BL10XU: High Pressure Research

The undulator beamline BL10XU is dedicated for X-ray diffraction experiments at high pressure and low/high temperature using a diamond anvil cells (DAC) (Figure 1) [1]. The high-resolution monochromatic angle-dispersive X-ray diffraction patterns obtained at BL10XU allow us to the accurate determination of equations of state, precise determination of phase relation, accurate structural refinements by Rietveld analysis, and charge density distribution analysis in crystals submitted to extreme pressures. High pressure is possible to change physical and chemical properties of matter through a change of its volume or distance between atoms (or molecules). The properties of matter at high pressure are drastically different from those known at ambient pressure. To have a better understanding of high-pressure research using a combination of synchrotron radiation and a DAC technique through this BL practice course, in situ high-pressure X-ray diffraction experiments will be carried out under hydrostatic conditions with a pressure-transmitting medium of helium that enables to give us high-quality data.

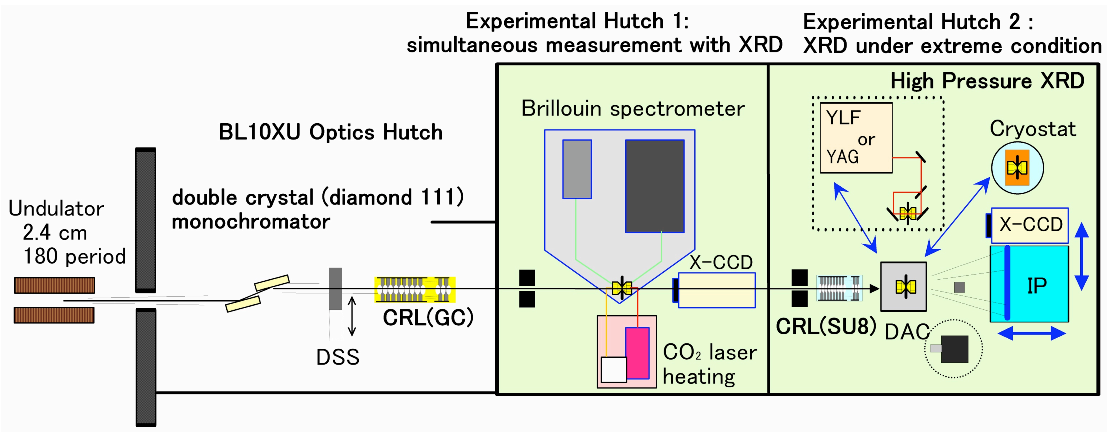

Figure1. Schematic layout of beamline BL10XU [1].

— GLOSSARY —

Diamond anvil cell

Diamond anvil cell is one of high-pressure generation techniques by static compression. The sample is placed in a pressure chamber created between the flat parallel faces (culets) of two opposed diamond anvils and the hole penetrating a hardened metal foil (the gasket) (Figure 2). Pressure is applied by forcing the diamonds together. Diamond is the premier anvil material because of hardest substance and transparency to electromagnetic radiation over a wide spectral range from the infrared to hard X-rays.

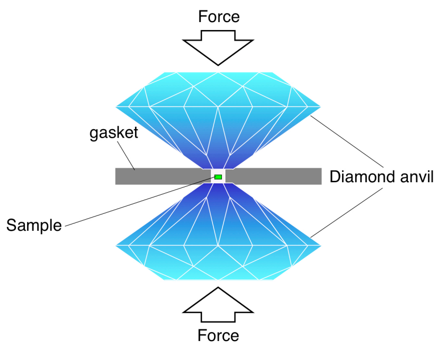

Figure 2. Diamond-anvil cell technique.

– Practice –

Obtain the parameters of "Equation of State" (EOS) for NaCl from experimental compression data by high-pressure X-ray diffraction method.

1) Energy calibration

Angle dispersive x-ray diffraction (XRD) requires a monochromatic X-ray beam. The most important requirements for the structure determination (or the measurement of the unit-cell parameters) of a material are the accurate determination of the wavelength for incident X-ray beam and of the distance between sample and detector of imaging plate (IP). In this practice, we use photon energy tuned to 30 keV for angle dispersive XRD measurement. The determination of the X-ray wavelength and the distance is based on the standard material of cerium oxide (CeO_2). Determine incident X-ray wavelength and the distance between sample and IP. Before the determination, we need obtain XRD patterns of the standard material at desired distance, and then convert the X-ray image to conventional one-dimensional X-ray pattern with the software.

