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Structural stability and depolarization of manganese-doped $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ relaxor ferroelectrics

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This work reveals that 0.5 mol. % manganese (Mn) doping in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ ($x = 0$ and 0.075) solid solutions can increase structural thermal stability, depolarization temperature (T_d), piezoelectric coefficient (d_{33}), and electromechanical coupling factor (k_t). High-resolution X-ray diffraction and transmission electron microscopy reveal coexistence of rhombohedral (R) $R\bar{3}c$ and tetragonal (T) $P4bm$ phases in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.925}\text{Ba}_{0.075}\text{TiO}_3$ (BN7.5BT) and 0.5 mol. % Mn-doped BN7.5BT (BN7.5BT-0.5Mn). $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) and BN7.5BT show an R–R+T phase transition, which does not occur in 0.5 mol. % Mn-doped BNT (BNT-0.5Mn) and BN7.5BT-0.5Mn. Dielectric permittivity (ϵ') follows the Curie-Weiss equation, $\epsilon' = C/(T - T_0)$, above the Burns temperature (T_B), below which polar nanoregions begin to develop. The direct piezoelectric coefficient (d_{33}) and electromechanical coupling factor (k_t) of BN7.5BT-0.5Mn reach 190 pC/N and 47%. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4898322>]

I. INTRODUCTION

Lead-free bismuth sodium titanate $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) is considered as a promising piezoelectric material.¹ Its relaxor ferroelectric properties are closely related to the random placements of Bi^{3+} and Na^+ ions on the A sites of the perovskite structure. BNT-based materials have attracted attention because of their promising piezoelectric and electromechanical properties, which are comparable to those of lead-containing $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) piezoceramics.¹ BNT has a high ferroelectric Curie temperature and undergoes a transition sequence of ferroelectric rhombohedral (R)–ferroelastic tetragonal (T)–cubic phases.² Neutron scattering and X-Ray diffraction (XRD) indicate coexistence of R and T phases.³ The direct piezoelectric coefficients d_{33} and electromechanical coupling factors k_t are respectively 60–80 pC/N and 20%–30% for (001)-cut BNT crystal, and 120–145 pC/N and 45%–55% for 1 at. % Mn-doped BNT crystal.^{4,5}

BNT-based materials have been developed for large piezoelectric and strain responses.^{6–13} The most studied BNT-based compounds include BNT- BaTiO_3 or $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$,^{6–8} BNT- $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$,⁹ BNT- KNbO_3 ,¹⁰ BNT- BiFeO_3 ,¹¹ BNT- SrTiO_3 ,¹² and BNT-BT- $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$.¹³ $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ (abbreviated as BN100xBT) exhibits a morphotropic phase boundary (MPB) between the R and T structures near $x = 0.06 \sim 0.07$,^{14,15} accompanied by polar nanoregions (PNRs) and large E -field-induced piezoelectricity.^{16–18} The large piezoelectricity and strain are associated with an E -field-induced transformation of the polar nanostructures,¹⁹

which allows lower energy barriers for dipole reorientation.⁷ The free energies of the $P4bm$ polar nanoregions and $P4mm$ ferroelectric phase are similar, so the transition from the PNRs to the long-range-ordered ferroelectric phase can occur under an E field.^{20,21} Local monoclinic nanotwins in an overall rhombohedral symmetry have been proposed in BN100xBT compounds to act as the bridging phase for polarization rotation between the rhombohedral and tetragonal structures.^{22,23}

Appropriate Mn doping in $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ferroelectrics can reduce conductivity and enhance electromechanical coupling due to multivalent effects in which the oxidation states of the Mn ion are sensitive to the calcination and sintering processes.²⁴ Sapper *et al.* reported that the depolarization temperatures (T_d) of poled 0.5 mol. % Mn-doped BN100xBT ($x = 0.03, 0.06$, and 0.09) shift to higher temperatures under a dc field.²⁵ A recent report has shown that BN7.5BT possesses the highest piezoelectric coefficient ($d_{33} \sim 186$ pC/N) among the BN100xBT compositions.¹⁸ With respect to applications of BN100xBT system, higher depolarization T_d and structural thermal stability are essential for piezoelectric actuators and transducers. The aim of this work is to explore the effects of 0.5 mol. % Mn doping on structural thermal stability, dielectric permittivity, depolarization transition, PNRs, ferroelectric polarization, field-induced strain, and piezoelectricity of $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ ($x = 0$ and 0.075) piezoceramics.

