BL02B2
Powder Diffraction

1. Introduction

BL02B2 is a bending-magnet beamline designed specifically for high-resolution powder X-ray diffraction studies of crystalline powder materials. These diffraction experiments help elucidate the relationship between crystal structure and physical properties through phase identification, precise structural analysis, and *in situ* observations under different external conditions. The beamline offers monochromatic X-rays with an energy range of 12–37 keV ($\Delta E/E$ is approximately 2×10^{-4}). Powder diffraction patterns are captured using six one-dimensional (1D) microstrip MYTHEN detectors [1]. There are two types of experiments conducted: (i) high-throughput powder diffraction experiments utilizing a sample changer, and (ii) *in situ*/time-resolved powder diffraction experiments under various conditions. The high-throughput experiments can automatically process up to 50 capillary samples within a temperature range of 30 to 1100 K.

For *in situ* powder diffraction experiments under various conditions, additional equipment needs to be installed in the powder diffractometer. A furnace and a cryostat are available for conducting experiments at high temperatures (up to 1473 K) and low temperatures (down to 5 K), respectively. A remote gas handling system is used for controlling gas and vapor pressures within a capillary [2]. Additionally, users can conduct *in situ* powder diffraction experiments using specialized equipment they bring, such as electric field generators for ceramics, charging/discharging cells for batteries, and light irradiation systems. A two-dimensional (2D) flat panel detector (FPD), XRD3025, has been added to enhance *in situ* powder diffraction measurements using high-energy X-rays, enabling the evaluation of crystal grain size.

In the previous year, to facilitate the utilization of experiments under gas atmospheres, we installed a new gas control and analysis system [3] under high-temperature conditions using a remote gas handling system [2], mass spectrometer, and gas chromatography with a high-temperature stage (Linkam TS-1500). As a consequence, it became possible to measure powder diffraction up to 1673 K under gas atmospheres. Thus far, we have focused on the development of the sample environment in relation to the temperature and gas atmospheres. On the other hand, there is also a large demand for applying pressure; in particular, *in situ* experiments with precise pressure adjustment in the region of tens or hundreds of MPa, which is difficult to control with other high-pressure experimental devices, have been impossible until now. To solve this problem, we developed a new high-pressure cell for powder diffraction, which is now available for use since FY2023.

2. Development of high-pressure cell

In FY2023, we newly developed an *in situ* synchrotron X-ray diffraction system under high-pressure conditions (0.1–400 MPa). Figure 1 shows a photograph of the high-pressure cell installed in the beamline BL02B2. The measurement samples can be mounted in the sample chamber (20 mm in diameter and 0.5–1.0 mm in thickness), which is

filled with water as the pressure medium. We control water pressure manually with a pump. The pressure is monitored using a pressure transducer, and then the sample pressure can be obtained directly without pressure markers. The uncertainty of pressure is estimated to be less than 10 MPa. An example of peak shift due to pressurization is shown in Fig. 2. In addition, heaters are also installed in the cell and we can control the temperature up to 180 ℃. A K-type thermocouple is installed in the cell to measure the temperature near the sample chamber. The sample temperature is maintained within 0.1 ℃ by a proportional–integral–differential controller. The maximum heating and cooling rates are about 3 and 1 ℃/min, respectively. The temperature uncertainty is less than 1 ℃. A pressure increase of 7–10 MPa occurs upon heating from room temperature to 170 ℃, but we can maintain arbitrary pressures by fine control of the pump.

The powder sample should be packed using waterproof materials, such as Kapton, and it is fixed with Kapton tape directly on the wall of the downstream side of the sample chamber of the cell. This easy sample fixing enables us to change samples within 10 min. Not only hydrostatic compression but also uniaxial compression experiments can be performed by changing the packing of the powder sample.

