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Ceramic Processing Research

# Electrical conduction properties of La-substituted bismuth titanate single crystals

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Single crystals of lanthanum-substituted bismuth titanate were grown by a self-flux method, and electrical conductivities were investigated at high temperatures. Lanthanum substitution suppressed Bi vaporization during annealing and decreased the electrical conductivity in both the a- and c-axes. It is suggested that lanthanum substitution stabilizes the perovskite blocks and hence decreases the concentrations of oxygen vacancies and holes as the conduction carriers. An *ab-initio* calculation indicated that the formation energy of an oxygen vacancy in the perovskite block is increased by lanthanum substitution, supporting the above experimental results.

Key words: bismuth titanate, lanthanum substitution, single crystal, Ab initio calculation, oxygen vacancy.

#### Introduction

Bismuth titanate (Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>: BiT) has attracted much attention over the past decades because of its ferroelectric properties and lead-free nature. Many studies have focused on its applications for nonvolatile random access memory and lead-free piezoelectrics [1, 2]. In the structure of BiT, a pseudo-perovskite block  $(Bi_2Ti_3O_{10})^{2-}$  and bismuth oxide layer  $(Bi_2O_2)^{2+}$  are stacked alternately [3]. BiT undergoes a ferroelectric transition at its Curie temperature ( $T_c = 675 \text{ °C}$ ) from a high- temperature I4/mmm tetragonal to ferroelectric B1a1 monoclinic structure [4], and shows a large spontaneous polarization (48-50  $\mu$ C/cm<sup>2</sup>) along the *a*axis at room temperature [5, 6]. However, BiT suffers from a low durability against a repeated switching of polarization states [7], which is probably ascribed to lattice defects [8-11]. Furthermore, a high leakage current interferes with the polarization switching (poling) process, resulting in poor polarization and piezoelectric properties.

We have previously reported that BiT single crystals showed oxide ionic-*p*-type mixed conduction at 700 °C [10]. Oxide ion was the principal carrier along the a(b)axis, while *p*-type conduction was dominant along the *c*-axis. In addition, vanadium doping at the perovskite B (Ti) site in single crystals largely decreased the ionic and hole conductivities along the a(b)-axis [12]. The vanadium doping was assumed to decrease effectively the concentrations of oxygen vacancies and holes in the perovskite blocks.

In recent years, it has been reported that lanthanumsubstituted BiT (BLT) thin films showed a relatively large remanent polarization ( $P_r$ ) and fatigue-free property that  $P_r$  does not decrease after 10<sup>11</sup> switching cycles [13]. However, a single crystal study showed that BLT (Bi<sub>3.15</sub>La<sub>0.85</sub>Ti<sub>3</sub>O<sub>12</sub>) has a smaller  $P_r$  of 20 µC/ cm<sup>2</sup> along a(b) axis than 49 µC/cm<sup>2</sup> of BiT [14]. It is not clear why polycrystal and thin films of BLT show better polarization properties than BiT does, in spite of the small spontaneous polarization expected in single crystals. In the present study, electrical conduction properties of BLT single crystals were examined, and defect formation energies were calculated to clarify the effects of lanthanum substitution.

#### **Experimental procedure**

 $Bi_4Ti_3O_{12}$  [BiT] and  $La_xBi_{4-x}Ti_3O_{12}$  [BLT(x)] single crystals were grown by a self-flux method using a mixture of BiT or BLT(x) powders and Bi<sub>2</sub>O<sub>2</sub> flux as follows. Firstly BiT and BLT(x) polycrystalline powders were synthesized by a conventional solid-state reaction method.  $Bi_2O_3$ ,  $La_2O_3$  and  $TiO_2$  were weighed for the stoichiometric composition of BiT and BLT(x) (x = 0.25, 0.75, 1.00 and 2.00), and then ball-milled in polyethylene pots with ethanol. Dried powders were calcined in almina crucibles at 800-1050 °C. Calcined BiT and BLT(x) were confirmed as single phases from X-ray diffraction (XRD) patterns. BLT(0.25) and BLT (0.75) powders were used for single crystal growth, while BLT(1.0) and BLT(2.0) were used in thermogravimetric measurements. Next, synthesized powders and  $Bi_2O_3$  were mixed with a weight ratio of 1:9.6, and packed in platinum crucible. The mixture was melted

