Dielectric, ferroelectric, and depolarization properties of B-site manganese-doped $0.925(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - 0.075BaTiO_3 solid solutions

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ABSTRACT

$(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.925}\text{Ba}_{0.075}(\text{Ti}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0, 0.2, 1.0$, and 2.0 mol%) ceramics were prepared by solid-state-reaction method to study dielectric, ferroelectric, and depolarization properties.

The manganese (Mn) doping can suppress dielectric permittivity and increase relaxor behavior. Coercive field (E_c) increases, while remanent polarization (P_r) decreases as the Mn content increases. P_r exhibits discontinuous anomalies as a function of temperature in all compositions, implying a polarization reorganization of local domains. The depolarization temperature (T_d) reaches the highest value ($\sim 152^\circ\text{C}$) in 0.2% Mn, and decreases as MnO_2 content increases. The increased T_d in 0.2% Mn is due to two-phase coexistence and structural thermal stability induced by Mn ions. This work suggests that the moderate Mn doping can enhance T_d in lead-free piezoceramics for applications at elevated temperatures.

Key words: Mn doping, dielectric permittivity, ferroelectric hysteresis loop, thermal stability, depolarization.

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1. Introduction

Recently, sodium bismuth titanate, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (BNT), based ceramics are extensively studied to replace lead-containing piezoelectric ceramics. Among them, the BNT-BaTiO₃ (BNT-BT) system is one of the most interesting owing to the existence of morphotropic phase boundary (MPB) and the relatively high piezoelectric properties for the compositions near the MPB [1]. Nevertheless, in order to meet the stringent requirements for specific applications, physical properties need to be improved, for example, by doping various oxides. Nagata and Takenaka [2] have found that the addition of MnCO_3 to BNT decreased T_C , while increased k_{33} and electrical resistivity ρ . Jiang *et al.* obtained the best piezoelectric properties with $k_p = 30\%$ for 0.2 wt.% Mn^{2+} doped $(\text{Na}_{0.5}\text{K}_{0.2})_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ [3]. The 0.5wt% manganese (Mn) doped $(\text{Na}_{0.5}\text{K}_{0.2})_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ exhibited strong ferroelectricity with remanent polarization $P_r = 38 \mu\text{C}/\text{cm}^2$ and Mn doping restrained the phase transition of ferroelectric→antiferroelectric because of oxygen vacancies [3]. Hu *et al.* [4] studied microstructure and electrical properties of lead-free piezoelectric $0.74(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - $0.208(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ - 0.052BaTiO_3 - $x\text{MnCO}_3$ (BNKBT) ceramics. Their experiments showed that the addition of MnCO_3 reduced the tetragonality c/a and increased the unit cell volume. It also revealed that the suitable addition of MnCO_3 can promote the sintering and increase the densities of BNKBT ceramics. Due to the effect of the crystal lattice, grain growth, and relaxor behavior, the optimal electric properties were realized at MnCO_3 addition $x = 0.16$ with dielectric permittivity $\epsilon_r = 1047$, $\tan\delta = 0.022$, piezoelectric strain $d_{33} = 140 \text{ pC}/\text{N}$, mechanical coupling $k_p = 0.18$, and mechanical quality $Q_m = 89$. Zhang *et al.* [5] reported that ferroelectric and piezoelectric properties could be enhanced notably by Mn doping in BN100xBT single crystals. The piezoelectric constant and electromechanical coupling coefficients were found to be $d_{33} \sim 483 \text{ pC}/\text{N}$, $k_t \sim 0.56$, and $k_{31} \sim 0.40$. It was found that the suitable substitution of Mn ion into the B site induces the lattice distortion of perovskite

MnO-doped $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.92}\text{Ba}_{0.08}\text{TiO}_3$ piezoceramics. Besides, the sintering properties could be improved by adding a small amount of MnO, thus increasing grain size and relative density [6].