2) Sample preparation

The sample is set up in a chamber created between the culets of two opposed diamond anvils and the gasket hole. The gasket in anvil devices serves three critical functions: (1) encapsulating the sample, (2) building a gradient from ambient to the peak pressure, and (3) supporting the tip of anvils. Gasket material, hole size of sample chamber, and thickness are critical for generating high pressure. In this practice, 300-μm culet anvil and a drilled rhenium gasket is prepared for the experiments with helium pressure-transmitting medium to compress the sample to the desired pressure. Mounting the sample into the chamber should be performed with preparation needle, together with tiny ruby chips for a pressure marker (see below).

3) Compressed gas loading

Hydrostaticity is an important parameter in high-pressure experiment, because non-hydrostatic stress affects the position and profile of diffraction peaks, resulting in inaccurate data [2]. The use of inert gases as pressure medium could significantly reduce pressure anisotropy and inhomogeneity, which causes non-hydrostatic condition, in the DAC. To perform loading of compressed helium gas at elevated pressures (195 MPa or 0.195 GPa), we use the large-volume gas-loading apparatus that enable to fill gas at high densities in the pressure chamber.

Note that a BL staff operates the apparatus for safe.

4) Pressure measurement

The ruby scale, which has been calibrated against primary shock-wave experiments on several metals, is commonly used for DACs: tiny ruby grains are loaded in the sample chamber with sample, and the pressure-shift of ruby fluorescence wavelength can be easily probed with a laser beam through the diamond window. Determine the pressure with empirical quasi-linear relationship: P (GPa) = $1904[(\lambda/\lambda_0)^B - 1]/B$, where $B = 7.665$ for quasihydrostatic conditions, for the correlation of the measured wavelength shift λ (in nm) of the R_1 line with applied pressure [3].

5) XRD data collection at high pressures

We use a DAC with pneumatic driving mechanism where pressure can be changed on-line by controlling the gas pressure on a membrane, enabling the pressure to be changed smoothly and remotely. In-situ high-pressure XRD experiments are carried out with the following three steps: (1) loading to the desired pressure, (2) pressure determination with ruby scale, and (3) acquirement of XRD images with IP. Collect XRD images at pressure intervals of 5 GPa for determination of the EOS parameters.

6) Data analysis

The basic principle of the X-ray diffraction is the Bragg's law: $\lambda = 2d\sin\theta$, where λ is the wavelength of the X-ray, d the lattice spacing, θ the angle of the incident beam and the diffracting lattice plane. The diffraction peaks are observed when the *d*-spacing satisfied the Bragg's law.

First, convert the X-ray image to conventional one-dimensional X-ray pattern with the software. Next, calculate *d*-spacing for each peak from 2theta value using the Bragg's law. Then, perform peak indexing. Finally, refine the unit-cell parameter and volume.

Note that sodium chloride (NaCl) has face-centered cubic (fcc) structure with space group of *Fm3m*, called B1-type (or NaCl-type) structure. Its structure transforms from the B1 to B2 (CsCl) structure at 29.3 GPa.

7) Determination of the EOS parameters

The equation of state (EOS) is the most fundamental parameter obtained from high-pressure research. The EOS describes the relationships among the thermodynamic parameters volume, pressure, and temperature (energy). In this practice, we try to obtain the EOS parameters of zero-pressure bulk modulus and its pressure derivative for B1-type NaCl from pressure-volume data at room temperature. Plot the P-V data, and then fit the EOS with the Birch-Murnaghan equation.

Note that the Birch-Murnaghan equation of state is based on the Eulerian strain [4] and is widely used for mineralogists:

$$P = 3K_{T0}/2\ [(V_0/V)^{7/3} - (V_0/V)^{7/3}]\{1 - 3/4(4 - K'_{T0})[\ (V_0/V)^{2/3} - 1]\}$$

, where P is pressure, K_T zero-pressure bulk modulus, K'_T its pressure derivative, V the volume at P, and the subscript "0" refers to ambient pressure conditions.

8) Comparison with other materials

Compare the EOS parameters of NaCl with other materials. The parameters for ionic, covalent, and metal crystals will be given in table.

References:

[1] Ohishi *et al.* (2008) *High Press. Res.*, in press.
[2] Takemura (2001) *J. Appl. Phys.* **89**, 662.
[3] Mao *et al.* (1986) *J. Geophys. Res.* **91**, 4673.
[4] Birch (1952) *J. Geophys. Res.* **57**, 227.