

Growth of Lanthanum-substituted bismuth titanate single crystals and observation of their domain structure

Masayuki Soga, Yuji Noguchi, and Masaru Miyayama

Institute of Industrial Science, The University of Tokyo,
4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan.
Fax +81-3-5452-6341, e-mail: miyayama@iis.u-tokyo.ac.jp

ABSTRACT

Effects of lanthanum substitution on the structure distortion and domain structure were investigated using powder samples prepared by solid-state reaction and single crystals grown by self-flux method. With increasing La content (BLT, $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$), parameter a and unit-cell volume decreased, while parameter b and c increased. X-ray Photoelectron Spectroscopy (XPS) revealed that the La content x in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals was about twice as much as that of BLT powder used for the crystal growth. The analysis of domain structures of single crystals in the a - b plane with an optical microscope showed that $\text{BiT}(\text{Bi}_4\text{Ti}_3\text{O}_{12})$ had a striped 90-deg domain structure and the average domain width was about $8.5\mu\text{m}$. The substitution of La led to a decrease in domain size, and $\text{BLT}(x \approx 1.5)$ showed a fine domain structure with about $2.5\mu\text{m}$ domain width.

Key words: bismuth layered-structured ferroelectrics, BLT, Rietveld analysis, single crystals, domain structure

1. INTRODUCTION

Bismuth layer-structured ferroelectrics are thought to be promising materials as lead-free ferroelectric oxides for their device applications to sensors, actuators, and nonvolatile random access memories (NvRAMs). Among them, ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) has been intensively studied for use in NvRAMs because of its low coercive field, low leakage current, and excellent fatigue endurance even when in the form of thin films with Pt electrodes.^{[1]-[3]} However, the remanent polarization (P_r) of SBT is not sufficient for the high-density integration of NvRAMs, and relatively high processing temperatures prevent SBT thin films from becoming fully commercialized.

Recently, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) has attracted much attention for potential utilization of thin films for NvRAMs, due to its large spontaneous polarization (P_s).^[4] Figure 1 shows the crystal structure of BiT. The perovskite blocks composed of three TiO_6 octahedral layers with Bi at the A site are sandwiched between Bi_2O_2 layers along the c axis. The spontaneous polarization (P_s) lies along the a axis at the angle of about 5 deg with the a - b plane. The polarization measurements for BiT single crystals have revealed that the P_s value along the a axis reaches $45\text{-}50\ \mu\text{C}/\text{cm}^2$,^{[4]-[5]} which is three times as large as that of SBT^[6]. In spite of prodigious efforts to integrate BiT into device applications, the thin films^{[7]-[10]} and ceramics^[11] of BiT suffer from high leakage electric current and domain pinning due to defects, leading to a small $2P_r$ of $\sim 15\ \mu\text{C}/\text{cm}^2$. Thin films of lanthanum-substituted BiT (BLT, $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$) has been reported to have a relatively large $2P_r$.^[12] Although much effort has been paid for an improvement of thin-film properties of BLT, the fundamental nature and domain structure are not fully

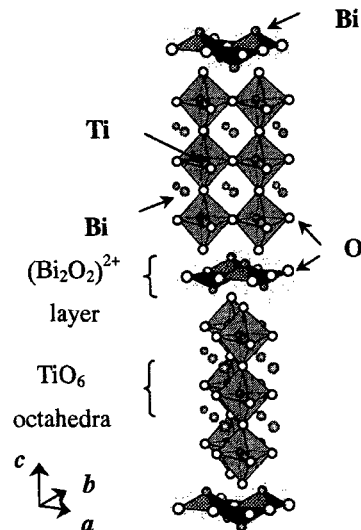


Fig.1 Crystal structure of BiT.

understood, probably because of the lack of BLT single crystals.

In this study, we grew BLT single crystals by self-flux method using BLT powder prepared by solid-state reaction. The effects of lanthanum substitution on the structure distortion and domain structure were investigated.

2. EXPERIMENTS

Powder samples of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLT(x); $x=0, 0.25, 0.50, 0.75, 1.00$) were prepared by solid-state reaction. Powders of Bi_2O_3 of 99.9999% purity and TiO_2 and La_2O_3 of 99.99% purity were mixed with the stoichiometric composition in a ball mill for 12 h. The mixed powders were calcined at

1000 °C for 10 h, crushed, and then sintered at 1000 °C for 7 h again for powder X-ray diffraction (XRD) measurements. The patterns obtained were analyzed by Rietveld method (the RIETAN2000 program^[13]) on the basis of the *B2cb* orthorhombic symmetry. Diffraction data were collected in the 2θ range of 10–120° in a step scanning mode with a step length of 0.02° and a step-counting time of 3 s.

