

Large electrostrictive strain in lead-free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--BaTiO}_3\text{--KNbO}_3$ ceramics

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Abstract In the present work, $(1 - x)(0.935\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - 0.065\text{BaTiO}_3) - x\text{KNbO}_3$ (BNT–BT–KN, BNT–BT–100xKN) ceramics with x ranging from 0 to 0.1 were prepared by the conventional ceramic fabrication process. A large electrostrictive coefficient of $\sim 10^{-2} \text{ m}^4 \text{ C}^{-2}$ is obtained with the composition x ranging from 0.02 to 0.1, which is close to the well-known electrostrictive material $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. Under an electric field of 4 kV/mm, the electrostrictive strain can reach as high as 0.08%. Besides, the electric field induced strain behavior indicates a temperature independent behavior within the temperature range of 20 to 150°C. The large electrostrictive strain is suggested to be ascribed to the formation of non-polar (NP) phase developed by the KNbO_3 substitution, and the high electrostrictive coefficient of BNT–BT–KN ceramics makes them great candidates to be applied in the new solid-state actuators.

1 Introduction

Piezoelectric materials, which realize the electrical and mechanical energy conversion through electromechanical coupling, play an important role in various electronic devices and microelectromechanical systems [1]. Since their discovery, the $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) based multi-component systems have become the dominant materials in the piezoelectric fields due to their high electromechanical properties [2].

However, due to the concerns about their toxicity, environmental legislation in the European Union [3], parts of Asia, and the US has been passed, and lead has been expelled from many commercial applications such as solder, glass. As candidates for lead-free piezoelectric ceramics, various perovskite-structured ferroelectrics have been developed recently, and great progress has been achieved [4–10]. Among them, the $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) has been regarded as one promising candidate of the lead-free systems, and BNT based solid solutions have shown excellent piezoelectric properties of piezoelectric constant d_{33} over 200 pC/N, electromechanical coupling coefficient k_p over 40% [6, 7]. Quite recently, Ren et al. reported another exciting lead-free system of $\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3 - (\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BTZ–BCT), indicating ultrahigh d_{33} of ~ 620 pC/N, entirely comparable to the PZT systems [11].

Nevertheless, these new systems suffer from several common problems, especially the strong temperature dependence of obtainable electric-field-induced strain. Taking the BTZ–BCT, for example, the working temperature cannot exceed 70°C [11], which greatly restricts the practical application prospective. Recently Zhang et al. proposed a new concept of using lead-free antiferroelectrics as electrostrictors, which can provide high strain and minimal losses at room temperature combined with minimal temperature dependence [12, 13]. Such a concept has also been proposed in the PLSZT system [14, 15]. Compared with the piezoelectric effect, the electrostrictive effect has several unique advantages: possessing little or no hysteretic loss up to high frequencies, being temperature stable, and exhibiting a fast response time [16]. Besides, antiferroelectrics indeed have witnessed great interest in the past because of the field-induced phase transition into the ferroelectric state accompanied by a large-volume change, making them an interesting alternative for strain and force generators [17].

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In this paper, we report the development a new lead-free electrostrictive system based on BNT ceramic which can deliver a giant strain with little strain hysteresis. The electrostrictive coefficient Q can reach as high as $0.029 \text{ m}^4 \text{ C}^{-2}$. Besides, the electric-field-induced strain indicates temperature independent behavior with the temperature range of 20 to 150°C , indicating great potential in new high-precision positioning and other solid-state actuators.

