TECHNICAL REPORT

In-house-built single-crystal anomalous X-ray diffraction measurement system using white X-rays and an energy dispersive detector

Rayko SIMURA^{1,†}, Hisanori YAMANE¹, Terutoshi SAKAKURA¹ and Kazumasa SUGIYAMA²

¹Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Aobaku, Sendai 980–8577, Japan

²Institute for Materials Research, Tohoku University (IMR), Aobaku, Sendai 980–8577, Japan

A single crystal X-ray diffraction (XRD) measurement system composed of white X-rays from an in-house X-ray generator, a four-circle diffractometer, and a compact energy dispersive detector was constructed to acquire XRD data including the effect of anomalous scattering of X-rays with selective energy. The obtained data are available for crystal structure analysis to determine the atomic positions of a specific element by the δ -synthesis method. A single crystal of $\text{Sr}_3\text{Y}(\text{BO}_3)_3$ containing neighboring elements of Sr and Y, which could not be distinguished by conventional XRD analysis, was tested to demonstrate the performance of the present system.

©2021 The Ceramic Society of Japan. All rights reserved.

Key-words : In-house-built measurement system, Anomalous X-ray scattering, Single crystal X-ray diffraction, Site occupancy, X-ray absorption edge, Elemental identification

[Received March 22, 2021; Accepted July 1, 2021]

1. Introduction

In regular X-ray crystal structure analysis, the electron density distribution is calculated by Fourier synthesis with X-ray diffraction (XRD) data, such as Miller indices (hkl) and intensities of the XRD reflections, and the phases provided from a structure model. Atomic positions (atomic sites) in a unit cell are determined at the peak positions of the electron density distribution. Similar electron density distributions of neighboring atoms mean that it is generally difficult to distinguish between the atoms of neighboring elements by regular XRD analysis. However, the phenomenon of anomalous X-ray scattering (AXS) that occurs near the X-ray absorption edge of a specific atom can be used to directly determine the atomic sites for the atom. One of the typical methods to distinguish neighboring elements by AXS is δ -synthesis, which utilizes the difference of the XRD intensities acquired by X-rays of two different energies near the absorption edge.^{1)–3)} Data collection for δ -synthesis has been performed using high intensity synchrotron radiation monochromatized with an incident monochromator.^{4)–10)} The monochromatic process of white X-rays significantly reduces the intensity of the incident X-rays. The intensity of X-rays generated with in-house X-ray equipment is lower than that of synchrotron X-rays; therefore, research reports on δ -synthesis using an in-house X-ray generator have been limited to cases with

powder XRD data measured using a two-axis diffractometer with an incident monochromator.^{5),11)}

A solid-state detector (SSD) is an energy dispersive detector, and it can detect intensities at specific X-ray energies, which makes it possible to acquire XRD intensity data at a specific X-ray energy without a significant decrease in the intensity of the incident X-rays. In previous studies, XRD intensities measured with an SSD installed at a fixed diffraction angle were plotted against the X-ray energies (energy dispersive XRD) to identify crystalline phases and to analyze crystal structures.^{12),13)} A measurement system that used a four-circle diffractometer, an SSD, and an in-house white X-ray generator with a Cr or W target was constructed by Sakamaki et al. (1980).¹⁴⁾ In this system, a 7.5 L liquid nitrogen tank was set on a metal frame above the diffractometer, and liquid nitrogen was automatically fed to the tank from a 50 L Dewar on the floor because it was necessary to cool the SSD with liquid nitrogen during measurements. This system was used to measure XRD data with AXS information at a specific energy, and the phases of the structure factors were analyzed by the Patterson map method.¹⁵⁾ Lange and Burzlaff (1992)¹⁶⁾ constructed an XRD intensity measurement system composed of a δ diffractometer (θ , ν , ω , δ), which was different from a typical four-circle diffractometer (θ , ω , χ , ϕ), and a scintillation detector of NaI(Tl) with a multi-channel analyzer (MCA). The system could measure Laue XRD intensities, excluding harmonics, for single crystal structure analysis. However, the energy resolution of the scintillation detector (ca. 660 eV full width at half

[†] Corresponding author: R. Simura; E-mail: ray@tohoku.ac.jp

maximum at 5.9 keV¹⁷⁾, which was four times larger than that of an SSD (Ge-SSD; ca. 165 eV at 5.9 keV), was not sufficient to obtain XRD data for δ -synthesis.

