BL02B2
Powder Diffraction

1. Introduction

BL02B2 is a bending-magnet beamline dedicated to high-resolution powder X-ray diffraction (XRD) measurements of crystalline powder materials. Powder diffraction experiments clarify the correlation between the crystal structure and physical properties through phase identification, accurate structural analysis, and *in situ* powder diffraction experiments under various external conditions. This beamline provides monochromatic X-rays with an energy range of 12–37 keV ($\Delta E/E$ is approximately 2×10^{-4}). Powder diffraction patterns are recorded with six one-dimensional microstrip MYTHEN detectors [1]. Two types of experiment are conducted: (i) high-throughput powder diffraction experiments using a sample changer and (ii) *in situ*/time-resolved powder diffraction experiments under various conditions. The former type of experiment is automatically carried out for up to 50 capillary samples, and the measurement temperature can be changed from 30 to 1100 K.

For *in situ* powder diffraction experiments under other external conditions, an additional apparatus must be installed into the powder diffractometer. A furnace and a cryostat are available for high-temperature (up to 1473 K) and low-temperature (down to 5 K) conditions, respectively. The remote gas handling system is applicable for controlling the gas and vapor pressures inside a capillary [2]. In addition, users can perform *in situ* powder diffraction experiments using carry-in equipment such as an electric field generator for ceramics, a charging/discharging cell for batteries, and light irradiation systems. Recently, a two-dimensional (2D) flat-panel detector (FPD), XRD3025, has been installed to improve the performance of *in situ* powder diffraction measurements with high-energy X-rays. This FPD can also rapidly evaluate the crystalline grain size using an online-readable 2D area detector.

In the previous year, for switching equipment around the sample environment, we developed an automatic equipment switching system to gain more effective beamtime and reduce hard work. As a result of this development, *in situ* experiments can be performed efficiently in a larger sample space on the powder diffractometer. Therefore, a new high-temperature stage system was developed in FY2021.

2. Development of new high-temperature transmission XRD measurement systems

In FY2021, we installed a compact high-temperature stage (Linkam TS-1500) to realize transmission powder XRD measurements in high-temperature regions. The heating stage includes a Pt wire attached to a small alumina heater block with a diameter of ~7.5 mm and a depth of ~2.5 mm. The measurement sample is set inside the heater block. The stage temperature is controlled using a Type S thermocouple near the heater block and ranges from room temperature to 1773 K. The maximum heating rate is 200 K/min. To easily and accurately conduct transmission powder XRD using the high-temperature stage, we have made the following developments and improvements.

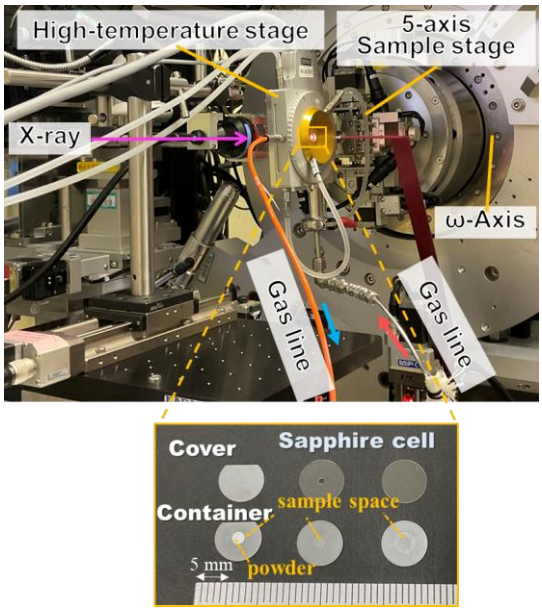

Fig. 1. Photograph of high-temperature transmission XRD measurement system using Linkam TS-1500 heating stage.

To achieve high-temperature transmission XRD using powder samples with high temperature reproducibility and sample exchange time as short as possible, we have developed a new sample cell made from a single sapphire crystal with high heat resistance (see Fig. 1). The sapphire cell consists of a container with a hole of 2 or 3.5 mm diameter and 0.15 mm depth and a cover of 0.2 mm thickness. A powder or pellet sample can be placed in the hole in the container and then capped with the cover. The measurement sample cell can be easily fixed using a SUS or W metal ring seal in the alumina heater block in a short time. Furthermore, by using the same types of sapphire cell with a thickness of ~0.65 mm including a cover, temperature reproducibility is ensured. The X-ray window of the heating stage is made of sapphire single crystals instead of standard quartz to reduce the background signal as mentioned below. Temperature control software was developed by using LabVIEW. The compact heating stage is easily set to the five-axis sample stage (see Fig. 1). Moreover, sample oscillation using the ω-sample stage can be possible during exposure, which improves the particle statistics of XRD data. The gas line of the heating stage is connected to a remote gas control system [2], allowing the external control of gas pressure and gas flow rate. The stage can be used under various gas environments, such as vacuum and gas flow conditions (N_2, Ar, Ar/H_2 (<1073 K), etc).

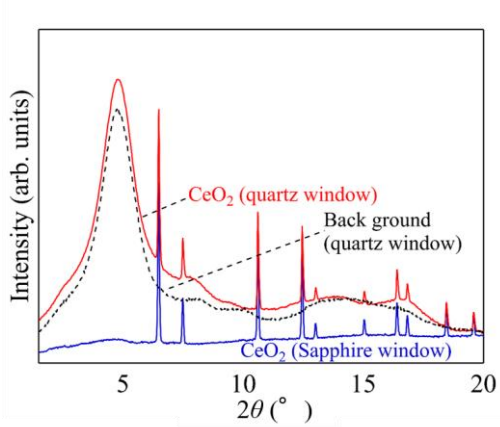

Fig. 2. Typical XRD pattern obtained using Linkam TS-1500 heating stage. XRD patterns of CeO_2 measured with quartz and sapphire X-ray windows and background data with a quartz window are shown.

Figure 2 shows the XRD pattern of CeO_2 in the high-temperature stage with sapphire and quartz X-ray windows. 2D XRD images were acquired using the FPD detector. By masking diffraction spots from sapphire single crystals on 2D XRD images, low-background 1D XRD patterns without diffraction peaks from the sapphire can be obtained when using the sapphire window. The sample temperature at the sample position was evaluated by

the offline microscopic observation of the melting temperature of pure metals and the XRD observation of structural phase transition temperatures. After temperature calibration, the maximum temperature was around 1678 K at the sample position (thermocouple temperature was 1723 K). By using this high-temperature transition XRD system, the high-temperature phase transition of ZrO_2 (~1443 K) and the high-temperature synthesis of $BaZrO_3$ (1350–1500 K) on heating (10 K/min) were clearly observed.

In summary, this development easily enables *in situ* high-temperature powder XRD measurements in wide temperature ranges without major measurement setup changes at BL02B2. In addition, now, an automatic sample preparation system used to fill powder into a capillary is currently undergoing trial operation. This system automates the filling of powder samples into thin capillaries (0.1–0.5 mm in diameter), which was previously conducted manually by hand. Thus, various developments of automated equipment and *in situ* measurement devices are proceeding at BL02B2.

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