High-throughput and high-resolution powder X-ray diffractometer with innovative automation system

Powder X-ray diffraction plays an essential role in material characterization and is important in the fields of material science and engineering. When combined with synchrotron radiation sources, it enables a high angular and temporal resolution across a wide Q range in a significantly reduced time. Consequently, several synchrotron facilities worldwide have dedicated powder diffraction beamlines. SPring-8 BL02B2 beamline has been in operation since 1999 and has contributed significantly to material research by utilizing a two-dimensional (2D) imaging plate detector for accurate data collection and charge density studies [1]. In the 2010s, six sets of one-dimensional (1D) Si microstrip MYTHEN detectors were introduced into a powder diffractometer [2] to meet the requirements for *in situ* measurements under various sample conditions. This allows for faster and more automated data collection by rapidly collecting the whole powder pattern with a high angular resolution [3].

Recent trends indicate that user needs are becoming even more diverse, and the following issues remain to be addressed to meet a wider range of user needs: (i) the Q range ($Q = 4\pi\sin\theta/\lambda$) needs to be wider than 20 Å^{-1} to investigate partially disordered materials; (ii) rapid *in situ* experiments require measurement times shorter than 1 s, and a highly automated measurement system capable of acquiring large amounts of diffraction data is needed to accelerate high-throughput measurements; and (iii) sample environments larger than 100 mm^3 should be available for *operando* experiments. To overcome these challenges, we installed a new powder diffractometer at the ID beamline SPring-8 **BL13XU** for highly automated and high-speed data collection, *in situ* and *operando* experiments, and data collection for pair distribution function (PDF) analysis.

Figure 1 shows the high-resolution powder diffractometer [4] developed in the third experimental hutch of BL13XU. The diffractometer is equipped with six sets of 2D CdTe detectors (LAMBDA 750k, X-Spectrum GmbH), and it is possible to acquire data with high detection efficiency even for high-energy X-rays. Three scan modes (standard, single-step, and high-resolution) were developed. In the standard scan, data with Q-values exceeding 20 Å^{-1} at 35 keV can be acquired in tens of seconds. In the high-resolution mode, measurements with a full width at half maximum of less than 0.01° can be acquired at low 2θ angles. In single-step mode, in which multiple detectors are asymmetrically arranged in the positive and negative 2θ directions, continuous data acquisition in milliseconds is possible. Capillary samples can be set on a 6-axis spinner, which can rotate at speeds of up to 200 rpm. Small *in situ* cells can also be mounted on the spinner. In addition to these measurement systems, we developed various automation systems. A maximum 100 powder capillary samples can be mounted on the sample changer. This allows capillary alignment by image recognition in addition to automatic sample exchange. A fully automatic system using a combination of temperature control nitrogen gas blowers and a robotic sample changer allows automatic measurements in the temperature range from 90 K to 1100 K in a short time. This sample changer is mounted on an automatic equipment switching system and can be automatically inserted in front of the diffractometer. The switching system is also equipped with a large sample table that can accommodate a maximum weight of 500 kg and

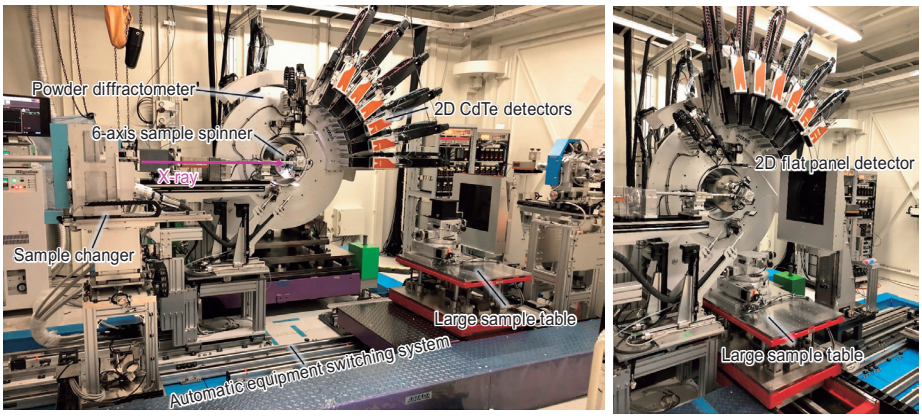

Fig. 1. Photographs of the high-resolution powder diffractometer equipped with six sets of 2D CdTe detectors and various automation systems at the third experimental hutch of BL13XU.

more than 1 m of external equipment. This provides a large sample space and allows for the development of a variety of *in situ* and *operando* experiments. Automatic measurements using a sample changer and *in situ* measurements using a large sample table can be easily switched on a PC. In addition, the alignments of the sample changer and the table are automatically adjusted with reference to the diffractometer position.

