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Synthesis and ferroelectric properties of bismuth layer-structured $(Bi_{7-x}Sr_x)(Fe_{3-x}Ti_{3+x})O_{21}$ solid solutions

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Bismuth layer-structured $(Bi_{7-x}Sr_x)(Fe_{3-x}Ti_{3+x})O_{21}$ (BSFT) ceramics were synthesized and the ferroelectric properties and crystal structure were investigated. X-ray powder diffraction profiles and refinement of the lattice parameters indicated single phase BSFT was obtained in the composition range 0–1.5. The lattice parameter *b* of BSFT remained almost constant, while a slight decrease in the lattice parameter *a* was observed by the Sr and Ti substitution for Bi and Fe, respectively, which indicated an increase in the orthorhombicity. The dependence of the BSFT lattice parameter on temperature implied a phase transition from the orthorhombic to the tetragonal phase, which was in good agreement with the Curie temperature. The remnant polarization P_r, of BSFT was significantly improved by the Sr and Ti substitution for Bi and Fe, and ranged from 9 to 16 μC/cm^2, although no remarkable variation in the coercive field E_c was observed. As a result, a well-saturated *P*–*E* hysteresis loop of BSFT ceramic was obtained at $x=0.5$ with a P_r of 30 μC/cm at an applied voltage of 280 kV/cm.

1. Introduction

Of the variety of ferroelectric materials the Aurivillius family of Bi-containing oxides are well known materials, and are considered to be attractive candidates for commercial applications; therefore, the ferroelectric properties of these ferroelectric materials have been intensively studied to date [1–3]. The crystal structure of the Aurivillius family is described as a combination of the perovskite block of $[A_{n-1}B_nO_{3n+1}]^{2-}$ with $[Bi_2O_2]^{2+}$ layers, where *n* represents the number of perovskite blocks. The A-site in the perovskite block is occupied by mono-, di-, or trivalent cations, while the B-site in the BO_6 octahedron is typically occupied by Ti^{4+}, Nb^{5+}, Ta^{5+}, or W^{6+} cations. Recently, the ferroelectric properties of $Bi_2Bi_{n-1}(Ti,Fe)_nO_{3n+n}$ compounds in the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system have been characterized [4–6]. The crystal structures of $Bi_2Bi_{n-1}(Ti,Fe)_nO_{3n+n}$ with $n=3$, 4, 4.5, and 6 were characterized by Krzhizhanovskaya et al. [7], and they investigated the relationship between the temperature dependence of the lattice parameters and phase transitions of $n=3$, 4, 4.5, and 6 compounds by crystal structural refinement and differential thermal analysis (DTA). In particular, the crystal structure of the $Bi_7Fe_3Ti_3O_{21}$ compound ($n=6$) has been reported to be orthorhombic with a space group of *F2mm* (No. 42) and lattice parameters of $a=5.4699(3)$, $b=5.4924(3)$, and $c=57.551(3)$ Å [7]. Moreover, $Bi_7Fe_3O_{21}$ was also reported to exhibit a phase transition from orthorhombic to tetragonal at approximately 650 °C, based on variations in the lattice parameters and DTA curves. In addition to the characterization of the crystal structure of $Bi_7Fe_3Ti_3O_{21}$ (BFT) ceramic, although the temperature dependence of dielectric constant and magnetic behavior of BFT ceramic has been reported by Srinivas et al. [8], the effect of Sr and Ti substitution for Bi and Fe on ferroelectric properties and crystal structure of $(Bi_{7-x}Sr_x)(Fe_{3-x}Ti_{3+x})O_{21}$ $(0 \le x \le 1.5)$ (BSFT) solid solutions have not been clarified to date. Therefore, BSFT solid solutions were synthesized and the ferroelectric properties of these solid solutions were investigated.

