MULTIPLE-DETECTOR SYSTEM FOR POWDER DIFFRACTION USING SYNCHROTRON RADIATION

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ABSTRACT

A multiple-detector system for powder diffraction using synchrotron radiation was built and has been operated at the Photon Factory in Tsukuba since May, 1995. The optics design is based on a flat-specimen-reflection geometry using parallel-beam, and the intensity data are collected by using asymmetric 2θ-step-scanning at a fixed incident angle. The multiple-detector system makes it possible to collect the high-resolution diffraction data in a moderate data collection time of 4 to 7 hours per sample. The performance of the detector system and some applications to Rietveld structure refinement are described.

INTRODUCTION

The use of high-resolution diffraction data becomes more and more important in structure analysis using powder data. The success in ab initio structure determination depends on the number of reflections decomposed without a constraint such as of equipartition\(^1\). The accuracy of structure refinement can be improved by the use of high-resolution diffraction data\(^2\). The synchrotron radiation light source makes it possible to use high-resolution powder diffraction data, which is superior in both resolution and signal-to-noise ratio to laboratory X-ray sources\(^3\), while the problem of intolerably long scan times has arisen\(^4\). A simple calculation will derive a scan time, for example, of 39 hours for a single arm scan in the 2θ range of 140° at a step interval of 0.002° and fixed counting time of only 1s in addition to 1s for moving the counter to the next step. The number of researchers who like to use synchrotron radiation facilities for powder diffraction experiments is increasing, while the chance and time of available machine time is limited. The problem is expected to become more and more serious with growing recognition of advantages of high-resolution powder diffraction data in structure analysis. One- or two-dimensional detector systems like position-sensitive detectors or imaging plates can be used as the means of fast data collection. A Debye-Scherrer transmission geometry
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using capillary specimens is adopted in these detectors. On the other hand, a single arm scan has long been used in a flat-specimen reflection geometry for laboratory X-rays and synchrotron radiation. The multiple-detector system (hereafter called MDS) in a flat specimen-reflection geometry was first introduced to the Photon Factory in Tsukuba, and has been tested and operated since May, 1995. In the present report, some characteristic features and applications to Rietveld structure refinements of the MDS are described.

INSTRUMENTATION

Design concepts

A multiple-detector scanning in a flat-specimen reflection geometry was realized by using the asymmetric 2θ scan technique at a fixed incident angle. A notable feature of parallel-beam geometry is that the diffraction profile is not degraded even with a glancing incidence of the X-ray beam onto a flat specimen. Thus a number of detectors can be set and operated simultaneously. On the other hand, only one detector can be operated at a focusing point in a para-focusing geometry.

There were two possible choices for the analyzer: a crystal analyzer or long horizontal parallel slits. The former is superior in angular resolution and signal-to-noise ratio while the latter in diffracted intensity. A great advantage of the latter, in particular for building the MDS, is that there is no need to make alignment each time when changing wavelength. Five Ge (111) flat crystals were, however, used as the analyzer for reasons: 1) the importance was put on high-resolution and 2) the high uniformity in efficiency that would be obtainable in preparing a set of analyzers. They were mounted on respective detector arms together with Soller slits with an angular aperture of 2° and a scintillation counter (Fig. 1).

The analyzer crystals were contained in steel

Fig. 1. Multiple-detector system (MDS) and multi-purpose detector arm (MPA).
boxes in order to avoid interference among the adjacent counters. The detector arms are radially set at acute angles of 25°. The rotation of MDS by 25° in 2θ can measure the intensity of the whole pattern in the 2θ range of 125°.

The sixth long detector arm (MPA) at the right corner of Fig. 1 can be used for a multi purpose. Various kinds of analyzers can be attached on the MPA for general user experiments.

The diffractometer is described in detail in reference 5.

Experimental station
The diffractometer was installed at the BL-4B2 experimental station at the Photon Factory in Tsukuba. This beam line was reconstructed in the summer of 1995. The present beam-line consists of a bending magnet light source (positron with energy of 2.5GeV and beam current of 360 to 260mA), water-cooled double-crystal Si(111) monochromator at 17m from a light source, a Rh-coated Si mirror at 18m, and the diffractometer with a sample position at 29.5m.

SOME CHARACTERISTICS OF THE MDS

Angular resolution and profile shape

Fig. 2 shows fitting results for the (111) reflections from Si powder measured with the MDS in asymmetric 2θ-scan using three wavelengths of 1.54, 1.0, and 0.7 Å.

$$\lambda = 1.54 \text{Å}$$

$$\lambda = 1.0 \text{Å}$$

$$\lambda = 0.7 \text{Å}$$

Fig. 2. Observed (solid squares) and calculated (solid lines) diffraction profiles of the (111) reflections from Si powder for three different wavelengths. Their differences are plotted at the bottom of the diagram.
1.0, and 0.7 Å. The observed profile shapes, fitted with the pseudo-Voigt function, were virtually symmetric except for the case of 0.7 Å, in which the axial divergence at low 2θ angle is pronounced. The formulas for the full-width at half-maximum (FWHM), which were least-squares fitted to the observed data, were: 

\[ H(2θ) = (0.00142 \times \tan^2 2θ - 0.00042 \times \tan 0 + 0.00056)^{1/2} \]

and

\[ H(2θ) = (0.00187 \times \tan^2 2θ - 0.00059 \times \tan 0 + 0.00054)^{1/2} \]

for asymmetric 2θ and symmetric θ-2θ scans, respectively, giving the minimum FWHM of 0.022°. As has been expected, the FWHM were virtually the same for both data sets obtained by the two scan modes.