II. EXPERIMENTAL PROCEDURE

$(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$, $(\text{Bi}_{0.5}\text{Na}_{0.5})(\text{Ti}_{0.995}\text{Mn}_{0.005})\text{O}_3$ (BNT-0.5Mn), $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.925}\text{Ba}_{0.075}\text{TiO}_3$ (BN7.5BT), and

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(Bi_{0.5}Na_{0.5})_{0.925}Ba_{0.075}(Ti_{0.995}Mn_{0.005})O₃ (BN7.5BT-0.5Mn) ceramics were prepared by using the solid state reaction technique. High purity (>99%) powders of Bi₂O₃, Na₂CO₃, BaCO₃, TiO₂, and MnO₂ were used as starting materials. Stoichiometric amounts of powders were ball-milled for 24 h in ethanol. The mixture was calcined at 900 °C (2 h) and a Retsch PM100 planetary ball mill was used to reduce particle size. The calcined powders were then pressed into 1.0 cm-diameter disks for sintering at 1150 °C (2 h), 1170 °C (2 h), 1200 °C (2 h), and 1200 °C (2 h) for BNT, BNT-0.5Mn, BN7.5BT, and BN7.5BT-0.5Mn, respectively.

Grain morphologies of as-sintered ceramics were obtained using a scanning electron microscope (SEM; HITACHI S-3400N FE-SEM). A Rigaku Multiplex Diffractometer with wavelengths $K\alpha_1$ (1.5406 Å) and $K\alpha_2$ (1.5444 Å) was used to analysis structure. A high-resolution transmission electron microscope (TEM) (JEOL JEM-2100 LaB6) was used to study nanoscale morphologies and structures. The (111) and (200) XRD peaks were fitted with Gaussian profiles to study structures and lattice parameters. A Wayne-Kerr Analyzer PMA3260A was used to obtain the real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity. Three processes were used in the dielectric measurements. The first two are called “zero-field-heated” (ZFH) and “zero-field-cooled” (ZFC) in which the data were taken upon heating and cooling without any prior E -field poling. In “prior-poled before zero-field-heated” (PP-ZFH), the sample was poled at room temperature with a dc field of $E = 40$ kV/cm for 5 min before the ZFH process was performed. The depolarization current density (J_d) is current density measured in the prior-poled sample upon heating or cooling without a dc bias voltage. Hysteresis loops were taken by using a Sawyer-Tower circuit for measuring frequency $f = 125$ Hz. Direct piezoelectric coefficients d_{33} were measured using a Model ZJ-6B piezometer as dc poling E field was increased by steps. Electromechanical coupling factors (k_t) were measured for poled samples (poling field $E = 40$ kV/cm) using a Wayne-Kerr Precision Impedance Analyzer 6420.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra and SEM grain morphologies of as-sintered ceramics, indicating no second phase. The average grain sizes are 6.80 μm , 16.31 μm , 2.43 μm , and 2.11 μm for BNT, BNT-0.5Mn, BN7.5BT, and BN7.5BT-0.5Mn, respectively. The XRD peaks obey the Bragg law, $2d_{hkl} \sin \theta_{hkl} = n\lambda$, where (hkl) is crystallographic orientation. For the rhombohedral structure, two (111) and one (200) XRD peaks are expected from the eight crystallographic orientations, i.e.,²⁶

$$\begin{aligned} d_{(111)}^2 &= [a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)] / \\ &\quad [3\sin^2\alpha + 6(\cos^2\alpha - \cos\alpha)]; \\ d_{(11\bar{1})}^2 &= [a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)] / \\ &\quad [3\sin^2\alpha - 2(\cos^2\alpha - \cos\alpha)]; \\ d_{(200)}^2 &= [a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)] / (4\sin^2\alpha) \end{aligned} \quad (1)$$

For the tetragonal (T) structure, one (111) and two (200) XRD peaks are expected from the six orientations, i.e.,

FIG. 1. XRD spectra and SEM grain morphologies.

$d_{(111)} = (\frac{2}{a_T^2} + \frac{1}{c_T^2})^{-1/2}$, $d_{(200)} = \frac{a_T}{2}$, and $d_{(002)} = \frac{c_T}{2}$. a_T and c_T are the lattice parameters of the tetragonal unit cell.

