Analysis of crystal structure for bismuth layer-structured oxides

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Introduction

Ferroelectric $SrBi_2Ta_2O_9$ (SBT), one of the promising candidate materials for nonvolatile random-access memories, has a layered structure. Thin films with compositions deviating from the stoichiometry of SBT have been extensively studied to improve ferroelectric properties. Noguchi *et al.*[1] reported that the remanent polarization (P_r) of the films with Sr-deficient and Bi-excess composition, $Sr_{0.8}Bi_{2.2}Ta_2O_9$, is larger than that of stoichiometric SBT. In spite of extensive efforts to improve the ferroelectric properties of thin films, the fundamental nature and the crystal structure of Sr-deficient and Bi-excess SBT have not yet been elucidated. This report describes the results of the structure refinement for stoichiometric SBT and $Sr_{0.73}Bi_{2.18}Ta_2O_9$ through the Rietveld analysis of synchrotron-radiation diffraction.

Experimental

Ceramic samples with nominal compositions of $SrBi_2Ta_2O_9$ (stoichiometric SBT), $SrBi_{2.04}Ta_2O_9$ (Bi-ex. SBT), $Sr_{0.73}Bi_{2.27}Ta_2O_9$ and $Sr_{0.73}Bi_{2.18}Ta_2O_9$ were prepared by the conventional solid-state reaction from ground powders of $SrCO_3$, Bi_2O_3, and Ta_2O_5 of 99.99% purity. The final sintering was performed at 1200 °C for 4 h. The samples obtained had a density of over 98 % of the theoretical density. For diffraction measurements, the calcined powder was fired at 1100 °C for 4 h to prevent grain growth and preferred orientation.

Synchrotron-radiation diffraction patterns were obtained using a powder diffractometer with a multiple-arm system at BL-4B2 of the Photon Factory in KEK[16]. The patterns obtained were analyzed by the Rietveld method (the RIETAN program) using the $A2_1am$ orthorhombic symmetry. For the values of anomalous scattering factors, f' and f'', a table calculated by Sasaki was used.

Results and Discussion

Figure 1 shows the result of the Rietveld analysis of the powder diffraction pattern. In the analysis, excess Bi was assumed to be substituted with cation vacancies at the perovskite A-site. The calculated pattern fits the observed data fairly well, confirming a single phase with SBT structure. The composition at the A-site determined by the Rietveld analysis was $(Sr_{0.73(3)}Bi_{0.18(3)} \square_{0.09})$, where $\square$ indicates cation vacancies. This analysis reveals that the charge neutrality in the crystal of $Sr_{0.73}Bi_{2.18}Ta_2O_9$ is satisfied through the substitution of Bi with cation vacancies at the A-site. Thus, these Rietveld results become direct evidence that Bi ions are substituted as *trivalent ions* with cation vacancies at the A-site [2].

In the SBT structure with the $A2_1am$ orthorhombic symmetry, the a axis is the polar axis, and constituent ions are displaced along the a axis. The spontaneous polarization (P_s) can be calculated by:

$$P_s = \Delta_i (m_i \times \Delta x_i \times Q_i e) / V, \qquad (1)$$

where m_i is the site multiplicity, Δx_i is the atomic displacement along the a axis from the corresponding position in the parent tetragonal ($I4/mmm$) structure, $Q_i e$ is the ionic charge for the ith constituent ion, and V is the volume of the unit cell. Using the formal charge (+2 for Sr, +3 for Bi, +5 for Ta, –2 for O) in the calculation, P_s of stoichiometric SBT was estimated to be 16 $\mu C/cm^2$, which agrees well with the value determined from the data on the basis of the single-crystal structure analysis performed by Rae *et al.*[5] For A-def. SBT, P_s was found from calculation to be 20 $\mu C/cm^2$ using the result of our Rietveld analysis, and this increase in P_s is consistent with our polarization hysteresis measurements shown in Fig. 3. The structural analysis indicates that the substitution of Bi with cation vacancies at the A-site enhances the intrinsic ferroelectricity of SBT.
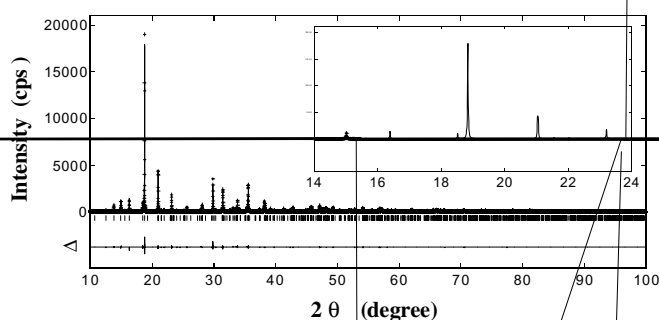

Fig. 1 Result of the Rietveld analysis of the powder synchrotron-radiation diffraction pattern for $Sr_{0.73}Bi_{2.18}Ta_2O_9$. A wavelength of 0.1 nm was used to collect the diffraction data. Δ indicates the difference between the observed and calculated values.