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Erratum

Nanoscale origins of small hysteresis and remnant strain in $Bi_{0.5}Na_{0.5}TiO_3$-based lead-free ceramics

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ABSTRACT

$BiAlO_3$-doped $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$ (BA-doped BNT-BKT) ceramics are greatly concerned due to their sufficient electric-field-induced strain with small hysteresis and remnant strain for high precision positioning devices and other actuators. In this paper, the structural analysis especially the high-resolution transmission electron microscope (HRTEM) is used to reveal the origin of excellent properties obtained in 0.96(0.75BNT-0.25BKT)-0.04BA, which exhibits a large strain of 0.21% at ~70 kV/cm, a small strain hysteresis of only 24% and a near-zero remnant strain. Using HRTEM, the antiferroelectric nano-domains composited by three variants of in-phase $a^0a^0c^+$ octahedral tilting coexisted with the remnant ferroelectric nano-domains of anti-phase $a^-a^-a^-$ octahedral tilting are directly identified. Then a continuous tilting model is proposed to interpret the gradually transitional tilting involving nano-domains leading to the small hysteresis and near-zero remnant strain. The findings may pave a way for further optimizing the properties through creating stable antiferroelectric nano-domains in BNT-based ceramics and the analogues.

1. Introduction

$Bi_{0.5}Na_{0.5}TiO_3$ (BNT) based lead-free ceramics are considered to be one of the most promising candidates to replace the commercialized $Pb(Zr,Ti)O_3$ (PZT) based ceramics due to their excellent properties such as giant strain [1–3], high electric energy densities [4,5], etc. Though pure BNT ferroelectric prototype ceramics have strong ferroelectric properties, the large remnant polarization (P_r) of 38 μC/cm^2 and coercive field (E_c) of 73 kV/cm hinder them to be applicable in high precision devices [6]. So far, intensive research work has been conducted by tailoring the composition in a BNT-based solid solution to acquire reduced P_r and E_c with a slim hysteresis loop. Sasaki et al. reported that the reduced P_r of 19.9 μC/cm^2 and E_c of 31 kV/cm were obtained in $0.80Bi_{0.5}Na_{0.5}TiO_3$-$0.20Bi_{0.5}K_{0.5}TiO_3$ (0.80BNT-0.20BKT) at room temperature (R.T.) [7]. Also, the P_r and E_c were both reduced to about 20 μC/cm^2 and 25 kV/cm after doping with $BaTiO_3$ (BT) in the compound of 0.95BNT-0.05BT [8]. To further meet the small hysteresis and remnant strain required by the applications in high precision positioning devices and other actuators, Zhang et al. proposed the concept of lead-free antiferroelectric electrostrictors based on $K_{0.5}Na_{0.5}NbO_3$ (KNN)-doped BNT-BT ceramics with small P_r and E_c [2]. Ullah et al. reported that a significant decrease in P_r and E_c with only a small decrease in maximum polarization was obtained in $BiAlO_3$ (BA) modified 0.75BNT-0.25BKT ceramics [9]. Besides, the small hysteresis has been acquired in other BNT-based solid solutions such as $Bi_{0.5}Na_{0.5}TiO_3$–$Bi_{0.5}K_{0.5}TiO_3$–$Bi(Mg_{0.5}Ti_{0.5})O_3$ [10], $(Bi_{0.5}Na_{0.5})TiO_3$–$KNbO_3$–$SrTiO_3$ [11], and $Ba(Zr_{0.05}Ti0.95)O_3$-modified BNT-BKT [12], making BNT-based ceramics be one of the most promising candidates for high precision positioning devices.