Figure 2 shows (111) XRD spectra before and after poling at $E = 40$ kV/cm in which two-peaks rhombohedral (R) structure is the dominant phase and the tetragonal (T) structure is enhanced after poling. The calculated lattice parameters (a_R and α) of the R structure are given in the figure, revealing a slightly distorted R unit cell. After poling, the α angles become smaller and the lattice parameters (a_R) increase.

Figure 3 shows the (200) XRD spectra before and after poling at $E = 40$ kV/cm, which confirms a dominant rhombohedral (R) phase. After poling at $E = 40$ kV/cm, two broad tetragonal (T) peaks appear in BNT, BN7.5BT, and BN7.5BT-0.5Mn. The unpoled BN7.5BT and BN7.5BT-0.5Mn possess a coexistence of R (major) and T (minor) phases at room temperature. The poled BNT shows an E -field-induced T phase, but BNT-0.5Mn remains in the R phase after poling. The broadness of the XRD peaks is likely associated with nanostructures. Polar nanostructures are often found in relaxor ferroelectrics to accommodate lattice distortions.²⁷ The nanostructure is often smaller than the coherence length of the X-ray radiation, so diffracted waves from various nanostructures can coherently superimpose and broaden the diffraction peak. The calculated lattice parameters are given in the figure.

FIG. 2. (111) XRD spectra before and after poling at $E = 40$ kV/cm. The solid and dashed lines correlate to $K\alpha_1$ and $K\alpha_2$ radiations. The black line is the sum of fitting curves.

Figure 4 shows the ZFH dielectric permittivities and losses ($\tan \delta = \epsilon''/\epsilon'$). Compared with BNT and BN7.5BT, BNT-0.5Mn, and BN7.5BT-0.5Mn exhibit weaker frequency dispersion in the lower temperature regions. The dielectric-maximum temperatures (T_m) of BNT-0.5Mn and BN7.5BT-0.5Mn shift 20 and 15 °C lower than those in BNT and BN7.5BT, respectively. The losses exhibit broad frequency-dependent maxima in the region of 100–200 °C, suggesting a progressive ferroelectric–relaxor transition upon heating. BNT-0.5Mn and BN7.5BT-0.5Mn show smaller dielectric losses than BNT and BN7.5BT at room temperature, respectively.

A phase-shifted conductivity is evident at higher temperatures (>400 °C), above which the dielectric loss is larger than 1.0 and rises exponentially with increasing temperature. This phase-shifted conductivity is mainly due to the thermally activated ionic conduction across intrinsic barriers.²⁸ A frequency-dependent shoulder maximum near 400 °C in the loss $\tan \delta$ of BN7.5BT-0.5Mn is likely due to ionic hopping

FIG. 3. (200) XRD spectra before and after poling at $E = 40$ kV/cm. The solid and dashed lines correlate to $K\alpha_1$ and $K\alpha_2$ radiations. The black line is the sum of fitting curves.

conductivity across more widely spaced and higher extrinsic barriers. This is evidenced by the shoulder disappearing at higher frequency (>10 kHz) because at higher frequencies few carriers have time to drift to these higher barriers.²⁸

A strong dielectric thermal hysteresis takes place in the region of 200–300 °C in the unpoled BNT as seen in Fig. 5(a), suggesting a first-order phase transition. The (200) XRD spectra of BNT in Fig. 6(a), reveal that the tetragonal phase begins to appear near 200 °C and becomes the dominant phase above 250 °C. This evolution suggests a first-order $R - R + T$ structural transition in the region of 200–250 °C. Here, $R + T$ represents a coexistence of R and T phases. Note that a transition sequence of $R - R + T - T - C$ was observed near 250, 315, and 530 °C in a (001)-cut unpoled BNT single crystal.²⁹ In Fig. 5(b), unpoled BNT-0.5Mn exhibits a relatively weaker thermal hysteresis than BNT. Fig. 6(b) evidences no structural transition in unpoled BNT-0.5Mn near the dielectric maximum.

FIG. 4. ZFH dielectric permittivity (ϵ') and loss $\tan \delta$.

BN7.5BT exhibits a broad dielectric thermal hysteresis in the region of 100–320 °C as shown in Fig. 5(c), implying a first-order transition. In Fig. 6(c), the (200) XRD temperature evolution confirms a significant growth of tetragonal phase near 100 °C. Unpoled BN7.5BT-0.5Mn, as seen in Fig. 5(d), exhibits a rather smaller dielectric response and weaker thermal hysteresis than unpoled BN7.5BT. Fig. 6(d) reveals no structural transition in unpoled BN7.5BT-0.5Mn. These results suggest that 0.5 mol. % Mn doping can enhance structural thermal stability to reduce development of the tetragonal phase as temperature approaches T_m .