BLT single crystals were grown from BLT ($x=0.25, 0.50, 0.75, 1.0$) powder samples by self-flux method using Bi_2O_3 of 99.9999% purity as a flux. The differential thermal analysis showed that La substitution increased the melting temperature almost linearly from 1200 °C (BiT) to 1250 °C (BLT($x=1.0$)). The BLT powder prepared by solid-state reaction was mixed with Bi_2O_3 powder as a flux at a molar ratio of 1 : 10.4. The mixture was melted in Pt crucible at the temperature just below its peritectic point by about 25 °C, and kept for 10 h, very slowly cooled to 1050 °C at a rate of 2 °C/h, slowly cooled to 900 °C at a rate of 5 °C/h. The single crystals obtained were plate-like thin sheets, with 0.2–0.3 mm thickness and approximately 10 x 10 mm² transverse dimension, the *c* axis normal to the large plane. The lanthanum content *x* in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals was determined with X-ray photoelectron spectroscopy (XPS). The domain structures in the *a*-*b* plane were investigated with an optical microscope.

3. RESULTS AND DISCUSSION

Figure 2 shows the powder XRD patterns of BiT and BLT ($x=0.25$ –1.00) obtained from powders heat-treated at 1000 °C for 7 h. For all the samples, the single phases were obtained. **Figure 3** shows the fitting results of the Rietveld analysis for BLT (0.75), assuming that all of La is randomly substituted at the A site (Bi) of the perovskite block. A good agreement was obtained between measured and calculated data, ($R_{\text{wp}} = 14.98\%$, $S = 1.24$). Osada *et al.*^[14] reported through the Raman spectroscopy that for BLT with *x* over 0.75 La began to occupy at the Bi site in Bi_2O_2 layers as well as the A site. However, our Rietveld analysis did not indicate a partial substitution of La at the Bi site in Bi_2O_2 layers

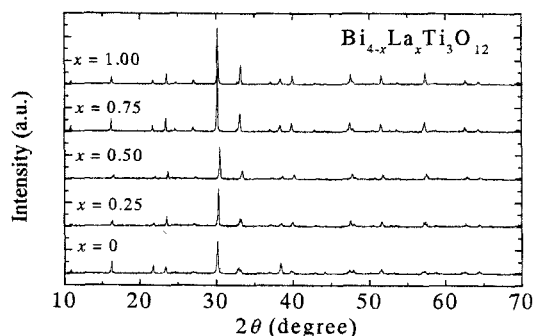


Fig.2 XRD patterns of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ powder prepared by solid-state reaction.

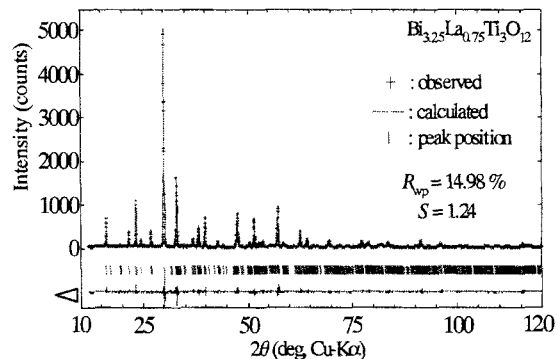


Fig.3 Fitting result of Rietveld analysis of powder XRD pattern of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x = 0.75$). Δ indicates the difference between calculated and observed values.