The Mn-doped NBT-6%BT single crystals have shown that the tetragonal domain states could be stabilized by *E*-field poling along the [001] direction and piezoelectric coefficient d_{33} could reach 570 pC/N [7]. Sapper *et al.* [8] discovered that Mn-doped BN100xBT piezoceramics stabilized macroscopic polarization and consequently shifted depolarization temperature (T_d) to higher temperatures as compared to the undoped BN100xBT. With respect to applications of BNT-BT systems, a high T_d is desirable to extend the possible range of applications. In our previous work [9], we reported that manganese doping could enhance structural thermal stability toward higher temperatures in $0.925(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - 0.075BaTiO_3 (BN7.5BT) ceramics. The 0 and 0.2% Mn showed a two-phase coexistence (rhombohedral and tetragonal) whereas, 1 and 2% Mn showed an orthorhombic structure [9]. In this work, we report effects of manganese doping on depolarization temperature, dielectric, ferroelectric, and piezoelectric properties in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.925}\text{Ba}_{0.075}(\text{Ti}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0, 0.2, 1.0, \text{ and } 2.0 \text{ mol\%}$) ceramics. T_d can reach 152 °C for 0.2% manganese (0.2% Mn) doping and decreases for higher Mn concentrations ($> 0.2\%$).

2. Experimental procedure

$(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.925}\text{Ba}_{0.075}(\text{Ti}_{1-x}\text{Mn}_x)\text{O}_3$ (BN7.5BT- $x\text{Mn}$) ($x = 0, 0.2, 1.0, \text{ and } 2.0 \text{ mol\%}$) ceramics were prepared by using solid state reaction. High purity ($> 99\%$) powders of Bi_2O_3 , Na_2CO_3 , BaCO_3 , TiO_2 , and MnO_2 were used as starting materials. Stoichiometric amounts of powders were ball-milled for more than 24 hours in ethanol. The mixture was calcined at 900 °C (2 hrs) 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 1170 °C (2 hrs). All polished sintered samples were annealed at 1000 °C for 30 mins to remove residual stress. The dielectric permittivity was taken upon zero-field heating (ZFH) and cooling (ZFC) by using Wayne–Kerr Analyzer PMA3260A. To determine the Mn electronic valence, the soft X-ray absorption spectra (XAS) of Mn L₃-edge were recorded in total electron yield via sample current mode at beamline 6.3.1.1 of Advanced Light Source Berkeley National Laboratory. Absorption measurements were made at room temperature with linear photon polarization and normal incidence. High-resolution TEM (JEOL JEM-2100 LaB6) observations were performed to study polar nanoregions. Thermal evolution of polarization versus E field (P-E hysteresis loop) was studied using Sawyer-Tower circuit at $f = 46$ Hz. To measure depolarization temperature T_d , the samples were previously poled at room temperature with a dc field of $E = 40$ kV/cm, then thermal depolarization current was measured upon heating without a dc field. d_{33} was measured using the Model ZJ-6B piezometer after various poling E fields.

3. Results and discussion

Figure 1 shows temperature-dependent dielectric permittivity (ϵ') and loss tangent ($\tan\delta$) in the frequency range of 50 kHz-1 MHz upon heating. Dielectric permittivity at room temperature decreases as MnO₂ content increases. This can be related to the pinning effect by the dopant dipolar defects, which can suppress dielectric permittivity. The substitution of MnO₂ in BNBT shows the acceptor-doping feature, and therefore induces hard character in BN7.5BT ceramics. The reduction of T_m (temperature corresponding to the dielectric permittivity maximum) could be caused by the reduced sizes of the polar clusters due to the shift from two-phase coexistence to an orthorhombic phase as MnO₂ was added.

Dielectric permittivity ϵ' characterized by strong permittivity maxima and frequency dispersion suggests a relaxor ferroelectric behavior. The relaxor behavior is due to dynamical fluctuations of polar nanoregions (PNRs), which is embedded in polarizable medium. Polar nanoregions have been observed in many ABO₃ relaxors above T_m , and play a crucial role for the dielectric relaxation [10]. The presence of PNRs was evidenced from the bright-field TEM images as shown in Fig. 2. As labeled in Fig. 2, average size of PNRs gradually decreases as Mn concentration increases. The PNRs are mobile and ergodic at high temperatures, leading to the diffuse phase transition in dielectric responses. It was observed that MnO₂ doping can increase relaxor behavior.

