

Structure dependence of the ferroelectric properties of $\text{Bi}_{3.25}\text{Ln}_{0.75}\text{Ti}_3\text{O}_{12}$ (Ln=La, Nd, Sm, Dy) ceramics

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Abstract We have fabricated rare-earth ion substituted bismuth titanate (BIT) ceramics, $\text{Bi}_{3.25}\text{Ln}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLnT; Ln=La, Nd, Sm, Dy), using the conventional solid-state reaction method and have investigated the changes in the structural distortion and electrical properties, which resulted from the substitution of the rare-earth ions in BIT ceramics. As the ionic radius of the rare-earth ion substituted into the BIT decreased, the structural distortion and decreases in the unit cell volume became more pronounced as well as the Curie temperature increased monotonically from 354 °C (BLaT) to 480 °C (BDyT). BNdT ceramics had relatively high remanent polarization value ($12.5 \mu\text{C}/\text{cm}^2$) at an applied electric field of 130 kV/cm. The extent of the structural distortion influenced the dielectric and ferroelectric properties of the BLnT ceramics.

Keywords Bismuth titanate · Rare-earth · Lattice distortion · Ferroelectricity

1 Introduction

Many studies have focused on the structures and the ferroelectric phase transitions of bismuth layer-structured

ferroelectrics (BLSF) ceramics and thin films because of their excellent piezoelectricity, ferroelectricity and lead-free compositions [1, 2]. BLSF ceramics have the general formula of $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, where $A=\text{Bi}$, Pb, Ba, Sr, La, Ca, Na, K; $B=\text{Ti}$, Nb, Ta, W, Mo, Fe, Co, Cr, and m is the number of BO_6 octahedrals in the pseudoperovskite block ($m=2, 3, 4, 5$) [1–16]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) is one of the more extensively studied materials among the BLSF family due to its large spontaneous polarization along the a -axis (approximately $50 \mu\text{C}/\text{cm}^2$), [4] low processing temperature, high Curie temperature, and lead-free composition. However, it is well known that oxygen-vacancy migration in BIT produces significant degradation problems associated with the ferroelectric properties such as high leakage current and small remnant polarization ($2P_r \sim 15 \mu\text{C}/\text{cm}^2$) [5, 6]. Recently, it has been reported that the oxygen-vacancy migration in BIT ceramics with the substitution of rare-earth ions has a significant effect on its electric properties. Rare-earth ion modified BIT ($\text{Bi}_{4-x}\text{Ln}_x\text{Ti}_3\text{O}_{12}$; Ln=La, Nd, Sm) films were reported to have relatively high ferroelectricity and good fatigue-free characteristics [7–9]. The ferroelectric property of the $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ceramics differs according to the value of x [3, 10]. When the value of x changes from $x=0$ to $x=1.50$, the ferroelectric phase transition temperature (T_C) of the $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ceramics shifts from 650 to -100 °C, as reported by Takenaka and Sakata [3]. They further suggested that the lattice distortion of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ appears at $x=0.75$. Park et al. reported that the $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ thin film exhibits fatigue-free characteristics and a large remnant polarization [8].

We have fabricated rare-earth ion substituted bismuth titanate ceramics, $\text{Bi}_{3.25}\text{Ln}_{0.75}\text{Ti}_3\text{O}_{12}$ (Ln=La, Nd, Sm, Dy; abbreviated to BLnT), using the conventional solid-state reaction method and have investigated their crystal structure and their dielectric and ferroelectric properties in order

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to clarify the influence of the substitution of various rare-earth ions for the Bi-site in BIT ceramics.

2 Experimental

Ceramic samples of $\text{Bi}_{3.25}\text{Ln}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLnT; Ln=La, Nd, Sm, Dy) were prepared by the conventional solid-state reaction method. Powders of Bi_2O_3 , TiO_2 , La_2O_3 , Nd_2O_3 , Sm_2O_3 and Dy_2O_3 of 99.9% purity were mixed in methyl alcohol with zirconia balls and then calcined at 850 °C for 2 h. The calcined powders were again milled using the same mixing conditions. To fabricate ceramic samples, the calcined powders were pressed into disk-shaped pellets of 15 mm diameter and approximately 1–3 mm thickness and then sintered at 1100 °C for 2 h in an air atmosphere. X-ray diffraction (XRD) with Cu – K_α radiation was used to determine the crystal structure. For electrical measurements, the specimen was lapped to 0.3 mm in thickness, and platinum electrodes of 6 mm in diameter were deposited on both sides of the specimens using dc sputtering. The ferroelectric P – E hysteresis loops were measured by a Sawyer–Tower circuit at 60 Hz frequency. The dielectric property was measured over the temperature range of 30–600 °C using an impedance analyzer (HP4192A). The amplitude of the ac signal was 0.1 V and the frequency was 10 MHz. The temperature ramp rate was 1 °C/min.