As indicated by the pink dashed lines in Fig. 5, the ZFH dielectric permittivity (ϵ') in the high temperature region was found to follow the Curie-Weiss equation, $\epsilon' = C/(T - T_0)$. The pink dashed lines are fits with $C = 2.85 \times 10^5$ °C and

FIG. 5. ZFH and ZFC dielectric permittivities (ϵ') for $f = 10$ kHz.

$T_0 = 230$ °C for BNT, $C = 3.05 \times 10^5$ °C and $T_0 = 230$ °C for BNT-0.5Mn, $C = 3.1 \times 10^5$ °C and $T_0 = 320$ °C for BN7.5BT, and $C = 2.5 \times 10^5$ °C and $T_0 = 310$ °C for BN7.5BT-0.5Mn. The temperature where ϵ' deviates from the Curie-Weiss equation is called the Burns temperature, below which PNRs begin to develop.³⁰ The weak dielectric response of the PNRs under the measuring E field causes the deviation from Curie-Weiss behavior.³¹ BNT, BNT-0.5Mn, BN7.5BT, and BN7.5BT-0.5Mn have Burns temperatures respectively near 380, 380, 420, and 420 °C, suggesting that 0.5 mol. % Mn doping does not change the temperature evolution of the PNRs.

By using high-resolution TEM as shown in Fig. 7, the PNRs are revealed to have sizes of 1–5 nm and 2–10 nm in unpoled BNT and BN7.5BT, respectively. Insets are the selected area diffraction patterns (SADPs) measured from representative grains. The [110]-viewed SADPs of in

FIG. 6. (200) XRD spectra of the unpoled samples upon heating. The solid and dashed lines correlate to $K\alpha_1$ and $K\alpha_2$ radiations. The black line is the sum of fitting curves.

Figs. 7(a) and 7(c) reveal $\frac{1}{2}\{ooo\}$ superlattice diffraction spots, which are due to tilted oxygen octahedral and indicate a rhombohedral $R3c$ phase.^{32–35} The [111]-viewed SADP in Fig. 7(d) shows $\frac{1}{2}\{ooe\}$ superlattice diffraction spots from the tilted oxygen octahedra, which is characteristic of tetragonal $P4bm$ symmetry with $a^o a^o c^+$ oxygen octahedron tilt.³⁶ “o” and “e” stand for odd and even Miller indices. The weak $P4bm$ superlattice diffractions reveal that tetragonal nanodomains are embedded in the rhombohedral matrix to form a coexistence of R + T phases.³⁷ The TEM results are consistent with the XRD spectra in Figs. 2 and 3.

Figs. 7(e) and 7(f) show the bright-field TEM images and diffraction patterns of BN7.5BT after poling at $E = 40$ and 60 kV/cm , respectively. The TEM images of poled BN7.5BT show long-range-ordered lamellar domains ($>100 \text{ nm}$), which are enhanced significantly as poling field increases. The insets correspond to the [111]-viewed SADPs, which show tetragonal $P4bm$ symmetry as revealed by the presence of $\frac{1}{2}\{ooe\}$ superlattice diffraction spots from oxygen octahedral tilts. A slight diffraction splitting is also observed and is possibly generated from twin planes, suggesting existence of tetragonal $P4mm$ phase. Fig. 7(g) shows

the $\frac{1}{2}\{ooo\}$ superlattice diffraction spots from a [110]-viewed SADP and confirms a rhombohedral $R3c$ structure. These TEM results confirm enhancement of long-range-ordered polarization and coexistence of R + T phases after E -field poling.

Fig. 8 shows PNRs of unpoled BNT-0.5Mn and BN7.5BT-0.5Mn with sizes less than 10 nm . Insets are the SADPs taken from representative grains. The [110]-viewed SADPs in Figs. 8(a) and 8(c) reveal $\frac{1}{2}\{ooo\}$ superlattice diffraction spots from oxygen octahedral tilts, indicating a rhombohedral $R3c$ phase. The [111]-viewed SADP in Fig. 8(d) reveals $\frac{1}{2}\{ooe\}$ superlattice diffraction spots and indicates a tetragonal $P4bm$ symmetry. The $\frac{1}{2}\{ooe\}$ superlattice diffraction spots do not appear in BNT-0.5Mn as evidenced in Fig. 8(b). The weak $P4bm$ superlattice diffraction spots in BN7.5BT-0.5Mn reveal that minor tetragonal nanodomains are embedded in the rhombohedral matrix.

