

BL02B2 Powder Diffraction

1. Introduction

BL02B2 is a bending-magnet beamline dedicated to high-resolution powder X-ray diffraction 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* observation 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 in a temperature range from 30 to 1100 K.

For *in situ* powder diffraction experiments under various conditions, additional apparatuses 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. A 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 yield the crystalline grain size using an online-readable feature.

In the previous year, to realize transmission powder diffraction measurements in high-temperature regions, we installed a compact high-temperature stage (Linkam TS-1500). As a consequence, it became possible to measure powder diffraction up to 1673 K without the use of capillaries. In FY2022, we constructed a new gas control and analysis system under high-temperature conditions, which combines this high-temperature stage, the existing remote gas handling system^[2], mass spectrometer, and gas chromatography. Furthermore, trial operations have begun for the automatic powder filling system used to fill powdered samples into a capillary, which has recently been developed by RIKEN. Thus, we will introduce its specifications and usage examples.

2. Exhaust gas analysis system combined with a high-temperature heating stage

In FY2021, we developed an *in situ* synchrotron X-ray diffraction system using a high-temperature stage to observe high-temperature phase changes of powdered samples^[3]. In FY2022, we integrated the developed heating system with gas control and analysis tools, including the remote gas handling system^[2], gas chromatography, and mass spectrometer. This combination enabled the analysis of solid–gas reaction processes by

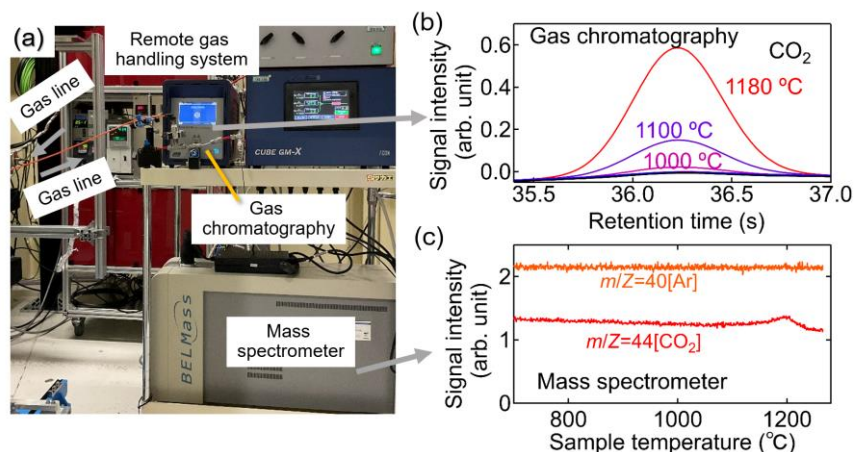


Fig. 1. (a) Photograph of the gas flow and exhaust gas analysis systems. (b) Gas chromatographs of the CO₂ signals collected during the *in situ* powder diffraction measurements at various temperatures. (c) Temperature dependence of the signal intensities of the gas components with mass numbers of ⁴⁰Ar and ⁴⁴CO₂, as determined by mass spectrometry.

monitoring the changes in the exhaust gas composition during chemical reactions.

Figure 1(a) shows a photograph of the gas flow and exhaust gas analysis systems. The gas inlet of the high-temperature stage was connected to the remote gas handling system to adjust the gas flow rate. High-temperature diffraction measurements can be conducted under various gas flow conditions, including inert gas, oxygen gas, air, and reduction gas (Ar/4% H₂). The gas outlet was linked to a gas chromatography–thermal conductivity detection system and a quadrupole-type mass spectrometer for exhaust gas component analysis. The utilization of the exhaust gas analysis system facilitates a comprehensive understanding of experimental conditions, such as residual oxygen content within the inert gas, thus contributing to the high reproducibility of high-temperature powder diffraction experiments under gas flow conditions. In addition, the system enables the detection of the change in exhaust gas components during chemical reactions. As an illustrative example, Figs. 1(b) and

1(c) display the outcomes of CO₂ detection during the synthesis process around 1423 K using gas chromatography and mass spectrometry, respectively, conducted simultaneously with the powder diffraction measurement. Thus, the newly developed system shows potential for use as an analytical tool for performing *in situ* observations during the high-temperature synthesis and phase change processes under various gas atmospheres.

3. Automatic powder filling system for a capillary sample

The high-throughput powder diffraction system at BL02B2 enables users to collect powder diffraction patterns for several tens of capillary samples within one-day beamtime. However, the significant amount of measurement sample preparation requires considerable effort. Therefore, we have introduced an automatic powder filling system to fill powdered samples into a capillary. The automatic powder filling system has recently been developed by RIKEN and the trial operation was

performed by JASRI.

Figure 2 exhibits the photograph of the automatic powder filling system that fills powder into a capillary. Users only need to complete the following three steps to perform sample preparation for powder diffraction measurements.

1. Fill powdered samples into a commercial sample bottle (2 mL) having a cap with a small hole of 0.3–0.5 mm in diameter. Place the sample bottle into a dedicated aluminum container and position it at the sample bottle table.
2. Place capillaries on the designated capillary table.
3. Create a sequence of powder filling conditions to operate the automatic powder filling system.

The process of automatic powder filling is briefly explained below. By shaking the sample bottle multiple times, an appropriate quantity of powder is ejected from the sample bottle into the capillary. Vertical oscillation and ultrasonic vibration of the capillary are employed to achieve efficient powder filling. Image recognition, facilitated by a camera, confirms the status of powder filling and automatically assesses whether further powder filling is necessary. The average powder filling time per sample is around 5 minutes, with variations depending on the sample and capillary diameter. It is possible to set up to 30 sample bottles and capillaries simultaneously. Recently, the trial operation of the automatic powder filling system has started.

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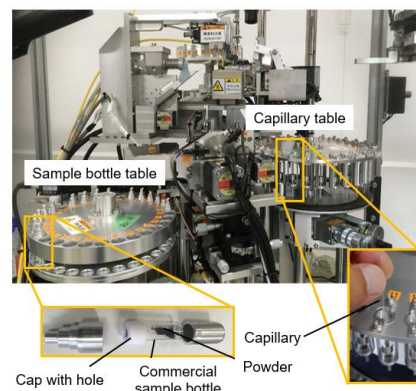


Fig. 2. Photograph of the automatic sample preparation system to fill powder into a capillary.

References:

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