Site Determination of Sr in Sr$_3$YB$_3$O$_9$ Crystals by Anomalous X-ray Scattering

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Abstract. The distribution of Sr in Sr$_3$YB$_3$O$_9$ crystals was determined by anomalous X-ray scattering. The Sr$_3$YB$_3$O$_9$ sample was grown by the floating-zone method in dry air. The Sr$_3$YB$_3$O$_9$ crystal has three cation sites (3a, 3b, and 18f). The results of single-crystal structural analysis using anomalous X-ray scattering at the Sr K-edge suggested that Sr is distributed at the 3a site as well as it is at the chemically disordered 18f site.

1. Introduction

Crystals of the strontium–yttrium double borate (Sr$_3$YB$_3$O$_9$ or SYB; $R^3$, $a = 1.2527(2)$ nm, $c = 0.9280(2)$ nm) doped with photogenic rare earth elements (REEs) have potential for use in laser and neutron scintillators [1-3]. A previously reported structural analysis of such SYB crystals has suggested that the crystals contain three cation sites: two Y sites at 3a and 3b and one Sr site at 18f (Fig.1). The sites at 3a and 3b are octahedrally coordinated by oxygen, and the interatomic distance in the case of Y$_{3a}$-O (0.251 nm) is greater than that for Y$_{3b}$-O (0.224 nm) [3]. The effective ionic radii of Y$^{3+}$(VI) and Sr$^{2+}$(VI) are 0.09 and 0.118 nm, respectively [4]. These values suggest the preferential distribution of Sr instead of Y at the 3a site. A single-crystal structural analysis using anomalous X-ray scattering (AXS) is necessary in order to elucidate the actual distributions of Sr and Y, which have similar atomic numbers.
2. Experimental
The SYB sample was grown by the floating-zone (FZ) method in dry air at the growth rate of 1 mm/h. Raw SrCO₃, Y₂O₃, and H₃BO₃ powders were stoichiometrically mixed and heated at 1000 °C for 24 h and then sintered to form feed/seed rods 7 mm in diameter for FZ growth.

A single crystal grain with a diameter of 50 µm was cut from the grown SYB crystal and used for single-crystal X-ray diffraction analysis. The AXS-based measurements were performed at the beamline 10 A of the Photon Factory (PF), Institute of Materials Structure Science (IMSS), High Energy Acceleration Organization (KEK), Tsukuba, Japan. The PF synchrotron was operated with a stored energy of 2.5 GeV and an electron current of 450 mA. The X-ray incident energies used for the AXS-based measurements were 16.083 keV and 15.958 keV; these values corresponded to levels 25 eV and 150 eV lower than the Sr K absorption edge (16.108 keV). The energies were tuned by using a Si(111) monochromator. The experimental setup and the data processing procedure were almost similar to those used previously [5-7]. The intensity data for sinθ/λ = 0.696 were collected for each energy using a vertical-type four-circle goniometer in the ω-scan mode. The number of reflections measured for the X-ray incident energies of 16.083 and 15.958 keV were 1278 and 1280, respectively. After averaging the equivalent reflections, 790 reflection pairs were used for the AXS-based analysis.

3. Structural analysis

3.1. R3 type A₃R₂B₃O₉ (A = Sr or Ba; R = rare earth element) crystal family

The crystal structures of the R3-type A₃R₂B₃O₉ crystal family, which includes compounds such as Ba₃DyB₃O₉ (BDB) [8], Sr₃ScB₃O₉ (SSB) [9], Ba₃YB₃O₉ (BYB) [10], and Sr₃YB₃O₉ (SYB) [3], have been reported previously (Table 1). These structures have been analyzed using two models. The first model is the "disordered" model: a divalent alkali earth element and a trivalent REE occupy the 3a and 3b sites, respectively, and the 18f site is a chemically disordered site occupied by either the alkali earth element or the REE, as in the case of BDB and BYB (i.e., 3a:3b:18f = A:R:A/R). The other model is the "ordered" model: the 3a and 3b sites are both occupied by trivalent REEs, and the 18f site is occupied solely by a divalent alkali earth element, as in the case of SSB and SYB [3] (i.e., 3a:3b:18f = R:R:A). The most important differences between these models are the valence states of the 3a site and whether the 18f site is chemically ordered or disordered. An investigation of the lengths of the bonds between the cation and the oxygen anions suggests that the 3a site may have a lower valence than that of the 3b site because the bond lengths at the 3b sites are smaller than those at the 3a sites. When the cation elements have significantly different atomic numbers, the site occupancy can be easily determined by ordinary X-ray structural analysis. However, in the case of Sr and Y, which have similar atomic numbers, the difference between the elements cannot be detected by ordinary X-ray
3.2. AXS-based X-ray diffraction of the SYB crystal

