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Piezoelectric and ferroelectric properties of lead-free $[Bi_{1-y}(Na_{1-x-y}Li_x)]_{0.5}Ba_yTiO_3$ ceramics

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Abstract

Lead-free $[Bi_{1-y}(Na_{1-x-y}Li_x)]_{0.5}Ba_yTiO_3$ (BNLB-*x*/*y*) piezoelectric ceramics were prepared by sintering the constituent oxides, and their piezoelectric and ferroelectric properties studied. The results of X-ray diffraction (XRD) suggest that Li^+ and Ba^{2+} diffuse into the $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) lattices to form a solid solution with a single-phase perovskite structure. The ceramics can be well sintered at 1100–1150 °C. The introduction of Li^+ and Ba^{2+} into $Bi_{0.5}Na_{0.5}TiO_3$ significantly decreases the coercive field, E_c but maintains the large remanent polarization, P_r of the materials. The ceramics exhibit relatively good piezoelectric properties and very strong ferroelectricity: piezoelectric constant, $d_{33} = 208$ pC/N, planar electromechanical coupling factor, $k_p = 37.0\%$, remanent polarization, $P_r = 38.5\ \mu C/cm^2$, coercive field, $E_c = 3.27$ kV/mm. The depolarization temperature, T_d of BNLB-0.075/0.04 ceramics is about 190 °C.

Keywords: (Bi, Na, Li, Ba)TiO_3; Piezoelectric properties; Ferroelectric properties; Perovskite

1. Introduction

$PbTiO_3$–$PbZrO_3$ (PZT) and PZT-based multi-component ceramics are widely used in electronic and microelectronic devices due to their superior electrical properties. The use of lead-based ceramics has caused serious environmental problems because of the toxicity of lead oxide and its high vapor pressure during sintering. Therefore, to reduce lead pollution, it is necessary to develop piezoelectric ceramics that should be "lead-free at last".[1]

$Bi_{0.5}Na_{0.5}TiO_3$ (BNT) is a perovskite ferroelectric and considered an alternative lead-free piezoelectric material because of a large remanent polarization ($P_r = 38\ \mu C/cm^2$)[2]. However, pure BNT piezoelectric ceramics are difficult to pole adequately because of its relatively large coercive field ($E_c = 7.3$ kV/mm)[2] and therefore provide low piezoelectric properties. To enhance the piezoelectric properties of BNT ceramics, some BNT-based solid solutions have been developed and extensively studied, including BNT–$BaTiO_3$,[2,3] BNT–$Bi_{0.5}K_{0.5}TiO_3$,[4] BNT–$BiFeO_3$,[5] BNT–$NaNbO_3$,[6] BNT–$Bi_{0.5}K_{0.5}TiO_3$–$BaTiO_3$,[7] BNT–$KNbO_3$–$\frac{1}{2}(Bi_2O_3{\cdot}Sc_2O_3)$,[8] BNT–$Ba(Cu_{1/2}W_{1/2})O_3$[9] and $(Bi_{0.5}$-$Na_{0.5})_{1-1.5x}La_xTiO_3$.[10] However, the piezoelectric properties of these BNT-based solid solutions are not sufficient. To further improve the piezoelectric properties of BNT ceramics, a key point is to decrease efficiently the large coercive field but retain simultaneously the strong ferroelectricity of the materials. Therefore, the development of new BNT-based systems with larger remanent polarization and lower coercive field may be a promising approach to enhance significantly the piezoelectric properties of the materials.

In this paper, a new member of BNT-based lead-free ceramics, $[Bi_{1-y}(Na_{1-x-y}Li_x)]_{0.5}Ba_yTiO_3$, was fabricated by conventional ceramic processing and their piezoelectric and ferroelectric properties investigated.[11]

2. Experimental

Conventional ceramic fabrication technique was used to prepare BNLB-*x*/*y* ceramics. Industrial-grade metal oxides or carbonate powders of Bi_2O_3, Na_2CO_3, Li_2CO_3, $BaCO_3$ and TiO_2 were used as starting raw materials. The raw materials were mixed by ball-milling and calcined at 850 °C for 2 h. After calcination, the powders were granulated by adding PVA as a binder, pressed into discs and then sintered at 1100–1200 °C for 2 h in air. The sintered ceramic specimens were coated with silver

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paste to form electrodes on both sides and fired at 810 °C. The specimens were poled in a silicone oil bath with a dc field of 3–4 kV/mm at 80 °C for 20 min.

