



Electric field forced *c*-axis oriented growth of polar nanoregions and rapid switching of tetragonal domains in BNT-PT-PMN ternary system



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ARTICLE INFO

Article history:

Received 20 July 2015

Received in revised form 12 October 2015

Accepted 14 October 2015

Available online 27 October 2015

Keywords:

Relaxor ferroelectric

Ergodic and nonergodic phase

Strains

Domain switching

ABSTRACT

A normal to relaxor ferroelectric phase transition was observed to accompany a tetragonal to pseudocubic phase transformation in $(1-x)(0.84(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-0.16\text{PbTiO}_3)-x\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BNT-PT-*x*PMN) ceramics. The addition of PMN was found to gradually refine the domain morphology, such that the morphotropic phase boundary intrinsically evolved into coexisting tetragonal ferroelectric microdomains and pseudocubic nonergodic polar nanoregions (PNRs). The mechanism of generating remarkably enhanced electrostrains was ascribed to the oriented growth of PNRs and subsequently rapid switching of tetragonal domains along the electric field direction by means of in situ synchrotron X-ray diffraction, through which the symmetry of PNRs was found to be intrinsically tetragonal. The key reason for an additional polarization current peak was attributed to a significant reduction of the unit cell anisotropy at a critical field at which a simultaneous shrinkage of the lattice constant c_t led to a relatively low electrostrain compared to those previously reported in other bismuth-containing relaxor ferroelectrics.

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1. Introduction

Giant electrostrains of up to $\sim 0.4\%$ have attracted lots of attention in recent years in some perovskite-structured relaxor ferroelectric ceramics such as $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BNT) and $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BMT) based solid solutions [1–7]. The compositional modification could induce an evolution of dielectric relaxation behavior, during which a normal ferroelectric to relaxor phase transition temperature (T_{fr}) or an ergodicity to nonergodicity freezing temperature (T_f) was gradually shifted close to room temperature (RT). Because of the appearance of ergodic relaxor phases, the response of ferroelectric ceramics to external electric fields was gradually dominated by a reversible transition process from ergodic to long-range ferroelectric ordering, leading to a significant enhancement of electrostrains [2,6,8]. According to the literature survey, contributions to large strains seemed to be concerned with the electric field induced phase transition, domain switching, electrostrictive effects and converse piezoelectric effects. However, the features of strains in response to electric fields are extremely different with varying compositions, even in the same matrix compositions but modified by different additives, involving the response speed of strains to electric fields, the hysteresis degree

of strains during loading and unloading [9,10], the threshold fields for generating large strains and the thermal stability of strains in addition to the strain magnitude [10,11]. Although large-strain-generating compositions were frequently reported, yet these issues seemed to need more cares. Particularly, how to optimize each contribution to strains would be a more urgent and fundamental issue. Further investigation of the physical mechanism for generating large strains would be of much interest as well because a couple of questions are still not well understood.

BNT and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) are typical relaxor ferroelectrics in lead-free and lead-containing perovskite family, respectively. Both of them can form a complete solid solution with PbTiO_3 (PT) and simultaneously exhibit an obvious change in structural symmetry, dielectric ferroelectric and electromechanical strain behaviors. As shown in Fig. 1, a morphotropic phase boundary (MPB) between rhombohedral (*R*) and tetragonal (*T*) phases was observed as 10–15 mol% PT was added into BNT [12] or as ~ 32 mol% PT substituted for PMN [13]. According to the phase diagram of BNT-PT systems [12], a typical ferroelectric to antiferroelectric phase (called as nonpolar phases later) transition anomaly disappeared as PT content exceeded 15 mol%. The temperature at this dielectric anomaly was usually called as the depolarization temperature (T_d) of BNT-based piezoelectric ceramics. It intrinsically corresponded to T_{fr} at which an electric field induced ferroelectric to relaxor phase transition occurred, and mostly tended to decrease as donor dopants or other perovskite phases were added [1,7,14].

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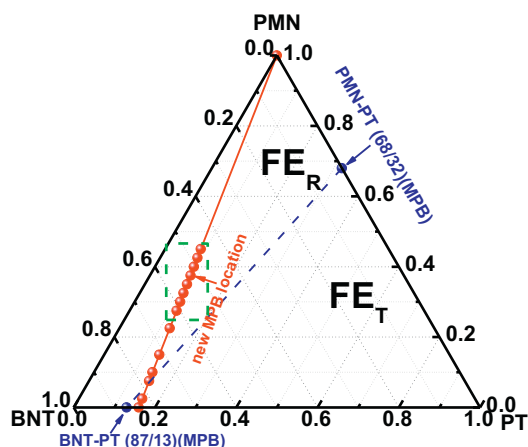


Fig. 1. Schematic phase diagram of BNT-PT-PMN ternary system.