The AXS method has been described in detail in previous research [6-7]. When the X-ray diffraction intensities of the sample are measured using two different X-ray incident energies (16.083 and 15.958 keV) in the close vicinity of the absorption K-edge of Sr, the detected variation in the structural factors is attributable to the anomalous scattering terms of Sr (Δf” = 1.86, Δf’’’ = 0 [11]). This is because the anomalous dispersion effects arising from the other elements such as Y, B, and O are insignificant at these energy levels. The distribution map of Sr, ρ_Sr(x,y,z), can be obtained by following Fourier transformation:

$$\rho_{Sr}(x,y,z) = \frac{1}{V} \sum \sum \sum \{ |F_{hk,15.98keV}| e^{i\alpha_{hk,15.98keV}} - |F_{hk,16.08keV}| e^{i\alpha_{hk,16.08keV}} \} e^{-2\pi(ux+vy+wz)}$$

where V is the volume of a unit cell, |F_{hk,Ek}v| and e^{i\alpha_{hk,Ek}} are the structural factor of an absolute unit and the phase term for an hkl reflection measured at the energy E keV, respectively.

4. Results and discussion

The isosurfaces of electron density obtained by ordinary single-crystal X-ray diffraction at 15.958 keV and the isosurfaces of electron density obtained by AXS at the Sr K-edge are shown in Fig. 2. In the isosurfaces shown in Fig. 2(b), elements other than Sr are omitted by the AXS analysis, and the electron density from Sr is observed only at the 3a, 3b, and 18f sites. This implies that the disordered model is suitable for modeling the structure of SYB.

The maximum intensity in the distribution map of Sr at the 18f site was about five-sixth of that at the 3a site, suggesting that the 18f site was a mixed site of Sr and Y, the two elements present in a ratio of 5:1. Consequently, the crystal structure of SYB could be constructed using three types of coordination polyhedrons: three Sr-centered octahedrons at the 3a site, three Y-centered octahedrons at the 3b site, and eighteen Sr/Y(=5:1)-centered irregular-shaped dodecahedrons at the 18f site, together with eighteen BO₃ triangles in the unit cell.

For laser and scintillator applications, a small amount of a photogenic REE is doped in SYB. Judging from the structure of SYB determined in this study, photogenic REEs that have ionic radii greater than that of Y³⁺ (0.09 nm), such as Ce³⁺ (0.101 nm), Pr³⁺ (0.099 nm), and Nd³⁺ (0.0983 nm), among others, can be assumed to occupy the 18f site (d = 0.266 nm), which is larger, rather than the 3b site (d = 0.224 nm).
Figure 2. (a) Isosurface three-dimensional (3D) image obtained by ordinary single-crystal X-ray diffraction analysis. (b) Isosurface 3D image obtained by AXS-based analysis at the Sr K-edge. The intensity thresholds used for the isosurfaces in (a) and (b) were $5.0 \times 10^{-3}$ electron/nm$^3$ and $1.0 \times 10^{-3}$ electron/nm$^3$, respectively.

5. Conclusion

AXS-based analysis at the Sr absorption K-edge revealed clearly the location of Sr in the Sr$_3$YB$_3$O$_9$ crystal. It was found that Sr was distributed at the 3a site as well as it was at the chemically disordered 18f site. Hence, the combination of single-crystal X-ray diffraction analysis and AXS-based analysis can be considered an indispensable tool for determining the site occupancies of elements having similar atomic numbers.

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