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Depolarization temperature and piezoelectric properties of $(Bi_{1/2}Na_{1/2})TiO_3$–$(Bi_{1/2}Li_{1/2})TiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$ lead-free piezoelectric ceramics

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Abstract

The phase transition temperature and piezoelectric properties of $x(Bi_{1/2}Na_{1/2})TiO_3$–$y(Bi_{1/2}Li_{1/2})TiO_3$–$z(Bi_{1/2}K_{1/2})TiO_3$ [$x + y + z = 1$] (abbreviated as BNLKT100y–100z) ceramics were investigated. BNLKT100y–100z ceramics were prepared by conventional ceramic fabrication. The depolarization temperature T_d was determined by the temperature dependence of the dielectric and piezoelectric properties. This study focuses on the effect of Li^{1+} and K^{1+} ions on T_d and the piezoelectric properties of BNT ceramics. BNLKT100y–100z (y = 0–0.08) has a morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases at z = 0.18–0.20, and high piezoelectric properties were obtained at the MPB composition. The piezoelectric constant d_{33} increased with increasing y; however, T_d decreased above y = 0.06. The d_{33} and T_d values of BNLKT4-20 and BNLKT8-20 were 176 pC/N and 171 °C, and 190 pC/N and 115 °C, respectively.

Keywords: C. Piezoelectric properties; Morphotropic phase boundary; Depolarization temperature; Lead-free piezoelectric ceramics

1. Introduction

Lead-free piezoelectric ceramics for replacing $Pb(Zr,Ti)O_3$ (PZT)-based ceramics have recently become required from the viewpoint of environmental protection. Therefore, recently various lead-free piezoelectric solid solutions with a perovskite structure, such as $KNbO_3$ [KN]-, $(Bi_{1/2}K_{1/2})TiO_3$ [BKT]-, $BaTiO_3$ [BT]-, and $(Bi_{1/2}Na_{1/2})TiO_3$ [BNT]-based ceramics have been actively studied [1–12].

BNT has a perovskite structure with rhombohedral symmetry at room temperature. The phase transition temperature of the rhombohedral–tetragonal phase T_{R-T} and the Curie temperature of the tetragonal–cubic phase T_C are approximately 300 and 540 °C on heating, respectively, for a BNT single crystal [13]. Moreover, BNT-based ceramics shows relatively high piezoelectric properties; therefore, they are highly promising lead-free piezoelectric materials [8–12]. However, a significant problem of BNT ceramics is their low depolarization temperature T_d of 185 °C for practical use as a piezoelectric actuator. In our previous paper, the T_d had been investigated accurately by measuring the temperature dependence of the piezoelectric properties of such ceramics [10]. In addition, how to determine the phase transition temperatures in detail for BNT–BKT–BT ternary systems had been demonstrated in our previous work [12] and the behavior of T_d and T_{R-T} for BNT-based solid solutions had been revealed [12,14,15].

Recently, an excellent piezoelectric constants d_{33} (d_{33} meter value) of 231 pC/N was obtained at the morphotropic phase boundary (MPB) composition of $(Bi_{1/2}Na_{1/2})TiO_3$–$(Bi_{1/2}Li_{1/2})TiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$ ternary systems [11], however, the relationship between T_d and d_{33} did not clarify. Therefore, the purpose of the present study is to clarify the relationship between T_d and the piezoelectric properties of $(Bi_{1/2}Na_{1/2})TiO_3$–$(Bi_{1/2}Li_{1/2})TiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$ ternary systems.

2. Experimental procedure

$x(Bi_{1/2}Na_{1/2})TiO_3$–$y(Bi_{1/2}Li_{1/2})TiO_3$–$z(Bi_{1/2}K_{1/2})TiO_3$ [$x + y + z = 1$] (abbreviated as BNLKT100y–100z) ceramics

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were prepared by conventional ceramic fabrication process. Raw materials with purities higher than 99.9% were used to prepare the ceramics. Sintered ceramics were then cut and polished to measure the electrical properties. The crystal structures and lattice constants of the sintered ceramics were determined by X-ray powder diffraction analysis using an X-ray diffractometer (Rigaku; RINT2000). The temperature dependences of the dielectric properties were measured using an automated dielectric measurement system with a multifrequency LCR meter (YHP 4275A and WK6440B). The piezoelectric properties were measured by a resonance–antiresonance method using an impedance analyzer (HP 4294A).

