# Applications of the two-dimensional detector HyPix-3000 in X-ray diffractometry

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## 1. Introduction

Various types of detectors have previously been used in X-ray diffractometers[1]. Scintillation counters (SC) have been used as zero-dimensional (0D) detectors, position-sensitive proportional counters (PSPC) and semiconductor detectors as one-dimensional (1D) detectors, and devices such as imaging plates (IP) and CCD detectors as two-dimensional (2D) detectors. IP and CCD detectors are 2D detectors still in use today, but they have problems such as slow read-out speed and narrow dynamic range, and thus their applications are limited. The HyPix-3000[2] hybrid multi-dimensional pixel detector is a 2D detector with the following features not available with IP or CCD detectors.

- Wide dynamic range
- Measurement with low background
- High-speed measurement with zero dead time
- Maintenance-free

Due to the wide dynamic range, the HyPix-3000 works advantageously in cases, such as thin-film samples, where there is a need to simultaneously measure faint diffraction peaks from the film, and strong diffraction peaks from a single-crystal substrate. Since energy resolution is high, low-background measurement is possible even with samples in which the background rises due to production of fluorescent X-rays, and it is possible to acquire measurement data with an outstanding S/N ratio. In addition, the HyPix-3000 can achieve essentially zero dead time (time loss) for data read-out. By achieving this high-speed measurement with zero dead time, it is possible to carry out continuous time-slice measurement via shutterless mode operation. For example, even in *in-situ* measurement involving heating, it is possible to conduct measurement which follows the sample's response such as transformation of crystal structure. Another feature of the HyPix-3000 is that it can be used without any need for troublesome maintenance such as the gas replacement required for gas detectors or the maintenance for the cooling equipment needed by CCD detectors.

In addition, by installing the HyPix-3000 in the SmartLab intelligent X-ray diffraction system, it can be used not only as a 2D detector, but also as a 0D and 1D detector. Therefore, there is no need to individually prepare each type of detector, as was done before, and go through the troublesome process of moving the sample to different detectors to suit the application. For this reason, a combined SmartLab-HyPix-3000 system (Fig. 1) can be used to measure a variety of samples, including powders, thin films and bulk samples. In addition, various measurement methods can be used to evaluate these samples, such as $2\theta/\theta$ measurement, and pole figure measurement employing a 2D detector. This paper introduces examples of measuring powder, single-crystal, bulk and thin-film samples by actually using this system.

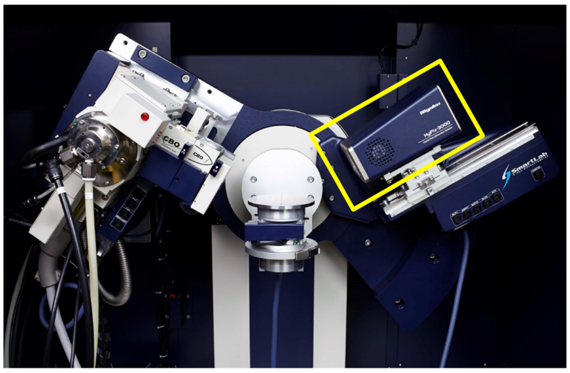

**Fig. 1.** SmartLab intelligent X-ray diffraction system equipped with HyPix-3000 hybrid multi-dimensional pixel detector.

## 2. Examples of measurement

### 2.1. The quantitative analysis by the Rietveld refinement of a mixed powder sample

Methods such as the calibration curve method and RIR method are generally used when performing quantitative analysis of crystalline phases using X-ray diffractometry. These are outstanding methods, but the former requires standard samples for the calibration curve, and both methods have the disadvantage of being difficult to apply to components which can easily exhibit a preferred orientation texture such as layered compounds or needle crystals. The Rietveld refinement[3], on the other hand, is a technique for crystal structure refinement in which analysis is carried out by fitting calculated data, created from crystal structure information, to measurement data. However, when it is applied to samples comprised of multiple phases, it is possible to obtain quantitative values for crystalline phases. In addition, this analysis technique enables correction[4] of variation in peak intensity

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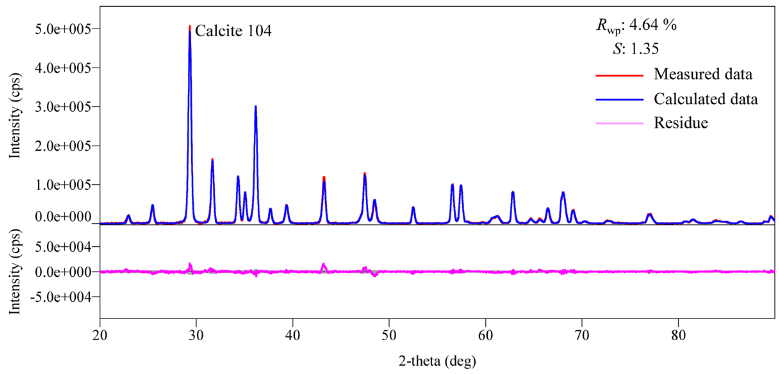