3 Results and discussion

The $\text{Bi}_{3.25}\text{Ln}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLnT; Ln=La, Nd, Sm, Dy) ceramics consist of plate-like grains around 5 μm in width and 0.5 μm in thickness. The grain sizes of the BLnT ceramics were similar to each other. The crystal structures of the BLnT ceramics were confirmed by XRD patterns and the lattice parameters were also calculated (Fig. 1). All specimens were crystallized into an orthorhombic or pseudo-tetragonal structure with a layered perovskite structure without a detectable secondary phase that was similar to that of BIT, no matter what kind of rare-earth ion was substituted. The variations of the lattice parameters and the unit cell volume of the BLnT ceramics with various rare-earth ionic radii are shown in Fig. 2. Here, the radii of 6 coordinated rare-earth ions proposed by Shannon et al. [17] are used for comparison because those of 12 coordinated ions have not yet been reported. The lattice constant and unit cell volumes decreased slightly as the radii of the rare-earth ions decreased.

Figure 3(a) shows the behaviour of the dielectric constant of the BLnT ceramics as a function of temperature. The dielectric constant and the T_C of the BLnT ceramics were shifted by the substitution of various rare-earth ions.

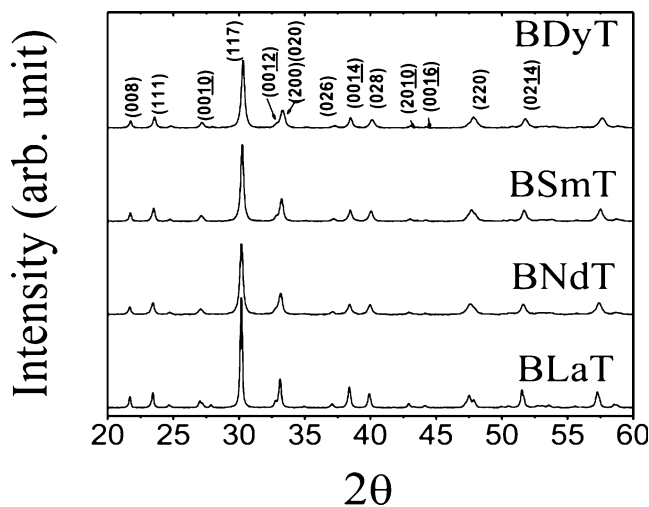


Fig. 1 XRD patterns of the BLnT ceramics

As the radius of the rare-earth ions decreased, the T_C increased monotonically from 354 °C (BLaT) to 480 °C (BDyT) as shown in Fig. 3(b). This relationship further suggested that the substitution of rare-earth ions for Bi^{3+} (A -site) on the BIT led to a change in the lattice parameters and the T_C as influenced by the variations of the structure. Shimakawa et al. [14, 16] reported on $\text{ABi}_2\text{Ta}_2\text{O}_9$ ($A=\text{Ca}$, Sr , Ba , and $\text{Sr}_{0.8}\text{Bi}_{2.2}$) and found that the size of the A -site cation significantly influences the structural distortion, which causes changes in the T_C and P_s . They found that as the size of the A -site cation decreases from Ba^{2+}