The silicon drift detector (SDD), a new type of SSD, was recently developed. An SDD is operated without liquid N₂ cooling and has good energy resolution (ca. 125 eV at 5.9 keV). The size of an SDD is comparable with that of typical scintillation detectors. Therefore, an SDD can be easily attached to a typical four-circle diffractometer. In the present report, an in-house-built XRD measurement system (δ -AXS measurement system) was constructed, which has made it possible to measure single-crystal XRD intensities for elemental identification by the δ -synthesis method. Sr₃Y(BO₃)₃ with neighboring elements of Sr and Y was used as a test sample, and the measurement conditions and analysis procedure are described.

2. Experimental

2.1 Single crystal δ -AXS measurement system

White X-rays radiated from a W target (Rigaku, 9407M8) on a tube-type general-purpose X-ray generator (Rigaku, CN4037, 2.0 kW) operated at 40 kV and 40 mA, an SDD (Amptek, XR-100SDD), and an MCA (Amptek, PX5) were used. The SDD was attached as a detector to a four-circle diffractometer (Rigaku, AFC7, collimator 500 μ m), and a single crystal sample was placed on the goniometer head (Huber, Goniometer Head 1004). Stepping motor controllers (Tsuji Denshi, UPM4C-01 and UPM2C-01) and stepping motor drivers (Niki Glass, NIKI-PMD-4ch and NIKI-PMD-2ch) were used for operation of the four-circle diffractometer, and to set the widths of the horizontal and vertical slits in front of the detector, respectively. A rotary solenoid driver (NIKI, NIKI-RSD) was used to control an incident X-ray shutter, and horizontal and vertical half shutters. Measurements were performed with the SPEC software (Certified Science Software). The rotation of the ϕ circle occurs in tandem with that of the χ circle ($\phi = \chi/2$); therefore, pre-processing and post-processing macro commands were added to properly control the ϕ and χ circles. The positive and negative directions of the circle axes were chosen as in Busing and Levy (1967).¹⁸⁾

As shown in **Fig. 1**, white X-rays from a W target are diffracted by a single crystal sample, and the diffracted X-rays have a certain width ΔD , in the 2θ horizontal plane [$\Delta D = R(2\theta_1 - 2\theta_2)$], where R is the diffractometer radius ($R = 235$ mm), d is the distance between adjacent lattice planes (d -spacing), and θ is the diffraction angle. For example, ΔD for $\Delta E = \pm 60$ eV ($E_1 = 16.94$ keV and $E_2 = 17.06$ keV) of an X-ray energy of $E = 17$ keV ($\lambda = 0.73$ Å), the energy of which is near the Sr K X-ray absorption edge, is $\Delta D = 0.24$ – 2.0 mm, where $d = 5$ – 0.7 Å. Therefore, a 0.24– 2.0 mm slit in front of the detector, which corresponds to a 0.03– 0.25° slit, is required. How-

Fig. 1. Schematic diagram of the δ -AXS system constructed in this study.

ever, it is possible to obtain XRD data with sufficient resolution, even with a wider slit, because the overlapping of XRD lines with different X-ray energies is eliminated by energy decomposition using the SDD. Slits of 5×5 mm were used in this study.

Zr–Cu–Ag metallic glass, which gives no Bragg peaks, was used for energy calibration of the SDD. **Figure 2(a)** shows the fluorescent X-rays of Cu, Zr, and Ag emitted from the metallic glass and the characteristic X-rays of W radiated from the X-ray tube. MCA channels were calibrated with the energies of these X-rays and a linear relation was confirmed, as shown in **Fig. 2(b)**. This relation was used to set the X-ray energy range for measurements [region of interest (ROI)].