The degree of relaxation in relaxor ferroelectric materials can be estimated in the region above dielectric maximum temperature T_m by using the power relation [11],

$$\frac{1}{\epsilon'(f,T)} = \frac{1}{\epsilon_m(f)} \{1 + [T - T_m(f)]^\gamma / 2\Delta^2\} \quad (1)$$

where ϵ_m is the maximum dielectric permittivity at T_m , γ is the degree of relaxation, and Δ is the broadening constant. γ is 2 for a perfect relaxor [12], whereas $\gamma = 1$ for a perfect ferroelectric state. From the linear fit of $\ln [\epsilon_m - \epsilon']$ vs. $\ln(T - T_m)$, γ and Δ were obtained as shown in Fig. 3. It is noted that the degree of relaxation (γ) increases with increasing MnO₂ content. In the ABO₃ oxides, substituting ions of different sizes, valences, and polarizabilities at A and B sites can produce dipolar defects and disorder so as to break translational symmetry and prevent the formation of a long-range-ordered state [13].

Figure 4 shows the Mn L₃ XAS in 2%Mn sample and references of Mn₂O₃ and MnTiO₃ powders at room temperature. The absorption spectra were normalized to the area of the L₃ peak and the number of *d*-holes for the references. The binding energy at the absorption edge for each standard Mn reference is indicated with an arrow. The measured spectra can be well fitted from a linear combination of two referenced spectra to give an

indication of the average Mn valence. Mn changes valence from mostly +2 to more +3, indicating a reduction of Mn valence. This result indicates an effective equilibrium of divalent Mn^{2+} (~45%) and trivalent Mn^{3+} (~55%) although manganese presents as tetravalent Mn^{4+} in the dopant oxide MnO_2 . In MnO_2 -doped BN7.5BT, three species of ions (Mn^{2+} , Mn^{3+} and Ti^{4+}) are most likely to occupy the B-site with the sizable radii [14]. The sizable radii of the B-site ions are beneficial for the reconstruction of the disordered state, and hence MnO_2 addition can enhance the dielectric dispersion.

To study the nature of phase transition, the dielectric permittivity as a function of temperature was recorded upon heating and cooling and all compositions show significant thermal hysteresis as shown in Fig. 5. The thermal hysteresis regimes for 0, 0.2, 1 and 2% Mn are 120-400 °C, 30-550 °C, 30-450 °C, and 30-250 °C, respectively. The broad thermal hysteresis suggests a gradual first-order-like phase transition. As indicated in Fig. 5, the Burns temperature (T_B) was determined by the deviation from the Curie–Weiss equation,

$$\varepsilon'(T) = \frac{C}{(T-T_0)} \quad (2)$$

The green dashed line is the fit of Curie–Weiss law with parameters given in Fig. 5. The polar nanoregions begin to appear below the Burns temperatures but they do not percolate large enough to trigger a macroscopic phase transition. These polar nanoregions (PNRs) dynamically slow down their fluctuations at $T \leq T_m$, leading to an overall isotropic relaxor state with random orientations [10]. As shown in Fig. 5, the Burns temperature (T_B) gradually increases toward higher temperature as Mn concentration increases, suggesting that the Mn doping prefers the PNRs development in the paraelectric cubic region.

Figure 6 shows the hysteresis loops (polarization vs. electric field) for various Mn-doped compositions at room temperature. The coercive field E_c increases with increasing Mn content and remanent polarization P_r is slightly smaller in 1% and 2% Mn-doped compositions. The increased coercive field is possibly due to the pinning of polar

nanoregions by oxygen vacancies in the Mn-doped compounds. Under low-field application, the electrical energy is not enough for destabilizing the network of oxygen vacancies. This is in agreement with the fact that the acceptor dopants such as manganese are known to increase coercive field E_c and stabilize the dipolar domain distribution [15,16].

