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) [Ohishi *et al.* (2008) *High Press. Res.*, **28**, 163.]. The high-resolution monochromatic angle-dispersive X-ray diffraction patterns obtained at BL10XU allow us to make an accurate determination of equations of state, precise determination of phase relation, structure refinement by Rietveld analysis, and charge density distribution analysis in crystals submitted to extreme pressures. High pressure is possible to change physical, chemical, and structural characteristics of materials through a change of its volume or distance between atoms (or molecules). The high-pressure properties are drastically different from those known at ambient pressure. Pressure thus serves as a versatile tool in material research, and it is also important in the investigation of the deep interior of the Earth and other planets. To learn high-pressure phenomena in the BL practice course, in-situ high-pressure X-ray diffraction experiments will be performed using a combination of synchrotron radiation and a DAC technique.

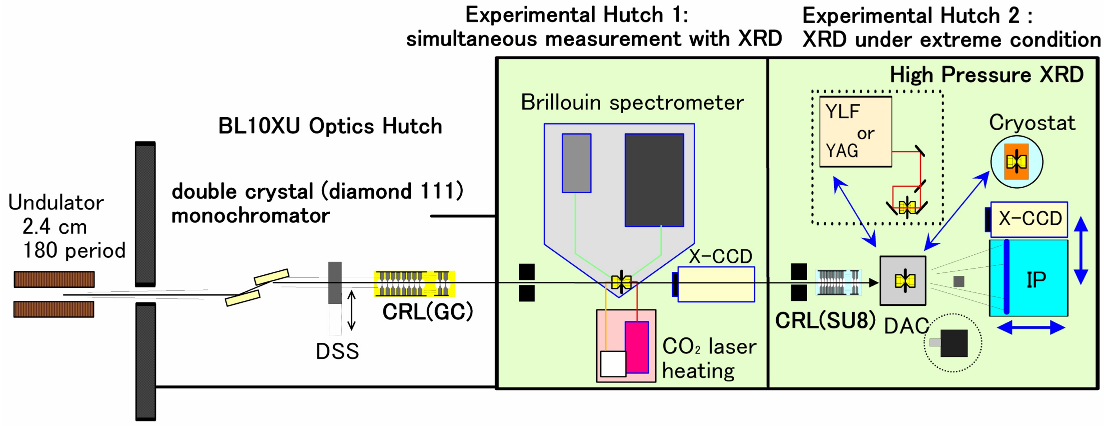


Figure1. Schematic layout of beamline BL10XU [1].

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.

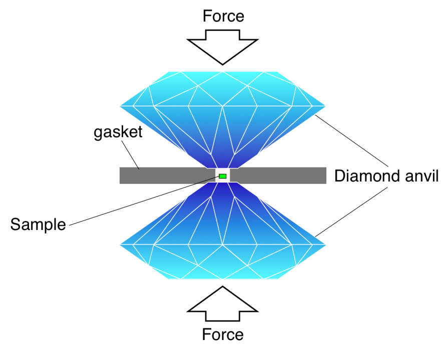


Figure 2. Diamond-anvil cell

Energy calibration

Angle dispersive X-ray diffraction (XRD) requires a monochromatic X-ray beam. The accurate determination of the wavelength for incident X-ray beam and of the distance between sample and detector of imaging plate (IP) allow to determine precise crystal structures and the unit-cell parameters of materials. In this practice, we use photon energy tuned to 30 keV (0.4133 Å) for the XRD measurement. The calibration of the X-ray wavelength and the distance is based on the standard material of cerium oxide (celia, CeO_2).

– Practice –

Observe a structural phase transition of sodium chloride (NaCl) at high pressure and obtain the parameters of Equation of State (EOS) for NaCl from in-situ X-ray diffraction data.

1) 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, for efficiency measurement we use a gas-membrane DAC. A sample of NaCl powder is placed in a chamber hole drilled in a rhenium foil, together with tiny ruby chips for a pressure marker.

2) XRD data collection at ambient and high pressures

In-situ high-pressure XRD measurements are carried out with the following steps: (1) first measurement at ambient pressure, (2) loading to the desired pressure, (3) pressure determination with ruby scale, and (4) collection of XRD images with IP. Collect XRD images at pressure intervals of 5 GPa up to 35 GPa.

3) High-pressure generation and pressure measurement

In a gas-membrane DAC, pressure is generated online, smoothly, and remotely through controlling the gas pressure in a membrane.

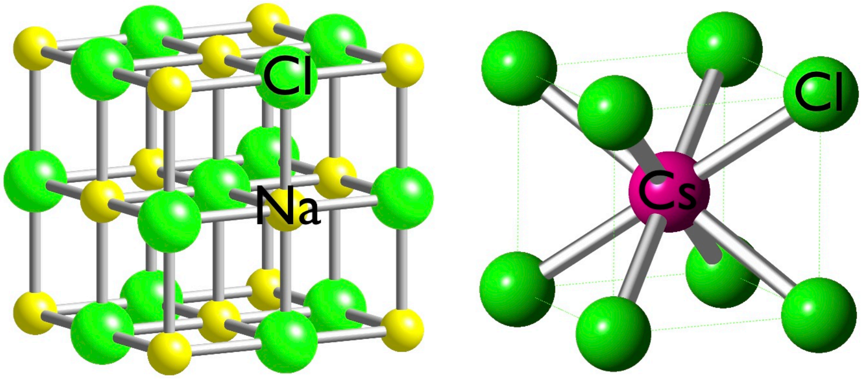
Pressure in the DAC is determined by ruby pressure scale [Mao *et al.* (1978) *J. Appl. Phys.* **49**, 3276.]. The ruby scale, which has been calibrated against primary shock-wave experiments on several metals, is commonly used for DACs: the pressure-shift of ruby fluorescence wavelength can be easily 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 $B = 5$ for non-hydrostatic conditions, for the correlation of the measured wavelength shift λ (in nm) of the R_1 line with applied pressure.

4) Data analysis and peak indexing

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 2θ 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 *Fm*3*m*, called B1-type (or NaCl-type) structure. At ambient conditions, the lattice parameter of NaCl is 5.630 Å. Its structure transforms from the B1 to B2 (CsCl) structure at 29.3 GPa.



5) Determination of the EOS parameters

An EOS is the relationships among the thermodynamic parameters volume, pressure, or temperature. The EOS is useful to describe the properties of solid, fluid, and even the interior of planets and stars. In this practice, obtain the EOS parameters of zero-pressure bulk modulus and its pressure derivative for a low-pressure phase of 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 [Birch (1952) *J. Geophys. Res.* **57**, 227.] 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.

6) Comparison with other materials

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

Material	K_0 (GPa)	K'_0	Ref.
Diamond	444.5	3.98	[1]
Na	6.310	3.886	[2]
Si	97.9	4.16	[3]
Al	73	4.54	[4]
Au	167	5.46	[5]
Pt	277	5.08	[4]
MgO	160.2	3.99	[6]
Al_2O_3	253	4.30	[7]
H_2	0.162	6.813	[8]
Ne	1.42	8.03	[9]
NaCl	23.83	5.09	[10]

References: [1] Occelli et al. (2003); [2] Hanfland et al. (2002); [3] Knittle (1995); [4] Dewaele et al. (2004); [5] Takemura (2007); [6] Speziale et al. (2001); [7] Syassen (2008); [8] Loubeyre et al. (1996); [9] Dewaele et al. (2008); [10] Dorogolupets and Dewaele (2007).