Powder diffraction patterns can be collected using both 1D and 2D detectors simultaneously at BL02B2. A wide angular aperture allows the acquisition of diffraction patterns up to $2\theta = 35°$ when using only a 1D or 2D detector (Fig. 3). The X-ray transmission windows of the cell are made of a single crystal of diamond, enabling the collection of powder diffraction patterns without or with a small number of diffraction spots from window materials compared with other window materials such as sapphire. To obtain powder diffraction patterns with sufficient particle statistics, powder diffraction measurements can be conducted by oscillating the high-pressure cell by several degrees using the oscillation stage during exposure. The oscillation stage is set on the table with motorized XYZ stages in BL02B2, enabling the adjustment of the sample position to an appropriate sample-to-detector length. As shown in Fig. 3, sharp diffraction peaks are observed even at high pressure, and Rietveld analysis can be applied to the data obtained using the high-pressure cell. The control and monitoring of pressure, temperature, stage position, oscillation, and measurement can be performed from outside the experimental hutch. This system, including the cell, oscillation stage, and pump, is compact enough to be carried by one person.

In summary, the described development enabled *in situ* high-pressure XRD measurements of 0.1–400 MPa at room temperature to 180 ℃. The XRD patterns obtained are of sufficient quality for studying the crystal structure by Rietveld analysis. This system was developed for XRD measurement at BL02B2 but can be used in other beamlines in SPring-8, and thus contribute to various measurements such as SAXS under high pressure.

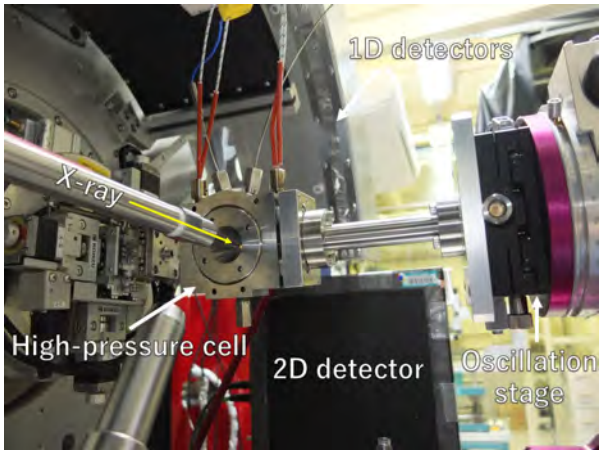

Fig. 1. Photograph of the high-pressure cell installed on BL02B2.

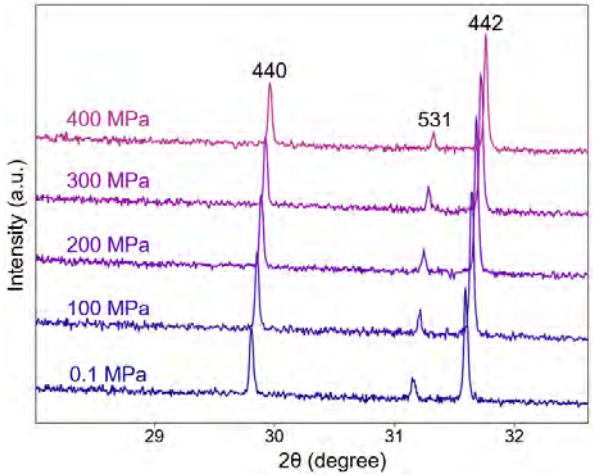

Fig. 2. A part of XRD patterns of NaCl under ambient and high pressures. Measurement was performed with 25 keV incident X-ray energy. Numbers labeled on peaks are Miller indices.

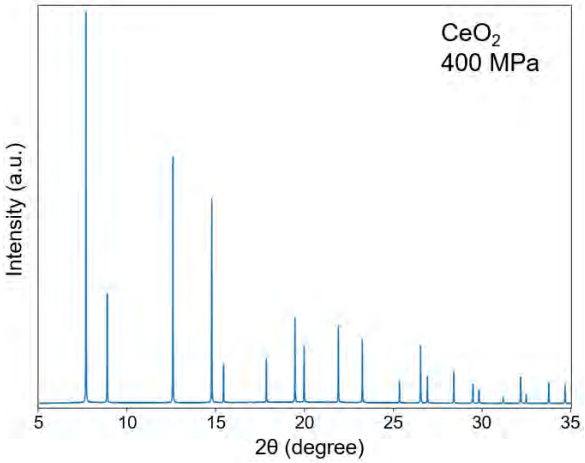

Fig. 3. XRD pattern of CeO_2 at 400 MPa and room temperature. Measurement was conducted using a 0.42 Å incident X-ray wavelength and 1D detectors.

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