Dielectric and Piezoelectric Properties of $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$-$NaNbO_3$ Lead-Free Ceramics

YUE-MING LI,[1,2] WEN CHEN,[1,*] QING XU,[1] JING ZHOU,[1] HUA-JUN SUN[1] & MEI-SONG LIAO[1]

[1]*Institute of Materials Science and Engineering, Wuhan University of Technology, Wuhan, 430070, Hubei, People's Republic of China*
[2]*Jingdezhen Ceramic Institute, Jingdezhen, 333001, Jiangxi, People's Republic of China*

Abstract. The ternary lead-free piezoelectric ceramics system of $(1 - x)$ $[0.88Na_{0.5}Bi_{0.5}TiO_3\text{-}0.12K_{0.5}Bi_{0.5}TiO_3]$ $- x NaNbO_3 (x = 0, 0.02, 0.04, 0.06, 0.08, 0.10)$ were synthesized by conventional solid state reaction method. The crystal structure, dielectric, piezoelectric properties and *P-E* hysteresis loops were investigated. The crystalline structure of all compositions is mono-perovskite phase ascertained by XRD, and the lattice constant was calculated from the XRD data. Temperature dependence of dielectric constant ε_r and dissipation factor $\tan \delta$ measurement revealed that all compositions experienced two phase transitions: from ferroelectric to anti-ferroelectric and from anti-ferroelectric to paraelectric, and these two phase transitions have relaxor characteristics. Both transition temperatures T_d and T_m are lowered due to introduction of $NaNbO_3$. *P-E* hysteresis loops show that $0.88Na_{0.5}Bi_{0.5}TiO_3$-$0.12K_{0.5}Bi_{0.5}TiO_3$ ceramics has the maximum P_r and E_c corresponding to the maximum values of electromechanical coupling factor K_p and piezoelectric constant d_{33}. The piezoelectric constant d_{33} and electromechanical coupling factor K_p decrease a little, while the dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ improves much more when the concentration of $NaNbO_3$ is 8 mol%.

Keywords: dielectric properties, piezoelectric properties, $Na_{0.5}Bi_{0.5}TiO_3$, perovskite, relaxor

1. Introduction

In recent years, lead-free piezoelectric ceramics have attracted considerable attention as important piezo-electric materials because of outstanding advantages in free control atmosphere and no lead pollution. $Na_{0.5}Bi_{0.5}TiO_3$ composition (abbreviated as NBT) is one of the important lead-free piezoelectric materials with perovskite structure discovered by Smolenskii et al. in 1960 [1]. As NBT has a remanent polarization $P_r = 38 \ \mu C/cm^2$, a coercive field $E_c = 7.3$ kV/mm and high Curie temperature $T_c = 320°C$ [2–4], it has been considered to be a good candidate of lead-free piezoelectric ceramics to replace the widely used lead-based piezoelectric materials. It reveals a very interesting anomaly of dielectric properties as a result of low temperature phase transition from ferroelectric to

*To whom all correspondence should be addressed. E-mail: chenw@public.wh.hb.cn

anti-ferroelectric phase at 200°C. However, NBT has a drawback of high conductivity and high coercive field E_c which causes problems in poling process. To improve its properties, solid solution of NBT with $BaTiO_3$ (BT) [2], $SrTiO_3$ (ST) [5], $K_{0.5}Bi_{0.5}TiO_3$ (KBT) [6, 7] have been investigated. Lanthanum [La_2O_3] was also introduced to modify NBT's properties [8].

The morphotropic phase boundary (MPB) of $(1 - x)$ NBT-xKBT system locates at $x = 0.16–0.20$ with relative high piezoelectric properties [6, 7]. Wang [7] reported that the maximum remanent polarization P_r was located at $x = 0.13$ and the solid solution belongs to rhombohedral structure with low dielectric constant ε, relatively high piezoelectric constant d_{33} and good electromechanical coupling factor k_p. Another binary system is NBT-$NaNbO_3$ (NN) that $NaNbO_3$ is an anti-ferroelectric with orthorhombic symmetry [9]. This strategy is adopted in the development of PZT, where $PbTiO_3$ is ferroelectric and $PbZrO_3$ is anti-ferroelectric. X-ray diffraction data

showed that rhombohedral–orthorhombic MPB exists at $x = 0.90 \sim 0.92$ in system $(1-x)\,\text{NBT} - x\text{NN}$. The coupling factor K_{33} reaches a maximum at $x = 0.03$ with a piezoelectric constant $d_{33} = 71$ pC/N.

