Development of a synchrotron powder diffractometer with a one-dimensional X-ray detector for analysis of advanced materials

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1 Introduction

Crystallographic information obtained by powder X-ray diffraction is basic information for search and development of materials with new functions or better properties. We often try to synthesize new materials varying chemical composition of starting materials or synthetic procedures and try to determine crystal structure of the products. Such investigations may reveal relation between material properties and crystallographic information. However, the investigation usually requires accumulation of a large quantity of powder diffraction data of the products. Powder X-ray diffraction experiments with high-efficiency is required for material development.

The Powder diffraction has been a basic application of synchrotron radiation. Many powder diffractometers have been constructed from an early stage of synchrotron radiation utilization. However, traditional type $\theta$–$2\theta$ scanning powder diffractometers were confronted with a problem of increase of measurement time. Low divergence of synchrotron radiation made the width of the diffraction peaks narrow. The narrow peak forced to make step scan width extremely fine and the fine steps causes the increase of measurement time.

In order to solve the problem, many types of synchrotron powder diffractometers were developed. One approach was $2\theta$ scanning by a multiple detector system (MDS). The MDS enabled to decrease measurement time by simultaneous data collection using several sets of an analyzer monochromator and a point detector. Further, in order to achieve more rapid data collection including time resolved measurement, MDS equipping several one-dimensional detectors instead of point detectors were developed recently. Another approach was use of area detectors. Especially, Debye–Scherrer cameras using an imaging plate (IP) have been the most successful apparatus for synchrotron powder diffraction. These Debye–Scherrer cameras not only reduced measurement time, but also expanded the application of powder diffraction to electron density analysis by maximum entropy method or in situ experiments under extreme conditions.

The disadvantage of IP cameras is the interruption of measurement sequence by the IP readout process due to limitation of IP size and the number of diffraction images recorded on it. Hence, we have examined possibilities of a full-automatic powder diffraction data collection system by applying a one-dimensional X-ray detector instead of an IP to the IP camera of BL15XU at SPring-8. The new diffractometer with a one-dimensional X-ray detector was successfully developed for the purpose of full-automatic powder diffraction experiments with high angular resolution and rapid data collection.

2 Synchrotron powder diffractometer with a one-dimensional X-ray detector

The new diffractometer was constructed by modifying the IP Debye–Scherrer camera of BL15XU, an insertion device beamline of the National Institute for Materials Science (NIMS) at SPring-8, a 3rd generation synchrotron radiation facility in Japan. A silicon semiconductor one-dimensional X-ray detector, Mythen, produced by Dectris Co. of Swiss was applied for the detector. The one-dimensional detector was set on the $2\theta$ arm of the BL15XU’s diffractometer where the sample-to-detector distance would be 955 mm. Detector surface size was $64 \times 8$ mm$^2$ and the long side was set parallel to the $2\theta$ direction.
(Fig. 1). The surface size of 64 mm corresponded to 3.84 degrees in 2θ for the sample-to-detector distance. The surface with 64 mm was divided into 1280 channels, thus size of one pixel was 0.05 x 8 mm² and the minimum interval of 2θ was approximately 0.003 degrees. The sample-to-detector distance and the minimum 2θ interval were designed to be equal to that of the IP camera. Table 1 summarizes the features of the diffractometer with a one-dimensional X-ray detector.

Due to the limitation of 2θ measurement area, several times of exposure at every 2θ angle by step scanning were required to collect a whole powder diffraction pattern. The collection procedure was similar to that of the IP camera developed at BL15XU. A sample exchanger and a position adjusting mechanism had been prepared for automatic data collection in advance. The whole diffractometer system including the sample exchanger, the sample position adjusting mechanism, the diffractometer axes and the one-dimensional detector, was controlled in a sequential measurement procedure by an originally developed measurement program. Full-automatic synchrotron powder diffraction data collection was achieved successfully.