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Chemical compositions of the single crystals were determined by inductive coupled plasma (ICP) analysis. Powder morphology and non-stoichiometry of BiT and BLT(x) were analyzed with scanning electron microscopy (SEM) and thermogravimetry (TG). Some BiT single crystals were annealed in air at 1000 °C for 48 h to examine the effects of Bi vaporization. Annealed BiT is denoted as "Bi-def BiT" hereafter.

For electrical measurements, single crystals obtained were cut along the a(b)-axis using a polarization microscope. Gold electrodes were pasted on cross sectional surface and co-fired. Electrical conductivities were evaluated by an AC-impedance method (impedance analyzer: Agilent HP4192A) in the temperature range of 25 to 750 °C [15].

To estimate the stability of Bi and oxide ions in the crystal structure in the high-temperature paraelectric state, we have performed an *ab-initio* band structure calculation within density functional theory via the generalized gradient approximation [16] using a plane wave basis set. The projector-augmented wave (PAW) method [17] was applied using the Vienna Ab-initio Simulation Package (VASP) [18]. A cutoff energy of 400 eV and k-point sampling grid of  $7 \times 7 \times 3$  were used. At first, we have optimized the crystal structure of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> and Bi<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>12</sub> with I4/mmm tetragonal symmetry, in which all of the La is assumed to occupy the perovskite A site. An atom was deleted at a specific site from the  $2a^{*}2a^{*}1c$  supercell composed of the optimized structure was created, and then the selfconsistent-field calculation of the defective supercell was performed. Considering the total energies of the optimized crystals and the defective supercells and the chemical potential of Bi gas and oxygen molecule, the vacancy formation energy of Bi and oxide ions in the structure was estimated.

# **Results and Discussion**

#### Single crystal growth and thermal stability

BiT and BLT single crystals finally obtained were transparent and mica-like; a typical size is  $5 \times 5 \text{ mm}^2$  and 0.1 mm normal to the *a-b* plane and the *c*-axis, respectively, as shown in Fig. 1. ICP and XRD analyses showed that grown crystals were single phase and their chemical compositions were Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, Bi<sub>3.52</sub>La<sub>0.46</sub>Ti<sub>3</sub>O<sub>12</sub> [BLT(0.46)] and Bi<sub>2.80</sub>La<sub>1.20</sub>Ti<sub>3</sub>O<sub>12</sub> [BLT(1.20)].

Bismuth vaporization under annealing was examined. Figure 2 shows the SEM images of calcined BiT and BLT powders. The mean particle size decreased with increasing La content. The measured particle sizes r were 1.47, 1.40, 0.75 mm for BiT, BLT(0.46) and BLT(1.20), respectively. Thermogravimetric profiles of



Fig. 1. Single crystals of BiT and BLT(0.46).



3 *μ*m

BLT(1.0)



3 *μ*m





**Fig. 2.** Scanning electron micrographs of powders of BiT, BLT(1.0), BLT(2.0).



Fig. 3. Bismuth deficiency of BiT and BLT(x) powders during annealing in  $N_2$  at 1000 °C.