**Fig. 2.** Results of the Rietveld refinement of mixed powder sample (measurement time: approx. 10 minutes).

**Table 1.** Results of quantitative analysis by the Rietveld refinement of mixed power sample.

| Crystal phase | mass% | |
|---|---|---|
| | Preparation value | Analysis value |
| Calcite ($CaCO_3$) | 43.91 | 42.25 (15) |
| Corundum ($\alpha$-$Al_2O_3$) | 33.64 | 35.62 (17) |
| Zincite (ZnO) | 22.45 | 22.13 (7) |

Figures in parentheses indicate standard deviation.

ratio due to the effects of texture with a preferred orientation, and thus it is possible to perform analysis with higher reliability than the calibration curve method and RIR method, which both use a single diffraction peak for quantitative analysis. When performing the Rietveld refinement, it is necessary to have X-ray diffraction data with high-intensity (about 10,000 counts for the maximum diffraction peak) and a wide measurement range, and thus it has required a long time to perform measurement with conventional detectors, but the HyPix-3000 can also be used as 1D detector, and this enables acquisition of measurement data for the Rietveld refinement in a short time. In addition, the pixel size of the HyPix-3000 is an extremely small 100 $\mu$m, and as a result it is possible to achieve measurement at a high resolution on a par with the case where SC is used with a receiving slit size of 0.1 mm (=100 $\mu$m). Thus here an attempt was made to carry out measurement for approximately 10 minutes using the HyPix-3000 of a mixed powder blending 3 types of powdered raw material—calcite ($CaCO_3$), corundum ($\alpha$-$Al_2O_3$), and zincite (ZnO)—and then to conduct the Rietveld refinement of the obtained measurement data. The results of Rietveld refinement are shown in Fig. 2. The residue of the measurement data and calculated data was small, and the two matched well. Table 1 shows the results of quantitative analysis obtained through analysis. The 104 diffraction peak of calcite is known to be predominant in powder XRD profiles due to its preferred orientation texture. Therefore, the present Rietveld refinement was performed by taking into account the presence of the preferred orientation texture for calcite, where the peak intensity ratios were corrected. There was a good agreement between the preparation values and analysis values after correcting the effects of preferred orientation with the Rietveld refinement. It was thus confirmed that the HyPix-3000 in 1D mode enables a data acquisition in a short time, whose data quality is applicable to the Rietveld refinement.

## 2.2. Analysis of a stony-iron meteorite

The HyPix-3000 is a 2D detector with an effective detection area of approximately 3000 $mm^2$, and this wide area works advantageously in various types of measurement. As an example, this section describes measurement of a stony-iron meteorite[(5)]. Inside of a stony-iron meteorite, there are transparent parts which look like glass, and opaque parts which look like metal. The transparent parts were thought to be non-crystalline (amorphous). However, when measurement of the transparent part was actually performed, only one diffraction peak was observed. To carry out analysis in more detail, measurement was done in the 2D mode using the HyPix-3000. In general, when measurement is done with a 0D detector or 1D detector, the range in which diffracted X-rays can be detected is limited to a certain region. (Here, this region is the area marked with yellow broken lines in Fig. 3.) At that time, the diffraction peaks indicated with red arrows are within the scanning range, and therefore can be detected. In contrast, the diffraction peaks indicated with white arrows are observed in a region which cannot be detected with a 0D or 1D detector, and, as shown in Fig. 3, only one diffraction peak attributable to the spot indicated by the red arrow appears in the X-ray diffraction pattern. For this reason, it is difficult with this sample to detect diffraction peaks observed in the form of a spot using a 0D or 1D detector due to small detection area. On the other hand, it is possible to acquire information on multiple lattice plane, as shown in Fig. 4, by using the HyPix-3000, which has a wide effective detection area. Oscillating samples during the measurements greatly contributes for collecting information on multiple lattice planes. When the 2D diffraction image obtained in Fig. 4 was converted to a $2\theta$-I profile and qualitative analysis of the transparent

