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Temperature dependent phase transition of $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ lead-free piezoelectric

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Abstract

Phase transformation and electric properties of lead-free piezoceramics $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ with $x=0.05$, 0.06, and 0.07(BNB5T, BNB6T and BNB7T) were investigated using dielectric, piezoelectric and ferroelectric measurements. Electric field induced strain measurement shows "W" shape bipolar strain characteristics for BNB5T with typical ferroelectric *P–E* curve, while BNB6T and BNB7T, possessing pinch-off *P–E*, exhibit "V" shape field-induced strain. All the BNB*x*T specimens exhibit relaxor characteristic, identified by the Debye Law. Dielectric properties measured at elevated temperatures with the frequency variation (10–500 kHz) reveal frequency dispersion below the T_d point, but no dispersion between T_d and T_m, which may be ascribed to an intermediate phase transition. By adding more Ba^{2+} ions, the region of intermediate phase, distinguished by frequency dependence dielectric constant, expands to lower temperature. Moreover, the ferroelectric properties measured at elevated temperature were carried out below and at the depolarization temperature to well investigate the existence of this phase. Much less ε–*T* profile dispersion were observed during the investigation of BNB6T and BNB7T, leading to possible existence of an intermediate phase in the investigated compositions. The results suggest that the linear field-induced-strain of $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ are expected to be attributed to the intermediate phase.

Keywords: C. Ferroelectric; D. Perovskites; C. Piezoelectric

1. Introduction

Many studies have been performed on the $(Bi_{0.5}Na_{0.5})$-TiO_3 (BNT) system as BNT was thought to be one of promising lead-free piezoceramics Some studies focused on dielectric properties, while others focused on piezoelectric properties. The aim is to determine how dopants influence the structural and electrical properties of the material. Both A-site and B-site dopants have been studied to determine how they affect the properties of BNT, and these dopants include Ba, Sr, Zr, La, K, Pb, etc.[1–11]. One of the advantages of doping with Ba^{2+} is that the formation of morphotropic phase boundary (MPB) between rhombohedral (Fα)–tetragonal (Fβ) phases of the structure [1], which may exhibit excellent piezoelectric properties [4,12]. Even though, the piezoelectric properties were observed to be markedly improved but depolarization temperature (T_d) decreased to around 100 °C [13,14]. The determination of T_d point is still in controversy. Some researchers disclaimed the existence of AFE phase below 100 °C, at which doped-BNT material would exhibit optimum piezoelectric properties [15–17]. In this study, we investigated the temperature dependence of dielectric properties (ε–*T* curve) and ferroelectric hysteresis loops in $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ with $x=0.05$, 0.06, and 0.07 piezoceramics to study phase transition from electrical properties measurement.

2. Experimental

(Bi0.5Na0.5)1−*x*Ba*x*TiO3 with $x=0.05$, 0.06, and 0.07 ceramics were prepared by an oxide mixing method. The commercially available materials Bi_2O_3, Na_2CO_3, $BaCO_3$, and TiO_2 with purity higher than 99.9% were mixed in

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ethanol and milling with zirconia balls for 24 h. Then, the mixing powders were calcined at 850 °C in alumina crucible for 2 h and then ball milling again for 24 h. The powders were formed into disks with 10 mm diameter and about 1 mm thickness under 98 MPa and then sintered at 1200 °C for 2 h in ambient atmosphere. Because of the evaporation of Bi and Na, the disks were embedded in the matching calcined powder.

The crystal structure and morphology were investigated using x-ray diffraction (XRD, D-2 phaser, Bruker AXS), scanning electron microscope (SEM, JEOL JSM-6393). For electric measurement, the samples were electroded with a silver paste fired at 750 °C for 30 min. The electric fields induced ferroelectric (*P–E* curve) and strain (*S–E* curve) hysteresis loops were investigated using Radiant Precision Workstation 2000 System connected with fotonic sensor MTI 2000 at room temperature. The dielectric constant and loss tangent were measured using a gain-phase analyzer, HP4194, in frequency 10–500 kHz and the temperature range from 25–400 °C. For further observation on phase transition existing below curie temperature (T_c), the ferroelectric measurement was carried out at elevated temperature up to temperature at the first peak anomaly in ε–*T* curve.

