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Nb doping effects on ferroelectric and electrical properties of ferroelectric $Bi_{3.25}La_{0.75}(Ti_{1-x}Nb_x)_3O_{12}$ ceramics

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Abstract

Nb-doped $Bi_{3.25}La_{0.75}(Ti_{1-x}Nb_x)_3O_{12}$ ceramics were prepared by a solid state reaction. A crystal structure with Bi-layered structured ferroelectrics is confirmed by a X-ray diffraction (XRD). With increasing Nb concentration, the Curie temperature decreased, and the dielectric constant peak broaden. The remanent polarization (P_r) increased at a small Nb doping of $x = 0.03$–0.05. At temperature above 120 °C, the electrical conductivity decreased by Nb doping. For the high-valence Nb^{5+} substitution for Ti^{4+} in BLT ceramic, the effects of Nb doping on ferroelectric and electrical properties were investigated by the dielectric constant, ferroelectric *P–E* hysteresis loop and electrical conductivity.

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1. Introduction

For ferroelectric random access memory (FRAM) and piezoelectric applications, the ferroelectric and electrical properties have been intensively investigated for ceramic and thin films [1,2]. Currently, isotropic perovskite ferroelectrics $Pb(Zr,Ti)O_3$ (PZT) and Bi-layer structrued ferroelectrics (BLSFs), $SrBi_2Nb_2O_9$ (SBN), $Bi_4Ti_3O_{12}$ (BIT) and $SrBi_2Ta_2O_9$ (SBT), are known as a useful ferroelectric material [3–10]. The BLSFs structure can be written with a general formula of $(Bi_2O_2)^{2+}$ $(A_{n-1}B_nO_{3n+1})^{2-}$ where A can be mono-, di-, trivalent ions or a mixture of them, B represents Ti^{4+}, Nb^{5+}, Ta^{5+}, etc., and *n* can have values of 2, 3, 4, ... For practical FRAM application, it is necessary to develop a new ferroelectric material with a high remanent polarization, high fatigue endurance, low leakage current and low processing temperature [1–6].

To improve the ferroelectric properties in BLSFs, the effects of ion doping have been investigated [11–16]. Currently, La substituted BIT ($Bi_{3.25}La_{0.75}Ti_3O_{12}$, BLT) thin films have attracted much attention for potential FRAM material due to polarization fatigue endurance and large spontaneous polarization (P_s) [7]. However, BLT and BIT materials are known to suffer from high leakage current which leads to a small remanent polarization. The conducting process is known as p-type electrical conductivity [10], which caused the high leakage current and domain pinning. A particular dopant change the ferroelectric and electrical properties depending on the ionic charge and radius. In this work, Nb-doped BLT (BLTN) ceramics were prepared by substituting high-valence Nb^{5+} for Ti^{4+} ions on the B site. The effects of Nb doping on the ferroelectric and the electrical properties were investigated.

2. Experimental

$Bi_{3.25}La_{0.75}$ $(Ti_{1-x}Nb_x)_3O_{12}$ (BLTN, $x = 0$, 0.01, 0.03, 0.05, 0.07, 0.10) ceramic were prepared by solid-state reaction and abbreviated as BLT, BLT-Nb01, BLT-Nb03, BLT-Nb05, BLT-Nb07 and BLT-Nb10 ceramics. The desired BLTN composition of the Bi_2O_3, La_2O_3, TiO_2, and Nb_2O_5 powders were mixed in methyl alcohol. The mixed BLTN powders were calcined at 750 °C for 4 h. To make

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BLTN ceramics, the calcined powder was pressed into pellets and sintered at 950–1000 °C for 5 h. The pellets were cut and polished to plate with 1 mm thick. Powder X-ray diffraction (XRD) with Cu Kα radiation were carried out to check a single phase or presence of different phase. To investigate the electrical properties, Pt electrodes were coated onto the polished surface using dc sputtering. The ferroelectric properties were investigated by polarization–electric field (*P–E*) hysteresis loops. The capacitance and loss tangent were measured by an impedance analyzer (HP4194A) in the frequency range of 100 Hz–1 MHz and the temperature range of 30–500 °C.

3. Result and discussion

3.1. Ferroelectric properties—ferroelectric polarization–electric field (P–E) hysteresis loops

Single phases and ferroelectric properties were characterized by XRD and *P–E* hysteresis loop, respectively. Fig. 1 shows the XRD patterns of BLTN ceramics, which agreed with those of BLT ceramic. The indexed XRD peaks show Bi-layered perovskite (1 1 7) peak and other perovskite (0 0 1) peak, which indicates that single phases with a Bi-layered perovskite structure were formed at different Nb concentrations. Doped Nb^{5+} ion seems to be incorporate at the Ti^{4+} sites in the perovskite structure because the ion radius of Nb ($r = 0.69$ Å) is similar to that of Ti ($r = 0.605$ Å).