The crystal structure of the sintered samples was examined by X-ray diffraction technique (DX-1000X, China). The microstructures of the sintered samples were observed using scanning electron microscopy (S-450, Japan). The bulk densities of the sintered samples were measured by Archimedes' method. The planar electromechanical coupling factor, k_p was determined by the resonance-antiresonance method according to IEEE standards using an impedance analyzer (HP4194A). The piezoelectric constant, d_{33} was measured using a piezo-d_{33} meter (ZJ-3A, China). The dielectric properties of the ceramics were measured using a capacitance meter (HP 4287A). The *P–E* hysteresis loops were obtained using Radiant Precision Workstation.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of BNLB-*x*/*y* ceramics between 39 and 48°. The complete pattern (not shown in Fig. 1) indicates that the ceramics have a perovskite structure. No second phase could be detected suggesting that Li^+ and Ba^{2+} diffuse into the BNT lattices to form a solid solution, whereby Li^+ enters Na^+ sites and Ba^{2+} occupies $(Bi_{0.5}Na_{0.5})^{2+}$ sites. Fig. 1 shows that the crystal structures of BNLB-*x*/0.06 ceramics with $x = 0.025$ and 0.05 are rhombohedral phases. However, the single peak at (2 0 2) of BNLB-*x*/*y* ($x < 0.075$ and $y \leq 0.06$) ceramics splits into two peaks at (0 0 2) and (2 0 0) of BNLB-*x*/*y* ($x \geq 0.075$ and $y \geq 0.06$) suggesting a tetragonal structure. Therefore, it can be inferred that a morphotropic phase boundary (MPB) of the BNLB-*x*/*y* ceramic system exists near $x = 0.075$ and $y = 0.06$, at which composition the rhombohedral turns into tetragonal symmetry.

The compositional dependency of the relative densities of BNLB-*x*/*y* ceramics is shown in Fig. 2. The BNLB-*x*/*y* ceramics sintered at 1100 °C for 2 h have bulk densities of 5.42–5.88 g/cm^3. BNLB-0.075/*y* ceramics ($0.02 < y < 0.12$) sintered at 1100 °C for 2 h provide high relative densities of 96.2–98.6% (Fig. 2a). In contrast, BNLB-0.025/*y* ceramics can

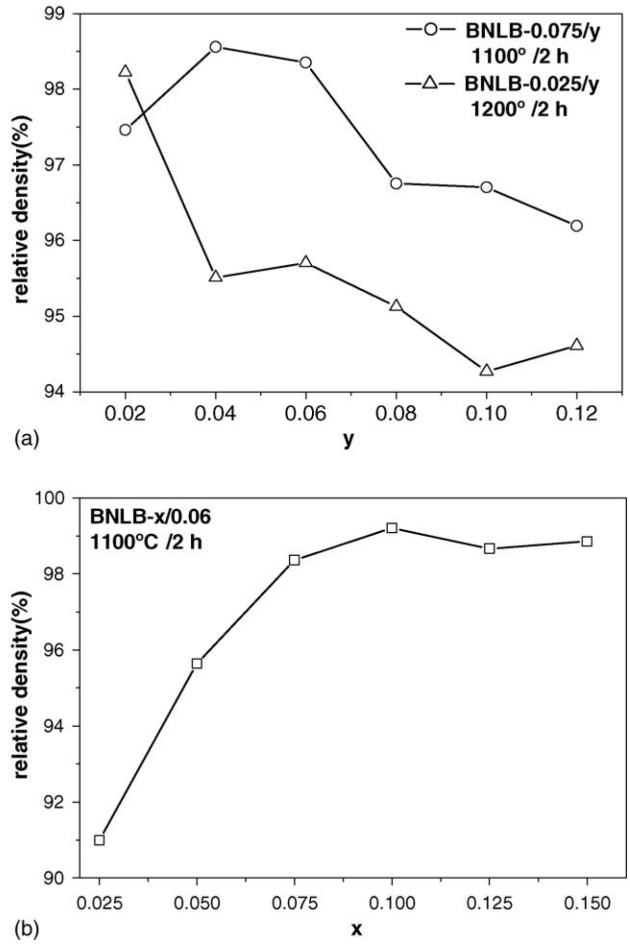

Fig. 2. (a) Relative density of BNLB-0.075/*y* ceramics sintered at 1100 °C for 2 h and BNLB-0.025/*y* ceramics sintered at 1200 °C for 2 h as a function of the atomic fraction *y* of Ba and (b) relative density of BNLB-*x*/0.06 sintered at 1100 °C for 2 h as a function of the atomic fraction *x* of Li.