The detection efficiency of the SDD is more than 40 % for an energy range $E = 1.1$ – 18 keV,¹⁹⁾ which corresponds to a wavelength range of $\lambda = 11.3$ – 0.69 Å. Considering the energy resolution of SDD through MCA, a shift of 3 to 4 channels of MCA, corresponding to ca. 120 eV, is necessary to separate and distinguish one energy from another. Therefore, the ROI should be set to an appropriate value for sufficient XRD intensity and energy separation for the two energies near the absorption edge of the target element. In this study, the XRD intensities were measured with ROI of which the centers were set at -190 and -70 eV from the Sr K absorption edge ($E_{\text{edge}}^{\text{Sr}} = 16.108$ keV), and the width of the ROI was 4 channels (the energy of the center for the ROI: $E_{\text{far}}^{\text{Sr}} = 15.919$ keV, $E_{\text{near}}^{\text{Sr}} = 16.037$ keV, ROI: $\delta E_{\text{far}}^{\text{Sr}} = 15.860$ – 15.980 keV, $\delta E_{\text{near}}^{\text{Sr}} = 15.975$ – 16.095 keV, as shown in **Fig. 3**). Anomalous scattering factors for the constitute elements of Sr₃Y(BO₃)₃ near the Sr K absorption edge at $E_{\text{far}}^{\text{Sr}}$ and $E_{\text{near}}^{\text{Sr}}$ are listed in **Table 1**.²⁰⁾ The difference of the real part (f'_{Sr}) of the anomalous scattering factors for Sr at $E_{\text{far}}^{\text{Sr}}$ and $E_{\text{near}}^{\text{Sr}}$, which is written as $\Delta f'_{\text{Sr}}$, is more than an order of magnitude

larger than $\Delta f'$ for Y, B, and O. The Sr distribution function in real space, ρ_{Sr} , is expressed as:

$$\rho_{\text{Sr}}(x, y, z) = \frac{1}{V} \sum_{h,k,l} \left[|F_{hkl}^{E_{\text{far}}}| e^{-i\alpha_{hkl}^{E_{\text{far}}}} - |F_{hkl}^{E_{\text{near}}}| e^{-i\alpha_{hkl}^{E_{\text{near}}}} \right] e^{-2\pi i(hx+ky+lz)}, \quad (1)$$

where the crystal structure factor $F = \sum_{j=1}^N f(Q, E) e^{2\pi i(hx_j+ky_j+lz_j)}$, atomic scattering factor $f(Q, E) = f^0(Q) + f'(E) + f''(E)$, $f^0(Q)$ is the normal atomic scattering factor, $f'(E)$ is the real part of anomalous

scattering factor, $f''(E)$ is the imaginary part of anomalous scattering factor, $Q = 2 \sin \theta / \lambda$, and E is the energy. Taking the difference between the structure factors obtained at $E_{\text{far}}^{\text{Sr}}$ and $E_{\text{near}}^{\text{Sr}}$, the energy-independent $f^0(Q)$ term is eliminated. The equation showing the distribution of Sr, $\rho_{\text{Sr}}(x, y, z)$, is calculated only from the terms related to the real-part of the anomalous scattering factor [$f'(E)$], because $\Delta f''$ is almost 0 in this case, as shown in Table 1 and Fig. 3.

2.2 Procedure for measurements and data analyses

Raw chemicals, SrCO_3 (98 %), Y_2O_3 (99.99 %), and H_3BO_3 (99.99 %), were stoichiometrically weighed, mixed in an agate mortar, and pressed to form a disk-shaped pellet. The pellet was sintered at 1250 °C for 20 h. The sintered pellet was an aggregate of colorless transparent $\text{Sr}_3\text{Y}(\text{BO}_3)_3$ single crystals of around 100 μm in size. A single crystal with a size of ca. 75 μm in diameter was separated from the aggregate, placed on the top of a glass fiber with epoxy resin, and set on the goniometer head. A conventional XRD intensity measurement was first conducted with a conventional single crystal X-ray diffractometer, a semiconductor two-dimensional detector, and Mo $K\alpha$ radiation (Bruker, D8 Quest). Software (Bruker, APEXIII) was used to determine the setting parameters (UB matrix) and unit cell parameters, acquire the crystal shape parameters (distance of a surface plane from the center and the plane index), and execute a typical crystal structure analysis.

Fig. 2. (a) MCA chart of Zr-Cu-Ag metallic glass at 40 kV, 20 mA, and $2\theta = 30^\circ$. Vertical bars in the bottom of the figure indicate the position of the characteristic X-rays of Cu, Zr, Ag, and W, (b) a linear correlation between the energies of characteristic X-rays and the channel number of MCA shown in (a). Linear regression equations are shown in the graph.

Fig. 3. Variations of anomalous scattering factors, f' and f'' , for Sr are plotted against the energy around the Sr K absorption edge (Data taken from the NIST webpage²⁸). The vertical dotted lines show the ROIs for SDD ($\Delta E_{\text{far}} = 15.8615\text{--}15.9795$ keV, $\Delta E_{\text{near}} = 15.9705\text{--}16.09795$ keV) used in this study.