Figure 9 shows PP-ZFH dielectric permittivities and losses. The dielectric measuring field is parallel to the prior poling E field direction. The room-temperature PP-ZFH dielectric permittivities were reduced due to enhancement of the ordered polarization after E -field poling as evidenced in the

FIG. 7. Bright-field TEM images and diffraction patterns of (a)–(d) unpoled BNT and BN7.5BT. (e)–(g) TEM images and diffraction patterns of BN7.5BT after poling at $E = 40$ and 60 kV/cm.

TEM images of Figs. 7(e) and 7(f). A sharp dielectric anomaly (that does not occur in the ZFH process of Fig. 4) appears at the depolarization temperature T_d , revealing a transition from a

long-range-ordered ferroelectric state to a short-range-ordered relaxor state. The depolarization temperatures (T_d) of BNT, BNT-0.5Mn, BN7.5BT, and BN7.5BT-0.5Mn are respectively

FIG. 8. Bright-field TEM images and diffraction patterns of unpoled BNT-0.5Mn and BN7.5BT-0.5Mn.

FIG. 9. PP-ZFH dielectric permittivity (ϵ') and loss $\tan \delta$.

165, 170, 80, and 100 °C, suggesting that 0.5 mol. % Mn doping enhances the polarization ordering and shift T_d to higher temperatures. Note that $T_d \sim 100$ °C in BN7.5BT-0.5Mn is higher than $T_d \sim 65$ °C reported in BN6BT-0.5Mn.²⁵ Frequency dispersion reappears above T_d as observed in the ZFH process of Fig. 4. Irregular frequent-dependent shoulders or maxima appear above 300 °C for lower frequencies ($f \leq 10$ kHz), likely due to ionic hopping conductivity across extrinsic barriers, which can be activated in the high-temperature region and often causes frequency-dependent maxima in dielectric permittivity and loss.²⁸

Figure 10 shows dielectric permittivities (for $f = 10$ kHz) and depolarization current densities (J_d) obtained from the PP-ZFH and ZFC (after the PP-ZFH) processes. The PP-ZFH J_d exhibits a strong Barkhausen-noise-like peak at T_d .

FIG. 10. Red and blue curves correspond to PP-ZFH depolarization current density (J_d) and ϵ' ($f = 10$ kHz). Insets are enlargements of PP-ZFH J_d near T_d . Green curves are ZFC depolarization current density after the PP-ZFH process. Pink dashed curves are fits to the Curie-Weiss equation.

This dramatic current response confirms dynamic polarization reorganization and enhancement of domain correlation. The T_d values of BNT-0.5Mn and BN7.5BT-0.5Mn are ~ 170 and ~ 100 °C, which are respectively higher than ~ 165 and ~ 80 °C in BNT and BN7.5BT. Depolarization current density (J_d) is a measurement of temperature evolution of local polarizations, i.e.,

$$J_d = -\partial P / \partial t = -(\partial P / \partial T)(dT/dt), \quad (2)$$

dT/dt is the temperature change rate and is 3 °C/min in this study. J_d is associated with the bound surface charge density ($\sigma_b = \vec{P} \cdot \hat{n}$) and bound volume charge density ($\rho_b = -\nabla \cdot \vec{P}$), which are functions of local polarization $\vec{P}$. The sharp peak of

J_d confirms significant reduction of polarization at T_d , above which the correlation of polar domains decreases. The direction of depolarization current is associated with reorientation of local domains and can be randomly positive or negative. The insets in Fig. 10 are enlargements near T_d , revealing asymmetric multi-peak depolarization processes possibly resulting from responses of mixed phases or PNRs. Similar features in 0.5 mol. % Mn doped BN6BT²⁵ and high-strain relaxor ($\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$)_{0.94}(PbTiO_3)_{0.06} (Ref. 38) were attributed to different types of PNRs. The coexistence of tetragonal and rhombohedral PNRs, which respond differently to external field, is likely responsible for the irregular depolarization behavior.

Figure 10 shows additional broad dips (or peaks) in J_d near 440, 440, and 480 °C for BNT-0.5Mn, BN7.5BT, and BN7.5BT-0.5Mn, respectively. These temperatures are consistent with the Burns temperatures (T_B), and these dips are likely caused by dynamically gradual decay of PNRs as temperature approaches T_B upon heating. Depolarization current rises exponentially above 500 °C mainly due to thermally activated ionic conduction. There is no depolarization anomaly in the ZFC (after the PP-ZFH) process as indicated by the green curves, revealing that the E -field induced polarized state can be erased by thermal annealing.