be well sintered at 1200 °C for 2 h to reach relative densities of 94.3–98.2%, somewhat lower than those of BNLB-0.075/*y* ceramics sintered at 1100 °C for 2 h. Generally, Li-free BNT-based ceramics can be sintered to obtain near theoretical densities at 1175–1250 °C for 2 h. However, the addition of Li significantly improves the sintering performance, decreases the sintering temperature of BNT ceramics, and greatly assists in densification of BNT-based ceramics. The dependency of the relative density of BNLB-*x*/*y* on the atomic fraction of Li is shown in Fig. 2b. With increasing atomic fraction *x* of Li, the relative density of BNLB-*x*/0.06 sintered at 1100 °C for 2 h significantly increases up to $x = 0.075$ and then remain constant at 98.3–99.2%. This may be ascribed to the low melting temperature of Li compounds that appears to promote formation of a liquid phase during sintering.

Fig. 3 shows the microstructure of BNLB-*x*/*y* samples sintered at different temperature. All of samples are very dense with almost no porosity.

Fig. 4 shows the dependencies of piezoelectric and dielectric properties of BNLB-0.075/*y* on the atomic fraction *y* of Ba. The piezoelectric constant, d_{33} and planar electromechanical coupling factor, k_p of the BNLB-0.075/*y* ceramics sintered at

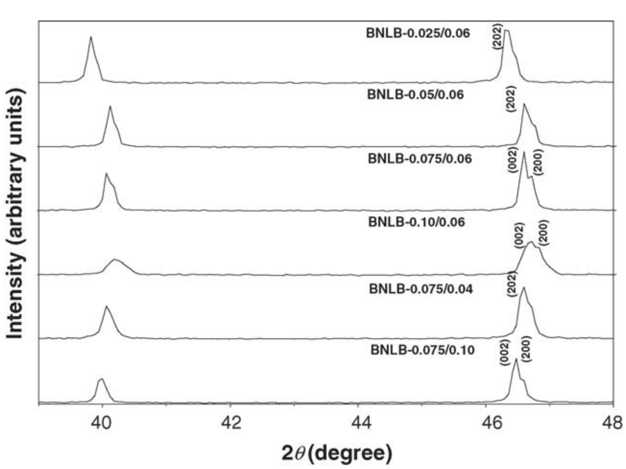

Fig. 1. X-ray diffraction pattern of BNLB-*x*/*y* ceramics.

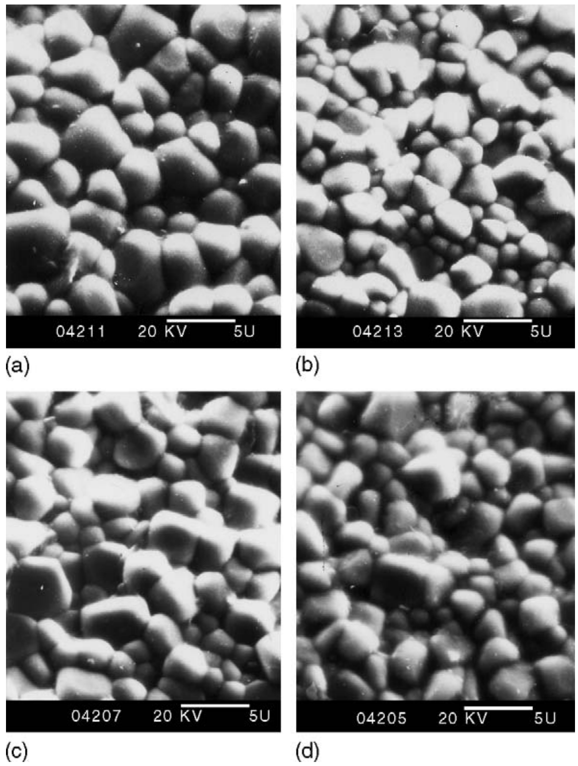

Fig. 3. SEM micrographs of the sintered samples: (a) BNLB-0.075/0.02 sintered at 1100 °C for 2 h; (b) BNLB-0.075/0.10 sintered at 1100 °C for 2 h; (c) BNLB-0.05/0.06 sintered at 1150 °C for 2 h; and (d) BNLB-0.10/0.06 sintered at 1125 °C for 2 h.