Temperature-dependent P - E hysteresis loops at chosen temperatures are shown in Fig. 7 for all compositions. The coercive field E_c decreases, while the saturated polarization (P_{sat}) increases as temperature increases. In Mn-doped compositions, local dipoles can be aligned with the external field to a higher degree due to the de-pinning of nanoregions. As a result, P_{sat} is large despite the fact that the P_r is strongly reduced. Fig. 8 presents remanent polarization (P_r) as a function of temperature. P_r exhibits discontinuous anomalies in all compositions. A sudden dip near 80 °C was seen in 0%Mn. P_r reaches a maximum respectively at 160, 120, and 90 °C in 0.2, 1, and 2%Mn, and then declines upon further increasing temperature. These discontinuous changes imply a polarization reorganization of local domains [17]. The pinching of hysteresis loop appears at higher temperatures and cannot be attributed to aging, which often occurs in acceptor ferroelectrics [18]. The pinching shape in the P - E loop signifies presence of nonpolar phase or weakly polar phase converting to a polar phase under an E -field poling [19]. It is noted that the P - E loop still exhibits hysteresis feature even at 200 °C instead of a linear paraelectric behavior. It implies that the FE order is disrupted over a wide range of temperatures and does not vanish completely even at fairly high temperatures.

Figure 9 shows the pre-poled-zero-field-heated (PP-ZFH) dielectric permittivity (ϵ') and depolarization current density (J_d). Depolarization current density is an evolution of local polarization as temperature changes, i.e.

$$J_d = -\frac{\partial P}{\partial t} = -(\partial P / \partial T)(dT / dt) \quad (3)$$

dT/dt is the heating 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 temperature at which J_d exhibits a sharp peak is denoted as depolarization temperature (T_d). The sharp J_d peak confirms a significant reduction of polarization at T_d , above which the average correlation length of local polar domains decreases dramatically as the sample goes from a long-range-ordered ferroelectric to a short-range-ordered state. It is noted that the dielectric curves of pre-poled-zero-field-heated (PP-ZFH) samples display a ferroelectric transition from ferroelectric phase to a relaxor phase at temperature marked by a kink (shown in black arrow), which nearly coincides with T_d .

It is known that the non-ergodic phase in ferroelectric disordered ABO_3 relaxors can be transformed into ferroelectric phase by a dc E -field poling [20-22]. The application of an electric field first aligns randomly oriented polar nanoregions or nanodomains along the E -field direction. Then, the formation of long-range ferroelectric domains can be developed with a further increase of E -field strength [23]. In bulk ceramics, mismatch of the polarization of neighbor grains was often expected due to charge and compositional disorder [24]. As a result, a depolarization field can appear [25] and reaches a maximum at pore surfaces [24]. Depolarization can be suppressed in relaxor ferroelectric compounds by an external poling field [26,27]. After removing the poling field, the depolarization field can lead to complete back-switching of domains at T_d . According to Lehnen et al.[28], the back-switching occurs predominantly at the interface between the induced superficial macrodomains and the adjacent PNRs [28]. Upon heating, it transits from an aligned domain structure to an ergodic relaxor state with polar nanoregions at T_d .

The depolarization temperature T_d reaches the highest value (~152 °C) in 0.2%Mn and decreases as MnO_2 content increases. The increased T_d in Mn-doped BN7.5BT (0.2%Mn) is

likely associated with two-phase coexistence and the structural thermal stability induced by Mn ions [9]. As Mn doping concentration increases, the composition exhibits an orthorhombic structure [9]. The corresponding insets in Fig. 9 show the enlargements of J_d near T_d , revealing asymmetric multi-peak depolarization possibly due to mixed phases or various PNRs in the ceramic matrix [17,29]. In 0 and 0.2% Mn, the coexistence of tetragonal and rhombohedral PNRs, which respond differently to external field, is likely responsible for the irregular depolarization behavior [29]. This picture is in agreement with neutron diffuse scattering result of $(\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3)_{0.92}(\text{PbTiO}_3)_{0.08}$ single crystals [30], which showed the tetragonal and orthorhombic PNRs were aligned differently under external E field. Whereas, in 1 and 2% Mn, asymmetric depolarization is more likely due to different size or polarization response of the PNRs [31].