Intensity

The focusing of the incident beam in both the vertical and horizontal directions at the sample position by using the mirror increased the observed diffracted intensity by factors of 3 to 6. The observed diffracted intensities for the (111) reflection from Si powder exceed 10^5 counts per s at the peak tops, where the correction is not applied to the dead-time of the counters (Fig. 2). It should be noted that the intensity in asymmetric 2θ scanning at a fixed incident angle is enhanced compared to that in the case of symmetric θ-2θ scanning^{11}.

Uniformity and reproducibility of the MDS

Five segments of the whole powder pattern are output from the MDS consisting of five detectors. They must be normalized so they look like the intensity data collected with a single detector arm. They are further combined as a single pattern for Rietveld refinement. Thus the uniformity of the intensity data collected with respective detectors is one of the points of interest. Test results using the (111) reflection from CeO₂ powder showed: the mean deviation for the integrated intensities from their average was 4.6% while that for the profile width was 1.7%. The difference between the two integrated intensities for the same detector arm, one of which was collected in one day and the other in another day, was 1.4% at the maximum and 0.6% in average, giving a good reproducibility^{5}.

Uneven intensities collected with five detectors will be partly adjusted by careful alignment of the tilt of the analyzer crystal etc. The difference in counter efficiency is, however, inevitable since, for example, the pulse-height analyzer must be tuned each time when the wavelength is changed. Therefore, they are processed in a further step by software. The five powder patterns are recorded in the 2θ-range of more than 25°. The intensity data in the overlapping region, which are common for two adjacent patterns, are used for the least-squares fitting, in which the differences in intensity, background, and 2θ-zero point are adjusted. A specially written computer program DATAPRO (the name of first version was PROESS) is now available for all data processing.

APPLICATIONS TO STRUCTURE ANALYSIS

Fig. 3 shows the diffraction patterns of Mg₂SiO₄ observed by the MDS at a fixed incident angle of 7° (λ = 1.2 Å, 2θ-range = 10°-129°, step size = 0.005°,
counting time at each step = 1s, 480 reflections, 23981 data points). Five segments of powder patterns with the common 2θ range of 7.96° were connected by using DATAPRO. The pattern in the 2θ range from 10° to 70° and that from 70° to 129° are presented with different scales to show the details of the pattern in the high angle region. A total of 480 independent reflections are present in the whole 2θ-range. The background counts are less than 25 counts/s in the high-angle region, giving a good signal-to-noise ratio. Well resolved peaks will be observed (Fig. 3). It took just 4.6 hours to collect the whole-pattern data.

We have recently started a study on the accuracy of Rietveld refinement\textsuperscript{12).}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diffraction_pattern}
\caption{Diffraction patterns of Mg$_2$SiO$_4$ observed by the MDS at a fixed incident angle of 7°. The vertical axis of the pattern in the 2θ-range from 70° to 130° is scaled up by factor of 30.}
\end{figure}
The accuracy of refined structural parameters was measured by the root-mean-square deviation ($\sigma_x$) in angstrom unit, which is defined by $\sigma_x = \sqrt{\frac{\sum (x_i - x_{\text{single}})^2}{n}}$, where $x_i$ is the positional parameters adjusted by Rietveld refinement, $x_{\text{single}}$ are those obtained by a single crystal technique, and $n$ is the number of positional parameters summed over $i$. In a present example, four sets of intensity data of Mg$_2$SiO$_4$ (11 variable positional parameters) were collected with diffractometers with different angular resolution (CuK$\alpha$, CuK$\alpha_1$, SR ($\lambda=1.54\text{Å}$), and SR ($\lambda=1.2\text{Å}$)), and two of them (SR) were measured with the MDS. Fig. 4 shows the plots of $\sigma_x$ against the degree of angular resolution. The improvement of the accuracy with increasing the resolution will be clearly seen, although not only the resolution but also a higher $\sin\theta/\lambda$ range will contribute to improving the $\sigma_x$ in the fourth data set.

Fig. 4. Plots of $\sigma_x$ for four data sets with different angular resolution (CuK$\alpha$, CuK$\alpha_1$, SR($\lambda=1.54\text{Å}$), and SR($\lambda=1.2\text{Å}$)) for Mg$_2$SiO$_4$.

CONCLUSIONS

Excellent cost-performances of the MDS in collecting high-resolution powder diffraction data have been demonstrated. Recently, the construction of a nine crystal multiple-detector system at the ESRF is reported. The multiple-detector system is expected to become an indispensable device in powder diffraction experiment using synchrotron radiation.

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References