

Large electric-field-induced strain in B-site complex-ion $(\text{Fe}_{0.5}\text{Nb}_{0.5})^{4+}$ -doped $\text{Bi}_{1/2}(\text{Na}_{0.82}\text{K}_{0.12})_{1/2}\text{TiO}_3$ lead-free piezoceramics



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ARTICLE INFO

Keywords:

Lead-free piezoceramics
Doped
Large strain
Phase transition
Phase coexistence

ABSTRACT

In order to obtain a new system of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BNT) based lead-free incipient piezoceramics with large strain for practical applications of actuators, we investigated the effect of B-site complex-ion $(\text{Fe}_{0.5}\text{Nb}_{0.5})^{4+}$ (FN)-doped $\text{Bi}_{1/2}(\text{Na}_{0.82}\text{K}_{0.12})_{1/2}\text{TiO}_3$ ceramics on the phase structure, dielectric, ferroelectric, piezoelectric and electric-field-induced strain properties. All samples exhibited single perovskite phase with pseudocubic symmetry. The room temperature electric-field-induced polarization (P - E) and strain (S - E) hysteresis loops indirectly illustrated ferroelectric-to-relaxor (FE-RE) phase transition. The increasing content of FN doping decreased the FE-RE phase transition temperature, $T_{\text{F-R}}$ to below room temperature and induced the reversible FE-RE phase transition, giving rise to a large strain of 0.462% with a normalized strain, d_{33}^* of 660 pm/V at a critical composition of $x = 5$. A fluctuation of the dielectric curve for BNKT-5 mol% FN ceramics in the spectra around 80 °C before and after polarization suggested that the large strain response can be induced via delicate mixing of the FE and RE phase.

1. Introduction

Lead-based piezoelectric ceramics represented by the lead zirconate titanate (PZT) have been extensively employed in modern electronic devices, such as the actuators, sensors and ultrasonic transducers for their excellent dielectric, piezoelectric and electromechanical properties [1,2]. Nevertheless, these materials contain more than 60 wt% lead elements which are volatile easily during sintering and can cause serious environment issues, resulting in intensive studies being given to lead-free piezoelectric ceramics [3–8]. Among them, $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) are considered to be promising candidates due to their excellent electric properties [9]. However, it is extremely difficult to obtain the practical application due to its high coercive field ($E_c = 73$ kV/cm) and electrical conductivity. In order to improve the electromechanical properties, many BNT-based ceramics were developed in recent years such as $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - BaTiO_3 (BNT-BT) [10,11], $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (BNT-BKT) [12,13], and $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - SrTiO_3 (BNT-ST) [14,15] because of the optimum performances of morphotropic phase boundary (MPB) [16,17]. Although significant improvements have been made on piezoelectric properties, BNT-based ceramics still can't compete with the lead-containing ones in terms of the overall

electrical properties. There is an urgent demand to find innovative piezoelectric lead-free materials for practical application.

In 2007, Zhang et al. [18] reported a giant strain of 0.45% at 80 kV/cm with normalized strain d_{33}^* ($S_{\text{max}}/E_{\text{max}}$) is 560 pm/V in a lead-free BNT-BT modified with $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (BNT-BT-KNN) system. Later, Seifert et al. [19] introduced BKT in place of BT in the BNT-BT-KNN system and reported a larger $S_{\text{max}}/E_{\text{max}}$ of 600 pm/V. Pham et al. [20] studied a Nb-doped $\text{Bi}_{1/2}(\text{Na}_{0.82}\text{K}_{0.18})_{1/2}\text{TiO}_3$ (BNKTN) ceramics near the morphotropic phase boundary (MPB) and obtained a large unipolar strain of 0.448% at 7 kV/mm. So far, the origin of the large strain in the BNT-based system remains unsettled and none of the proposed mechanisms for these superior properties induced by doping is conclusive enough to outweigh the others. A series of in-situ diffraction studies in an electric field environment [21,22], transmission electron microscope (TEM) [23,24] and piezoresponse force microscopy (PFM) [25,26] measurements have revealed that the large strain is due to a reversible phase transformation from ergodic relaxor (RE) phase to a long-range ferroelectric (FE) phase.

In general, the most effective and convenient method to obtain the optimized strain properties in BNT-based ceramics is to construct components of the material to the proximity of a composition-induced

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phase transition between FE and RE phases [27–29]. Meanwhile, the phase transition will decrease ferroelectric-to-relaxor (FE-RE) transition point T_{F-R} down to the room temperature (RT) [30,31]. Thus, to obtain an expected large strain, one of estimate criterion concerning the effect of the modifier is whether it can lower the T_{F-R} to RT.