3. Experimental

Powder diffraction experiments were conducted in order to examine performance of the new diffractometer and origin of measurement errors. The synchrotron radiation X-rays provided by the undulator of BL15XU were monochromatized to X-rays with a wavelength of 0.065298 nm by a liquid-nitrogen cooling Si(111) double crystal monochromator. An X-ray total-reflecting double-mirror system reduced the higher-harmonics in the X-rays. Beam focusing was not applied. The beam size at sample position was 0.5(h) x 0.8(v) mm². NIST CeO2 standard powder stuffed into a Lindemann glass capillary with a diameter of 0.1 mm was used. Powder diffraction data were collected by 2θ step scanning with an interval of 3.5 degrees. The diffraction data up to 60 degrees were collected and required number of steps was 18. Diffraction intensity data was accumulated for 4 s at every step.

The collected data was merged and corrected by an originally developed program. The details of the correction are stated in a later section. Diffraction peak profiles and angular resolution were compared with that of the IP camera of BL15XU. Further, diffraction intensity data quality for crystal structure refinement was evaluated by Rietveld analysis.

4. Results and discussions

4.1 Origin of measurement errors

The examinations of the origins of measurement errors of the new diffractometer revealed that the following factors strongly affected measurement errors;

(1) Effect of flat detector surface
(2) Deviation of detector center (Pv-Pc)
(3) Sample-to-detector distance (r)
(4) Deviation of 2θ rotation center from sample position
(5) Anomalous counting near detector edges
(6) Decrease of intensity by a shadow of a detector frame

The symbols in this section are shown in Fig. 2.

The factors through (1) to (4) were mainly related to 2θ angle error. The flat detector surface of Mythen affected the 2θ angle. The effect could be calculated geometrically without approximation. Observed peak position, 2θobs, is given by the following formula.

$$2\theta_{\text{obs}} = 2\theta + \psi = 2\theta + \tan^{-1}(Px - Pv) \times Ps/r$$

2θ: 2θ angle for measurement, Px: diffraction peak position on the detector surface, Pv: Foot of a perpendicular line from the

Table 1. Feature of the new synchrotron powder diffractometer with a one-dimensional detector

| Feature                                | Specification                  |
|----------------------------------------|--------------------------------|
| Diffractometer                         | Debye-Scherrer Geometry        |
| Sample-to-detector length              | 955 mm                         |
| Number of samples in a pallet          | 50                             |
| Detector                               | One dimensional type (Mythen)   |
| Energy range                           | 5-30 keV                       |
| Quantum efficiency                     | 5 keV:90%, 8 keV:96%, 15 keV:49%, 30 keV:8% |
| Dynamic range                          | 24 bit                         |
| Counting rate (8 keV)                  | $2 \times 10^3$/cps/strip      |
| Readout time                           | 0.3 msec                       |
| Size                                    | $64 \times 8$ mm²              |
| Number of channel                      | 1280                           |
| Pixel size                             | 0.05 x 8 mm²                   |
| Minimum 2θ step                        | 0.003 deg                      |
| Width in 2θ                            | 3.84 deg                       |
sample to the detector surface, $Ps$: one pixel size of the detector, $r$: sample-to-detector length. $Pv$ was determined experimentally by comparing observed and calculated diffraction peak positions of NIST-CeO$_2$ standard powder.

The sample-to-detector distance($r$) and the deviation of 2$\theta$ rotation center from sample position were estimated by the peak position difference of NIST-CeO$_2$ standard powder between observation and calculation, which was the same procedure used for the IP camera of BL15XU.9)

The factors (5) and (6) effected diffraction intensity measurements. Anomalous counting, which supposed to be caused by detector edge effect, was observed near both edges of the detector (Fig. 3). The observed intensity within about 10 pixels from detector edge was enhanced 30–40%. Decrease of X-ray intensity around the lower 2$\theta$ edge of the detector was observed. The shadow of the supporting frame of the detector reduced X-ray intensities [Fig. 1(b)]. To avoid these effects to the intensity, we simply cut off intensity data of 30 pixels from both edges of the detector. Thus, only the intensity data of 1220 pixels in the center region of the detector was applied as diffraction data. Less effect of other factors, such as difference of distance of sample-to-detector surface (ex. OPx-OPv), difference of incident angle to detector surface ($\beta$) etc, were observed. After corrections of those factors, the powder diffraction data were applied for further crystallographic analysis.