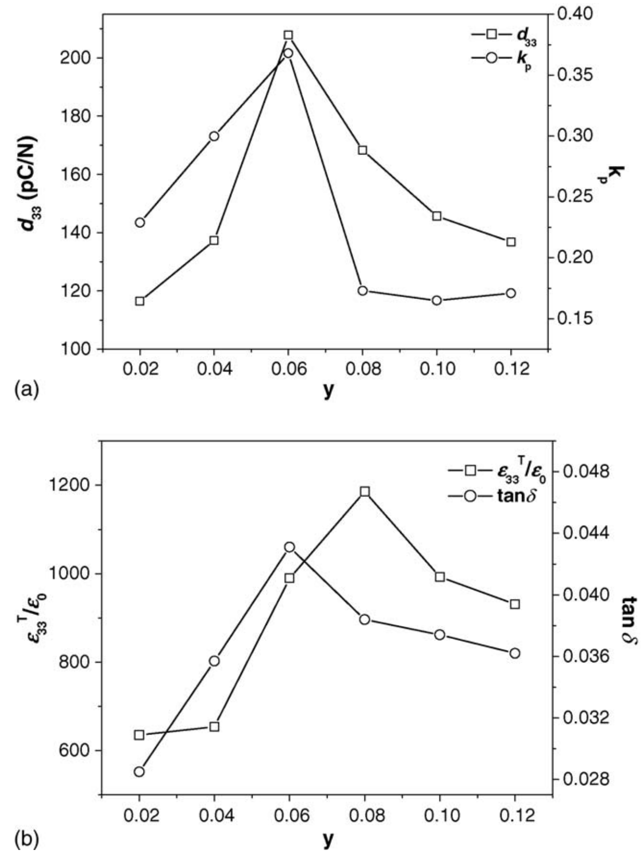

Fig. 4. Piezoelectric and dielectric properties of BNLB-0.075/y ceramics as a function of the atomic fraction y of Ba: (a) piezoelectric constant, d_{33} and planar electromechanical coupling factor, k_p and (b) relative dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ and the dissipation factor tan δ.

1100 °C for 2 h reach the maximum values of 208 pC/N and 37.0% at $y = 0.06$ (Fig. 4a). The relative dielectric constant and the dissipation factor show the maximum values of 1186 and 0.043 at $y = 0.80$ and 0.06, respectively (Fig. 4b).

Fig. 5 shows the dependencies of piezoelectric and dielectric properties of BNLB-x/0.06 on the atomic fraction x of Li. The maximum values of d_{33} (208 pC/N) and k_p (37.0%) of the BNLB-x/0.06 ceramics are observed at $x = 0.075$, and the BNLB-x/0.06 ceramics with $x = 0.075$–0.10 provide relatively good piezoelectric properties (Fig. 5a). Greatly different from the dependency of dielectric properties on the atomic fraction y of Ba shown in Fig. 4b, Fig. 5b shows that $\varepsilon_{33}^T/\varepsilon_0$ and tan δ increase significantly with increasing molar fraction x of Li. The BNLB-0.075/0.06 ceramics possess the best piezoelectric properties (Fig. 4a), which may be attributed to the very high relative density and a composition near the MPB where the number of the possible spontaneous polarization direction of the materials increases and the ceramics can be easily poled.

