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Polarization and Piezoelectric Properties of La-substituted $Bi_{0.5}Na_{0.5}TiO_3$ Ceramics

Yoichi Kizaki*, Yuji Noguchi*,**, and Masaru Miyayama*

*RCAST, The University of Tokyo,
4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan.
**PRESTO, Japan Science and Technology Agency,
4-1-8, Hon-cho, Kawaguchi, Saitama 332-0012, Japan.
Fax: 81-3-5452-5083 e-mail: miyayama@rcast.u-tokyo.ac.jp

ABSTRACT

$Bi_{0.5}Na_{0.5}TiO_3$ (BNT) and La-substituted BNT ($La_{0.05}Bi_{0.475}Na_{0.475}TiO_y$) ceramics were prepared by a conventional mixed oxide method. The temperature dependence of dielectric loss measurement indicates that the phase transition temperatures from rhombohedral-to-tetragonal and tetragonal-to-cubic lowered by La substitution. The remanent polarization of BNT and La-BNT ceramics were 29 $\mu C/cm^2$ and 12 $\mu C/cm^2$ at 25°C, respectively. Polarization measurements show that narrower but apparent ferroelectric features remained up to 160°C for both systems. The maximum strain over the maximum electric field (S_{max}/E_{max}) of La-BNT was 160 pm/V, which was much larger than that of BNT (64 pm/V). While the maximum strain of La-BNT reached 0.2% at 120 kV/cm, the strain curve showed a hysteresis loop. High-temperature strain measurements indicate that the S_{max}/E_{max} of La-BNT was over 100 pm/V up to 190°C.

Key words: ferroelectrics, piezoelectric, bismuth sodium titanate (BNT), rare earth substitution

1. INTRODUCTION

Lead zirconium titanate (PZT) ceramics have been widely used for piezoelectric applications, such as sensors, actuators and other electronic devices. PZT-based ceramics, however, contain a large amount of toxic lead, and the use of lead element in these electronic devices would be restricted in the near future by the RoHS directives. Thus, lead-free materials with sufficient ferroelectric and piezoelectric properties are necessarily required in order to protect the environment and the ecosystem.

Bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$: BNT) with a perovskite structure has been regarded as a promising lead-free piezoelectric material, because of its relatively high transition temperature in addition to a large remanent polarization (P_r = 38 $\mu C/cm^2$) [1,2,3].

BNT-based ceramics have been extensively investigated for use in both piezoelectric and pyroelectric applications, since these ceramics have several advantages of [1] a high degree of sintering in air and [2] good mechanical properties [3,4,5]. BNT-based ceramics, however, suffer from a difficulty of polling due to its high coercive field (E_c), leading to a poor piezoelectric property. Several solid solutions of BNT with $SrTiO_3$, $BaTiO_3$ and $NaNbO_3$ have been studied to reduce E_c as well as to form a morphotropic phase boundary (MPB) [6,7,8,9]. Another way to improve the properties of piezoelectric ceramics is the substitution of rare earth at the *A*-site. Park *et al.* have reported that Lanthanum-substituted $Bi_4Ti_3O_{12}$ (BLT) shows a relatively large P_r with a high fatigue endurance against repeated polarization switching [10]. It has reported that the P_r of $SrBi_2Ta_2O_9$ (SBT) at low electric fields is enhanced by praseodymium substitution [11].

In this study, BNT and 5 at.%-La substituted BNT (La-BNT) ceramics were studied to investigate the effects of La substitution on dielectric, ferroelectric and piezoelectric properties. It is shown that La substitution leads to a higher electric-field-induced strain.

2. EXPERIMENTAL

BNT and La-BNT ceramics were prepared by a conventional mixed oxide method. Powders of Bi_2O_3, TiO_2 and La_2O_3 of 99.99% purity and Na_2CO_3 of 99.95% purity were used as starting raw materials. These powders were weighted and mixed by ball milling for 1 h. After drying, the mixed powder was calcined at 800°C for 4 h in an almina crucible. The calcined powder was ground by ball milling for 1 h. The milled powder was molded at 20 MPa and then pressed into disks using cold isostatic press technique at 100 MPa. The green compacts were sintered at 1100°C for 4 h. Powder X-ray diffraction (XRD) patterns were analyzed by the Rietveld method using the program RIETAN-2000 based on *R*3*c* rhombohedral symmetry [12]. The density of the sintered compacts was measured

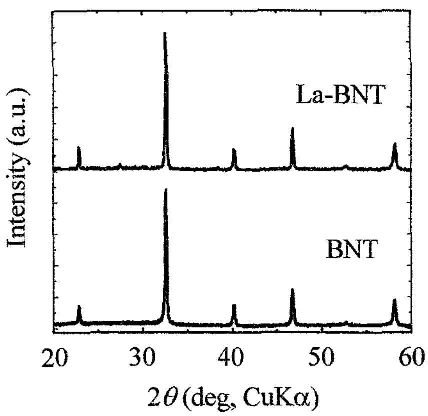

Fig.1 XRD patterns of the ceramics.

by Archimedes method. The sintered ceramics were cut and polished into thin disks with a diameter of 8-9 mm and a thickness of 0.1-0.2 mm, and then gold electrodes were sputtered onto the surfaces. The dielectric permittivity and loss of the ceramics were measured using an impedance analyzer (HP 4194A) over a temperature range of 30°C to 600°C. The polarization hysteresis properties were measured at 25°C and 160°C using an FCE-2STD (Toyo Technica, Japan) at 1 Hz. The electric field induced strain was measured using a contact-type displacement sensor at 1 Hz.