In this paper, we extended the binary system NBT-KBT and NBT-NN to ternary system NBT-KBT-NN. The effects of NN on crystal structure, dielectric, ferroelectric and piezoelectric properties of the ternary system were investigated.

2.   Experimental Procedures

Reagent grade oxide or carbonate powders of Bi_2O_3, Na_2CO_3, K_2CO_3, TiO_2 and Nb_2O_5 were used as starting raw materials. A conventional powder synthesis method was adopted to synthesize $0.88\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$-$0.12\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NKBTN0) and NaNbO_3 (NN), respectively. Raw materials were mixed using planetary milling with agate media and alcohol. The mixed powders were calcined at $900°\text{C}$ for 2 hours. According to $(1-x)\,\text{NKBTN0} - x\text{NN}$ with $x = 0$, 0.02, 0.04, 0.06, 0.08, 0.10 (hereafter named NKBTN100x), the synthesized powders of NKBTN0 and NN were mixed using planetary milling with agate media and alcohol for 6 hours. Then the mixed powders were pressed into disk of 20 mm in diameter and about 1.5 mm in thickness. After binder burnout, these pressed disks were sintered at $1150–1200°\text{C}$ with two hours soaking period in air. Silver paste was fired on both faces of the disks at $580°\text{C}$ as electrodes. The specimens for measurement of piezoelectric properties were poled in silicon oil at $80°\text{C}$ under $3–4$ kV/mm for 15 min.

X-ray powder diffraction (XRD) patterns were taken on a D/MAX-III X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5418$ Å) and graphite monochrometer. The diffraction data were recorded for 2θ between 20 and $80°$, with a resolution of $0.02°$. The lattice parameters were refined by a least-square method using Si as an internal standard. The dielectric constant ε_r and dissipation factor (tan δ) at room and elevated temperature were measured at 1, 10 and 100 kHz using TH2816 LRC meter. Piezoelectric constant d_{33} of the samples were measured by means of quasistatic d_{33} meter (ZJ-3A) based on Berlincourt method at 110 Hz. Dielectric and piezoelectric properties were measured by means of the resonance-anti-resonance method using a precision impedance analyzer (HP4294A). The electromechanical coupling factor K_p was calculated from the resonance and anti-resonance frequencies based on

the Onoe's formula [10]. The coercive field E_c and remanent polarization P_r were determined from P-E hysteresis loops obtained by Radiant Precision Workstation ferroelectric testing system.