2 Experimental

$(1-x)(0.935\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.065\text{BaTiO}_3)-x\text{KNbO}_3$ (BNT–BT–KN or BNT–BT– $100x\text{KN}$) ceramics with $x = 0, 0.02, 0.04, 0.06, 0.08, \text{ and } 0.1$ were prepared by a conventional ceramic fabrication method using Bi_2O_3 (99.0%), Na_2CO_3 (99.8%), K_2CO_3 (99.0%), BaCO_3 (99.0%), TiO_2 (98.0%), and Nb_2O_5 (99.5%) as starting raw materials. For each composition, the starting materials were weighed according to the stoichiometric formula and ball milled for 7 h in de-ionized water. The dried slurries were calcined at 850°C for 2 h and then ball milled again for 7 h. The powders were subsequently pressed into green disks with a diameter of 15 mm under 4 MPa. Then the sintering was carried out at 1200°C for 2 h in covered alumina crucibles. To minimize the evaporation of the volatile elements Bi, Na, and K, the disks were embedded in the powder of the same composition. Silver paste was coated on both sides of the sintered samples and fired at 650°C for 0.5 h to form the electrodes. The specimens for measurement of piezoelectric properties were poled in silicone oil bath with a dc field of 4–6 kV/mm at $50\text{--}60^\circ\text{C}$ for 15 min.

The crystal structures of the ceramics were characterized by powder XRD (D8 Focus, Germany) with unpoled sample powders. Dielectric permittivity and loss of the ceramics were measured using an impedance analyzer (Agilent HP4294A) in a temperature range of $30\text{--}320^\circ\text{C}$. P – E loops and S – E curves, where P , E , and S denote the polarization, the electric field and the strain, respectively, were measured at 50 mHz in silicon oil with the aid of a Sawyer–Tower circuit to apply an electric field with triangular waveform.

3 Results and discussions

Figure 1 shows the X-ray diffraction patterns of the BNT–BT– $100x\text{KN}$ compositions with x from 0 to 0.1. The patterns indicate that all ceramics were crystallized into a single-phase perovskite structure and no second phase existed. Besides, no obvious change in the positions and relative intensities of all reflections was observed, suggesting similar crystal structures for all compositions. Based on the XRD

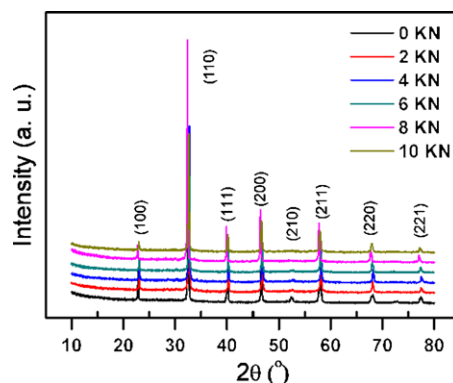


Fig. 1 The X-ray diffraction patterns of the proposed lead-free BNT–BT– $100x\text{KN}$ ceramics

results, pseudocubic (rhombohedral) phases for the ceramics with compositions x between 0.02 and 0.1 can be estimated by fitting the characteristic peaks of the perovskite structure. The lattice parameter of the angle α is only a little away from 90° , which is similar to the XRD results of the $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--BaTiO}_3\text{--K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (BNT–BT–KNN) system [12, 18].

Figures 2(a)–(d) and 3(a)–(d) illustrate the P – E loops and S – E curves of BNT–BT– $100x\text{KN}$ with the composition $x = 0, 0.02, 0.06, 0.1$, respectively, under an electric field of about 4 kV/mm at 50 mHz. For the pure BNT–BT composition of $x = 0$, a typical P – E loop (Fig. 2(a)) can be observed with the remnant polarization P_r of $\sim 27 \mu\text{C}/\text{cm}^2$, coercive field E_c of $\sim 3 \text{ kV}/\text{mm}$. The d_{33} of poled ceramic is about 120 pC/N. The strain curve indicates that under an electric field of 4 kV/mm, the minus strain can reach 0.07%, which is due to the ferroelectric domain and domain wall switching.