3. RESULTS AND DISCUSSION

All ceramics of BNT and La-BNT sintered at 1100°C had a high relative density of 94-96%. Figure 1 shows the XRD profiles of BNT and La-BNT powders. The Rietveld analysis indicates that the data observed fit fairly well to the calculation (R_{wp} = 10.0%, S = 1.19 for BNT and R_{wp} = 13.6%, S = 1.14 for La-BNT). The lattice parameters were determined to be a = 0.54745(3) nm and c = 1.34484(14) nm for BNT, and a = 0.54892(7) nm and c = 1.34291(9) nm for La-BNT. The La substitution led to an increase in parameter a axis and to a decrease in parameter c (polarization axis). This result indicates that spontaneous strain (c/a) originating from the ferroelectric displacements of the constituent ions is reduced by the La substitution.

Figure 2 shows the temperature dependence of dielectric permittivity (ε_r) of BNT and La-BNT ceramics at a frequency of 100 Hz. The ε_r as a function of temperature exhibited a broad peak for BNT. The La substitution resulted in an ambiguous dielectric anomaly, as can be seen from the broader dielectric peak in Fig.2. Jones *et al.* [10] have reported a detailed structural phase transition in BNT; low-temperature *R*3*c* rhombohedral, intermediate *P*4*bm* tetragonal and high-temperature *P*-3*m* cubic. These phase transitions gradually take place

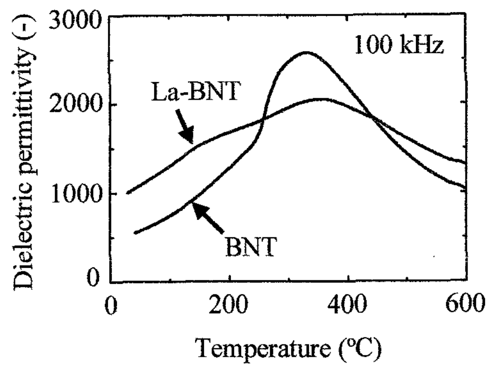

Fig.2 Dielectric permittivity as a function of temperature of the ceramics.

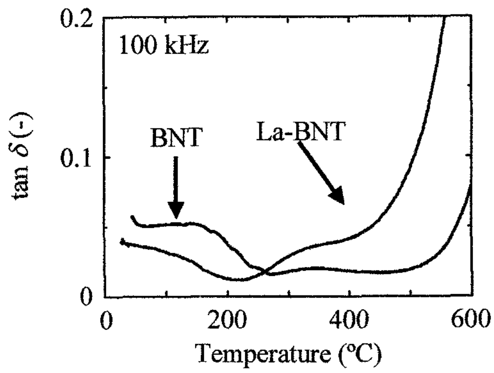

Fig.3 Dielectric loss property as a function of Temperature of the ceramics.

through the coexisting temperature region. This broad ε_r peak of La-BNT suggests that the coexisting temperature region was wider than that of BNT and more gradual phase transition occurred for La-BNT. The ε_r of La-BNT at room temperature was 1080, which was twice as large as that of BNT (550), suggesting its superior piezoelectric properties.

Figure 3 shows the temperature dependence of dielectric loss (tan δ) of BNT and La-BNT ceramics at a frequency of 100 Hz. The temperature dependence of tan δ can be divided into three regions, corresponding to the phase transitions in BNT reported by Jones *et al.* [10]. However, these phase transitions were not observed clearly in La-BNT. This result indicates that phase transitions occurred gradually in La-BNT, which is consistent with the result of the temperature dependence of ε_r. The La substitution lowered dip temperature of tan δ, suggesting the lower phase-transition temperatures for La-BNT compared with BNT.