Table 1. Anomalous scattering factors,²⁰⁾ f' and f'' , near the Sr K absorption edge for Sr, Y, B, and O, and differences of these factors at two energies, $\Delta f'$ and $\Delta f''$

	Energy	Sr		Y		B		O	
	keV	f'	f''	f'	f''	f'	f''	f'	f''
$E_{\text{near}}^{\text{Sr}}$	16037	−4.9334	0.5271	−2.4631	0.5885	0.0010	0.0008	0.0100	0.0074
$E_{\text{far}}^{\text{Sr}}$	15919	−3.9581	0.5343	−2.3668	0.5966	0.0010	0.0008	0.0103	0.0075
		$\Delta f'$	$\Delta f''$	$\Delta f'$	$\Delta f''$	$\Delta f'$	$\Delta f''$	$\Delta f'$	$\Delta f''$
		−0.9753	−0.0072	−0.0964	−0.0081	0.0000	0.0000	−0.0002	−0.0001

Table 2. Summary of measurements

Crystal data	
Chemical formula	Sr ₃ Y(BO ₃) ₃
M_r	1584.6
Crystal system, space group	Trigonal, $R\bar{3}$
Cell parameters, $a/\text{\AA}$, $c/\text{\AA}$	12.496 (2), 9.264 (2)
$V/\text{\AA}^3$	1252.7 (5)
Z	6
μ/mm^{-1}	12.98
Crystal size $l_{\min} \times l_{\text{ave}} \times l_{\max}/\text{mm}^3$	$0.064 \times 0.076 \times 0.078$
Data collection for ordinary crystal structure analysis	
X-ray source for structure determination	Mo $K\alpha$ X-ray bulb
Wavelength $\lambda/\text{\AA}$	0.71073
Goniometer	Bruker D8 Quest
Temperature T/K	300
Absorption correction	Multi-scan (SADABS ²⁷⁾)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10569, 646, 609
R_{int}	0.038
$(\sin \theta/\lambda)_{\max}/\text{\AA}^{-1}$	0.649
Data indices	$-16 < h < 16$, $-16 < k < 16$, $-12 < l < 12$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.056, 1.16
No. of reflections and parameters	646, 68
Weighting scheme	$w = 1/[s^2(F_o^2) + (0.0148P)^2 + 14.0415P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}/\text{e \AA}^{-3}$, $\Delta\rho_{\min}/\text{e \AA}^{-3}$	0.88, -0.91
Data collection for the δ -AXS	
X-ray source for AXS	white X-rays from W target (40 kV and 40 mA)
E_{far} (d E_{far})/keV	15.919 (15.860–15.980)
E_{near} (d E_{near})/keV	16.037 (15.975–16.095)
Goniometer	Rigaku AFC7
Temperature, T/K	300
Number of reflections (measured)	1006
Data indices	$0 < h < 8$, $-8 < k < 8$, $-8 < l < 8$
Scan mode	ω -scan
Scan width, $\Delta\omega/^\circ$	0.45
Scan step width, $\delta\omega/^\circ$	0.06
Scan step time, t/s	30

The goniometer head with the same single crystal sample was reloaded on the δ -AXS system constructed in this study. Setting parameters of the UB matrix for the δ -AXS system were refined at 0.70 $\text{\AA}$ in X-ray energy using the UB matrix obtained with APEXIII as the initial parameters of the refinement. The measurement conditions and results are summarized in **Table 2**. The δ -synthesis method was performed on the diffraction data of $I > 2\sigma(I)$ measured with the δ -AXS system. The data was corrected with the Lorentz-polarization factor, where the polarization correction factor for white X-rays from a W target is $P = 1/2 \cdot (1 + \cos^2 2\theta)$, and the Lorentz factor for a four-circle diffractometer with a single crystal is $L = 1/\sin 2\theta$. The intensity of X-rays radiated from an X-ray tube is dependent on the wavelength, which is expressed in Kramer's equation, $I(\lambda) = (k_1 i Z)/\lambda^2 \cdot (\lambda/\lambda_0 - 1)$, where I is the intensity of X-rays, λ is the wavelength, k_1 is an empirical parameter, i is the tube current, Z is the atomic number for the target material, and λ_0 is the critical wavelength. The maximum intensity difference of the incident X-rays in the energy region, 15.086–16.059 keV (0.82195–0.77215 $\text{\AA}$), is 0.4 %, and the difference at $E_{\text{far}}^{\text{Sr}}$ and $E_{\text{near}}^{\text{Sr}}$ is 0.2 % under