However, the improved properties of the BNT-based ceramics are essentially rooted in the microscopic features. The antiferroelectric (AFE) phase is commonly observed in these BNT-based materials, such as BNT-BT [13–15], BNT-BKT [16,17], and BNT-BT-KNN [1,18]. In BNT-BT system, Ma et al. discovered the existence of the AFE (rigorously uncompensated AFE) phase with *P4bm* symmetry [13]. The introducing of BT was found to refine the size of polar domains and make the AFE domains nanometer scale, which ultimately led to a relaxor behavior and resulted in the hystere-

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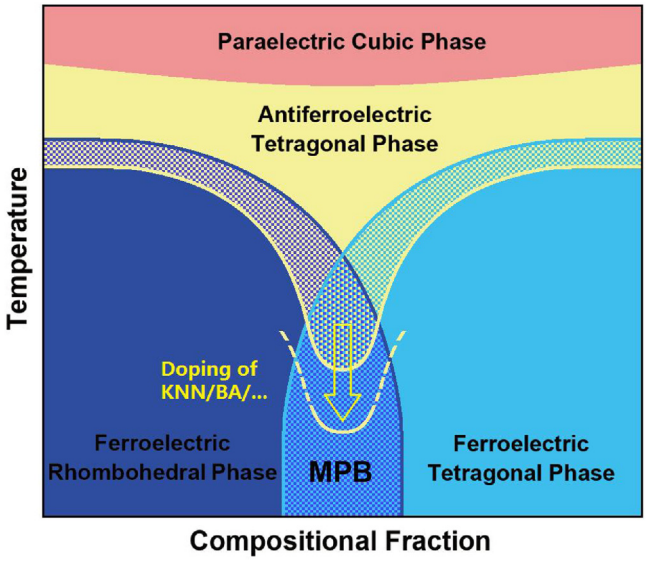

Fig. 1. Schematic of phase diagram for BNT-based materials with morphotropic phase boundary between rhombohedral and tetragonal sides based on Refs. [2,13,23,24].

sis reducing [13]. However, AFE *P*4*bm* phase could not be retained and the metastable ferroelectric *P*4*mm* phase could be induced after poling [19]. In order to stabilize the AFE *P*4*bm* phase, KNN was introduced and then the AFE *P*4*bm* phase could undergo a reversible phase transition under the electrical field [20,21]. Generally in the view of phase diagram illustrated in Fig. 1, an AFE phase with nano-domains morphology could be formed near the morphotropic phase boundary (MPB) between BNT rhombohedral side and BT tetragonal side, and the addition of KNN lowers the depolarization temperature and stabilized the AFE phase in BNT-BT system [2,5]. This scenario is also expected in BA-doped BNT-BKT system.

Recently, Ma et al. proposed a model that the AFE nano-domains with *P*4*bm* symmetry are embedded in an undistorted cubic matrix, by means of investigating the relationship between the AFE domain structures and the dielectric properties in BNT-BT ceramics [13]. The structural details of these AFE domains are particularly concerned due to the key role in the optimization of properties. Unfortunately, some important aspects of the AFE domains remain elusive. The coherence length of the AFE domains have been inferred to be nanometer according to the frequency dispersion of dielectric constant, but the direct evidence is still lacked [13,22]. The structure model that AFE nano-domains with the *P*4*bm* symmetry are embedded in the undistorted cubic matrix has been well accepted, but how these nano-domains separate from each other remains unknown. Up to now, the AFE domains were usually identified to be *P*4*bm* symmetry by selected area electron diffraction (SAED) and neutron powder diffraction, which actually gives a picture of the average structure [19–24]. However, the local structures at nanoscale or even several atoms lengths deviated from the average structure, arising from various octahedral tilting systems in BNT-based perovskite-type ceramics with pseudocubic structures, have not been well discovered. These obscurities hinder the understanding of the structure-property relations and further optimizing properties for application.

In this paper, high resolution transmission electron microscopy (HRTEM) techniques with Fourier-filtered reconstruction were applied to directly reveal the nature of the AFE nanoscale domains in BA modified 0.75BNT-0.25BKT solid solutions with small hysteresis and remnant strain, where AFE phase could be stabilized at MPB. A continuous tilting model is proposed to describe the gradual changes of octahedral tilting among distinct tilting systems based on the features of HRTEM images. Based on this inherent relation between the microscopic structures and the macroscopic properties, the BNT-based ceramics and the analogues can be tailored by creating nanoscale antiferroelectric domains from the ferroelectric prototypes to acquire small hysteresis and remnant strain to make the high precision devices practically viable.