The powder diffraction data for the NIST LaB_6 sample, measured using a high-resolution powder diffractometer, are shown in Fig. 2(a). High-energy X-rays of 60 keV were used for measurements in the standard scan mode. To facilitate the observation of the peaks in the high-Q region, the sample was cooled to 100 K using a cryostream nitrogen gas blower. Diffraction data over Q = 30 Å^{-1} were obtained, as shown in Fig. 2(b). The inset shows the data averaged over six repetitions of the same scan to compare intensities at high angles. By repeating the scans, a weak peak 4–5 orders of magnitude below the most intense peak was detected, even in the $Q \sim 30$ Å^{-1} region. The statistical quality of the high-angle data was enhanced owing to the amplified X-ray flux from the ID source and the improved detection efficiency of the 2D CdTe detectors. Thus, this diffractometer enables the rapid measurement of diffraction and scattering data up to the high-Q region, facilitating active research on nanoparticles and crystalline materials using Rietveld refinement and PDF analysis. The results of the crystal structure analysis based on the powder diffraction data measured in milliseconds are shown in Fig. 2(b). The CeO_2 data were measured using a single-step mode with 35 keV X-rays. The acquisition time was 2 ms. Rietveld refinement yielded an R_B value of approximately 3%, and the isotropic atomic displacement parameters could be refined. These results demonstrate the potential for visualizing continuous changes in the crystal structure on a millisecond timescale. The single-step mode provides continuous data acquisition within milliseconds. Although the measurable 2θ range is narrower than that of standard scanning, a sufficient Q range can be obtained even with high-energy X-rays such as 35 keV and 60 keV. Using this method, time-resolved experiments are frequently performed to observe the synthesis process of a large number of samples, structural changes under rapid temperature changes, gas adsorption, and reaction processes.

In summary, a high-throughput and high-resolution powder diffraction system was developed at the third experimental hutch of BL13XU. The system is equipped with six sets of 2D CdTe detectors for high-energy X-rays (16–72 keV), and includes automation systems for switching between large sample environments. This supports the Rietveld refinement and PDF analysis of the data collected under ambient and non-ambient conditions. Three scan modes—standard, single-step, and high-resolution—have been established with the ability to measure whole powder patterns at millisecond resolution and achieve high-Q data (exceeding 30 Å^{-1}) within seconds. This capability is expected to significantly contribute to new research using machine learning and artificial intelligence by leveraging the large amount of data obtained from high-throughput measurements. In addition, millisecond time-resolved powder diffraction measurements are required to elucidate the crystal structures of various chemical reactions and synthetic processes.

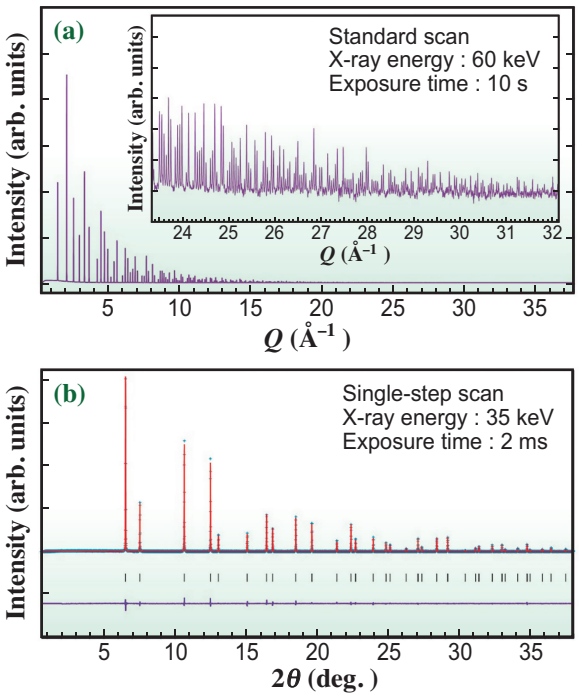

Fig. 2. **(a)** Powder diffraction pattern of NIST LaB_6 using the standard scan mode. **(b)** Rietveld refinements of NIST CeO_2 powder data obtained in the single-step scan mode.

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