BiT and BLT powders during annealing at 1000 °C in  $N_2$  ( $Po_2 = 20 Pa$ ) are shown in Fig. 3. The amount of Bi deficiencies y in the vertical axis were converted from TG data under an assumption that all the weight loss during annealing can be attributed to vaporization of bismuth oxide in the form of Bi<sub>2</sub>O<sub>3</sub>. In Fig. 3, BiT showed a larger weight decrease than BLTs. The weight loss was due to vaporization of Bi or Bi<sub>2</sub>O<sub>3</sub> as represented by;

$$Bi_{Bi} = Bi(gas) + V_{Bi}''' + 3h', \qquad (1)$$

$$Bi_2O_3 = 2Bi(gas) + 2/3O_2 + 2V_{Bi}''' + 3V_o'',$$
 (2)

where  $Bi_{Bi}$ ,  $V_{Bi}$ " and  $V_o$ " are Bi ion at the Bi site, Bi vacancy and oxygen vacancy with Kroeger-Vink notation. The  $Bi_2O_3$  vaporization occurs with generation of bismuth and oxygen vacancies, which largely affect electrical properties. As shown in Fig. 3, La substitution suppressed the Bi vaporization. Two reasons can be considered; the first one is due to a decrease in the amount of Bi in the lattice, and the second one is the stabilization of the perovskite A-site by La-substitution. Lanthanum is mainly substituted for provskite A-site (Bi site). As is widely known, La shows ionic properties and La-addition to perovskite materials generally raises their melting points or sintering temperatures, as observed in Fig. 2, suggesting the stabilization of the lattice by La. The BLT(2.0) has a half the Bi concentration of BiT, but the weight loss in BLT(2.0) is less than half of that in BiT. This indicates that the stabilization by La-substitution is more effective for suppression of vaporization.

# **Electrical properties**

The chemical composition of the Bi-def BiT was evaluated to be  $Bi_{3,9}Ti_3O_{11.85}$  from weight loss. Electrical conductivities of BiT and Bi-def BiT single crystals are compared in Fig. 4. As clearly shown in this figure, the conductivity of Bi-def BiT along the a-axis rose up by 60% with respect to that of BiT, while



**Fig. 4.** Temperature dependence of conductivity of BiT and Bi-def BiT single crystals.

there was a much smaller increase along the c-axis. This increase in conductivity along the a-axis can be understood to be due to an increase in oxygen vacancy concentration and subsequent increase in hole concentration during cooling, expressed as,

$$1/2O_2 + Vo^{"} = O_0^* + 2h^{"}.$$
 (3)

In our previous report on electrical properties of vanadium-doped BiT (V-BiT) [12], the conductivity along the a-axis largely decreased by vanadium doping, while that along the c-axis showed a much smaller change. Bismuth ions in the  $(Bi_2O_2)^{2+}$  layer are more stable than in the perovskite block, therefore, Bi defects exist mainly in the perovskie block and conductive carriers (holes and oxygen vacancies) move easily along the a-axis. The highly resistive  $(Bi_2O_2)^{2+}$  layer suppresses the conduction along the c-axis, which is the reason the electrical conductivity along the c-axis is much lower than that along the a-axis in BiT [19, 20]. The same mechanism can be applied for the anisotropic conductivity changes in the Bi-def BiT system. Since Bi vaporization mainly occured in the perovskite block, Bi vacancies and conducting carriers increased in the perovskite block. The combination of increased carrier concentration in the perovskite block and the highly resistive  $(Bi_2O_2)^{2+}$  layer leads to the anisotropic conductivity changes by Bi vaporizaion.

Electrical conductivities of BiT and BLT(0.46) and BLT(1.20) are shown in Fig. 5. Along the a-axis, the conductivity decreased with an increase of La content. Meanwhile, the conductivities of BiT and BiT(0.46) along the c-axis were very close to each other, and that of BLT(1.20) much decreased over the entire temper-



Fig. 5. Temperature dependence of conductivity of BiT and BLT(x) single crystals.