The ferroelectric *P–E* hysteresis loops were measured at an applied field of about 60 kV/cm. The remanent polarization (P_r) of BLT, BLT-Nb01, BLT-Nb03, BLT-Nb05, BLT-Nb07 and BLT-Nb10 ceramics were estimated to be 10.2, 10.3, 11.7, 12.2, 11.2, 9.9 μC/cm², respectively. Thus, the P_r seems to be increased at a small Nb doping of $x = 0.03$–0.05. The maximum value of P_r was observed for BLT-Nb05 ceramics. To compare the ferroelectric and electrical properties, we choose the BLT and BLT-Nb05 ceramic. Fig. 2 shows the *P–E* hysteresis loops of the BLT and BLT-Nb05 ceramics. In this figure, P_r and the coercive field (E_c) of the BLT-Nb05 ceramics were 12.2 μC/cm² and 37.9 kV/cm, respectively. Thus, the remanent polarization of the BLT-Nb05 was higher than that of the BLT ceramic with $P_r = 10.2$ μC/cm². The spontaneous polarization, P_s, of BIT single crystals along the *a*-axis was 45–50 μC/cm² and that along the *c*-axis was 4.5 μC/cm². The *c*-axis orientation of the BLT-Nb05 ceramic decreased, as was shown X-ray analysis. Thus, the remanent polarization was thought to be increased by the increased random grain orientation or by a decreased number of defects, such as oxygen vacancies. Thus, Nb doping is responsible for the larger remanent

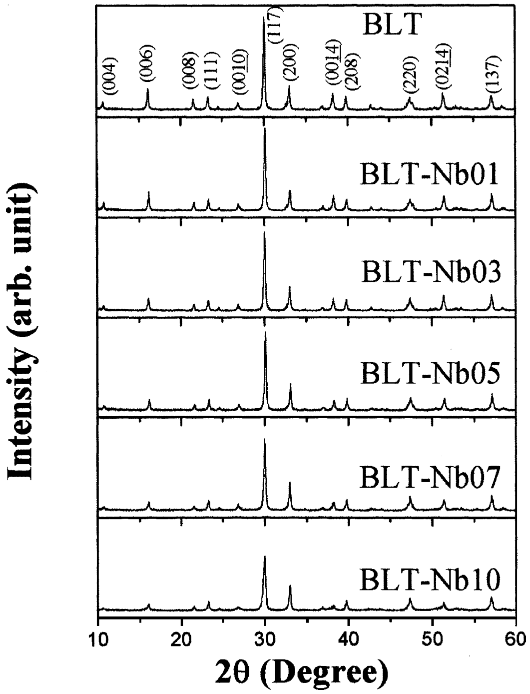
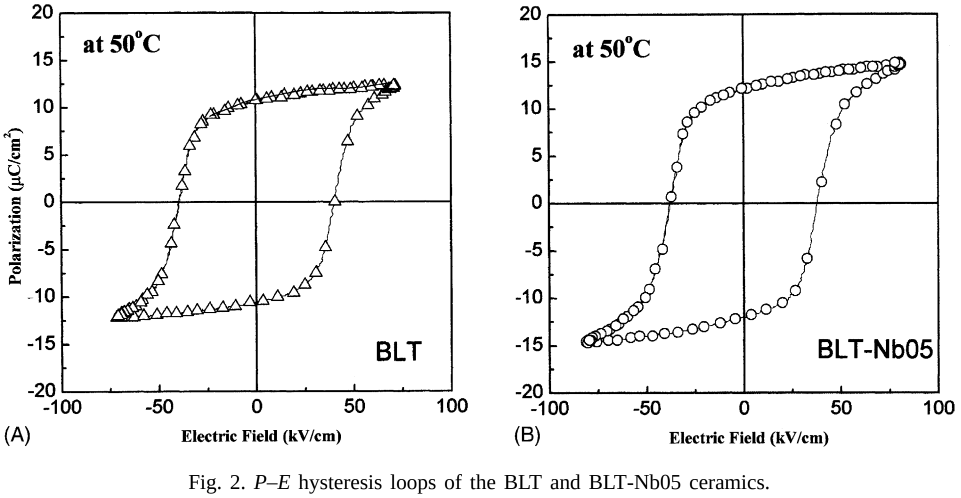


Fig. 1. XRD patterns of BLTN ceramics.