When KNbO_3 (KN) with the concentration of $x = 0.02$ was introduced into the BNT–BT system, the P_r and E_c decreased greatly and the loop became very slim as shown in Fig. 2(b). Strain curve follows the square of the polarization as shown in Fig. 4(a). The maximum polarization P and strain S (under the electric field of 3.3 kV/mm) reach $12.5 \mu\text{C}/\text{cm}^2$ and 0.04%, respectively. Correspondingly, the electrostrictive coefficient Q can be determined from the formula

$$S = QP^2 \quad (1)$$

where the S and P represent the strain and polarization, respectively. As a result, Q of the BNT–BT–2KN is calculated to be $0.0274 \text{ m}^4 \text{ C}^{-2}$. This value is even larger than that of the well-known electrostrictive material $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) having Q of $0.017 \text{ m}^4 \text{ C}^{-2}$ and also superior to the recently reported BNT–BT–KNN system [12, 18, 19].

With the KN concentration x further increased to 0.1, the P – E loops became slimmer as shown in Fig. 2(c) and (d). The maximum polarizations under the electric field

Fig. 2 The ferroelectric hysteresis loops for the BNT–BT–100 x KN ceramics with (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.06$, (d) $x = 0.1$

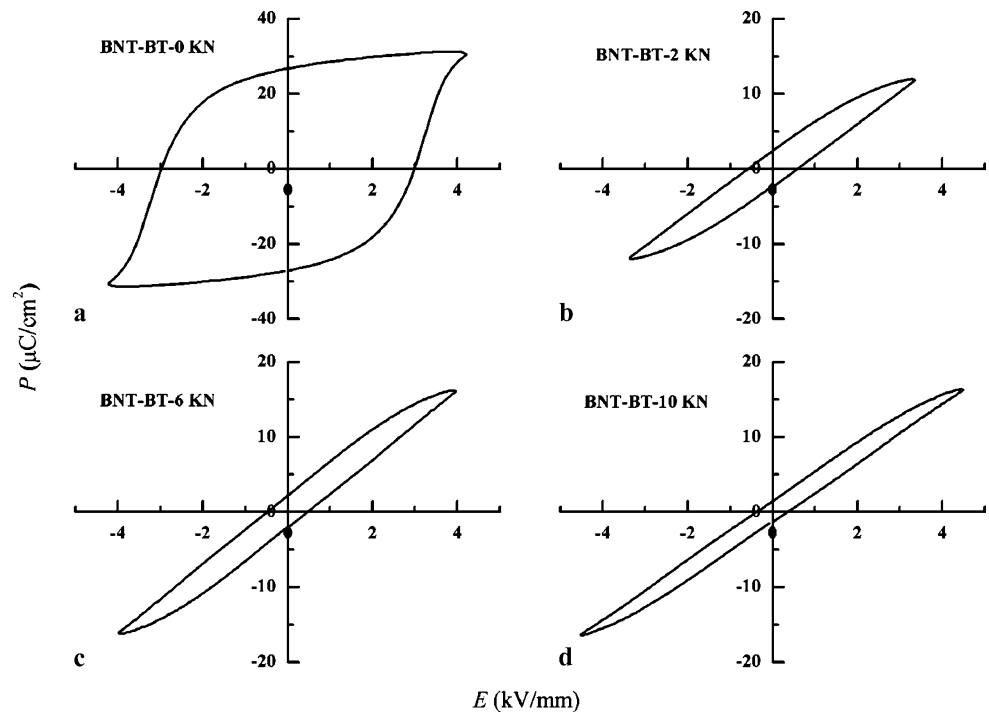
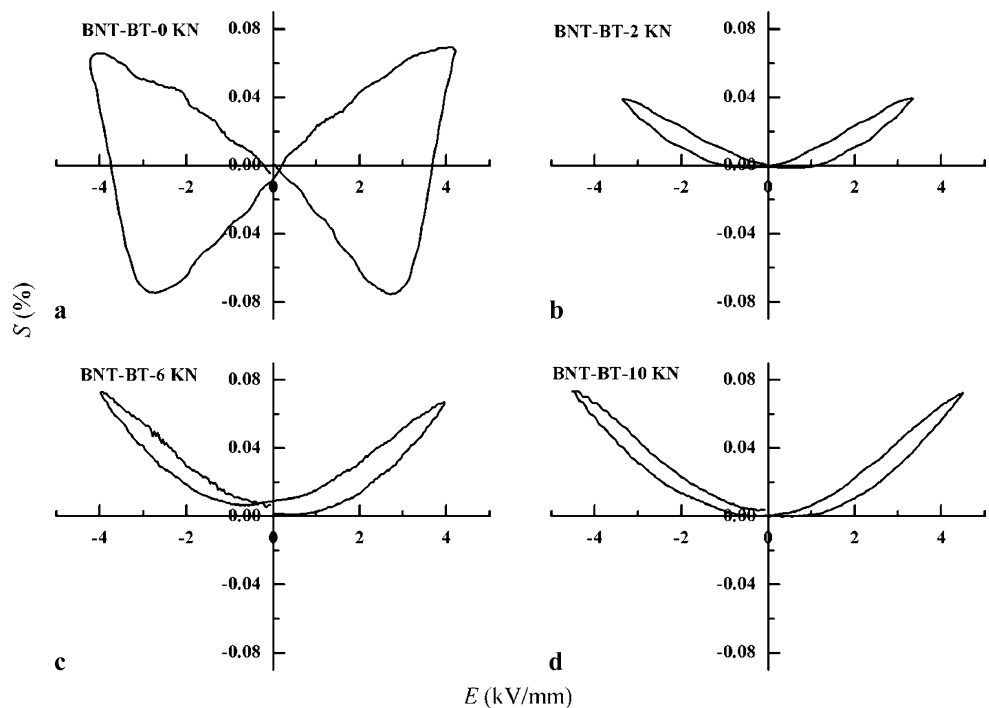