Figure 4 shows the lattice constants refined by the Rietveld analysis as a function of La content *x*. With increasing *x*, parameter *a* and unit-cell volume decreased, while parameter *b* and *c* increased. Though the ionic radius of La is likely to be almost the same as that of Bi at the 12-coordinated site, La substitution led to a linear decrease in unit-cell volume. Furthermore, La substitution resulted not only in a decrease of the orthorhombic distortion expressed as *a/b* but also in a longer *c*. These structural changes seem to be closely related to a lattice distortion in the perovskite blocks. In $\text{SrBi}_2\text{Ta}_2\text{O}_9$, the lattice distortion is divided into two categories: one is a TaO_6 octahedral rotation in the *a*-*b* plane and the other is a octahedral tilt from the *c* axis.^[6] The rotation angle in the the *a*-*b* plane is about 4 deg, while the tilt angle from the *c* axis is about 7 deg at 25 °C. The structural analysis of BiT single crystals performed by Rae *et al.*^[15] showed that the similar lattice distortion to SBT is present also in BiT. It can qualitatively be considered that the octahedral rotation and tilt are associated with the orthorhombic distortion (*a/b*) and the parameter *c*, respectively. The substitution of La led a lower Curie temperature (T_C),^[14] and a lattice relaxation occurred. As a result, the lattice distortion such as the rotation and tilt of TiO_6 octahedra is released, leading to a decrease in *a/b*, and an increase in *c*.

The La content *x* in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ single crystals was determined by XPS. The crystals were crushed into powder, and pressed softly onto indium plate for XPS measurements. The powder prepared by solid-state reaction was used as a reference for the composition determination. **Figure 5** shows $\text{Bi}4f$, $\text{Ti}2p$ and $\text{La}3d$ core-level spectra of BLT (1.5) single crystal obtained from BLT(0.75) powder sample. Any binding energy shift due to the sample charging was corrected by the $\text{C}1s$ (284.6 eV) peak as an internal reference. The presence of Bi metal was not confirmed from the $\text{Bi}4f$ spectra. Oxidation of La resulted in a splitting of the peaks of $\text{La}3d$.

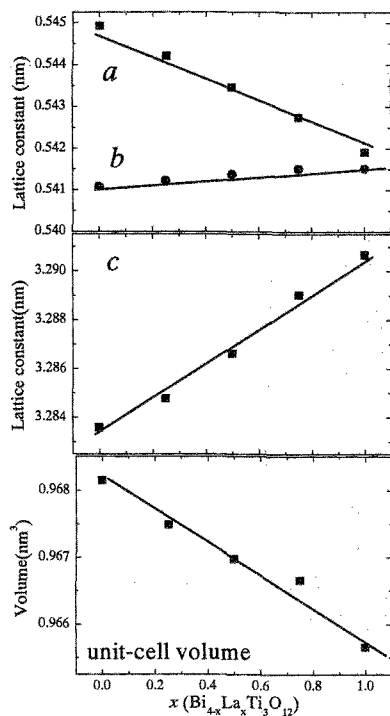


Fig.4 Lattice constants *a*, *b*, *c* and unit-cell volume as a function of *x* ($\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$).

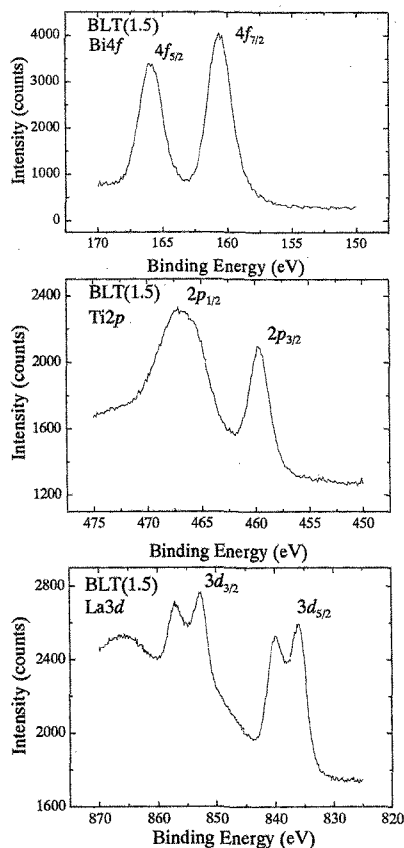
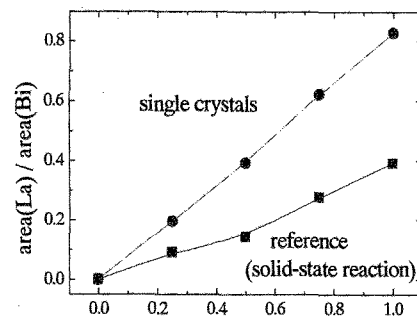


Fig.5 $\text{Bi}4f$, $\text{Ti}2p$ and $\text{La}3d$ spectra of BLT (1.5) single crystals.



x ($\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$) of the powder used for crystal growth

Fig.6 The relationship between *x* in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ powder used for crystal growth and the ratio of the area (La) to the area (Bi). The results of the powder prepared by solid-state reaction were depicted as a reference.