In the last decade, most of the studies on the A-site (or B-site) single-ion substitution and A/B-site complex ions replacement have been done for improving the electromechanical properties, such as $(0.935-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.065\text{BaTiO}_3-x\text{SrTiO}_3$ [32], $\text{Bi}_{1/2}(\text{Na}_{0.82}\text{K}_{0.18})_{1/2}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ [33] and $(1-x)\text{Bi}_{1/2}(\text{Na}_{0.82}\text{K}_{0.18})_{1/2}\text{TiO}_3-x\text{LaFeO}_3$ [34]. However, little effort has been paid to the effect of B-site complex ions substitution. Recently, Cheng et al. [35] studied a large strain of 0.442% ($S_{\text{max}}/E_{\text{max}} = 844 \text{ p.m./V}$) in (Fe, Nb) co-doped $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.935}\text{Ba}_{0.065}\text{TiO}_3$ piezoceramics, however, this sample showed a much larger remanent strain (S_r) value (0.2%). Li et al. [36] reported that the $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.935}\text{Ba}_{0.065}\text{Ti}_{1-x}\text{O}_3(\text{Al}_{0.5}\text{Sb}_{0.5})_x\text{O}_3$ (BNBT6.5- x AS) ceramics exhibited a large strain of 0.46% ($d_{33}^* = 573 \text{ p.m./V}$) at an applied field of 80 kV/cm. Although the strain of BNBT6.5- x AS ceramics is very large, antimony is toxic to human and environmental organisms and is even alleged to be carcinogenic. Based on the former researches, we designed a non-toxic new ternary solid solution through introducing B-site complex-ion $(\text{Fe}_{0.5}\text{Nb}_{0.5})^{4+}$ (FN) into the MPB solid solution $\text{Bi}_{1/2}(\text{Na}_{0.82}\text{K}_{0.18})_{1/2}\text{TiO}_3$. It is expected that the addition of $(\text{Fe}_{0.5}\text{Nb}_{0.5})^{4+}$ will play a similar role and may also result in a great enhancement of the electromechanical properties.

2. Experimental procedure

A conventional solid-state reaction method was utilized to prepare the $\text{Bi}_{1/2}(\text{Na}_{0.82}\text{K}_{0.18})_{1/2}\text{Ti}_{1-x}\text{O}_3(\text{Fe}_{0.5}\text{Nb}_{0.5})_x\text{O}_3$ (BNKT- x mol% FN, $x = 1, 2, 3, 4, 5, 5.5, 6$) ceramics. The raw materials Bi_2O_3 (99.0%), Na_2CO_3 (99.8%), K_2CO_3 (99.8%), Fe_2O_3 (99.5%), Nb_2O_5 (99.5%), and TiO_2 (99.5%) were weighed according to the nominal compositions. The powders were dried in an oven at 100 °C for 24 h before weighting. The weight of dried powders depended on stoichiometric formula. Then the dried raw powders were ball-milled with stabilized zirconia balls for 24 h in ethanol. The dried slurries were pulverized and calcined at 850 °C for 2 h, after which the ball milling process was repeated. Polyvinyl alcohol (PVA) was added to the dried mixture as a binder for granulation, thoroughly crushed, and passed through a 100-mesh sieve. The fine powder was pressed into green disks of 10 mm diameter and thicknesses of 0.6 mm under the pressure of about 100 MPa. Sintering was performed at 1120 °C in the covered alumina crucibles for 2 h in air. To prevent Bi, Na and K from volatilizing, the disks were embedded with their corresponding powders.

The phase structures of the sintered ceramics were characterized by powder X-ray diffraction (XRD) obtained by a diffractometer (PANalytical B.V., X'Pert PRO, the Netherlands) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at a voltage and current of 40 kV and 30 mA. XRD data were collected in the range of 20–80° in θ -2 θ locked-coupled scanning mode with a 0.02° step and scanning speed of 5°/min. The surface micrograph of the bulk ceramics were examined by scanning electron microscopy (SEM: Philip, XL30TM). For measuring the electrical properties, silver paste was coated on both sides of the pellets and fired at 520 °C for 20 min to form electrodes. Temperature and frequency dependent permittivity and dielectric loss were measured with a high-precision LCR meter (TH2832, Tonghui Electronic Co., Ltd., Jiangsu, China). The data were collected at four frequencies (0.5 kHz, 1 kHz, 10 kHz and 100 kHz) for every 1 °C from RT to 450 °C with a heating rate of 1 °C/min. The electric-field-induced polarization (P - E) and strain (S - E) hysteresis loops measurements of the samples were carried out using the commercial aixPES setup (aixACCT Systems GmbH, Aachen, Germany), which is equipped with a laser interferometer. The piezoelectric coefficient d_{33} of the poled samples was measured using a quasi-static d_{33} meter (ZJ-6A, Institute of Acoustic, Chinese Academic of Sciences, Beijing, China).