Fig. 6 shows the ferroelectric properties of BNLB-0.075/y ceramics as a function of the atomic fraction y of Ba. The remanent polarization, P_r increases slightly with increasing atomic fraction y of Ba up to $y = 0.06$ and then decreases quickly with further increasing Ba content. At $y = 0.06$, the remanent polarization, P_r reaches the maximum value of 38.5 μC/cm^2. The coercive field, E_c decreases almost linearly with increasing Ba content. As mentioned above, pure BNT ceramics possess a large remanent polarization ($P_r = 38$ μC/cm^2) and a large coercive field ($E_c = 7.3$ kV/mm). Compared with pure BNT ceramics, partial substitution of Na^+ by Li^+ and partial substitution of $(Bi_{0.5}Na_{0.5})^{2+}$ by Ba^{2+} effectively decrease the coercive field, E_c but simultaneously maintain the very high remanent polarization, P_r. This allows efficient poling of the ceramics, resulting in an significant enhancement of their piezoelectric properties.

The temperature dependencies of P–E hysteresis loops of BNLB-0.075/0.06 and BNLB-0.075/0.04 ceramics are shown in Fig. 7. At room temperature, the hysteresis loops of BNLB-0.075/0.06 and BNLB-0.075/0.04 ceramics are well rectangular ($P_r = 38.5$ and 36.3 μC/cm^2, $E_c = 3.27$ and 3.80 kV/mm, respectively) as typical for ferroelectrics. With temperature increasing, the loop of BNLB-0.075/0.06 ceramics (Fig. 7a) begins to narrow but up to 130 °C still keeps the typical ferroelectric feature with a rather large remanent polarization, P_r (26.4 μC/cm^2). However, at 150 °C the ferroelectricity of the ceramics weakens ($P_r = 8.33$ μC/cm^2) and the piezoelectric properties almost disappear. The hysteresis loop of the ceramics is deformed, becomes narrower and appears to form a double-like P–E hysteresis loop. As temperature further increase up to 180 °C, the hysteresis loop becomes even narrower ($P_r = 6.60$ μC/cm^2) than that at 150 °C. The depolarization temperature, T_d, at which the ferroelectricity of the materials begins to weaken, plays an important role in device applications. From the data it can be inferred that the T_d of BNLB-0.075/0.06 ceramics is about 150 °C.

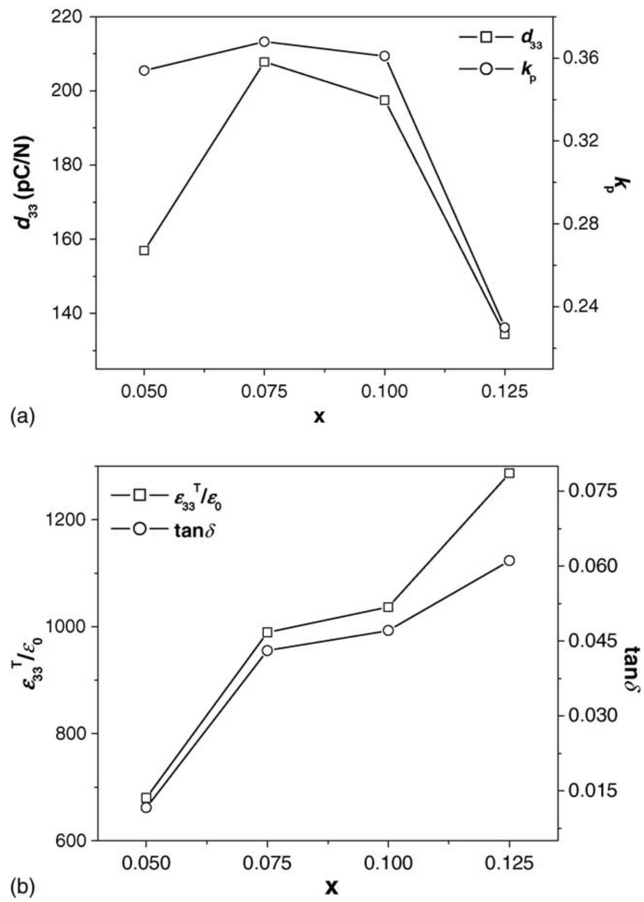

Fig. 5. Piezoelectric and dielectric properties of BNLB-*x*/0.06 ceramics as a function of the atomic fraction *x* of Li: (a) piezoelectric constant, d_{33} and planar electromechanical coupling factor, k_p and (b) relative dielectric constant $\varepsilon_{33}^{T}/\varepsilon_0$ and the dissipation factor tan δ.