Figure 4 shows the polarization hysteresis loops of the ceramics at room temperature and 160°C. BNT exhibited a saturated polarization hysteresis loop, a remanent polarization (P_r) of 29 $\mu C/cm^2$ and a coercive field (E_c) of 71 kV/cm at room temperature. These

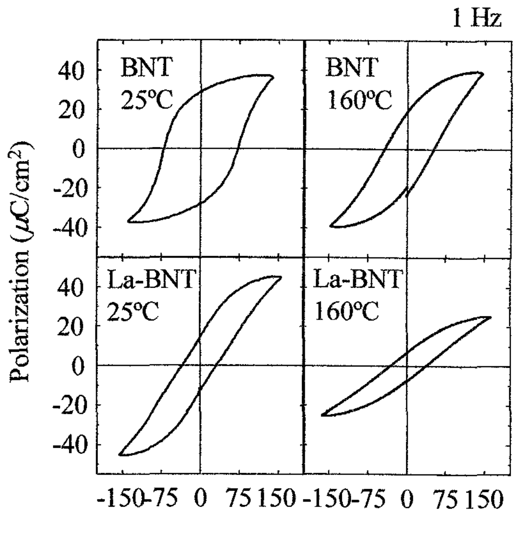

Fig.4 *P-E* hysteresis loops of the ceramics at 25°C and 160°C.

values were in good agreement with previous reports [13]. The La-substituted samples showed smaller values of P_r and E_c (12 μC/cm^2 and 33 kV/cm) than those of BNT at room temperature. The structural analysis has revealed that the ferroelectric distortion is weakened by the La substitution, which is responsible for the smaller P_r and lower E_c found for La-BNT.

Although BNT and La-BNT exhibited smaller P_r values at 160°C, apparent polarization hysteresis loops were observed for both samples. Some research reported that BNT ceramics undergo a transition from ferroelectric to antiferroelectric phase and did not show a ferroelectric hysteresis loop at 160°C [2]. However, direct evidence of long-range antiferroelectric ordering has not been provided yet. In this study, the *P-E* hysteresis loops of BNT and La-BNT at 160°C showed narrow but typical ferroelectric features. The detailed mechanism of the high-temperature ferroelectricity remains unclear, and further investigations are currently in progress.

Figure 5 shows the electric-field-induced strain of BNT ceramics at a frequency of 1 Hz. BNT showed a linear strain behavior. The maximum strain over the maximum electric field (S_{max}/E_{max}) was determined to be 64 pm/V, which is reasonably regarded as piezoelectric strain constant d_{33}. The La substitution resulted in a higher S_{max}/E_{max} of 160 pm/V and, the maximum strain reached 0.2% at an electric field of 120 kV/cm. These values are comparatively large among lead-free ceramics. The electric-field-induced strain of La-BNT showed a hysteresis loop. The polarization rotation of non-180-deg domains seems to be partially responsible for the larger S_{max}/E_{max} observed for La-BNT.

Figure 6 shows the temperature dependence of S_{max}/E_{max} at an electric field of 80 kV/cm. Dielectric

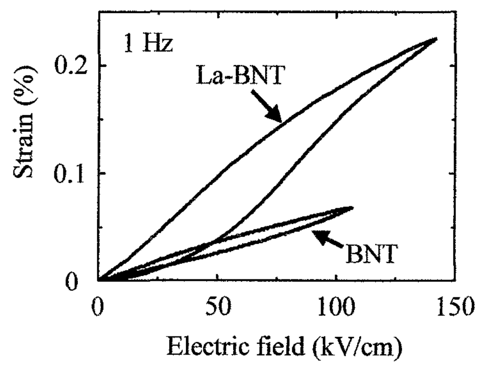

Fig.5 Electric-field-induced strain of the ceramics.

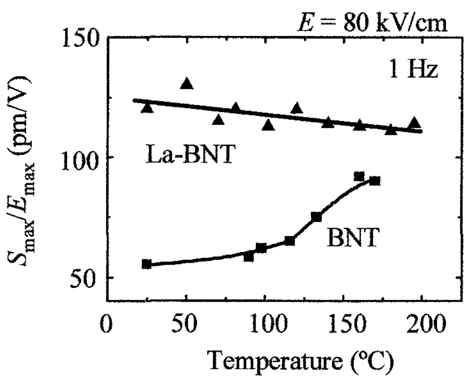

Fig.6 S_{max}/E_{max} property of the ceramics.

breakdown easily occurred above 80 kV/cm at high temperatures. The S_{max}/E_{max} of BNT was increased with increasing temperature. The higher ε_r is attributed to the enhanced piezoelectric properties for BNT ceramics. For La-BNT, the strain hysteresis observed at room temperature became smaller at higher temperatures, leading to a decrease in S_{max}/E_{max}. A relatively large S_{max}/E_{max} over 100 pm/V was maintained up to 190°C. La-BNT has been demonstrated to be advantageous over BNT for high-temperature actuator devices.

4. CONCLUSION

BNT and La-substituted BNT ceramics were prepared and their dielectric, ferroelectric and piezoelectric properties were investigated. The remanent polarization of BNT and La-BNT were 29 μC/cm^2 and 12 μC/cm^2 at 25°C, respectively. Although BNT and La-BNT exhibited smaller P_r values at 160°C, apparent polarization hysteresis loops were observed. The S_{max}/E_{max} of La-BNT was 160 pm/V, which was much larger than that of BNT (64 pm/V). While the electric-field-induced strain of BNT showed a linear strain behavior, that of La-BNT showed a hysteresis loop. For La-BNT, a relatively large S_{max}/E_{max} over 100 pm/V was maintained up to 190°C.

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