Rectangular shapes of 2 mm × 2 mm × 5 mm were prepared for piezoelectric measurements. These samples were poled in stirred silicone oil by applying DC electrical fields of 4–6 kV/cm at RT. The electromechanical coupling factor of the longitudinal extensional mode k_{33} was calculated from the series and parallel resonance frequencies f_s and f_p. The piezoelectric constant d_{33} was calculated using the following formula of

$$d_{33} = k_{33}\sqrt{\varepsilon_{33}^{T} \cdot s_{33}^{E}}, \quad (1)$$

where ε_{33}^{T} is the free permittivity, which is measured after poling at 1 kHz, and s_{33}^{E} is the elastic constant.

3. Results and discussion

The densities of the ceramics were measured by the Archimedes method. The ratios of the measured densities to the theoretical densities of the sintered ceramics were all higher than 96%. The phases of BNLKT100*y*–100*z* were characterized using X-ray diffraction patterns. A single-phase perovskite structure was obtained for BNLKT0-100*z*. Although BNLKT100*y*-0 shows a single-phase perovskite structure below $y = 0.24$, some impurity phases were observed for BNLKT28-0. This means that the solid solubility limit of Li^{+} (y) is 0.24 for BNLKT100*y*-0 because of the small ionic radius. The depolarization temperature T_d and the piezoelectric constant d_{33} of BNLKT100*y*-0 were shown in Fig. 1. The T_d and d_{33} of BNLKT0-0 (BNT) were 185 °C and 69.8 pC/N, respectively. d_{33} increased with increasing y for BNLKT100*y*-0, and the highest d_{33} was obtained for BNLKT16-0. On the other hand, T_d of $y < 0.06$ was higher than that of BNT for BNLKT100*y*-0, and T_d decreased with increasing y above 0.08. It is very important to increase d_{33} without reducing T_d, and the T_d and d_{33} values of BNLKT4-0 and BNLKT8-0 were 196 °C and 75.7 pC/N, and 170 °C and 85.3 pC/N, respectively. Therefore, in this study, T_d and the piezoelectric properties of BNLKT4-100*z* and BNLKT8-100*z* were investigated in detail.

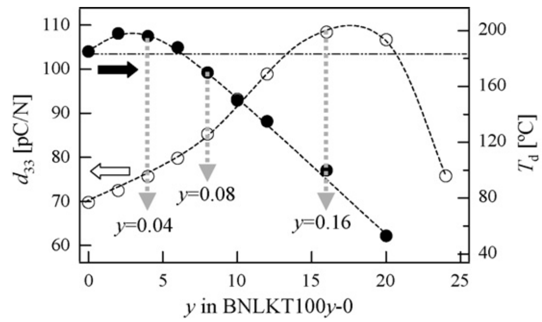

Fig. 1. Depolarization temperature T_d and piezoelectric constant d_{33} of BNLKT100*y*-0.

The lattice constants a and c, and rhombohedrality 90-α and tetragonality c/a of BNLKT4-100*z* are shown in Fig. 2(a) and (b). Although BNLKT4-100*z* showed rhombohedral symmetry for $z = 0$–0.18, BNLKT4-20 showed tetragonal symmetry. This means the MPB between the rhombohedral and tetragonal phases is $z = 0.18$–0.20 for BNLKT4-100*z*.

The temperature dependences of the coupling factor k_{33} and dielectric loss tangent tan δ after poling for BNLKT4-100*z* ($z = 0.08$, 0.12, 0.16, 0.20, 0.24, and 0.28) are shown in Fig. 3. It can be seen that T_d for the peak of tan δ is good agreement with the values determined from k_{33} for BNLKT4-100*z* ($z = 0.08$, 0.12, 0.16, 0.20, and 0.24). However, T_d determined from tan δ was 10 °C higher than that determined from k_{33} for BNLKT4-28 because of the internal stress caused by the poling treatment.

Fig. 4 shows the variation in T_d as a function of z for BNLKT0-100*z*, BNLKT4-100*z*, and BNLKT8-100*z*. It is realized that the T_d of BNLKT4-100*z* is higher than that of BNLKT0-100*y*. On the other hand, the T_d of BNLKT8-100*z* is smaller than that of BNLKT0-100*z*. These results indicate that a small amount of Li^{1+} can increase T_d. Moreover, the variation in T_d as a function of z in BNLKT4-100*z* is similar to those in 90-α and c/a, as shown in Fig. 2(b). Therefore, it is considered that T_d is probably related to the magnitude of 90-α and c/a.