2. Experimental method

$(Bi_{7-x}Sr_x)(Fe_{3-x}Ti_{3+x})O_{21}$ $(0 \le x \le 1.5)$ ceramics were prepared by the conventional solid-state reaction method. Stoichiometric amounts of high purity (99.9%) Bi_2O_3, $SrCO_3$, Fe_2O_3, and TiO_2 powders were ground in a mortar with ethanol and then heated in an alumina crucible at 700 °C for 5 h in air. The obtained powders were crushed and reground again in ethanol for 30 min. Powders mixed with 5 wt% polyvinyl alcohol as a binder were pressed into pellets of 12 mm diameter and 2 mm thickness at a pressure of 100 MPa. The pellets were sintered for 2 h at various temperatures ranging from 1000 to 1150 °C for each composition until the highest density was obtained. The sintered pellets were polished to thicknesses between 0.2 and 0.3 mm for electrical measurements and annealed at 400 °C for 2 h in air. Pt and Au electrodes were applied for measurement of the temperature

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dependence of the dielectric constant and *P*–*E* hysteresis measurement, respectively. X-ray powder diffraction (XRPD) and high-temperature-XRPD (HT-XRPD) was conducted by Rigaku RINT-2000 diffractometer using CuK$_\alpha$ radiation to characterize the crystallographic phases of the sintered samples. The lattice parameters of each compound at various temperatures were refined using the Le Bail method [9] to clarify the temperature dependence of the dielectric properties and crystal structure. XRPD profiles for refinement of the lattice parameters were obtained by step scanning in the range of 10–120° with a step size of 0.03°/step and a counting time of 5.0 s. The differential thermal analysis (DTA) was also performed to evaluate the possibility of phase transition by using Rigaku thermo plus TG-8120. The *P*–*E* hysteresis loops at 50 Hz and the temperature dependence of the dielectric constant at 1 MHz was measured using an TF analyzer 2000 (aixACCT) and precision LCR meter (Agilent 4284A). Morphological changes in the samples were investigated using field emission scanning electron microscopy (FE–SEM, JEOL JSM 6330F). The apparent density of the sintered samples was determined by the Archimedes method.

3. Results and discussion

Fig. 1 shows XRPD patterns of the BSFT ceramics sintered at optimum temperatures for 2 h in air. No XRPD peaks corresponding to the unreacted raw materials or impurity phases were detected in the composition range ($0 \le x \le 1.5$), which suggested that Sr^{2+} and Ti^{4+} cations were successfully substituted for Bi^{3+} and Fe^{3+} sites, respectively. A slight shift in the diffraction peak toward a lower angle of 2θ resulted from Sr and Ti substitution for Bi and Fe, as shown in Fig. 1. The lattice parameters of the BSFT ceramics were refined using the Le Bail method [9] to clarify the influence of Sr and Ti doping on the crystal structure of the ceramics. The variations in the lattice parameters of the BSFT ceramics are shown in Fig. 2. The refined lattice parameters of BSFT at $x=0$ were similar to those of $Bi_7Fe_3Ti_3O_{21}$ reported by Krzhizhanovskaya et al. [7]. All the lattice parameters of the BSFT ceramics varied linearly in the composition range ($0 \le x \le 1.5$), as shown in Fig. 2. Sr and Ti substitution for Bi and Fe resulted in significant variation of the lattice parameter *c* compared with that of lattice parameters *a* and *b*. The lattice parameter *b* remained almost constant, whereas the lattice parameters *a* decreased with increasing *x*. In the crystallographic data reported for $Bi_7Fe_3Ti_3O_{21}$ [7], the bismuth ions are 12-fold coordinate for the Bi(2), Bi(3), and Bi(4) sites, whereas the Fe^{3+} and Ti^{4+} cations are located within the $(Fe,Ti)O_6$ octahedra. The ionic radius of each cation in BSFT was compared to investigate the effect of Sr and Ti substitution for Bi and Fe on the lattice parameters. The ionic radius of the Sr^{2+} cation (1.44 Å) [10] is larger than that of the Bi^{3+} cation when the ionic radius of Bi^{3+} with 12-fold coordination is estimated to be 1.3 Å [11]; therefore, it is considered that Sr substitution for Bi would lead to an increase in the lattice parameters *b* and *c*. In contrast, the lattice parameter *a* decreased linearly; therefore, the ionic radii of the Fe^{3+} and Ti^{4+} cations may affect the lattice parameters *a*. According to the ionic radii of the Fe^{3+} and Ti^{4+} cations reported by Shannon [10], the ionic radius of 6-coordinate Ti^{4+} (0.605 Å) is smaller than that of the high spin Fe^{3+} cation (0.645 Å), though the low spin Fe^{3+} cation has a larger ionic radius than Ti^{4+}. Therefore, it is considered that the linear decrease in the lattice parameter *a* is due to the substitution of Fe for Ti.