(A) (B)

Fig. 2. *P–E* hysteresis loops of the BLT and BLT-Nb05 ceramics.

Table 1
Dielectric properties at 100 kHz and ferroelectric properties of BLT and BLT-Nb05 ceramics

Ceramics	T_c (°C)	ε (25 °C)	$\tan\delta$ (25 °C)	P_r (μC/cm^2)	E_c (kV/cm)
BLT	405	151	0.025	10.2	40.4
BLT-Nb05	307	222	0.027	12.2	37.9

polarization. Table 1 shows the dielectric and ferroelectric properties of BLT and BLT-Nb05 ceramics

3.2. Dielectric properties—temperature dependences of dielectric constant

Fig. 3 shows the temperature dependences of the dielectric constant of BLT and BLTN ceramics at measured frequency of 100 kHz. The Curie temperature T_c was obtained from the maxium peak of the dielectric constant. The T_c of the BLT-Nb01, BLT-Nb03, BLT-Nb05, BLT-Nb07 and BLT-Nb10 ceramics were estimated to be 389, 343, 307, 291 and 281 °C, respectively. Compared to the $T_c = 405$ °C of BLT ceramic, the Tc of BLTN ceramics tended to decrease with increasing Nb concentration. Also, the dielectric constant peak was broaden. It was caused by the partial substitution of Nb for Ti ion on B-site. Fig. 4 shows the dielectric constants of the BLT and the BLT-Nb05 ceramics at the several frequencies, 0.1, 1, 10, 100 kHz, and 1 MHz. With increasing temperature, a low-frequency dielectric dispersion was observed for the BLT ceramic. However, the low-frequency dielectric dispersion was remarkablely decreased for BLT-Nb05. A low-frequency dielectric dispersion of the BLT ceramic may be explained by the contribution of space-charge polarization at the grain boundary and ionic polarization by ionic motion [9]. The decrease of low-frequency dielectric dispersions for the BLTN ceramics agrees with the observation of higher-valence cation-doped ceramics [9]. This implies that Nb-doping reduces the space charge or the ion mobility, which caused the low leakage current and conductivity. Thus, the remanent polarization was increased and ferroelectric properties were improved.

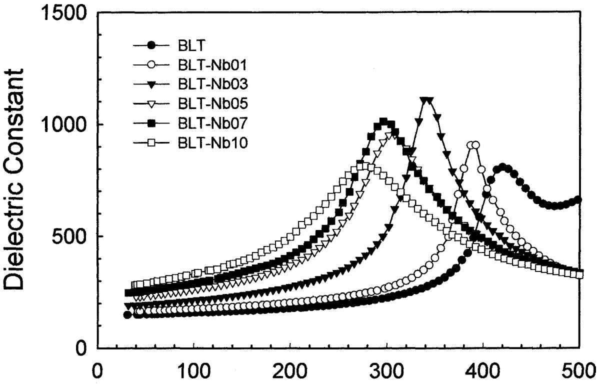


Fig. 3. The temperature dependences of the dielectric constant of BLT and BLTN ceramics at measured frequency of 100 kHz.

3.3. Electrical properties—temperature dependences of ac conductivity

Fig. 5 shows the temperature dependences of ac conductivity, σ_{ac}, versus the reciprocal temperature, $1/T$, measured at 100 kHz. In the low temperature region, the ac conductivity depend significantly on the frequency. Below T_c, the conductivity of BLT-Nb05 ceramics steadily increased while that of the BLT ceramic remarkably increased at temperatures above 100 °C. From the slope of the $\ln\sigma_{ac}$ versus $1000/T$ curve, the activation energy of BLT ceramic was 0.55 eV in the temperature range of 120–400 °C. In oxide ferroelectrics, doubly charged oxygen vacancies ($V_{\ddot{O}}$) are the