the tube voltage and current conditions of 40 kV and 40 mA in this study. Therefore, no correction was performed for the incident X-ray intensities. Analytical absorption correction was performed with the direction cosines¹⁸⁾ calculated with the refined UB matrix and the crystal shape parameters using the absorption correction program²¹⁾ included in PLATON²²⁾ (absorption coefficients for $E_{\text{far}}^{\text{Sr}}$ and $E_{\text{near}}^{\text{Sr}}$ are 4.751 and 4.652 mm^{-1} , respectively).

Lists of F_o and F_c with hkl (FCF files) were created from the corrected XRD intensities measured at $\delta E_{\text{far}}^{\text{Sr}}$ and $\delta E_{\text{near}}^{\text{Sr}}$ in conjunction with the unit cell parameters and atomic site positions of Sr₃Y(BO₃)₃ determined by conventional XRD analysis with the Mo $K\alpha$ data using the SHELXL-2014 program.²³⁾ The part of the AXS factor was eliminated for F_o in the FCF file output by SHELXL-2014 with the equation $F_o = |F|/|F_{\text{c}_a}| \cdot F_{\text{c}_n}$, where F is the observed structure factor, F_{c_a} is the structure factor calculated with scattering factors including AXS, and F_{c_n} is the structure factor calculated with scattering factors excluding AXS. For the δ -AXS analysis, $F_o = |F|/|F_{\text{c}_a}| \cdot F_{\text{c}_n}$ was calculated with $F_{\text{c}_n} = F_{\text{c}_a}$, where the anomalous scattering factors were set to be 0 in the instruction file of SHELXL-2014. The

crystal structure and Fourier synthesis map of $\rho_{\text{Sr}}(x, y, z)$ were drawn with the F_o lists of $\delta E_{\text{far}}^{\text{Sr}}$ and $\delta E_{\text{near}}^{\text{Sr}}$ using VESTA.²⁴⁾

3. Results and discussion

The crystal structure of $\text{Sr}_3\text{Y}(\text{BO}_3)_3$ (trigonal, space group $R\bar{3}$) has been analyzed for single crystals grown by the Czochralski method²⁵⁾ and the floating zone (FZ) method.²⁶⁾ The XRD data in the present study were indexed with hexagonal lattice parameters $a = 12.4956(3) \text{ \AA}$ and $c = 9.2644(2) \text{ \AA}$, which were almost the same as the previously reported parameters [$a = 12.527(2) \text{ \AA}$ and $c = 9.280(2) \text{ \AA}$,²⁵⁾ $a = 12.520(3) \text{ \AA}$ and $c = 9.260(2) \text{ \AA}$].²⁶⁾

In the crystal structure reported by Mączka et al. (2008),²⁵⁾ Y atoms are at $3a$ and $3b$ sites and Sr at $18f$ sites (the ordered model). On the other hand, Simura and Sugiyama (2014)²⁶⁾ analyzed the crystal structure by the δ -synthesis method with XRD data measured using synchrotron X-rays, and reported occupation of the $3a$ and $3b$ sites by Sr and Y atoms, respectively, and statistical occupation of the $18f$ site by Sr and Y atoms with occupancies of $5/6$ and $1/6$, respectively (the disordered model).

The XRD data for the $\text{Sr}_3\text{Y}(\text{BO}_3)_3$ single crystal prepared in the present study was measured with $\text{Mo } K\alpha$ and analyzed by the conventional method with anisotropic displacement parameters. The reliability indices R , for the structure refinement with the ordered and disordered models were 0.0433 and 0.0432, respectively, which indicated that the distribution of Sr and Y atoms in the structure could not be determined. In the subsequent analysis, Y atoms instead of Sr/Y were placed at all the $3a$, $3b$, and $18f$ sites, and a split site model was evaluated because the electron density distribution ellipsoid of the $3b$ site was elongated in the direction of the c axis. The $3b$ site was changed to a $6c$ site as a split site, and split sites of Y and O atoms were placed at the peak positions of the residual electron densities observed near the $\text{Sr/Y}3(18f)$, O1, O2, and O3 sites in the $F_o - F_c$ difference Fourier synthesis map. The occupancies of the original and split sites were ca. 0.8 and 0.2, respectively; therefore, they were refined with common values. The resultant occupancies were 0.801(6) and 0.199(6) and the R value of the refinement was reduced to be 0.022. The atomic arrangements around $\text{Sr/Y}1(3a)$, $\text{Sr/Y}2(6c)$, $\text{Sr/Y}3a(18f)$, and $\text{Sr/Y}3b(18f)$ are shown in Fig. 4. This model was used in the following analysis by the δ -synthesis method.