3. Results and discussions

The X-ray diffraction patterns of (Bi0.5Na0.5)1−x BaxTiO3 with $x=0.05$, 0.06, and 0.07 ceramics sintered in air at 1200 °C for 2 h are shown in Fig. 1. All sintered ceramics exhibit a perovskite-type structure without any secondary or impurities phases, implying that Ba^{2+} has diffused into the BNT lattices to form a solid solution. The insets of the peaks at around $2\theta=46°$ for BNB5T and BNB7T show details demonstration of characteristics splitting of pseudocubic notation (200) reflection into the tetragonal phase (200)/(002) peaks, indicating the phase transition occurred from rhombohedral symmetry to tetragonal symmetry.

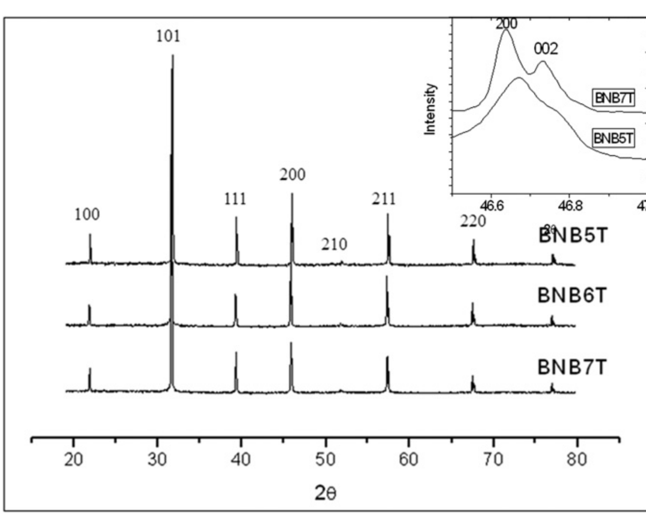

Fig. 1. XRD Patterns for BNBxT ($x=0.05$–0.07) are indexed according to pseudo-cubic structure and were measured with step size 0.05° and 0.2 s/step.

The piezoelectric property results are depicted in Fig. 2. It was found at room temperature BNB7T achieved the optimum piezoelectric properties. The electric field induced strain of BNB7T is achieved up to 0.32%, while others are ranging between 0.13 and 0.17%. The low strain region of BNB5T exhibits a "W" shape response containing a significant negative and a rapid increasing strain. Negative strain always appears as the value to denote the difference between zero field strain and the lowest strain and is only visible in the bipolar cycle [13,18]. While the "V" shape strain of BNB6T and BNB7T reveals none existence of negative strain, therefore the large strain is exhibited. Furthermore, the existence of the "V" shape strain can be correlated with is conceived by the kind of pinched hysteresis loop in Fig. 3 *P–E* curve. The *P–E* curves are resulted from ferroelectric property measurement at elevated temperature. As observed from hysteresis curves, Ba^{2+} exerts significant influence on the loops shape and polarization value. The remnant polarization, P_r, of samples decreased monotonously as the content of Ba^{2+} increases. The maximum P_r at room temperature is obtained by BNB5T which exhibits typical normal ferroelectric behavior containing a square shape *P–E* curve with $P_r=50$ μC/cm^2. By adding 1–2 mol% more Ba^{2+} into BNB5T, the Pr value decreases to 12 μC/cm^2. The spontaneous polarization, P_s, also gives a role on electrical properties behavior. The large strain is achieved by the large value of $[P_s–P_r]$, indicating that $[P_s–P_r]$ could be functioned as the possibility of the dipole switching in the large strain induced in this system. Moreover, the resultant data of ferroelectric properties measured at elevated temperature are combined in Table 1.