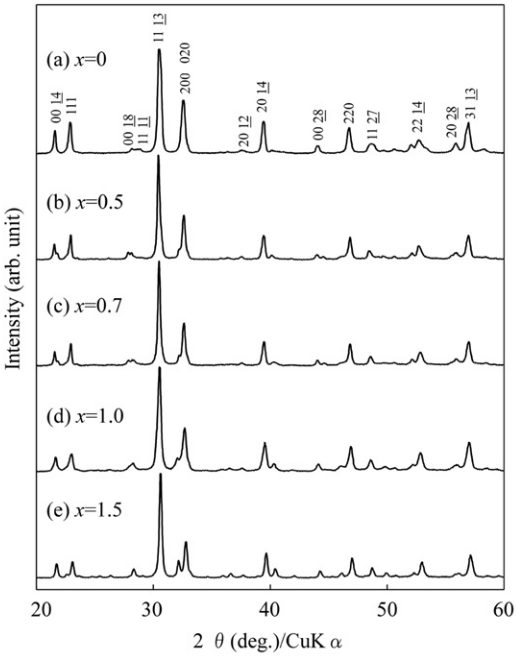

Fig. 1. XRPD profiles of BSFT ceramics sintered at optimum temperatures for 2 h in air.

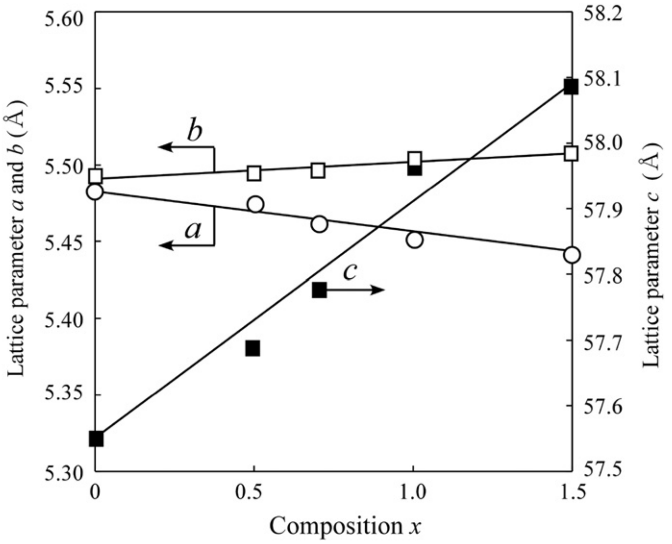

Fig. 2. Lattice parameters of $(Bi_{7-x}Sr_x)(Fe_{3-x}Ti_{3+x})O_{21}$ ($0 \le x \le 1.5$) as a function of *x*.

Such variations in the lattice parameters *a* and *b* (Fig. 2) imply an increase in the orthorhombicity of the BSFT ceramics, which is closely related to the ferroelectric properties. In order to clarify the effect of Sr and Ti substitution for Bi and Fe in the BSFT ceramics, the orthorhombicity, which is defined as $2(a-b)/(a+b)$ [12], was calculated using the obtained lattice parameters. Variations in the orthorhombicity of BSFT are listed in Table 1; the orthorhombicity of BSFT ceramics increased from 1.7×10^3 to 1.2×10^{-2} due to the variations in *a* and *b* lattice parameters. The increase in the orthorhombicity of the BSFT ceramics by Sr and Ti substitution for Bi and Fe is considered to enhance the ferroelectric properties of the ceramics, due to the close relationship of orthorhombicity and ferroelectric properties in BLSF ceramics [13].

The stability of perovskites and perovskite-related compounds have often been evaluated in terms of the ions comprising the unit cell using the tolerance factor (t), which is defined as

$$t=(r_A+r_O)/\sqrt{2}(r_B+r_O),$$

where r_A and r_B are the ionic radii of A- and B- site cations in the perovskite block, respectively, and R_O is the ionic radius of