Figure 5(a) shows the three-dimensional (3D) isosurface of Sr distribution calculated using Eq. (1) with the XRD data measured by the δ -AXS system and the model described here. Sr atoms clearly appeared at $\text{Sr/Y}1(3a)$, and around $\text{Sr/Y}3a(18f)$ and $\text{Sr/Y}3b(18f)$. This Sr distribution was consistent with that of the disordered model reported for a single crystal grown by the FZ method and analyzed using the δ -synthesis with synchrotron XRD data.²⁶⁾ The ratio of occupation for Sr in $3a$ ($\text{Sr/Y}1$) and $18f$ ($\text{Sr/Y}3a + \text{Sr/Y}3b$) estimated by subtraction of an average background value from the maximum value of the Sr distribution for each site was approximately 3:10.

Fig. 4. (a) Atomic sites around $\text{Sr/Y}1$, $\text{Sr/Y}2$, $\text{Sr/Y}3a$, and $\text{Sr/Y}3b$ of $\text{Sr}_3\text{Y}(\text{BO}_3)_3$, and arrangement of the site positions with (b) large and (c) small occupancies.

Fig. 5. Isosurfaces (arbitrary unit) for Sr distribution calculated by δ -synthesis for data with a resolution of (a) $0.9 \text{ \AA}$ and (b) $1.9 \text{ \AA}$.

$\text{Sr/Y}1(3a)$ is octahedrally coordinated by six oxygen atoms at $\text{O}3a(18f)$ or $\text{O}3b(18f)$ with occupancies of 0.801(6) and 0.199(6), respectively. The distance of $\text{Sr/Y}1(3a)\text{--O}3b(18f)$ [$= 2.77(2) \text{ \AA} \times 6$] is longer than that of $\text{Sr/Y}1(3a)\text{--O}3a(18f)$ [$= 2.480(4) \text{ \AA} \times 6$] and Sr is larger than Y; therefore, the $\text{Sr/Y}1(3a)$ site was assumed to be partly occupied by Sr with the same occupancy as that of

Table 3. Atomic positions, occupations, equivalent isotropic atomic displacement parameters $U_{eq}/\text{\AA}^2$, and anisotropic displacement parameters $U_{ij}/\text{\AA}^2$

		<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Occupancy
Sr1/Y1	3 <i>a</i>	0	0	0	0.0179 (2)	0.8134/0.1866 (8)
Y2	6 <i>c</i>	0	0	0.4736 (2)	0.0224 (6)	1/2
Sr3a/Y3a	18 <i>f</i>	0.25514 (7)	0.37562 (7)	0.0238 (2)	0.0221 (2)	0.783 (2)/0.0312 (2)
Sr3b	18 <i>f</i>	0.2286 (4)	0.3514 (4)	0.0201 (6)	0.0221 (2)	0.1866 (8)
B1	18 <i>f</i>	0.0512 (4)	0.2026 (3)	0.2485 (5)	0.0202 (8)	1.0
O1a	18 <i>f</i>	0.0557 (4)	0.1762 (4)	0.3895 (4)	0.0387 (9)	0.8134 (8)
O1b	18 <i>f</i>	0.003 (2)	0.198 (2)	0.397 (2)	0.0387 (9)	0.1866 (8)
O2a	18 <i>f</i>	0.2698 (4)	0.0208 (5)	0.2034 (6)	0.042 (2)	0.8134 (8)
O2b	18 <i>f</i>	0.234 (2)	−0.016 (2)	0.155 (3)	0.042 (2)	0.1866 (8)
O3a	18 <i>f</i>	0.1265 (4)	0.1817 (4)	0.1562 (5)	0.0386 (9)	0.8134 (8)
O3b	18 <i>f</i>	0.113 (2)	0.146 (2)	0.240 (2)	0.0386 (9)	0.1866 (8)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr1/Y1	0.0153 (2)	0.0153 (2)	0.0231 (4)	0.0077 (2)	0	0
Y2	0.0161 (3)	0.0161 (3)	0.035 (2)	0.0081 (2)	0	0
Sr3a/Y3a	0.0264 (5)	0.0145 (4)	0.0196 (2)	0.0060 (3)	−0.0042 (3)	−0.0022 (3)
Sr3b	0.0264 (5)	0.0145 (4)	0.0196 (2)	0.0060 (3)	−0.0042 (3)	−0.0022 (3)
B1	0.016 (2)	0.012 (2)	0.029 (2)	0.003 (2)	−0.003 (2)	0.001 (2)
O1a	0.054 (3)	0.035 (2)	0.031 (2)	0.025 (2)	−0.006 (2)	0.005 (2)
O1b	0.054 (3)	0.035 (2)	0.031 (2)	0.025 (2)	−0.006 (2)	0.005 (2)
O2a	0.020 (2)	0.046 (3)	0.058 (3)	0.016 (2)	0.014 (2)	0.024 (2)
O2b	0.020 (2)	0.046 (3)	0.058 (3)	0.016 (2)	0.014 (2)	0.024 (2)
O3a	0.029 (2)	0.035 (2)	0.046 (2)	0.011 (2)	0.011 (2)	−0.005 (2)
O3b	0.029 (2)	0.035 (2)	0.046 (2)	0.011 (2)	0.011 (2)	−0.005 (2)

