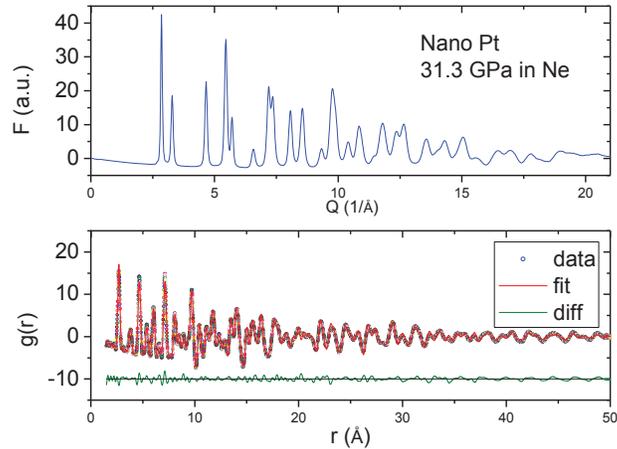


FIGURE 2. High-pressure pair distribution function (PDF) of nano Pt (50 nm) at 31.3 GPa using a focused X-ray beam. (Upper panel) Reduced total scattering function $F(Q)$. (Lower panel) Data points are the corresponding PDF function, $g(r)$, using an upper limit ($Q_{max} = 21.5 \text{ \AA}^{-1}$) for the Fourier transform. Lines are the simulated PDFs for the Pt structure solution with a fit residual, R_w , of 0.159. The bottom curve shows the difference between measured and simulated PDFs, offset for clarity.

The focused high energy X-ray beam can also improve the precision of conventional structure refinement in terms of the available high- Q data in comparison with a moderate X-ray beam (e.g. 30 keV) for DAC experiments. Figure 3 shows a typical Rietveld refinements for nanocrystalline Au (n-Au) at 2.1 GPa, using the Jana2006 software¹⁰. It can be seen that the lattice parameter refinements based on the simple FCC model display an obvious misfit in the intensity ratio of the 111 and 200 reflections, as reported earlier¹¹.

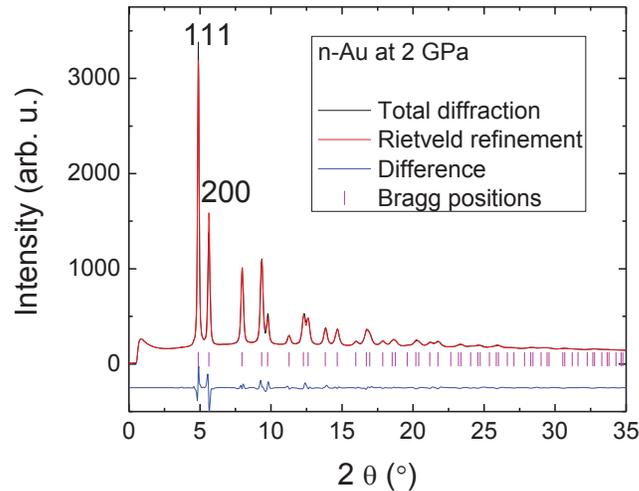


FIGURE 3. Rietveld refinements of the diffraction patterns of n-Au at 2.1 GPa

It is known that compression under non-hydrostatic conditions can yield a volume that lies as large as much as 10–20 % above the quasi-hydrostatic curve at a given pressure¹². As one of the most commonly used pressure transmitting media, methanol–ethanol (4:1) has a hydrostatic limit of 10.5 GPa, and its non-hydrostatic stresses increase rapidly above this pressure¹³ making it unsuitable for a precise equation of state (EOS) determination at pressures significantly above 10 GPa. To minimize the effect of uniaxial stress on the sample volume, we employed the solid noble gas neon as a pressure medium due to its low strength and chemical inertness¹³. Figure 4 shows the pair distribution function (PDF) of n-Pt at 35 GPa in methanol/ethanol (4:1) mixture (black) and quasi-hydrostatic Ne pressure-transmitting medium (red), respectively, indicating the existence of a slight non-hydrostatic effect on the PDF, $g(r)$, function. This is evidenced by the relatively slow oscillation in the sample using the methanol/ethanol (4:1) mixture (black). To address the size related stiffness in nanoparticles probed by DAC technique, solid noble gases, such as He, Ne or Ar as pressure media are needed.

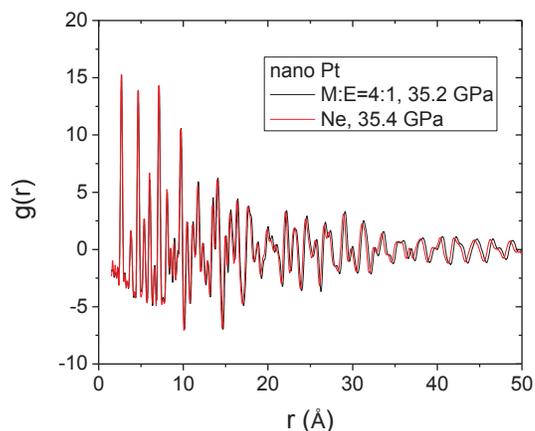


FIGURE 4. Pair distribution function (PDF) of n-Pt at 35 GPa in methanol/ethanol (4:1) mixture (black) and quasi-hydrostatic Ne pressure-transmitting medium (red), respectively.

CONCLUSION

The combination of Kirkpatrick-Baez (K–B) focusing mirrors with sagittally bent Laue monochromator provides a clean, high-energy X-ray focused beam which is well suited to the high-pressure pair distribution function (HP-PDF) measurement when coupled with the diamond anvil cell (DAC) technique.

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