Figure 10 shows piezoelectric coefficients (d_{33}) for different MnO_2 concentration as a function of poling E field. The maximal values obtained for 0, 0.2, 1 and 2% Mn are 186, 170, 157, and 145 pC/N respectively. The larger d_{33} in 0% Mn can be explained by the increase of structural competition due to rhombohedral distortion, enhancement of tetragonal phase, and polarization/domain ordering [10]. In Mn-doped samples, the hard character induced by Mn ions tends to stabilize dipoles leading to decrease in piezoelectric coefficient. Table 1 is the summary of dielectric, polarization hysteresis, and piezoelectric parameters in Mn-doped BN7.5BT ceramics.

4. Conclusions

The MnO_2 doping in BN7.5BT showed acceptor-doping feature and therefore induced hard character. Dopant dipolar defects induced by Mn ions suppressed the dielectric permittivity at room temperature. The MnO_2 doping increases coercive field E_c and decreases remanent polarization P_r at room temperature. Temperature-dependent P - E

hysteresis shows that the ferroelectric order is disrupted over a wide range of temperatures and does not vanish completely even at fairly high temperatures. The pinched shape in the P - E loop at higher temperatures signifies the presence of nonpolar phase or weakly polar phase converting to a polar phase under E -field application. The remanent polarization shows a discontinuous change as temperature increases, which can be attributed to the breakdown of the induced ferroelectric phase. The depolarization temperature T_d reaches $\sim 152^\circ\text{C}$ in 0.2%Mn, and decreases as MnO_2 content increases. The increased T_d in 0.2%Mn is due to a two-phase coexistence and the structural thermal stability induced by Mn ions.

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Figure captions

Fig. 1 Real part of dielectric permittivity ϵ' and dielectric loss ($\tan\delta$) as functions of temperature and frequency (50 kHz–1 MHz) of Mn-doped BN7.5BT ceramics.

Fig. 2 Bright-field TEM images of Mn-doped BN7.5BT ceramics.

Fig. 3 Fits of power relation of $\ln[\epsilon_m - \epsilon']$ vs. $\ln(T - T_m)$ with fitting parameters for $f = 1$ MHz in Mn-doped BN7.5BT ceramics.

Fig. 4 Mn L_3 -edge XAS in 2%Mn sample at room temperature. Red and black lines are references for various Mn valences. Blue line is the experimental data and green line is the sum of Mn^{2+} and Mn^{3+} spectra.

Fig. 5 Dielectric thermal hysteresis and fits of Curie–Weiss law for unpoled samples at $f = 1$ MHz.

Fig. 6 Hysteresis loops of polarization (P) versus E field for Mn-doped BN7.5BT ceramics at room temperature.

Fig. 7 Temperature evolution of P-E hysteresis loops for Mn-doped BN7.5BT ceramics.

Fig. 8 Variation of remanent polarization (P_r) as a function of temperature in Mn-doped BN7.5BT ceramics.

Fig. 9 Real part of dielectric permittivity ϵ' for PP-ZFH process and depolarization current density (J_d) upon heating. The inset is the enlargement of J_d near T_d .

Fig. 10 Piezoelectric coefficient (d_{33}) at different poling E fields in BN7.5BT ceramics with different MnO_2 concentrations.

Table caption

Table 1 Summary of dielectric, polarization hysteresis loop, and piezoelectric parameters in Mn-doped BN7.5BT ceramics.

Physical parameters	BN7.5BT (0%Mn)	0.2%Mn	1%Mn	2%Mn
ϵ' (at RT)	1570	1473	1330	1080
$\tan\delta$ (at RT)	0.089	0.052	0.066	0.055
T_m (°C)	272	243	233	215
T_B (°C)	417	420	424	429
T_d (°C)	93	152	128	100
P_r ($\mu\text{C}/\text{cm}^2$)	22	22	19	18
E_c (kV/cm)	21	32	35	37
d_{33} (pC/N)	186	170	157	145

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

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