2. Experimental procedure

0.75BNT-0.25BKT and 0.96(0.75BNT-0.25BKT)-0.04BA samples were prepared via a standard solid-state reaction. Powders of Bi_2O_3 (≥99.0%), Na_2CO_3 (≥99.8%), K_2CO_3 (≥99.0%), TiO_2 (≥99.0%), Al_2O_3 (≥99.0%) were used as starting materials, which were weighed according to the stoichiometric formula and ball-milled in ethanol for 12 h. The dried slurry was calcined at 850 °C for 3 h and then ball-milled again for 16 h. After drying, the calcined powders, mixed with 5 wt% polyvinyl alcohol solution as binder, were uniaxially pressed into disks with diameter of 13 mm and thickness of 1.5 mm. A two-step sintering method was carried out. After heated up to 1140 °C at a rate of 5 °C/min, the disks were immediately cooled down to 1000 °C at a rate of 20 °C/min and soaked for 5 h. The pellets were embedded in an atmospheric powder of the same compositions in order to prevent the evaporation of volatile elements during sintering.

The crystal structures of the ceramics were characterized using an X-ray diffractometer (XRD, SmartLab-3kW, Rigaku Ltd, Tokyo, Japan) in the range of 10°–80° at a step of 0.02° with a collecting rate of 10°/min. The TEM characterization was conducted on a JEM-2100F UHR TEM (200 kV). The TEM samples were prepared by dispersing 0.96(0.75BNT-0.25BKT)-0.04BA powders on lacey-carbon coated support grids. The selected samples were annealed at 600 °C for 2 h after dimpling and prior to ion-thinning to remove remaining residual stresses. Fast Fourier Transformation (FFT) and Inverse Fast Fourier Transformation (IFFT) were conducted using Digital Micrograph software (Gatan, Pleasanton, CA, USA). Ferroelectric hysteresis loops and unipolar strain curves were measured by a ferroelectric test system (Precision Premier II, Radiant Technologies. Inc., Albuquerque, USA) in silicone oil with the aid of a Sawyer-Tower circuit and laser displacement sensor respectively.

3. Results and discussion

3.1. P-E, S-E characterization and X-ray diffraction (XRD) analysis

The relative density of 0.75BNT-0.25BKT and 0.96(0.75BNT-0.25BKT)-0.04BA samples is 95.5% and 97.1% respectively with a representative micrograph of polished and thermally etched cross-section shown in Fig. 2. Fig. 3(a), (b) shows the comparison of P-E loop and S-E curve between 0.96(0.75BNT-0.25BKT)-0.04BA and 0.75BNT-0.25BKT ceramics at R.T. respectively. It is noted in Fig. 3(a) that a much reduced remnant polarization and coercive field, *i. e.* $P_r = 3.8\ \mu C/cm^2$, $E_c = 6.8$ kV/cm, were derived in the P-E loop for 0.96(0.75BNT-0.25BKT)-0.04BA (for pure 0.75BNT-0.25BKT, $P_r = 23.5\ \mu C/cm^2$, $E_c = 24.3$ kV/cm). However, the maximum polarization induced by the applied field only decreased a little. On the other hand, the considerably pinched slim P-E loop of 0.96(0.75BNT-0.25BKT)-0.04BA suggests a much reduced hysteresis and indicates a relaxor behavior due to the existence of AFE nano-domains, which will be later discussed [22,25]. Meanwhile, the strain hysteresis ($\Delta S/S_{max}$, ΔS and S_{max} are measured at $E_{max}/2$ and E_{max} respectively) calculated from the S-E curve (see Fig. 3(b)) is 24% for 0.96(0.75BNT-0.25BKT)-0.04BA, which is 22.6% less than that of 31% derived for 0.75BNT-0.25BKT, whereas the normalized strain S_{max}/E_{max} remains closely the same with each other [12]. Generally, a large strain is usually accompanied with a rel-

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