3.   Results and Discussions

3.1.   Crystal Structure

X-ray diffraction patterns are shown in Fig. 1 indicate that mono-perovskite phase formed in all samples. The lattice distortion in the NKBTN100x compound was investigated in the 2θ ranges $57–60°$. The indices (hkl) of the reflecting planes of the NKBTN100x in the 2θ ranges of $57–60°$ were determined to be (211), $(21\bar{1})$ with respect to the rhombohedral axes. Figure 2 shows a change in the diffraction peaks of NKBTN100x composition. The NKBTN0, NKBTN2, NKBTN4 and NKBTN6 still have a rhombohedral structure with a slight change in axial length and angle parameters (Table 1). The diffraction peaks in the stated 2θ ranges of NKBTN100x were altered for compositions above 8 mol%. It is observed that the $K_{\alpha 1}$ and $K_{\alpha 2}$ doublets in NKBTN10 split out, but no doublets in NKBTN8. The two K_α peaks in the 2θ ranges of $57–60°$ are identified as (211), with respect to a primitive cubic system. Thus, it can be concluded that no phase transition was observed for NKBTN100x when x is about 0–6 mol%. Moreover, the structure of the NKBTN100x with $x = 8$ mol% transformed to a pseudo-cubic and, subsequently, to a cubic form ($x = 10$ mol%).
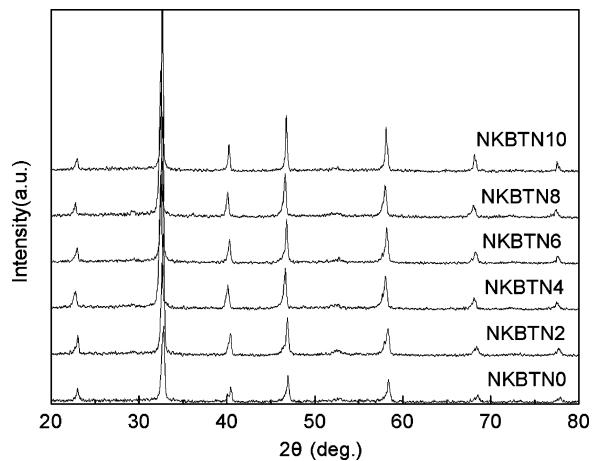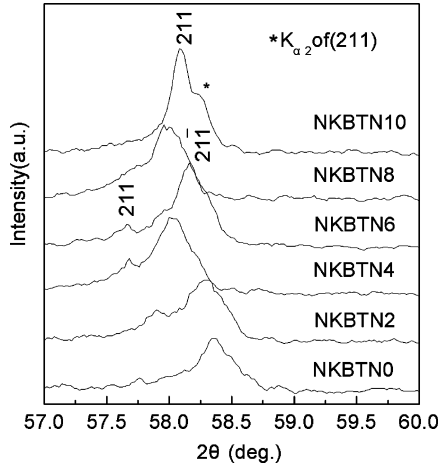

Fig. 1. XRD patterns of ceramics samples at room temperature.

*Table 1.* Lattice constant and rhombohedral distortion.

| Samples no.	x	a/Å	$\alpha/°$	Structure
NKBTN0	0	3.898	89.7	Rhombohedral
NKBTN2	0.02	3.917	89.8	Rhombohedral
NKBTN4	0.04	3.914	89.8	Rhombohedral
NKBTN6	0.06	3.976	89.6	Rhombohedral
NKBTN8	0.08	3.918	90	Pseudo-cubic
NKBTN10	0.10	3.916	90	Cubic

Fig. 2. XRD patterns at room temperature of samples at 2θ between $57°$ and $60°$.

It was reported that the MPB existed in NBT-KBT binary system at about 16 to 20 mol% of KBT [6]. In present work, KBT concentration in all samples is smaller than 16 mol%, XRD in 2θ range from $45°$ to $49°$ corresponding to (202) plane of rhombohedral structure (Fig. 1). No peak split related to tetragonal distortion is observed.