As indicated by the dashed lines in Fig. 10, the PP-ZFH ε' follows the Curie-Weiss equation, $\varepsilon' = C/(T - T_0)$, above

FIG. 11. Hysteresis loops of (a) polarization vs. E field and (b) strain vs. E field.

FIG. 12. Direct piezoelectric coefficient (d_{33}) as poling E field is increased by steps.

380, 440, 440, and 480 °C for BNT, BNT-0.5Mn, BN7.5BT, and BN7.5BT-0.5Mn, respectively. The Burns temperatures in the PP-ZFH process are higher than those in the ZFH process in Fig. 5. The fitting parameters are $C = 2.3 \times 10^5$ °C and $T_0 = 230$ °C for BNT, $C = 3.1 \times 10^5$ °C and $T_0 = 260$ °C for BNT-0.5Mn, $C = 2.7 \times 10^5$ °C and $T_0 = 320$ °C for BN7.5BT, and $C = 2.8 \times 10^5$ °C and $T_0 = 310$ °C for BN7.5BT-0.5Mn.

Figure 11 shows hysteresis loops of electric polarization and strain vs. E field. The remanent polarizations (P_r) and coercive fields (E_c) are respectively ~ 32 $\mu\text{C}/\text{cm}^2$ and ~ 40 kV/cm for BNT, ~ 38 $\mu\text{C}/\text{cm}^2$ and ~ 34 kV/cm for BNT-0.5Mn, ~ 42 $\mu\text{C}/\text{cm}^2$ and ~ 22 kV/cm for BN7.5BT, and ~ 40 $\mu\text{C}/\text{cm}^2$ and ~ 24 kV/cm for BN7.5BT-0.5Mn. Note that P_r and E_c values of BNT-0.5Mn are respectively larger and smaller than $P_r \sim 30$ $\mu\text{C}/\text{cm}^2$ and $E_c \sim 60$ kV/cm in the (001)-cut 1 mol. % Mn-doped BNT single crystal.³⁹ Field-induced strains for a poling field of $E = 60$ kV/cm are respectively about 0.061, 0.089, 0.152, and 0.120% for BNT, BNT-0.5Mn, BN7.5BT, and BN7.5BT-0.5Mn.

Direct piezoelectric coefficients d_{33} ($=d_{33}^D$) are given in Fig. 12 as poling E field increases by steps. The direct piezoelectric coefficient d_{ij}^D is defined by $P_i = d_{ij}X_j$, where P_i and X_j are polarization and external stress. d_{33} shows a rapid increase in 20–40 kV/cm for BNT and BNT-0.5Mn and in 10–20 kV/cm for BN7.5BT and BN7.5BT-0.5Mn. The rapid increase of d_{33} is likely associated with an enhancement of long-range-ordered polarization. The d_{33} values for a poling field of $E = 60$ kV/cm respectively reach 79, 90, 185, and 190 pC/N for BNT, BNT-0.5Mn, BN7.5BT, and BN7.5BT-0.5Mn. Electromechanical coupling factors (k_3) for a poling field of $E = 60$ kV/cm are about 40%, 44%, 46%, and 47% for BNT, BNT-0.5Mn, BN7.5BT, and BN7.5BT-0.5Mn, respectively.

IV. CONCLUSIONS

The 0.5 mol. % Mn doping enhances piezoelectricity, electromechanical coupling, and structural thermal stability and reduces the development of tetragonal phase as temperature approaches T_m upon heating. Coexistence of rhombohedral $R3c$

and tetragonal $P4bm$ phases is revealed in the unpoled BN7.5BT and BN7.5BT-0.5Mn. The poled BN7.5BT shows long-range-ordered lamellar domains (>100 nm), which are enhanced significantly as poling field increases. The poled BNT-0.5Mn and BN7.5BT-0.5Mn exhibit higher T_d and d_{33} than BNT and BN7.5BT, respectively. The unpoled BNT and BN7.5BT show a structural evolution of $R-R+T$, which does not occur in the unpoled BNT-0.5Mn and BN7.5BT-0.5Mn upon heating. This work suggests that 0.5 mol. % Mn-doping in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ can enhance piezoelectricity, electromechanical coupling, and structural thermal stability.

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