The dependency of the hysteresis loop of BNLB-0.075/0.04 ceramics on temperature is similar to that of BNLB-0.075/0.06 ceramics, but with a higher depolarization temperature, T_d at about 190 °C. Compared with the results reported,[3,7] BNLB-0.075/0.04 ceramics possess simultaneously good piezoelectric properties, strong ferroelectricity and high T_d.

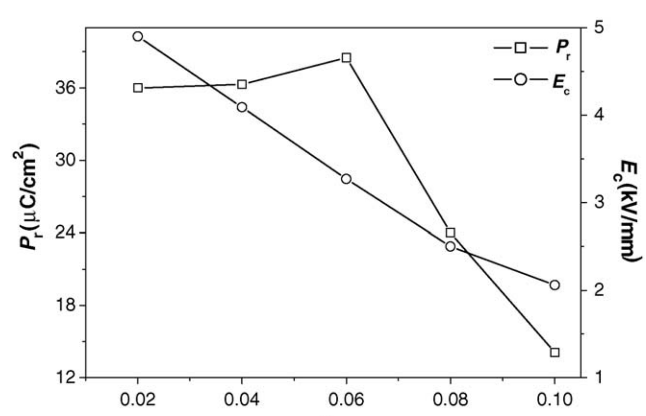

Fig. 6. Ferroelectric properties of BNLB-0.075/*y* ceramics as a function of the atomic fraction *y* of Ba.

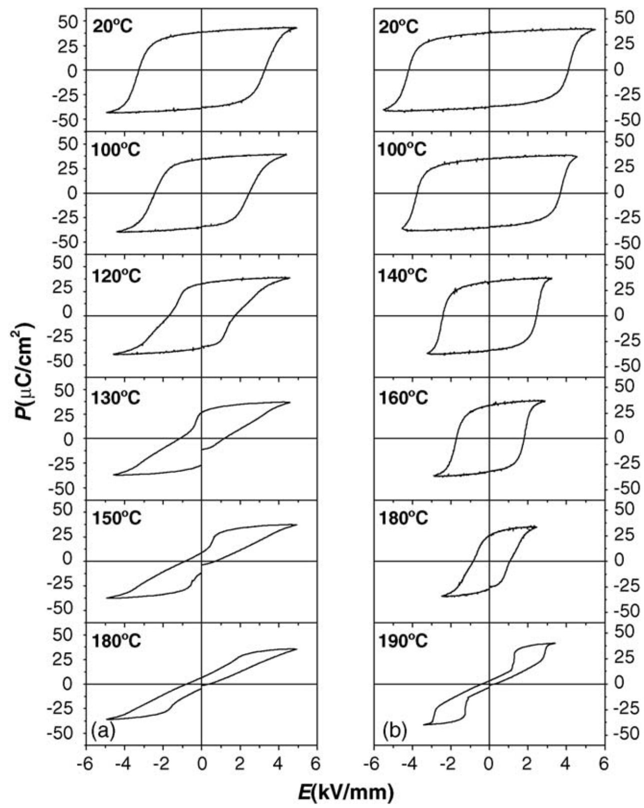

Fig. 7. *P–E* hysteresis loops of BNLB-*x*/*y* ceramics at different temperature for: (a) BNLB-0.075/0.06 and (b) BNLB-0.075/0.04.

4. Conclusion

New $[Bi_{1-y}(Na_{1-x-y}Li_x)]_{0.5}Ba_yTiO_3$ lead-free piezoelectric ceramics have been prepared by conventional ceramic technique. The ceramics possess a single-phase perovskite structure and an MPB may exist near $x = 0.075$ and $y = 0.06$. The ceramics with $0.075 < x < 0.10$ can be well sintered at 1100 °C and have the bulk densities of 5.74–5.88 g/cm^3 which is higher than 96% of the theoretical density. The addition of Li decreases the sintering temperature of BNT ceramics and greatly assists in the densification. The ceramics reach optimum piezoelectric and ferroelectric properties near the MPB: piezoelectric constant, d_{33} = 208 pC/N, planar electromechanical coupling factor, k_p = 37.0%, remanent polarization, P_r = 38.5 μC/cm^2, coercive field, E_c = 3.27 kV/mm. The depolarization temperature, T_d of the BNLB-0.075/0.04 ceramics is about 190 °C.

Acknowledgement

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