3.2. Dielectric Property

Figure 3 shows the dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ and dissipation factors $\tan \delta$ of poled ceramic samples at room temperature as a function of the amount of NN (x). It can be seen that the dielectric constant $\varepsilon_{33}^T/\varepsilon_0 = 1237$ and dissipation factors $\tan \delta = 0.0631$ of NKBTN8 are much more than that $\varepsilon_{33}^T/\varepsilon_0 = 575$ and $\tan \delta = 0.0299$ of NKBTN0. This is believed to be the result of doping donor ion Nb^{5+} in B-site. Figures 4 and 5 show the temperature dependence of dielectric constant ε_r and dissipation factor $\tan \delta$ of NKBTN0 and NKBTN8,
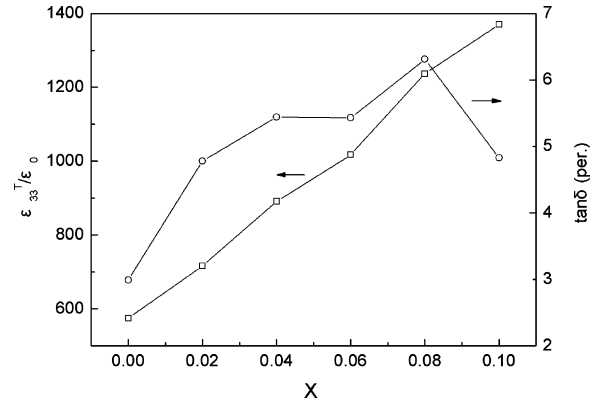
Fig. 3. Dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ and dissipation factor $\tan \delta$ of ceramics samples as a function of the NaNbO$_3$ concentration x.
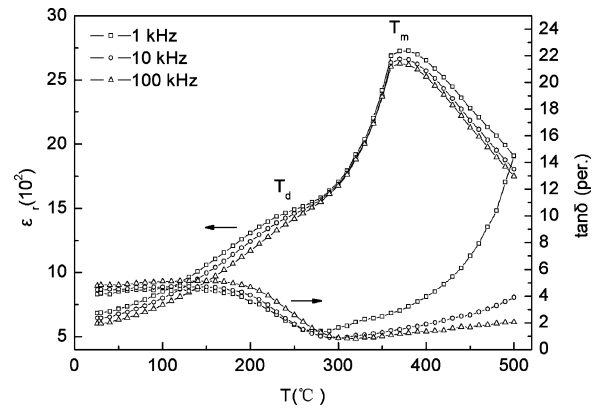
Fig. 4. Dielectric constant ε_r and dissipation factor $\tan \delta$ of NKBTN0 ceramics as a function of temperature and frequency.
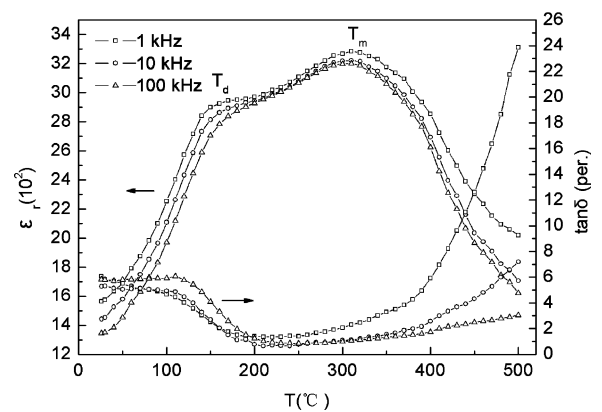
Fig. 5. Dielectric constant ε_r and dissipation factor $\tan \delta$ of NKBTN8 ceramics as a function of temperature and frequency.

respectively. It can be evidently seen that the three phases of ferroelectric, anti-ferroelectric and paraelectric exist in different temperature range for the samples similar to the results of NBT-BaTiO$_3$ [2], NBT-NN [9], NBT-KBT [6] binary system lead-free piezoelectric ceramics. Here, the transition temperature between ferroelectric phase and anti-ferroelectric phase is called as depolarization temperature (T_d) and the temperature corresponding to maximum value of dielectric constant is named as maximum temperature T_m. T_m could be considered as Curie point (T_c) because that T_c corresponds to the transition between anti-ferroelectric phase and paraelectric phase. It can be found that the samples have relaxor characteristics from the curves, i.e. both dielectric constant ε_r, transition temperature T_d and T_m are strongly measurement-frequency dependent, the higher the frequency, the lower the dielectric constant value and the higher the transition temperature T_d and T_m. It is thought that different ions random occupied the A or B-site sublattice of $(A'A'')(B'B'')O_3$-type perovskite unit cell, which would form numerous numbers of chemical micro-regions with distinctive composition of the A or B-site cations. Each micro-region possesses its own Curie temperature (T_c), leading to relaxor characteristics [11]. The representative compounds are $Pb(Mg_{1/3}Nb_{2/3})O_3$ [12], $Pb(Zn_{1/3}Nb_{2/3})O_3$ [13], et al., which have two kinds of ions of different valence at B-site of perovskite structure. In this work, the coexistence of Na^+, K^+ and Bi^{3+} ions at A-site, Ti^{4+} and Nb^{5+} co-occupied B-site may induce a relaxor ferroelectric behavior. The T_d and T_m measured at 1 kHz are given in Fig. 6 for all investigated samples. Both T_d and T_m first decrease and then increase as NN concentration increase.