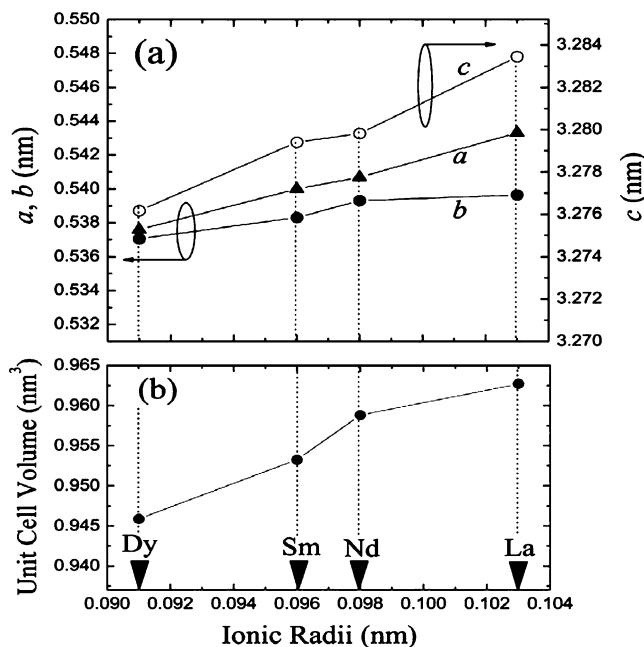


Fig. 2 The variation of (a) the lattice parameters and (b) the unit cell volume of the BLnT ceramics with different rare-earth ionic radii

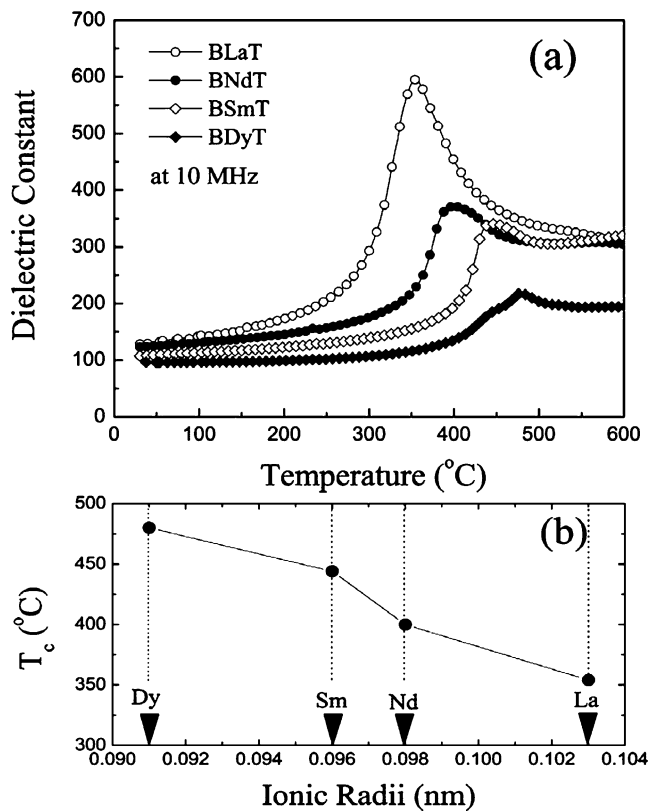


Fig. 3 The behaviour of (a) the dielectric constant of the BLnT ceramics as a function of temperature and (b) the T_C of the BLnT ceramics with different rare-earth ionic radii

(0.161 nm) to Ca^{2+} (0.134 nm), the lattice mismatch between the AO and TaO_2 planes increases; as a result, any structural distortion becomes more pronounced, which leads to a higher T_C . Therefore, the substitution of smaller rare-earth ions for the Bi^{3+} -site in BIT should cause the compressive stress in the perovskite-like unit to become pronounced and as a result, the mismatch between the perovskite-like unit and the Bi_2O_2 layer will increase for the BITs modified with smaller rare-earth ions, leading to a larger distortion in the TiO_6 octahedral. This structural distortion is related to the variations of the T_C . As the structural distortion increases, the T_C increases. However, the unit cell volume decreased slightly as the radii of rare-earth ions decreased. This indicated that the rattling space for the Ti^{4+} ions inside the TiO_6 octahedral would be reduced and therefore, the substitution of a smaller rare-earth ion for Bi^{3+} in BIT decreased the dielectric constant.