ature range. This anisotropic behavior can also be understood by taking the highly resistive  $(Bi_2O_2)^{2+}$ layer and stabilization of perovskite block by La-substitution. As mentioned above, BiT has Bi vacancies and oxygen vacancies mainly in the perovskite block, and conductive carriers can move there easily. La-substitution stabilizes the peovskite lattice and decreases carrier concentration, leading to lower electrical conductivities along the a-axis. In contrast, the high resistance of the  $(Bi_2O_2)^{2+}$  layer determines the conductivity along the c-axis. Therefore, small changes of the carrier concentration, as in BLT(0.46), did not affect the conductivity along the c-axis

A large decrease in conductivity was observed in BLT(1.20) along the c-axis. This may be due to a change in the La-substituting site in BLT with a high La content. It has been confirmed from Rietvelt analysis of XRD patterns that La ions substituted at the A site (Bi) of the perovskite blocks in BLT(0.75) [21]. However, La content dependences of lattice parameters suggested a change in substitution site above X = 1.0. Osada et al. reported through the Raman spectroscopy that La began to occupy at the Bi site in  $(Bi_2O_2)^{2+}$  layers as well as the A site [22]. Following the vacancy formation energy also supports the change in Lasubstituting site.

# Estimation of vacancy formation energy

Here we consider the vacancy formation energy  $(E_v)$ of an atom that is required for creating a vacancy at the site. Figure 6 indicates the optimized (tetragonal) structure of the paraelectric BiT. In the structure, there are two kinds of Bi: Bi1 at the perovskite A site and Bi2 in the Bi<sub>2</sub>O<sub>2</sub> layers. The  $E_v$  of Bi1 was much lower by about 2 eV than that of Bi2, showing that the Bi vacancy is created preferentially at the Bi1 site during heat treatment. The  $E_v$  of O4 was about 5 eV, which



Fig. 6. Crystal structure of tetragonal (paraelectric) BiT.

was higher than those of other oxide ions. In the case of a vacancy complex comprising a Bi vacancy and an oxygen vacancy, the  $E_V$  of the Bi1-O1 pair was lower by 2 eV than that of the Bi1-O2 pair. These results indicate that the vacancy formation of Bi1 acts as a trigger for oxygen vacancies at the O1 site for charge compensation. Furthermore, the strong Coulomb interaction between a positively charged oxygen vacancy and a negatively charged Bi vacancy is likely to stabilize the defect pair of Bi1 and the adjacent O1 in the perovskite layers.

Figure 7 exhibits the results of  $E_V$  of oxygen in BiT and BLT(2.0) calculated by an *ab-initio* study. The presence of La at the *A* site leads to a significant change in  $E_V$  of oxide ions. In particular, the La substitution increases the  $E_V$  of oxide ions (O1, O3, and O5) in the perovskite layers. The results for BLT suggest that the oxide ions in the perovskite layers in



**Fig. 7.** Vacancy formation energies of oxygens in BiT and BLT(2.0), estimated by *ab-initio* calculation.

BLT are stabilized by the La substitution. For BiT, the vacancies seem to be abundant in the perovskite layers, while the lower  $E_V$  of O2 for BLT indicates that oxygen vacancies accumulate in the  $(Bi_2O_2)^{2^+}$  layers. Thus, the La substitution will lead to a marked decrease in conductivity along the a- and c-axes, as shown in Fig. 5.

Substituting La for Bi in BiT thin films is known to improve ferroelectric properties, leakage current and fatigue behavior. The experimental and calculated results in the present study indicate that the stabilization of the perovskite block and the decrease in oxygen vacancy concentration by La substituting contribute to the improvements of ferroelectric properties.

# Conclusions

Lanthanum substitution in BiT decreased Bi vaporization during annealing at high temperatures and electrical conductivities in both a- and c-axes. It is suggested that lanthanum substitution stabilizes the perovskite blocks and hence decreases the concentrations of oxygen vacancies and holes. An *ab-initio* calculation indicated that the formation energy of oxygen vacancy in the perovskite block is increased by lanthanum substitution, supporting the above experimental results. These effects are assumed to contribute to the improvement of ferroelectric properties by lanthanum substitution.

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