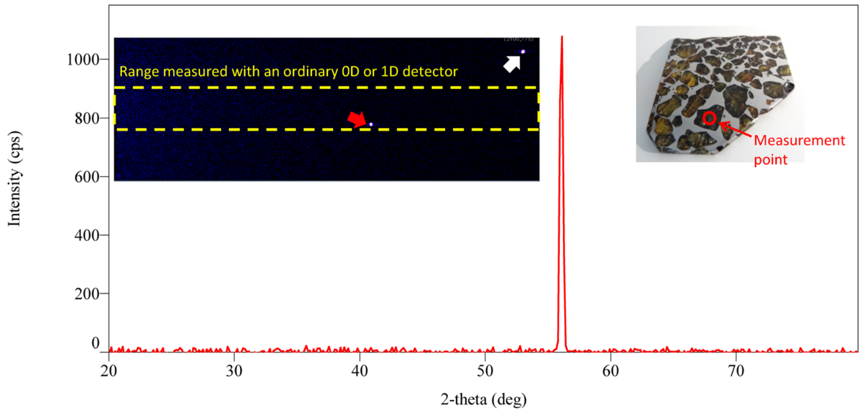


**Fig. 3.** X-ray diffraction pattern of glass-like transparent part when using a 0D or 1D detector.

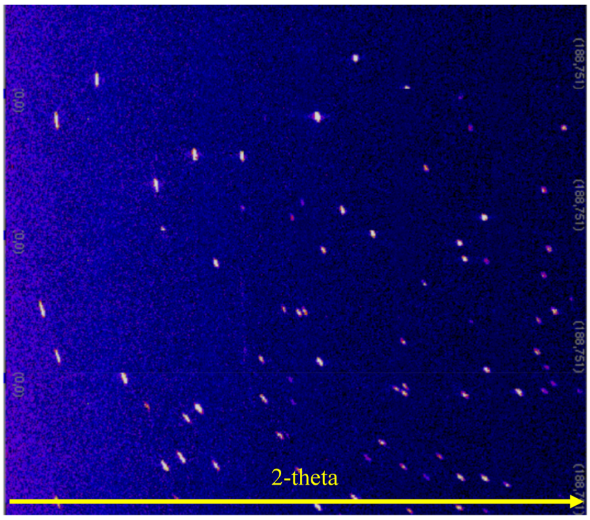


**Fig. 4.** 2D diffraction image of transparent part (with oscillation).

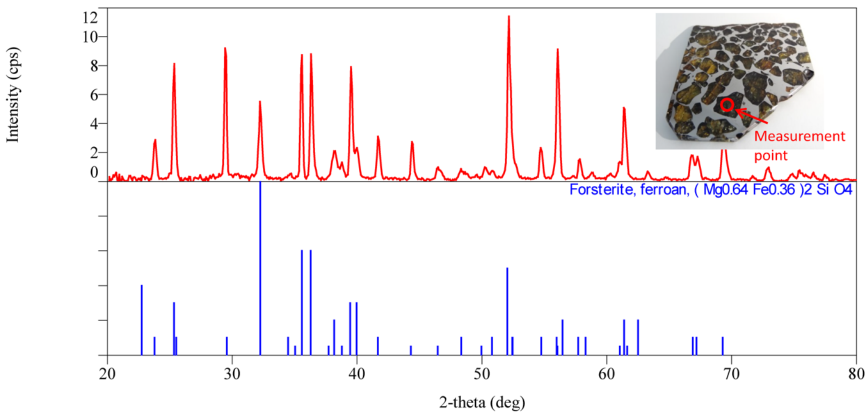


**Fig. 5.** Results of phase identification of transparent part.

part was carried out, it was possible to identify forsterite ($Mg_2SiO_4$) (Fig. 5). Since the diffraction spot were observed, it was conjectured that the glass-like transparent part is a single crystal or is comprised of an extremely small number of crystal grains.

### 2.3. Pole figure measurement of Nd magnet

In pole figure measurement[(6)], a goniometer is fixed at a diffraction angle for a certain lattice plane, and measurement is conducted by varying two parameters $\alpha$ (tilt angle of a sample) and $\beta$ (rotation angle of a sample). The crystallite orientation and distribution within the sample can be ascertained from the obtained intensity distribution. Figure 6 shows the 2D diffraction image for an Nd magnet (a sintered body of crystals, whose main components are Nd and Fe) measured at