Figure 4 shows the P - E hysteresis loops of the BLnT ceramics. The ferroelectric hysteresis loops were measured using a driven electric field of 130 kV/cm at a frequency of 60 Hz at room temperature. The shape of the P - E hysteresis loop changes with respect to the substitution of the various rare-earth ions. The BLaT and BNdT capacitors were characterized by a well-saturated P - E hysteresis curve but

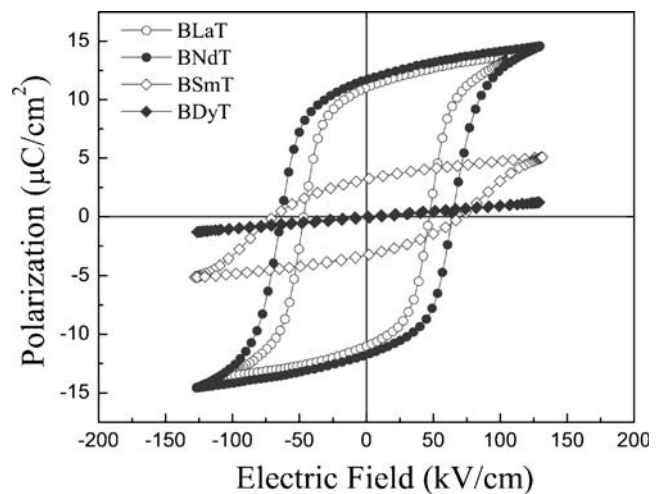


Fig. 4 P - E hysteresis loops of the BLnT ceramics

a saturated P - E loop for the BDyT capacitor was not observed at an applied electric field of 130 kV/cm because the coercive field of the BDyT ceramic was higher than 130 kV/cm. The coercive field increased correspondingly as the radii of the rare-earth ion decreased. These variations may be related to the large structural distortion and narrow rattling space. The substitution of smaller rare-earth ions for Bi^{3+} in the BIT should lead to a larger distortion of the TiO_6 octahedral and a smaller unit cell volume. This indicated that the rattling space for the atomic displacement was narrowed. So an A -site substitution with smaller rare-earth ions in BIT leads to a higher coercive field.

The remanent polarization (P_r) of the BNdT ($12.5 \mu\text{C}/\text{cm}^2$) was higher than that of the BLaT ($10.3 \mu\text{C}/\text{cm}^2$). The P_r of the BLnT ceramics suddenly decreased with the substitution of rare-earth ions with radii smaller than that of the Nd^{3+} ion. Shimakawa et al. reported that as the size of the A -site cation decreases, the structural distortion becomes more pronounced, which leads to a larger atomic displacement. So, when a smaller ion is placed at the A -site in layer structured ferroelectrics, the P_r is higher than if a bigger ion were placed at the A -site [14–16]. In the case of $\text{ABi}_2\text{Ta}_2\text{O}_9$ ($A=\text{Ca}, \text{Sr}$), the value of the ferroelectric polarization for $\text{CaBi}_2\text{Ta}_2\text{O}_9$ (with smaller A -site ions) along the a -axis is higher than that of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (with bigger A -site ions). According to our results, the BLaT and BNdT ceramics agreed with this rule. However the BSmT and BDyT ceramics did not agree with Shimakawa's results. These results suggested that the remnant polarization of the BLnT ceramics was influenced not only by the structural distortion but also the unit cell volume. As the size of the A -site cation decreased, unit cell volume was decreased, which led to a decrease in the rattling space such that the atomic displacement was reduced.

4 Conclusions

We have fabricated rare-earth ion substituted bismuth titanate ceramics, $\text{Bi}_{3.25}\text{Ln}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLnT; Ln=La, Nd, Sm, Dy), by using a conventional solid-state reaction method, and have investigated the crystal structure and the dielectric and ferroelectric properties of the BLnT ceramics in order to clarify the influence of the substitutions for the Bi-site on the ceramics. The BLaT and BNdT capacitors were characterized by well-saturated P – E hysteresis curves, but a saturated P – E loop for the BDyT capacitor was not observed at an applied electric field of 130 kV/cm because the coercive field of the BDyT ceramic was higher than 130 kV/cm. The lattice constant and the unit cell volumes decreased slightly as the radii of rare-earth ions decreased. The substitution of smaller rare-earth ions for Bi^{3+} on BIT should lead to a larger distortion in the TiO_6 octahedral and a smaller unit cell volume. This indicated that the rattling space for atomic displacement was narrowed. Correspondingly, substitution with smaller A -site ions in the BIT led to an increase of the T_C , a decrease of the dielectric constant, a higher E_C and a lower P_r .

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