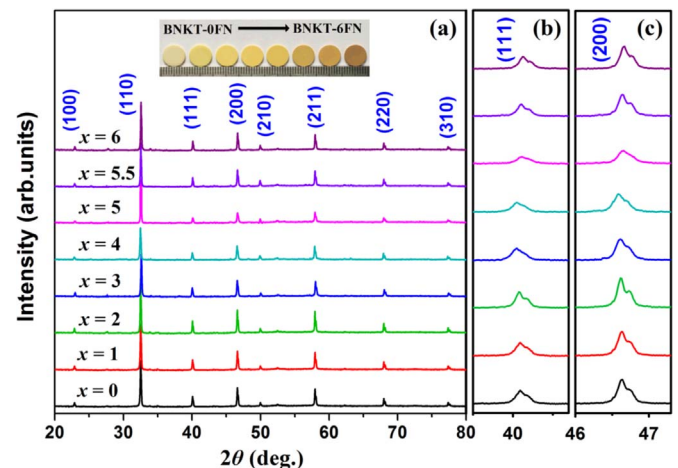


Fig. 1. X-ray diffraction (XRD) patterns for BNKT- x mol% FN ceramics before poling with 2θ ranging 20–80° (a), 39.5–40.8° (b), and 46–47.3° (c).

3. Results and discussion

Fig. 1(a) provides the XRD patterns of BNKT- x mol% FN ceramics. It can be seen that all of the samples exhibited a single perovskite structure without apparent secondary phases. This absence of second phases indicates that the Fe^{3+} and Nb^{5+} ions diffused into the BNKT lattice to form a homogeneous solid solution [37]. The characterization of the (111) and (200) peaks was investigated in detail to reveal the phase structure evolution, as shown in Fig. 1(b) and (c). Careful observation shows that the undoped ceramics possess the characteristics of a pseudocubic phase, as proved by the presence of non-split (111) and (200) peaks other than $\text{K}\alpha_1$ and $\text{K}\alpha_2$ peaks [31,38], supporting the fact that there is no obvious long-range non-cubic distortion [39]. However, considering the X-ray diffraction method limit, it is highly possible that the pseudocubic phase proved by the current diffraction experiments could be a consequence of the presence of a rhombohedral symmetry with a very small distortion [40].

Fig. 2 displays the SEM micrographs of the polished and thermally etched surfaces of BNKT- x mol% FN ceramics. The addition of FN greatly influenced the grain size and shape. Upon FN doping, the grain changes from a normal shape for $0 \leq x \leq 1$ to a larger but non-uniform strip shape for $2 \leq x \leq 5$, then change back to its normal shape for $x > 5$. This result shows that a proper FN doping promotes the grain growth, but a high concentration of FN may restrain the grain growth. The introduction of new components may produce compounds with low melting point. It can increase the speed of ion diffusion and lead to crystal growth. In addition, the crystal has a certain solid solubility for dopant, and excessive FN doping will lead to dopant accumulation at the grain boundaries, and crystal growth is limited.

Fig. 3(a) describes the P - E hysteresis loops of the BNKT- x mol% FN ceramics measured at the frequency of 1 Hz and room temperature. The characteristic parameters of the ceramics, maximum polarization (P_m), remanent polarization (P_r), and coercive field (E_c), are summarized in Fig. 3(b) as a function of the FN content. Obviously, the $P(E)$ of the pure BNT-BKT forms a fully saturated hysteresis loop with maximum and remanent polarizations of 39 $\mu\text{C}/\text{cm}^2$ and 32 $\mu\text{C}/\text{cm}^2$, respectively, and a coercive field of 41 kV/cm, which is typical for ferroelectric materials [1,41]. As can be seen from Fig. 3(a), with the increase of FN content slightly pinched hysteresis loop appears while the maximum polarization P_m is essentially unchanged for $0 < x \leq 5$, which indicates that the introduction of FN restrains a field-induced ferroelectric order [42]. It should be pointed out that, a significant pinched and slimmer polarization hysteresis loop appears at the critical FN content of $x = 5$. Such a sharply decrease resulted in a drastic drop in the P_r from 32 $\mu\text{C}/\text{cm}^2$ for pure BNKT to 9 $\mu\text{C}/\text{cm}^2$. The E_c also decreased from 41 kV/cm to

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