Temperature dependences of ε and tan δ for all ceramics at 10–500 kHz are shown in Fig. 4. All the ceramics exhibit two dielectric anomaly peaks in which is believed as T_d and T_c point. Since all ceramics situated at or near the MPB, the lower dielectric peak at T_d exhibit strong frequency dependences, implying that ceramics undergo a relaxor phase transition at T_d. In this study the Debye law is applied to observe the level of relaxor phenomena within the first anomaly peak at ε–*T* curve. The result of the calculation by the Debye Law could be seen in Fig. 5. The levels of relaxor are 0.980, 0.971, and 0.960 for BNB5T, BNB6T, and BNB7T, respectively. The s (slope) which indicates the level of relaxor phenomena shows constant value, reaches value near 1. This implies that the level of relaxation is higher at the composition near MPB.

For the ceramics which exhibit optimum piezoelectric properties, the first anomaly peak shifts to lower than room temperature and the second anomaly peak at maximum ε shifts to higher temperature. The tendency makes the phase transition broaden in larger range of temperature. In results, another phase believed as an intermediate phase before the ceramics reached the AFE-like state is observed.

The *P–E* shape transformation at elevated temperature is used to observe the existence of intermediate phase. From Fig. 3, the pinched hysteresis loop is observed in BNB5T at 115 °C, the pinched loop observed is similar to BNB6T and

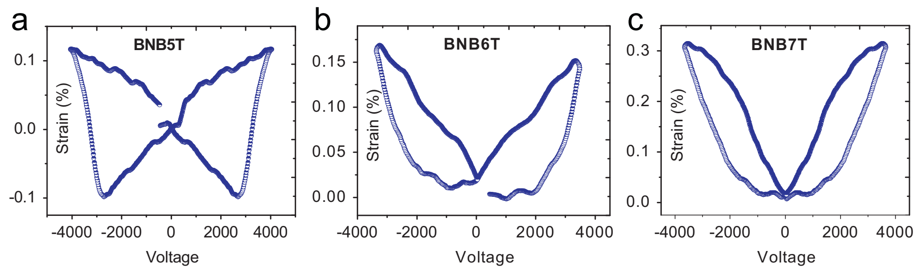

Fig. 2. Field induced bipolar strain hysteresis loops for BNB*x*T measured at 0.2 Hz; (a) BNB5T, (b) BNB6T and (c) BNB7T.