Fig. 3 The strain curves vs. electric field for the BNT–BT–100 x KN ceramics with (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.06$, (d) $x = 0.1$



of ~ 4 kV/mm reach ~ 15 $\mu\text{C}/\text{cm}^2$. In the poled samples, d_{33} is only 8–10 pC/N for the composition $x = 0.06$ –0.1. The strain curves also follow the square of the polarization as shown in Fig. 4(b) and (c), and the corresponding Q is calculated to be 0.0253 and 0.0296 $\text{m}^4 \text{C}^{-2}$, respectively. These are all impressive values for a lead-free electrostrictive material. Besides, it needs to be mentioned that here the maxi-

imum polarization and strain for BNT–BT–2KN is lower than for the BNT–BT–6KN and BNT–BT–10KN ceramics. This is related to the lower applied electric field during our measurement and comparable results can be expected if the same electric field is applied.

Figures 5(a)–(d) show the temperature dependence of dielectric constant and loss of the BNT–BT–100 x KN with the

Fig. 4 The strain vs. the square polarization for the BNT-BT-100xKN ceramics with (a) $x = 0.02$, (b) $x = 0.06$, (c) $x = 0.1$

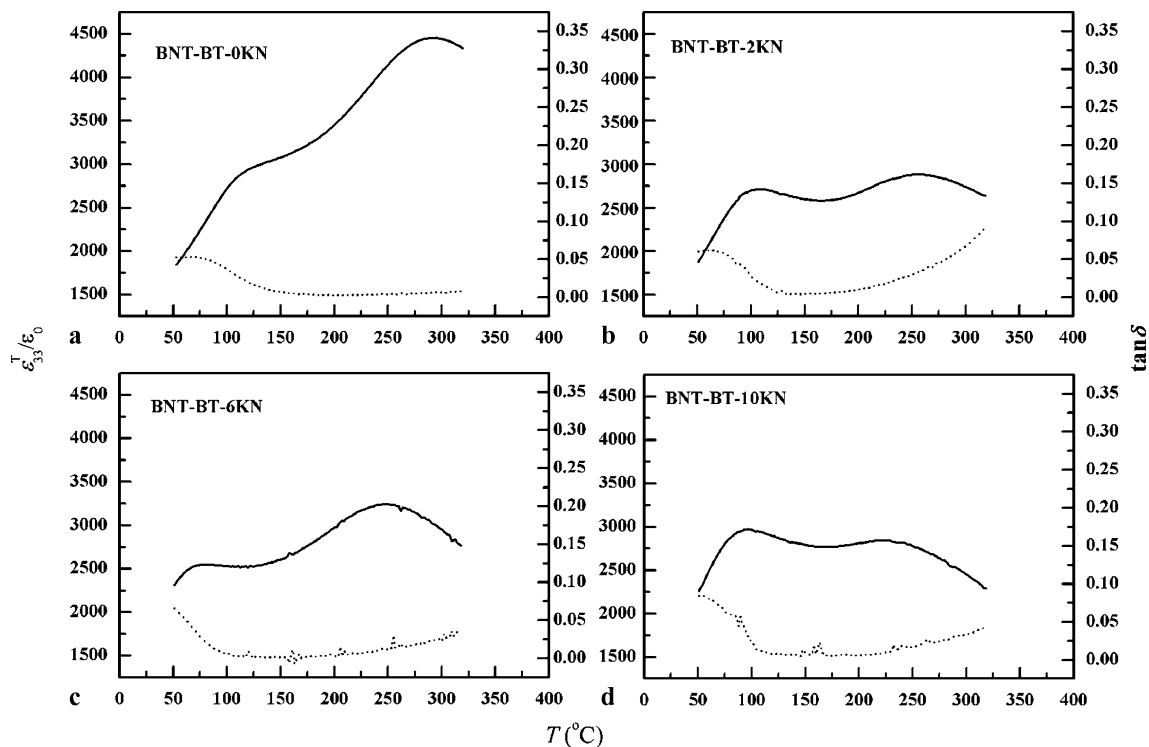
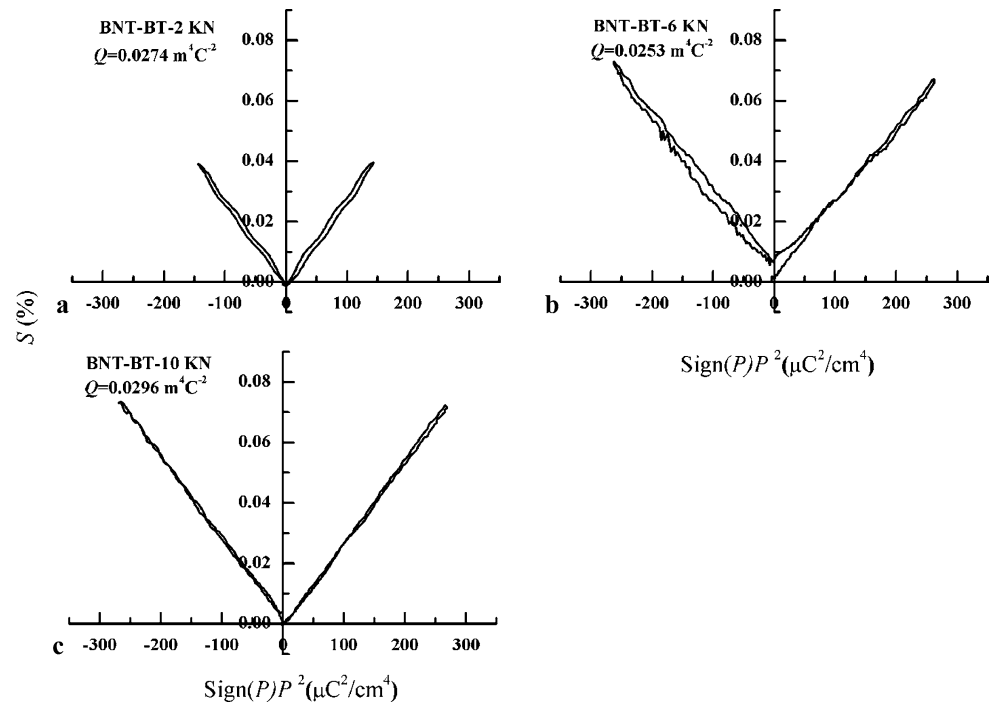