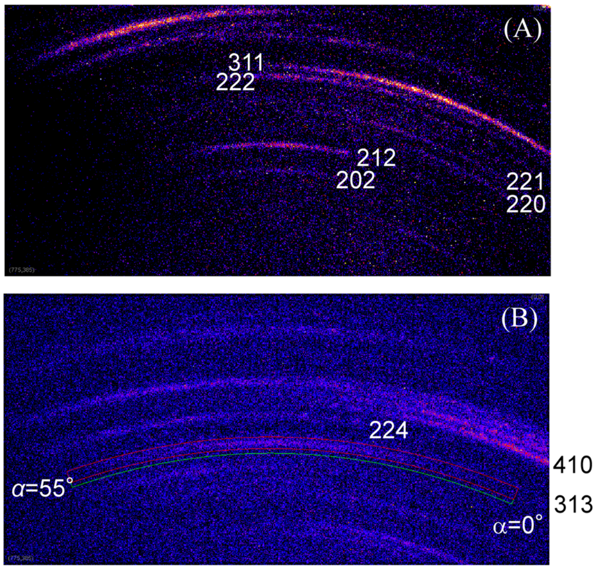


**Fig. 6.** 2D diffraction images of Nd magnet.
(A): Measured at $2\theta$=28° ($\alpha$=30°)
(B): Measured at $2\theta$=41° ($\alpha$=30°)

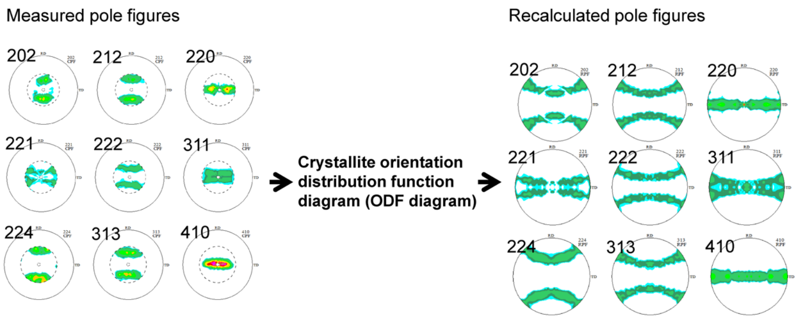


**Fig. 7.** Measured pole figures for Nd magnet (left) and recalculated pole figures by ODF analysis (right). Miller indices for reflections are shown by the number of three digits in each figure.

$2\theta$=28° ($\alpha$=30°) and $2\theta$=41° ($\alpha$=41°). From the two 2D diffraction images, it is possible to confirm that information has been acquired for a total of 9 relections: 202, 212, 220, 221, 222, 311, 224, 313, and 410. When HyPix-3000 is used as a 2D detector, data collection for multiple reflections is possible, since it covers a certain range of $2\theta_B$ (twice of Bragg angle) and $\alpha$ and $\beta$ angles in a single snapshot measurement. In contrast, if 0D detector is used for a pole figure measurement, data collections for the variations of $2\theta_B$, $\alpha$ and $\beta$ angles should be performed separately by changing these angles, thus it takes a long time(6). Pole figures for 9 reflections created from the obtained 2D diffraction images were shown in Fig. 7 (left). And the pole figures recalculated by using crystallite Orientation Distribution Function analysis (ODF analysis)(6) were shown in Fig. 7 (right). Pole figure measurements for various reflections required for ODF analysis can be done very easily and in a short time with a 2D detector.

## 2.4. Measurement of wide-area reciprocal space map for PLT thin film

Thin film materials are widely used, particularly in the field of electronic devices. Since these device performances have close correlation with physical properties of constituent materials, characterization of crystalline quality of these materials using X-ray diffraction techniques comes to be crucial. In epitaxial thin films, particularly, analysis of crystallographic orientation relationships between substrates and epitaxial films is very important. In X-ray diffractometry, crystallinity and crystallographic orientation have been evaluated using reciprocal space map measurement, but if a 0D detector is used, measurement takes as long as a few hours, and the usual approach is to evaluate by measuring only one specific reflection around out of multiple reflections. However, with this method it is often the case that, if there are unanticipated orientation domains, it is difficult to evaluate their presence.

Wide-area reciprocal space map measurement, in which a large amount of reflection information is obtained, is effective for confirming the existence of unanticipated domains, and evaluating the epitaxial orientation relation between substrates and films. In measurement using a 2D detector, diffraction angle and crystal orientation information are obtained at the same time within the image, and therefore it becomes possible to create a wide-range reciprocal space map through measurement over a short time. Here, we introduce an example of a wide-range reciprocal space map measurement applying for the characterization of a ferroelectric PLT ((Pb, La) $TiO_3$) epitaxial film. The layer structure of this sample is shown in Fig. 8.