All samples show similar dissipation factor behavior. Dielectric loss reaches minimum before the ferroelectric to anti-ferroelectric phase transition (Figs. 4 and 5). In the ferroelectric phase, the dielectric loss probably comes from domain wall movement and is frequency dependent. At higher temperature, the dielectric loss increases sharply which may be attributed the high electrical conductivity [14].

3.3. Ferroelectric Property

Figure 7 shows hysteresis loops of NKBTN system at room temperature as a function of the amount of NN (x). The hysteresis loops of the NKBTN system could easily be observed over a wide composition range of
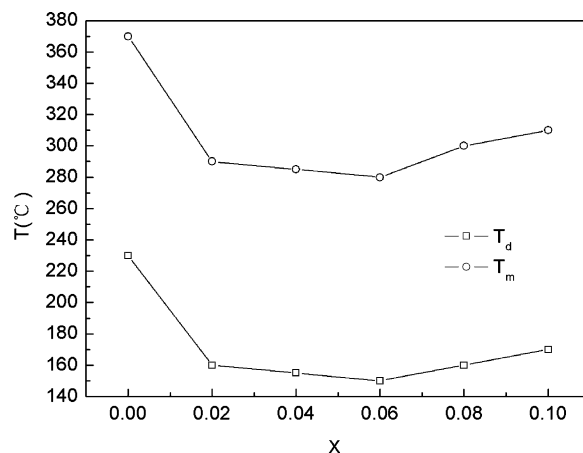

Fig. 6. Phase transition temperature T_d and T_m as a function of the NaNbO$_3$ concentration x.
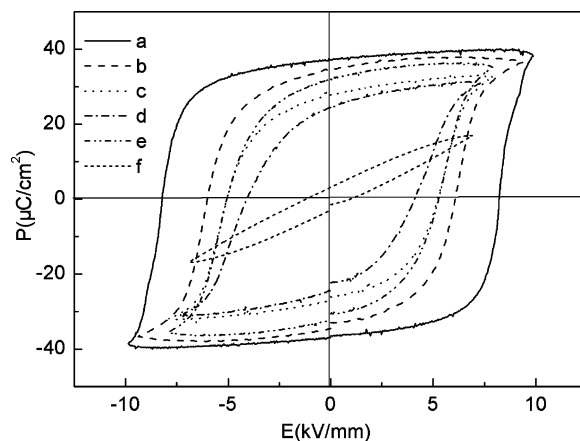

Fig. 7. *P-E* hysteresis loop of NBT-KBT-NN system ceramics at room temperature (a: NKBTN0; b: NKBTN2; c: NKBTN4; d: NKBTN6; e: NKBTN8; f: NKBTN10).

$x = 0$–8 mol% with a relatively large remanent polarization P_r and a high coercive field E_c. The P_r and E_c decrease with the increase of the amount of x in the range of 0–6 mol%. The P_r and E_c of NKBTN8 are larger than that of NKBTN6. It is thought that the reason for lower values of P_r in the NKBTN system is the decrease amount of Bi^{3+} ions with increase of NN concentration [4]. The P_r reaches a maximum of 37.2 μC/cm^2 at $x = 0$ where is correspond to the maximum value of the electromechanical coupling factors K_p. However, from Fig. 7 it can be seen that the P_r and E_c of NKBTN10 are very small, nearly equal 0. This
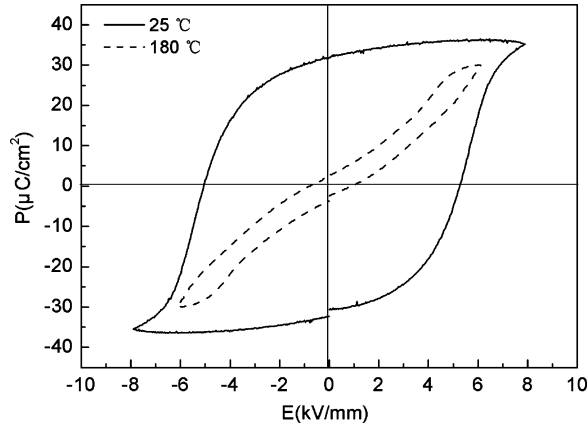
Fig. 8. *P-E* hysteresis loops of NKBTN8 ceramics at 25 and 180°C.

