Neutron powder diffraction of small-volume samples at high pressure using compact opposed-anvil cells and focused beam

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Abstract. Neutron powder diffraction techniques of small-volume samples at high pressure using compact opposed-anvil cells were developed at J-PARC pulsed neutron source. For this purpose we apply a few types of super-hard materials as opposed anvils with culet diameters between 3 to 5 mm. Generated pressures with these anvils were up to 9 GPa for 2 to 4 mm\textsuperscript{3} and up to 14 GPa for 0.7 mm\textsuperscript{3} sample volumes, which not only depends on the anvil geometry and material but even more depends on the metallic gasket geometry and material. A representative anvil geometry with 4 mm in culet diameter, along with TiZr “null alloy” metallic gasket containing varying sample volumes, were then applied to time-of-flight neutron powder diffraction experiments, where methane hydrate of 4 mm\textsuperscript{3} volume and lead of 0.7 mm\textsuperscript{3} volume were separately measured and their signal-to-background ratios were evaluated. A neutron-focusing optics was used to concentrate the neutron beam into these small-volume samples to increase the intensity of diffraction. Although spurious diffraction peaks from the anvils were prominent, more than seven diffraction peaks are clearly observed from both of the samples. In spite of the smaller sample capacity than previous standard high-pressure apparatus for neutron, it is concluded that the opposed-anvil cells will become alternative apparatuses for neutron scattering at strong pulsed neutron sources where sufficient neutron intensity was granted.

1. Introduction
Neutron plays the complementary role to x-ray in solid state physics and chemistry, geophysics, and material science at high pressures, because it is the unique probe for structural analysis of hydrogen-bearing materials which works effectively even at high pressures. Japan Proton Accelerator Research Complex (J-PARC) at Tokai, Japan now has become one of the strongest pulsed neutron sources which enable us to utilize this unique potential of the neutron beam. To make the best use of the
strongest pulsed neutron beam, we are developing the experimental techniques of neutron powder
diffraction of small-volume samples of the order of a few mm$^3$ at high pressures, which is compressed
by compact opposed-anvil cells. We are working at a state-of-the-art engineering diffractometer
TAKUMI (BL19) at J-PARC Materials and Life Science Experimental Facility (MLF), where time-of-
flight (TOF) neutron diffraction experiments at ambient condition and high pressure are conducted
with $L_1=40\text{m}$, $L_2=2\text{m}$ and 90-degree scattering geometry [1,2]. The compact anvil cells are designed
to work together with a neutron focusing optics previously designed and installed at TAKUMI [3].
Here we present our preliminary results using these apparatuses and facility.

2. Experimental

We expect that by using compact anvil cells with their best-optimized manner, detectable sample
volume for TOF neutron diffraction at high pressures will be significantly reduced from that of the
current standard Paris-Edinburgh (P-E) apparatus [4]. This is because the compact cells have not only
much wider opening angle from sample to see neutron detectors, but also equipped with much more
transparent anvils for the neutron beam than the P-E press. Therefore we expect a considerable
increase of signal-to-background ratio per unit sample volume which will compensate the intrinsically-
limited sample capacity of the compact cells. To evaluate this expectation, we have conducted neutron
powder diffraction experiments for sample volumes of one to two orders of magnitude smaller than
that of the P-E press.

Before touching the neutron, we applied several types of super-hard anvil materials as opposed
anvils with culet diameter of 3 to 5 mm, which is considerably larger than those used for previous
compact anvil cell experiments [5,6]. We thus evaluated pressure generation efficiency of the-largest-
order volume samples for the compact cells. First of all, culet sizes of single crystal diamond anvils at
$\leq 1\text{mm}$ are too much small, so that their application was not considered. Instead, we applied single
crystal moissanite (SiC) [5], sintered polycrystalline diamond (SD) [7], and nano-polycrystalline
diamond (NPD) [8]. The SiC anvil was made of synthetic gem-quality silicon carbide single crystal
commercially supplied from Charles & Colvard. Its size was 10 mm in outside diameter, 11 mm in
height, and 5 mm in culet diameter. The SD anvils were cut from a die commercially supplied from
Sumitomo Electric Industries. Its geometry was 13 mm in outside diameter, 12 mm in length, and 4 to
5 mm in culet diameter. The NPD anvils were cut from test pieces supplied from Sumitomo Electric
Industries, LTD (Itami, Osaka, Japan). Their sizes were 5 to 6 mm in outside diameter, 4 to 5 mm in
length, and 3 to 4 mm in culet diameter, which were precisely cut and shaped into the double-conical
geometry by laser-machining scheme [9]. These anvils and their surrounding supports were designed
to accept full lateral support while compressive force of the order of 100 kilonewtons (~10 tons) were
applied to compress the increased sample volume.

As the anvil culet size increased, our earliest designs of compact anvil cells for neutrons [6,10] are
required to be improved to generate even more forces, so that the cell designs were revised [11,12].
Using these cells and anvils, we conducted a series of pressure generation experiments, and found that
the generated maximum pressure strongly depends on the sample volume. We generated 9 GPa
pressure with moissanite or NPD on one side and SD on the other side of the sample, which was 2 to 4
mm$^3$ in volume between the 4 to 5 mm anvil culet diameters. We also generated 5 to 14 GPa pressures
using a pair of NPD with 4 mm in culet diameter; 5 GPa was for 3 mm$^3$ sample volume enclosed in a
Ti$_{52.5}$Zr$_{47.5}$ “TiZr null-alloy” gasket, while 14 GPa was for 0.7 mm$^3$ sample volume in a fully-hardened
Be-Cu 25 alloy gasket. Therefore, it was experimentally demonstrated that such a large difference in
generated pressure using the same anvil material and geometry came exclusively from the difference
in gasket geometry (especially in the sample volume) [13] and selection of its material. We note that
for measuring the sample pressures, microscope-based ruby fluorescence systems worked effectively,
which collected good fluorescence from the pressure sensors in sample chambers through transparent
moissanite and NPD anvils [6].
Considering the results of these pressure generation experiments, we selected a pair of the 4 mm culet NPD anvils and the TiZr gasket material as the working standard. Two representative samples with different volumes, 4 mm$^3$ of gas hydrate and 0.7 mm$^3$ of lead, were prepared and gently compressed with these anvils and gasket (Fig. 1).