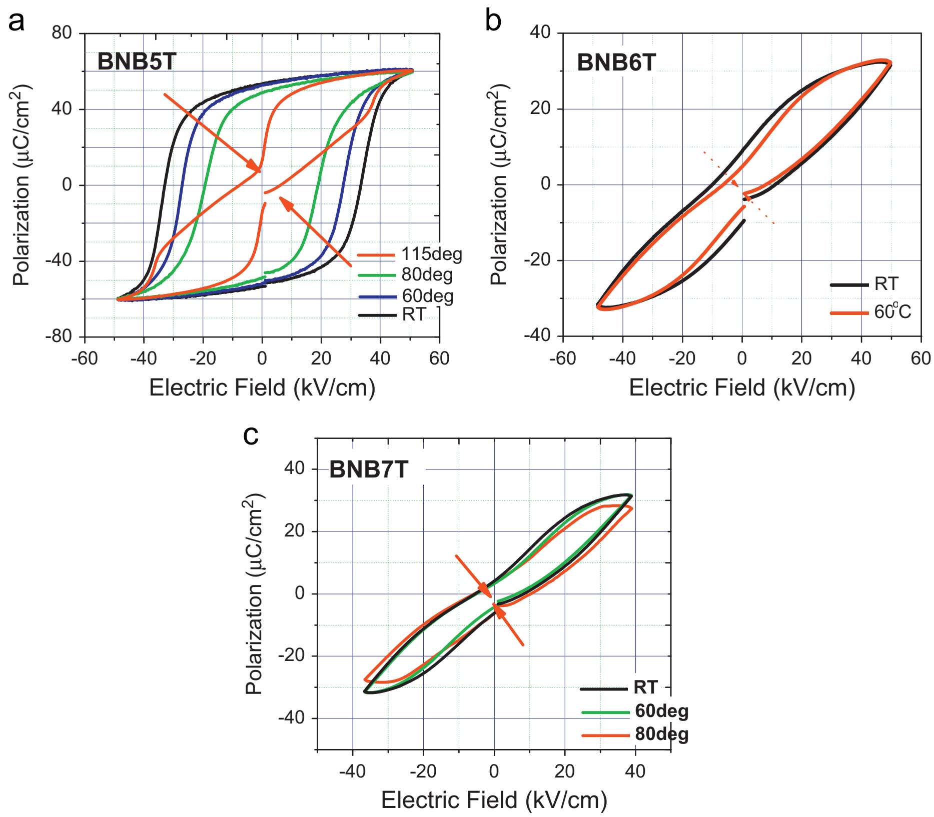

Fig. 3. Temperature dependence ferroelectric hysteresis loop of BNB*x*T piezoceramics; (a) BNB5T, (b) BNB6T and (c) BNB7T.

Table 1
The summaries of ferroelectric properties of BNB_xT piezoceramics.

BNB*x*T	Room Temperature (RT)				60 °C			
	P_r	P_s	E_c	$[P_s–P_r]$	P_r	P_s	E_c	$[P_s–P_r]$
BNB5T	54	58	34	4	52	56	27	4
BNB6T	10	24	7	14	7	24	6	17
BNB7T	12	45	13	33	8	22	12	14
	80 °C				115 °C			
BNB5T	48	52	20	4	14	50	7	36
BNB6T	–	–	–	–	–	–	–	–
BNB7T	7	20	11	13	–	–	–	–

BNB7T at RT. There is no conventional double loop hysteresis is observed in *P–E* curve, which is similar to the one reported as AFE phase in PZT-based materials [19].

At higher temperature measurement, the hysteresis loops of BNB6T and BNB7T, in which the intermediate phase exists, show lower maximum polarization, P_m. At higher temperature above the T_d point, the *P–E* curve of BNB6T and BNB7T ceramic almost show no transformation to double-like hysteresis loop, shown in Fig. 6. The evolution of *P–E* shape of BNB6T ceramic, measured at elevated temperature, provides the certainty of the existence of intermediate phase as the phase which occurs between the FE to AFE phase transition.

4. Conclusions

The existence of intermediate phase is investigated by *P–E* shape transformation at elevated temperature recorded during the ferroelectric property measurement. The recorded temperature range is determined by the first anomaly peak at Temperature dependences of ε and tan δ