Fig. 9. Piezoelectric constant d_{33} and electromechanical coupling factor K_p as a function of the NaNbO$_3$ concentration x.

is in accordance with the cubic structure which is paraelectric phase and it has no piezoelectric properties.

Figure 8 shows the *P-E* hysteresis loops of NKBTN8 ceramics obtained at room temperature and 180°C, respectively. At room temperature, it can be seen that the remanent polarization P_r is 32.0 μC/cm^2, and coercive field E_c is 5.16 kV/mm, which are lower than that of pure NBT. That is to say the lower E_c facilitate the domain walls movement leading to an increase in piezoelectric properties. At 180°C, *P-E* hysteresis loop reveals an obvious anti-ferroelectric features for the narrow double hysteresis loop. Thus it can be concluded that there exists a transition from ferroelectric to anti-ferroelectric phase for all samples during heating.

3.4. Piezoelectric Property

Figure 9 shows the piezoelectric constant d_{33} and electromechanical coupling factor K_p as a function of the amount of NN. It can be found the d_{33} and K_p decrease with the amount of NaNbO$_3$, and the relative low values are located at $x = 6$ mol%, then they are increased at $x = 8$ mol%. This is consistent with *P-E* hysteresis loop shown in Fig. 7 that the remanent polarization P_r of NKBTN6 is the minimum value at the range of $x = 0$–6 mol%. However, the piezoelectric property is fully diminished once the NN (x) concentration is 10 mol%. This is believed to be in accordance with a phase distortion from rhombohedral to cubic phase shown in Fig. 2. Figure 7 shows the P_r reaches a maximum of 37.2 μC/cm^2 at $x = 0$, where is corresponding to the
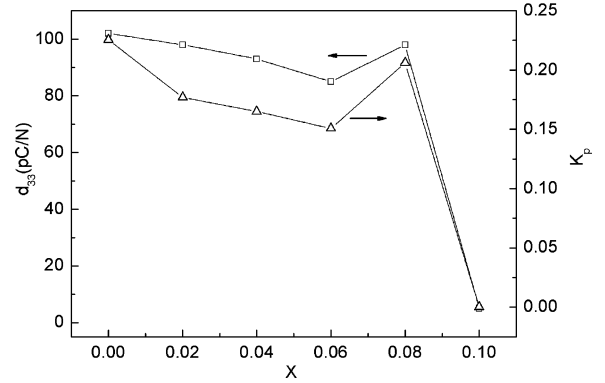
maximum values of K_p and d_{33}. Compared to the piezoelectric properties of NKBTN8 to that of NKBTN0, the d_{33} and K_p decrease a little, while the dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ increase much more as shown in Fig. 3. In contrast with NBT-NN binary system, the d_{33} and K_p of NBT-KBT-NN ternary system are higher, the ternary NKBTN ceramics are superior for NBT-based piezoelectric ceramics.

4. Conclusions

All compositions investigated in this work can form mono-perovskite solid solution. The varied crystalline structure can be ascertained by the powder X-ray diffraction patterns that from rhombohedral to pseudocubic, then to cubic with the increase concentration of NaNbO$_3$. All solid solution compounds experience two phase transitions at the range of room temperature to 500°C that ferroelectric to anti-ferroelectric and anti-ferroelectric to paraelectric phase transition with relaxor characteristics. Both phase transition temperatures are lowered due to introduction of NaNbO$_3$. *P-E* hysteresis loop shows that NKBTN0 ceramics has the maximum P_r and E_c corresponding to the maximum values of electromechanical coupling factor K_p and piezoelectric constant d_{33}. The piezoelectric constant d_{33} and electromechanical coupling factor K_p decrease a little, while the dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ improves much more when the concentration of NaNbO$_3$ is 8 mol%. Compared to NBT ceramics, the ternary NBT-KBT-NN system ceramics are superior for NBT-based piezoelectric ceramics.

Acknowledgments

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