Fig. 5 Composition dependence of dielectric constant and loss in the temperature range from 50 to 320°C at 1 kHz

composition $x = 0, 0.02, 0.06, 0.1$ with temperature range of 50 to 320°C at 1 kHz. With the composition increasing, the T_m corresponding to the temperature of maximum dielectric constant decreases. Broad dielectric peaks around T_m can be well observed, exhibiting diffuse phase transition

characteristics, which has been well observed in the BNT based solid solutions. This is correlated with the multiple complexes in the A-site (such as Bi^{3+} , Na^{1+} , Ba^{2+} , etc.) of perovskite compounds, which could lead to the compositional inhomogeneity on the nanoscale [20]. For the pure

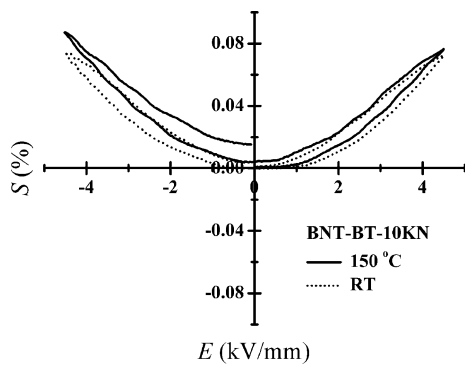


Fig. 6 The strain curves vs. electric field for the BNT–BT–10KN ceramic at room temperature (RT) and at 150°C

BNT–BT ceramic, the maximum dielectric constant reaches around 4500 at 1 kHz, which is a little lower than the previously reported one of about 5100 [21]. The reason for this should be correlated with the processing techniques such as the different balling process, the sintering conditions and poling procedure. Besides, in the whole temperature scale the dielectric constant changes a lot. In comparison, when the KN was introduced into BNT–BT, the variation of dielectric constant vs. temperature reduced greatly, indicating a weaker temperature-independent behavior. This is also compared to the temperature dependence of the strain behavior, with the strain curve at room temperature and at 150°C shown in Fig. 6. With the temperature increasing, the induced maximum strain under the electric field of about 4 kV/mm changes little and keeps around 0.08%. In comparison with the reported PMN and BNT–BT–KNN system, the electrostrictive strain of the present solution is lower than the relaxor PMN under the same field (about 0.12% at 4 kV/mm), however, obviously larger than the BNT–BT–KNN (about 0.05% at 4 kV/mm) [12, 18].

Based on the above obtained results, the decrease of the quasi-static piezoelectric constant d_{33} (from 120 pC/N to about 10 pC/N), large electrostrictive strain and weak ferroelectric response for the ternary solid solution were suggested to originate from the coexistence of the ferroelectric and non-polar (NP) phase developed by the KN substitution. When subjected to external electric field, the presence of the NP phase can easily bring the system to its original unpoled state after field removing so as to realize high strain response. Similar results have also been observed in recently-developed solutions such as the BNT–KNN and Zr-modified $\text{Bi}_{0.5}(\text{Na}_{0.78}\text{K}_{0.22})_{0.5}\text{TiO}_3$ [22, 23]. The high electrostrictive strain along with the good temperature stability would be much favorable for new solid-state actuator designs and applications.

4 Conclusions

In summary, a new type of lead-free electrostrictor BNT–BT–100xKN was proposed in the present work. The ferroelectric, dielectric and strain characteristics were investigated systematically. For the BNT–BT–100xKN ceramic with the composition $x = 0.1$, the electrostrictive coefficient Q can reach as high as $0.0296 \text{ m}^4 \text{ C}^{-2}$, even higher than that of the well-known PMN. Besides, this strain indicates a nearly temperature-independent behavior with little hysteresis in the temperature range from 20 to 150°C. All these properties make these ceramics quite suitable for environment-friendly high-precision solid state actuators.

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