### 4.2 Diffraction peak profiles and angular resolution

Diffraction peak profile and angular resolution of the new diffractometer were compared with those of the IP camera of BL15XU. The diffraction peak profiles of the new diffractometer and the IP camera almost coincided each other [Fig. 4(a)]. The calculated $\Delta d/d$ values for all 2$\theta$ regions were also equivalent [Fig. 4(b)]. No significant difference of peak profile and angular resolution was observed between the new diffractometer and the IP camera, as the sample-to-detector distance and the minimum 2$\theta$ interval of these apparatuses are equivalent. Powder diffractometer with multiple one-dimensional detectors have already been developed at Swiss light source5) and Australian Synchrotron.5) The diffractometers of Swiss light source and Australian Synchrotron can measure diffraction data up to 126 and 80 degrees in 2$\theta$ simultaneously and have advantage in rapid measurement and in situ time resolve diffraction experiments. On the other hand, sample-to-detector distances of those diffractometers are 760 and 720 mm and the minimum 2$\theta$ step size were 0.037 and 0.04 degrees. Those of the new diffractometer developed at BL15XU were 955 mm and 0.003 degrees and has advantage in angular resolution.

### 4.3 Result of Rietveld analysis

Intensity data quality of the new diffractometer for crystal structure analysis was examined by Rietveld refinement of NIST-CeO$_2$. Figure 5 shows the results of the Rietveld analysis. Table 2 shows the final atomic coordination parameters and reliable factors. The parameters were converged to the proper

![Fig. 3.](image1) Anomalous counting of the one-dimensional detector, Mythen, at detector edges. In several pixels near the detector edges, observed intensities were enhanced.

![Fig. 4.](image2) (a) Diffraction peak profiles and (b) observed $\Delta d/d$ values of NIST-CeO$_2$ powder obtained by a one-dimensional detector and an IP. Peak profile and angular resolution of both detectors were equivalent.

![Fig. 5.](image3) Results of Rietveld analysis of NIST-CeO$_2$ powder obtained by the diffractometer with a one-dimensional detector. Atomic coordination parameters converged to the proper values. Gray circle, black line, vertical bar and gray line presents observed intensity, calculated intensity, peak position and error, respectively.

| site | x  | y  | z  | $R_{int}(\text{Å})$ |
|------|----|----|----|-------------------|
| Ce   | 0  | 0  | 0  | 0.335(1)         |
| O    | 0.25 | 0.25 | 0.25 | 0.514(8)         |

$R_{wp} = 4.35\%$, $R_p = 3.21\%$, $R_B = 1.32\%$, $R_F = 1.34\%$, $S = 1.45$. 

Table 2. Results of Rietveld analysis using NIST CeO$_2$ diffraction data obtained by the diffractometer with a one-dimensional detector.
values. The result shows that the powder diffraction data obtained by the new diffractometer has enough quality for crystal structure refinement by Rietveld method.

4.4 Measurement efficiency

Calculated measurement time of the new diffractometer was compared with other cases. The calculation was performed for the diffractometer with one, two and four one-dimensional detectors and the IP camera. According to the number of detectors, the number of minimum steps for the measurements was presumed. Measurement range and movement time for 2θ were assumed to be from 0 to 60 degrees and 5 s per one movement, respectively. Readout time of the IP was not taken into account. The results are shown in Fig. 6. The diffractometer with a one-dimensional detector required approximately six times longer measurement time than that of the IP camera. It is obvious that the number of exposures was dominant for the measurement time. The present measurement efficiency of the diffractometer with a one-dimensional detector is not so high. Therefore simultaneous measurement with many one-dimensional detectors is essential for efficient diffraction data collection.

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Fig. 6. Simulation of measurement time of diffractometers with one-dimensional detectors and the comparison with the IP camera. The diffractometer with a one-dimensional detector required approximately six times longer measurement time than that of the IP camera.