O atoms at O3b(18*f*). Based on the formula of $\text{Sr}_3\text{Y}(\text{BO}_3)_3$ with $Z = 6$, other Sr atoms of $18 - 3 \times 0.1866 = 17.4402$ are distributed at the Sr/Y3a(18*f*) and Sr/Y3b(18*f*) sites, as indicated by the δ -synthesis. The average Sr/Y3a(18*f*)–O (= 2.61 Å) and Sr/Y3b(18*f*)–O (= 2.60 Å) distances are almost the same; therefore, the occupancy ratio of Sr and Y at both sites could be constrained to be the same ratio.

Adopting the information of the Sr distribution indicated by the δ -synthesis to the split site model, the refinement was performed again with the MoK α XRD data. The Y occupancy at Sr/Y3b was set to be 0 in the final refinement because the occupancy became a small negative value within a standard deviation. The results of the atomic positions, occupancy, and displacement parameters are listed in **Table 3**. The *R* value was 0.022, which is the same as the case for the analysis with only Y, and the common occupancies for the split sites were refined to be slightly different values of 0.8134(8) and 0.1866(8). The structure formula can be expressed as $(\text{Sr}_{0.1866(8)}\text{Y}_{0.8134(8)})_{0.5}\text{Y}_{0.5}(\text{Sr}_{0.969(2)}\text{Y}_{0.0312(2)})_3(\text{BO}_3)_3$, and the ratio of occupation for Sr at 3*a* (Sr/Y1) and 18*f* (Sr/Y3a + Sr/Y3b) sites is ca. 2:10, which is consistent with the ratio of 3:10 estimated by the δ -synthesis method.

Ten days were required to measure the data with 0.9 Å resolution for calculation of the Sr distribution 3D-map shown in Fig. 5(a). A similar Sr distribution map could also be obtained with the 1.2 Å resolution data, as shown in Fig. 5(b). In this case, the measurement time was reduced to approximately 2/3, and the data could be acquired in 6 days.

In the research and development of functional ceramics, partial ion substitution is a common method for improving properties and developing new performances. The δ -AXS system constructed in this study is expected to be useful for such research using neighboring elements because the atomic positions of the introduced neighboring elements can be easily identified in the laboratory.

4. Summary

A single crystal XRD system (δ -AXS measurement system) was constructed by the combination of an in-house white X-ray generator, a four-circle diffractometer, and an energy dispersive semiconductor detector. The Sr distribution in the crystal structure of $\text{Sr}_3\text{Y}(\text{BO}_3)_3$ synthesized by solid-state reaction and grain growth was revealed by the δ -synthesis method using the XRD intensity data at two energies near the Sr absorption edge measured with the δ -AXS system. The present study demonstrated that the XRD data containing AXS phenomena for the visualization of a specific atom distribution among the atoms with similar X-ray scattering powers in a crystal can be easily available with the in-house-built laboratory equipment.