In order to determine *x*, the area of each peak was calculated using fitting the spectrum on the basis of Gauss-Lorentz function (90% Gauss). The background was subtracted in the area estimation. **Figure 6** shows the relationship between *x* in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ and the ratio of the area (La) to the area (Bi). It is suggested that La content can be determined by XPS. It was revealed that BLT single crystals contained about twice as much La content as the powder used for crystal growth. It is considered that the substitution of La at the A-site (Bi) of the perovskite block increases the stability at high temperatures during crystal growth from the thermodynamics point of view, however the exact reason remains unclear.

Fig.7 shows the domain structures in the *a-b* plane of as-grown BiT and BLT ($x=0.5, 1.0, 1.5, 2.0$) single crystals investigated with an optical microscope. Since the spontaneous polarization (P_s) of about $50 \mu\text{C}/\text{cm}^2$ lies along the *a* axis at the angle of about 5 deg with the *a-b* plane, these pictures indicate an in-plane domain structure (so called *a-a* domain structure in the ABO_3 -type ferroelectrics such as PbTiO_3). Here, we do not care a component of P_s along the *c* axis, and then the domain wall is categorized into two groups. One is 90-deg domain wall, at which the direction of P_s in the neighboring two domains has the angle of 90-deg and polarization charge is compensated. The other is 180-deg domain wall, and the direction of P_s is different by 180-deg in the *a-b* plane. The 90-deg domain walls are visible with an optical microscope due to the elastic distortion at the boundary, while the 180-deg domain wall cannot be observed. BiT showed a striped 90-deg domain structure, and the average domain width was about $8.5 \mu\text{m}$. La substitution led to a decrease in domain size, and BLT ($x \approx 1.5$) showed a domain structure with about $2.5 \mu\text{m}$ domain width. The improvement of polarization properties observed for BLT thin films seems to be closely related to the domain structure. Further investigation is required to reveal the relation between domain structure and polarization properties.

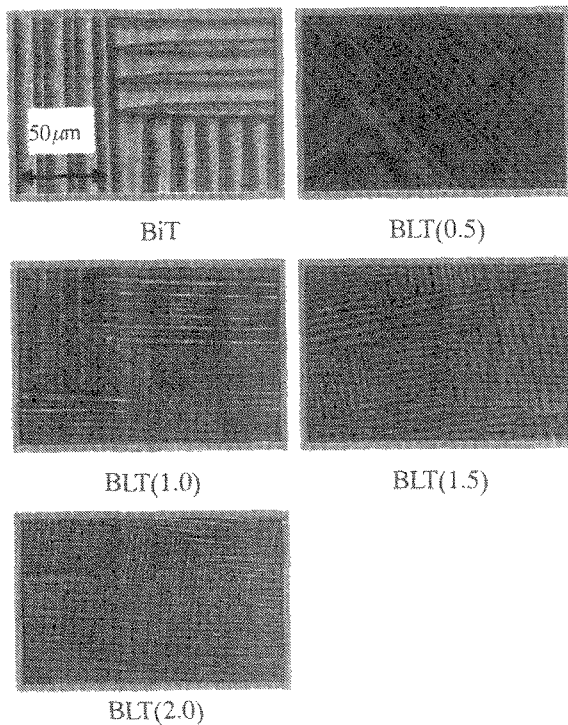


Fig.7 Domain structures of as-grown BiT and BLT ($x=0.5, 1.0, 1.5, 2.0$) single crystals with optical microscope.

4. CONCLUSIONS

BLT ($x=0.25, 0.50, 0.75, 1.00$) powder samples were prepared by solid-state reaction. With increasing La content, parameter a and unit-cell volume decreased, while parameter b and c increased. These structural change was attributed to the lattice relaxation in the perovskite blocks (TiO_6 octahedral rotation in the a - b plane and octahedral tilt from the c axis). BLT ($x=0.5, 1.0, 1.5, 2.0$) single crystals were grown by self-flux method, and the domain structures

in the a - b plane were investigated with optical microscope. BiT and BLT had striped 90-deg domain structure. The average domain width of BiT was about $8.5\mu\text{m}$. The substitution of La led to a decrease in domain size, and BLT ($x \approx 1.5$) showed a domain structure with about $2.5\mu\text{m}$ domain width.

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