The piezoelectric properties were measured by the resonance–antiresonance method. The electromechanical cou-

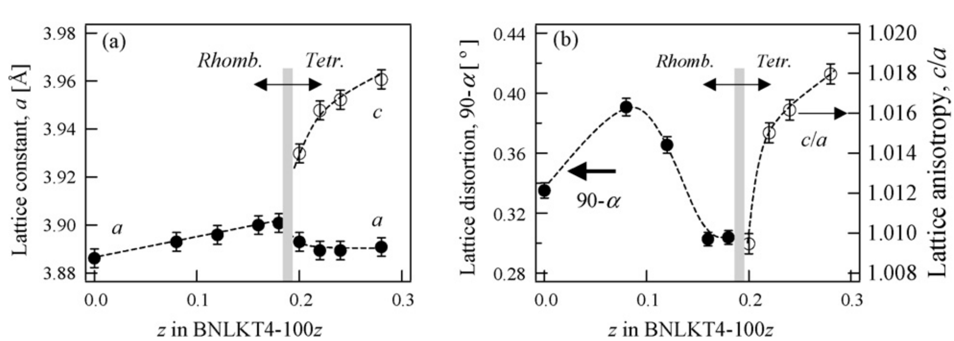

Fig. 2. Variations in (a) lattice constants a and c, and (b) rhombohedrality 90-α and tetragonality c/a as functions of z for BNLKT4-100*z* ceramics.

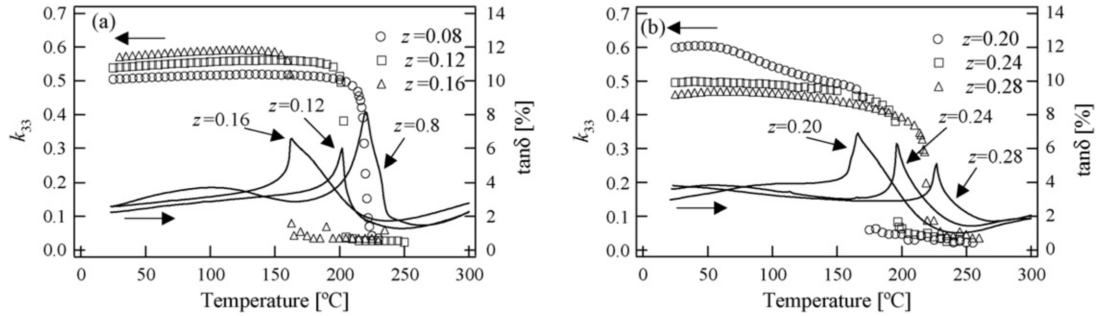

Fig. 3. Temperature dependences of coupling factor k_{33} and dielectric loss tangent after poling for BNLKT4-100z; (a) $z = 0.08$, 0.12, and 0.16 and (b) $z = 0.20$, 0.24, and 0.28.

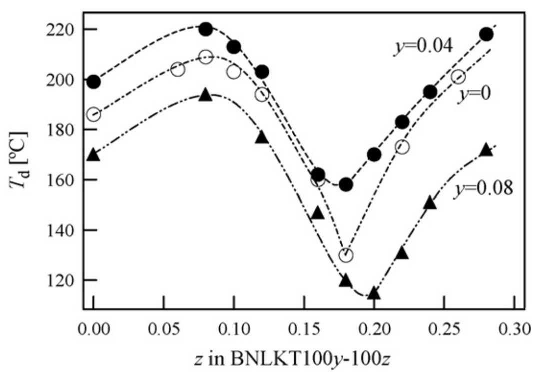

Fig. 4. Depolarization temperatures T_d of BNLKT0-100z, BNLKT4-100z, and BNLKT8-100z ceramics.