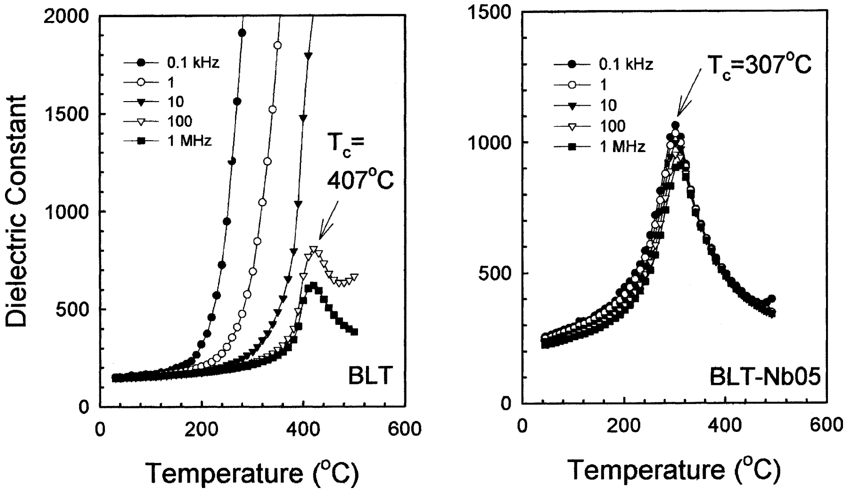


Fig. 4. The dielectric constants of the BLT and the BLT-Nb05 ceramics at the several frequencies, 0.1, 1, 10, 100 kHz, and 1 MHz.

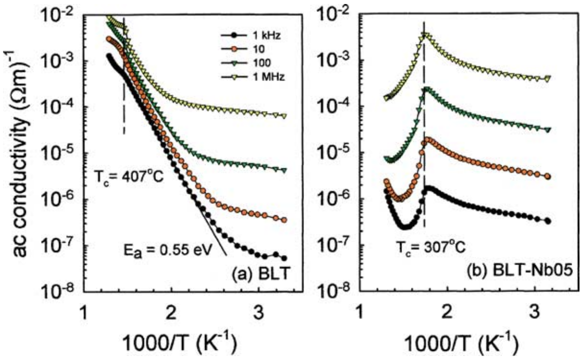


Fig. 5. The temperature dependences of ac conductivity, σ_{ac}, versus the reciprocal temperature, $1/T$, measured at 100 kHz.

most mobile charges and play an important role in the conduction process [8]. The motion of oxygen vacancies is well known to give rise to an activation energy of about 1 eV [9] in perovskite oxides at high temperature. Thus, the calculated activation energy of 0.55 eV is attributed to the thermal motion of the oxygen ion or for the formation of associations between oxygen vacancies and residual cations in the grain boundary. The ac conductivity of BLTN ceramics is independent of temperature up to 200 °C. The activation energies of BLTN ceramics were about 0.2 eV. Thus, Nb doping seems to be decrease the conductivity caused by oxygen vacancy. The role of the B-site substitution by high-valency cations is known mainly to compensate defects which cause fatigue and strong domain pinning [11–16]. Defects, such as bismuth and oxygen vacancies, are considered to be the most mobile charges and play an important role in polarization fatigue and conduction. Ti and Bi ions are known to be unstable. Bi ions easily evaporate during the sintering process, and Ti ions are Ti^{3+} and Ti^{4+}. Thus, defects, such as bismuth and oxygen vacancies, may exist in the perovskite layers. For a PZT thin film, oxygen vacancies move, reach the interface/electrodes, and are trapped at trap sites [1,2]. Thus, space charges are created at the boundaries/interfaces, and fatigue occurs in the PZT material. BIT and BLT suffers from a high leakage current and domain pinning due to defects, leading to a small remanent polarization after read/write cycles. Defects get trapped at sites like grain boundaries and grain-electrode interfaces and space charges are created. As high-valence Nb doping suppresses the formation of oxygen vacancies and then decrease bismuth defects accompanied by oxygen vacancies. Thus, Nb doping may be an effective way to decrease the conductivity. This results in a low accumulation of vacancies, a low space charge buildup, and low domain pinning.

4. Conclusions

For the Nb doped $Bi_{3.25}La_{0.75}(Ti_{1-x}Nb_x)_3O_{12}$ (BLTN, $x = 0, 0.01, 0.03, 0.05, 0.07, 0.10$) ceramics, the single phase with Bi-layer perovskite structure was confirmed by XRD. The P_r of BLT, BLT-Nb01, BLT-Nb03, BLT-Nb05, BLT-Nb07 and BLT-Nb10 ceramics were estimated to be 10.2, 10.3, 11.7, 12.2, 11.2, 9.9 μC/cm^2, respectively. The maximum P_r of the BLT-Nb05 ceramics ($P_r \approx 12.2\,\mu C/cm^2$) is higher than that of BLT ceramic ($P_r = 10.2\,\mu C/cm^2$). With increasing Nb doping, the T_c decreased and the dielectric constant peak broad. Below T_c, the conductivity of BLT-Nb05 ceramics steadily increased while that of the BLT ceramic remarkably increased at temperatures above 100 °C. High-valence Nb doping suppresses the formation of oxygen vacancies and then decrease bismuth defects accompanied by oxygen vacancies. It is explained by compensation of defect by donor doping of Nb^{5+} ion.

Acknowledgements

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