Figure 9 shows the wide-area reciprocal space map measurement data obtained and Fig. 10 shows the results of reciprocal space simulation of orientation relationships. Since the measurement results and simulation results match perfectly, the orientation model shown in Fig. 11 explains the epitaxial orientations in this sample. In addition, looking at the Pt reflection, its reciprocal lattice point is observed in the form of a spot, and thus it is predicted that variation in crystallographic orientation (ordinarily evaluated with rocking curve width) will be extremely small. On the other hand, the diffraction signal of PLT layer grown on Pt was observed to be extended as arcs, and thus it is evident that crystallographic orientation variation is larger than Pt. A tilting mosaicity of PLT layer was evaluated as 4.5° from FWHM of the spreading of these arcs.

The 2D-TDI measurement mode[1] of the HyPix-3000 was used for measurement. Using this measurement mode enables measurement via a continuous scan even though the system is operated as a 2D detector. In order to obtain diffraction peaks of an epitaxial film or single crystal substrate with good crystallinity, it was effective to measure with this mode, in which the angle of the incident X-ray changes continuously, and it was possible to obtain wide-area reciprocal space map measurement data, like that in this case, even with measurement for only 15 minutes.

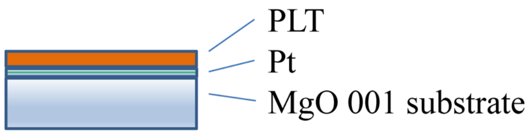


**Fig. 8.** Layer structure of epitaxial PLT film.

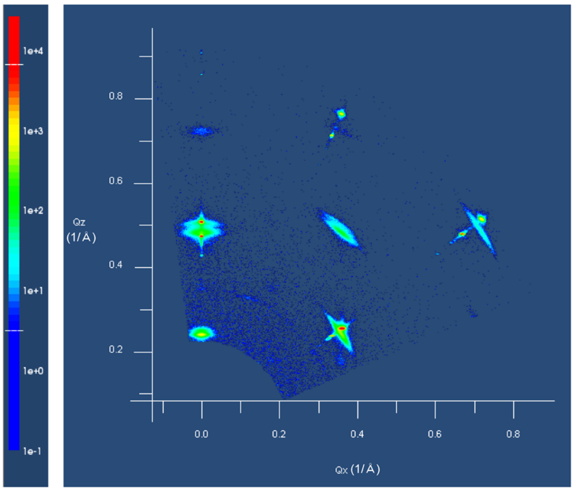


**Fig. 9.** PLT thin-film wide-area reciprocal space map obtained from measurement.

## 3. Conclusion

The HyPix-3000 functions not only as a 2D detector but also as a 0D or 1D detector, and by installing it in SmartLab, it can be used for the various types of

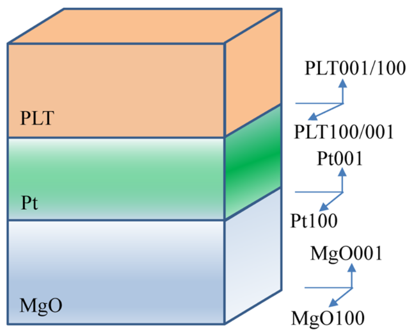


**Fig. 11.** Epitaxial orientation relationships of PLT/Pt/MgO sample.

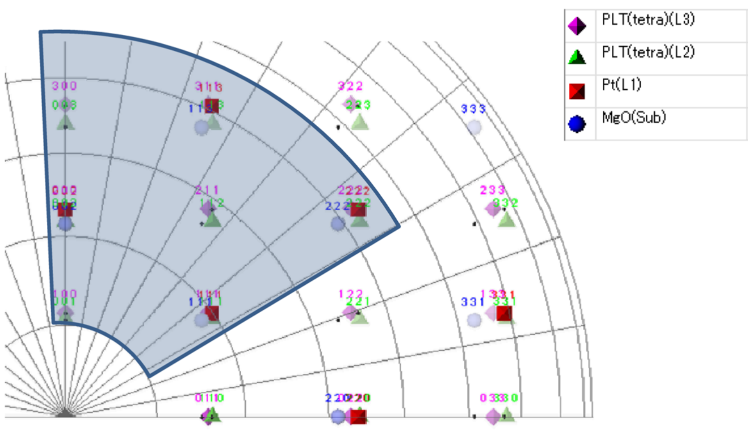


**Fig. 10.** Simulation of PLT thin-film wide-area reciprocal space map.
▷: Indicates measured range.

measurement indicated in this paper. In addition, aside from the examples of measurement in this paper, the system also enables measurement with a wide dynamic range and low background, and measurement using advantages such as high-speed measurement with no dead-time. (For examples of such measurement, see Reference (2).) In this way, using the HyPix-3000 enables measurement in a much shorter time than conventional detectors, and applications in research activities can be expected to expand going forward.

## References

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