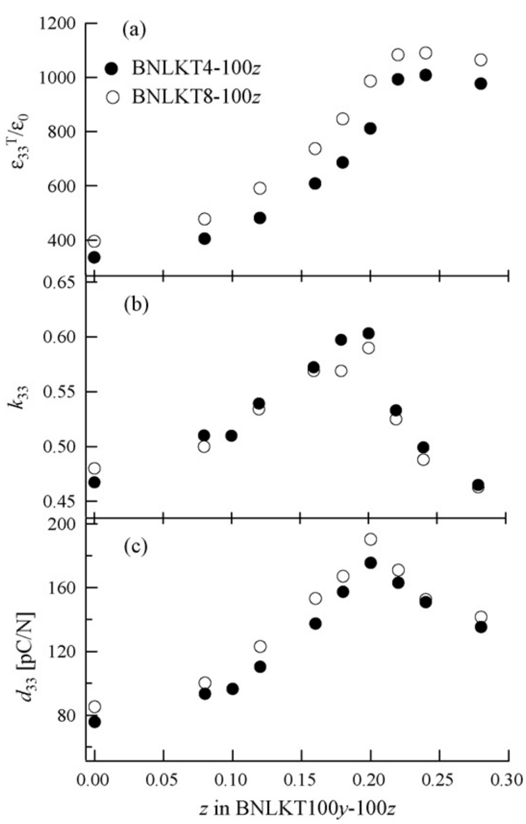

Fig. 5. (a) Free permittivities $\varepsilon_{33}^{T}/\varepsilon_0$, (b) electromechanical coupling factors k_{33}, and (c) piezoelectric constants d_{33} of BNLKT4-100z and BNLKT8-100z ceramics.

pling factor k_{33}, free permittivity ε_{33}^{T}, and piezoelectric constant d_{33} of BNLKT4-100z and BNLKT8-100z are shown in Fig. 5. The ε_{33}^{T} of BNLKT100y–100z increased markedly near the MPB composition, and the ε_{33}^{T} values of the tetragonal side were higher than those of the rhombohedral side. Moreover, the ε_{33}^{T} values of BNLKT8-100z were all higher than those of BNLKT4-100z because the T_d of BNLKT8-100z is lower than that of BNLKT4-100z, and the $\varepsilon_{33}^{T}/\varepsilon_0$ values of BNLKT4-100z and BNLKT8-100z at $z = 0.22$–0.28 were approximately equal at 1000 and 1100, respectively. On the other hand, the k_{33} values of BNLKT4-100z were almost the same as those of BNLKT8-100z, as shown in Fig. 5(b), and the highest k_{33} values were 0.603 for BNLKT4-20 and 0.590 for BNLKT8-20.

Fig. 5(c) shows d_{33} as a function of z for BNLKT4-100z and BNLKT8-100z. d_{33} was calculated using formula (1). For the BNLKT100y–100z system, the d_{33} values of BNLKT8-100z were higher than those of BNLKT4-100z, because the $\varepsilon_{33}^{T}/\varepsilon_0$ values of BNLKT8-100z were higher than those of BNLKT4-100z. The highest d_{33} values of BNLKT4-100z and BNLKT8-100z were 176 and 190 pC/N, respectively. Moreover, the highest d_{33} of BNLKT0-20 was 168 pC/N. These results indicate that the substitution of Li ions in the A-site of BNT is very effective for improving d_{33}.

From the viewpoint of the temperature property, T_d is actual working temperature; therefore, its T_d value is very important. The d_{33} values of MPB compositions were rather high; however, the T_d values of the MPB composition were very low. In this study, for BNLKT0-20, BNLKT4-20, and BNLKT8-20, showed 130, 171 and 115 °C, respectively. Although, high d_{33} (d_{33} meter value) of 231 pC/N was obtained for BNLKT10-20 [11], it is considered that the T_d of this composition is probably lower than 100 °C. Thus, considering its high d_{33} and high T_d, the MPB composition of BNLKT4-100x is thought to be the optimal composition for that of BNLKT100y–100z systems.

4. Conclusions

In this study, the depolarization temperature T_d and piezoelectric properties of BNLKT100y–100z were investigated. This study revealed that a small amount of Li ions can increase d_{33} without reducing T_d. The d_{33} values of BNLKT8-100z were higher than those of BNLKT4-100z; however, the T_d of BNLKT8-100z was lower than that of BNLKT4-100z. Considering its high d_{33} and high T_d, the MPB composition of

BNLKT4-100z is thought to be the optimal composition for that of BNLKT100y–100z systems.

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