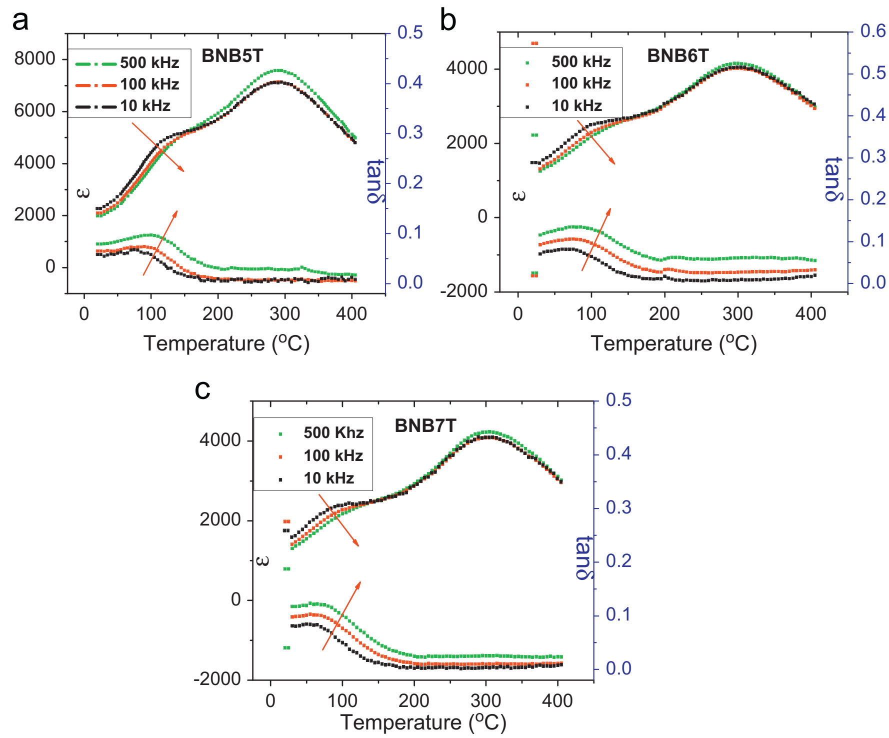

Fig. 4. Correlation between dielectric constant (ε) and tan δ as a function of frequency (10–500 kHz) and temperature (25–400 °C) for BNB*x*T piezoceramics;(a) BNB5T, (b) BNB6T and (c) BNB7T.

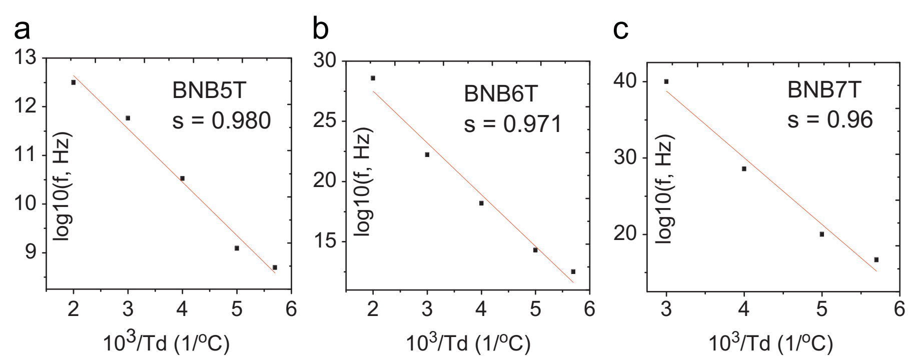

Fig. 5. Variation of log 10 (*f*, Hz) versus $10^3/T_d$ point for BNB*x*T piezoceramics; (a) BNB5T, (b) BNB6T, and (c) BNB7T.

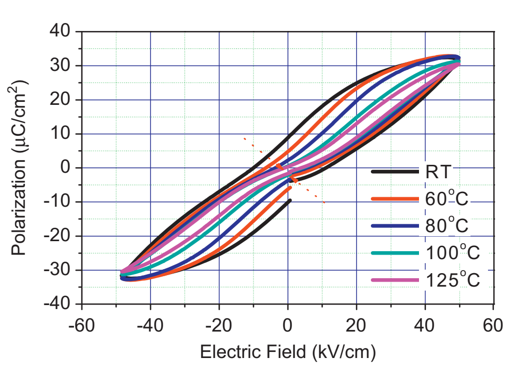

Fig. 6. Evolution of *P*–*E* shape from pinched loop to double loop of BNB6T ceramic, measured at elevated temperature.

curves. This peak is dependent on frequency, so called relaxor phenomena. Furthermore, the evolution of *P*–*E* shape of BNB6T ceramic, measured at elevated temperature, provides the evidence of the existence of intermediate phase in this ceramics. The results suggest that the linear field-induced-strain of $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ are expected to be attributed to the intermediate phase.

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