Acknowledgements Dr. T. Kawamata in Institute for Materials Research, Tohoku University is appreciated for supply of the Zr–Cu–Ag metallic glass for the energy calibration of the SDD. The authors thank Assoc. Prof. H. Okudera of Kanazawa University and Assoc. Prof. K. Shinoda of Tohoku University for fruitful discussions on controlling the AFC7 diffractometer and the in-house-built AXS system,

respectively. We are grateful to the editor and anonymous reviewers for their comments that helped us improve the manuscript. This work was supported by a Kakenhi Grant-in-Aid (No. JP18H05347) from the Japan Society for the Promotion of Science (JSPS).

References

- 1) R. Wulf, *Acta Crystallogr. A*, **46**, 681–688 (1990).
- 2) M. Wendschuhjosties, *Z. Kristallogr.*, **209**, 107–112 (1994).
- 3) J. L. Hodeau, V. Favre-Nicolin, S. Bos, H. Renevier, E. Lorenzo and J.-F. Barar, *Chem. Rev.*, **101**, 1843–1867 (2001).
- 4) R. Wulf, *Miner. Petrol.*, **52**, 187–196 (1995).
- 5) Y. Waseda, “Anomalous X-Ray Scattering for Material Characterization Atomic-Scale Structure Determination”, Springer, Berlin, Heidelberg (2002) p. 214.
- 6) K. Sugiyama, M. Genba, K. Hiraga and Y. Waseda, *J. Alloy. Compd.*, **494**, 98–101 (2010).
- 7) O. Oeckler, M. N. Schneider, F. Fahnrbauer and G. Vaughan, *Solid State Sci.*, **13**, 1157–1161 (2011).
- 8) E. Nishibori and M. Takata, *T. MRS Jap.*, **40**, 165–168 (2015).
- 9) H. Arima, Y. Tani, K. Sugiyama and A. Yoshiasa, *J. Miner. Petrol. Sci.*, **113**, 273–279 (2019).
- 10) D. Kitahara, H. Arima, T. Kawamata, K. Sugiyama and T. Mikouchi, *J. Miner. Petrol. Sci.*, **115**, 227–235 (2021).
- 11) K. Shinoda, K. Sugiyama, K. Omote and Y. Waseda, *Int. J. Soc. Mat. Eng. Res.*, **4**, 20–29 (1996).
- 12) P. Ballirano and R. Caminiti, *J. Appl. Crystallogr.*, **34**, 757–762 (2001).
- 13) G. M. Hansford, *J. Appl. Crystallogr.*, **44**, 514–525 (2011).
- 14) T. Sakamaki, S. Hosoya and T. Fukamachi, *J. Appl. Crystallogr.*, **13**, 433–437 (1980).
- 15) T. Sakamaki, S. Hosoya and T. Fukamachi, *Acta Crystallogr. A*, **36**, 183–189 (1980).
- 16) J. Lange and H. Burzlaff, *J. Appl. Crystallogr.*, **25**, 440–443 (1992).
- 17) L. Swiderski, M. Moszynski, W. Czarnacki, A. Syntfeld-Kazuch and M. Gierlik, 2006 IEEE Nuclear Science Symposium Conference Record (2006) pp. 1122–1128.
- 18) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457–464 (1967).
- 19) Amptek. Inc. Silicon Drift Detector (SDD) XR-100SDD. <https://www.amptek.com/-/media/ametkamptek/documents/products/xr-100sdd-silicon-drift-detector-sdd-specifications.pdf>.
- 20) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891–1898 (1970).
- 21) J. de Meulenaer and H. Tompa, *Acta Crystallogr.*, **19**, 1014–1018 (1965).
- 22) A. L. Spek, *Acta Crystallogr. D*, **65**, 148–155 (2009).
- 23) G. M. Sheldrick, *Acta Crystallogr. A*, **64**, 112–122 (2008).
- 24) K. Momma and F. Izumi, *J. Appl. Crystallogr.*, **44**, 1272–1276 (2011).
- 25) M. Mączka, A. Waśkowska, A. Majchrowski, J. Kisielewski, W. Szyrski and J. Hanuza, *J. Solid State Chem.*, **181**, 3211–3216 (2008).
- 26) R. Simura and K. Sugiyama, *J. Phys. Conf. Ser.*, **502**, 012028 (2014).
- 27) Bruker AXS Inc., “SMART, SAINT and SADABS”, Madison, Wisconsin, USA (1997).
- 28) NIST X-ray form factor, attenuation, and scattering tables. <https://physics.nist.gov/PhysRefData/FFast/html/form.html>.