At TAKUMI beamline, the incident neutron beam is shielded and collimated by the combination of boron rubber plate and hBN (boron nitride) rod collimators which stop the direct neutron beam, and also by cadmium foil surrounding the cell which stops scattered neutrons from the cell body (Fig. 1). A number of hBN collimators with different inner diameters were prepared to best-fit into the size of the sample. Fine tuning of the neutron focusing device works not only to increase the beam intensity at the sample position but also to reduce the background neutron intensity scattered from other materials than the sample. This device produces twice higher intensity of neutron beam at the sample position while keeping the resolution $\Delta d/d$ at around 0.6% which is only 0.1% larger than the original performance of TAKUMI [3].

![Figure 1](image.png)

**Figure 1.** An example of compact anvil cell and neutron beam path geometry. Boron rubber plate, hBN guide, and cadmium foil simultaneously shield and collimate the incident neutron beam from the bottom of the figure and reduce the background scattered from the cell body.
3. Results and Summary

Figs. 2 and 3 show the anvil cell setup and observed diffraction patterns for the two representative samples. Some of the strongest diffraction peaks shown with asterisks came from the two anvils directly contacting with the samples. These anvils were polycrystalline which intrinsically produce strong diffraction. Other indexed peaks were all coming from the samples.

![Diffraction pattern of partially-deuterated methane hydrate](image)

**Figure 2.** Setup and observed diffraction pattern of partially-deuterated methane hydrate with 4 mm$^3$ in volume before compression. The neutron beam came from the left of the cell. The small photo is the sample of ~2mm in diameter observed through the anvil by microscope. Experimental conditions were 120 kW proton power, 6.5 hours of accumulation, and radial collimator of 2 mm gauge volume installed only at the single side (north) detector bank. This pattern was constructed from that bank only.
Figure 3. Setup and observed diffraction pattern of lead with 0.7 mm$^3$ in volume before compression. The neutron beam came from the back of the cell at the centre of the photo. Experimental conditions were 100 kW proton power, 7 hours of accumulation, and radial collimator of 2 mm gauge volume installed only at the single side (north) detector bank. This pattern was constructed from that bank only.
It is noteworthy that more than seven diffraction peaks from both samples are clearly observed. Especially in Fig. 3, only 0.7 mm$^3$ sample volume gave enough diffraction intensity to accurately determine the lattice constant at high pressure by Le Bail fitting [14]. Therefore, in spite of the small sample capacity, the opposed-anvil cells gave very high signal-to-noise ratio per unit volume, and will become alternative apparatuses for powder neutron diffraction at high pressures at strong pulsed neutron sources where enough neutron intensity was granted.

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References
[1] Harjo S, Moriai A, Torii S, Suzuki H, Suzuya K, Morii Y, Arai M, Tomota Y, Akita K, Akiniwa Y 2006 Mater. Sci. Forum 524–525 199
[2] Hattori T, Fukazawa H, Okuchi T, Komatsu K, Arima H MLF Annual Report, in press
[3] Arima H, Komatsu K, Ikeda K, Hirota K, Kagi H 2009 Nucl. Instr. and Meth. A 600 71
[4] Besson J M, Nelmes R J, Hamel G, Loveday J S, Weill G, Hull S 1992 Physica B 180 & 181, 907
[5] Xu J, Mao H K, Hemley R J, Hines E 2004 Rev. Sci. Instrum. 75 1034
[6] Okuchi T, Sasaki S, Osakabe T, Ohno Y, Odake S, Kagi H 2010 J. Phys. Conf. Ser. 215 012188
[7] Klotz S, Besson J M, Hamel G, Nelmes R J, Loveday J S, Marshall W G, Wilson R M 1995 Appl. Phys. Lett. 66 1735
[8] Irifune T, Kurio A, Sakamoto S, Inoue T and Sumiya H 2003 Nature 421, 599
[9] Okuchi T, Ohfuji H, Odake S, Kagi H, Nagatomo S, Sugata M and Sumiya H 2009 Appl. Phys. A: Mater. Sci. Process. 96 833
[10] Okuchi T, Sasaki S, Ohno Y, Komatsu K, Kagi H, Arima H, Abe J, Hattori, T, Sano A, Osakabe T, Utsumi W, Harjo S, Ito T, Aizawa K, Irifune T 2010 Rev. High Press. Sci. Tech. 20 175 (in Japanese with english abstract)
[11] Okuchi T, Sasaki S, Ohno Y, Komatsu K, Kagi H, Arima H, Abe J, Hattori, T, Sano A, Osakabe T, Utsumi W, Irifune T 2010 Special Issue of Rev. High Press. Sci. Tech. 51 2B01 (in Japanese)
[12] Okuchi T, in preparation
[13] Ohno Y, Fujii T, Sasaki S, Osakabe T, Okuchi T, Kagi H 2010 Special Issue of Rev. High Press. Sci. Tech. 51 2P09 (in Japanese)
[14] Le Bail A, Duroy H, Fourquet J L 1988 Mat. Res. Bull. 23 447