However, giant strains reported in BNT-based binary or ternary systems were generally not observed in the proximity of T_{fr} but close to the T_f although this issue was mostly vague in the literatures. As reported, there was a much smaller difference between T_f and T_{fr} for BNT-based relaxor ferroelectrics than for BMT-based systems. This kind of difference was believed to probably contribute to different thermal stability of large strains [10]. Moreover, the achievement of large electrostrains usually requires a relatively high driving electric field of up to 6–7 kV/mm in most of BNT based solid solutions probably because of their specific domain structures [5–7,9,15,16]. By comparison, most of R PMN-PT solid solutions have a low coercive field (E_c) and exhibit a typical dielectric relaxor behavior. As a result, the substitution of PMN for BNT can be expected to modify the domain morphology and further to optimize the dielectric and electromechanical strain behavior.

In this work, a specially-designed new composition system of $(1-x)(0.84\text{BNT}-0.16\text{PT})-x\text{PMN}$ (abbreviated as BNT-PT- $x\text{PMN}$) was constructed by mixing two systems PMN and BNT-PT together in terms of their respective phase transition behavior and possibly different domain structures. The aim to do so is to see how the phase or domain structures of this system vary with changing the PMN content and the electric field magnitude, and how the ergodic phases or nonergodic phases respond to the variation of external electric fields, and particularly to further make clear the mechanism of generating large strains by means of temperature or composition dependent synchrotron X-ray diffraction (XRD), dielectric properties and polarization (strain) versus electric field (P(S)–E) curves.

2. Experimental

The BNT-PT- $x\text{PMN}$ ($x=0-0.45$) composition points were drawn as red dots in Fig. 1, being distributed on both sides of a theoretically predicted MPB line of BNT-PT and PMN-PT binary systems by fixing a constant ratio of BNT to PT. The ceramics with different x were synthesized by a conventional solid-state reaction method using high-purity oxides: Bi_2O_3 (99.0%), Na_2CO_3 (99.8%), PbO (99.0%), $(\text{MgCO}_3)_4\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ (99.0%), Nb_2O_5 (99.5%) and TiO_2 (99.0%) as raw materials. The powders were weighed and ball-milled with ethanol and zirconia media for 4 h, and calcined twice after drying in a closed alumina crucible at 850 °C for 2 h. After calcination, the powder mixture was ball-milled again for 6 h with 0.5 wt% PVB as a binder. The granulated powder was uniaxially pressed into discs with a diameter of 10 mm and a thickness of 1 mm. The compacted discs were sintered in the temperature range of 1100–1200 °C for 2 h. To minimize the vaporization of Pb, Na and Bi, sample discs were buried in the sacrificial powder of the same composition. For the electrical measurements, silver paste was painted on major

sides of the discs and fired at 550 °C for 30 min as electrodes. The specimens were polarized in a silicone oil bath at RT under a dc field of 3–4 kV/mm for 15 min.

The relative densities of sintered samples were evaluated by the Archimedes method. The phase structures were analyzed at RT using a conventional powder X-ray diffractometer (XRD, D/Mzx-rB; Rigaku, Tokyo, Japan) with $\text{CuK}\alpha_1$ radiation. The grain morphology was observed by using a field-emission scanning electron microscope (FE-SEM, SU8020, JEOL, Tokyo, Japan). Before the SEM observation, the samples were polished and thermally etched at ~950 °C for 30 min. The dielectric properties were measured using an LCR meter (Agilent E4980A, Santa Clara, CA) in a temperature range of 20–400 °C and at a frequency range of 0.1 kHz–1 MHz. The quasi-static piezoelectric strain constant d_{33} of poled samples was measured by a Berlincourt-meter (YE2703A, sinocera, Yangzhou, China). The planar electromechanical coupling factor k_p was determined by a resonance-antiresonance method with an impedance analyzer (PV70A; Beijing Band ERA Co. Ltd., Beijing, China). A ferroelectric testing system (Precision multiferroelectric, Radiant Technologies Inc., Albuquerque, NM) was used to measure the polarization-electric field (P–E) hysteresis loops and electric field-induced strain (S–E) curves. *In-situ* high-resolution synchrotron XRD measurement was carried out under various electric fields or at different temperatures at Shanghai Synchrotron Radiation Facility (SSRF) using beam line 14B1 ($\lambda = 1.2378 \text{ \AA}$).

3. Results

3.1. Phase structural transition, microstructure and normal ferroelectric to relaxor phase transition

Fig. 2 demonstrates RT XRD patterns of BNT-PT- $x\text{PMN}$ ceramics. A single perovskite structure could be clearly identified for all compositions according to their typical diffraction patterns. Moreover, a typical T symmetry could be identified as $x < 0.325$, as evidenced by both the peak splitting of the (0 0 2) and (2 0 0) diffraction lines and the single (1 1 1) diffraction peak. When $x \geq 0.4$, a sharp and narrow peak profile of both (2 0 0) and (1 1 1) diffraction lines suggested a pseudocubic (PC) structure. Slowly scanned (2 0 0) diffraction lines in a 2θ range of 45–46.5° were fitted by using a Gaussian peak shape function for samples with $x = 0.275-0.425$, as shown in Fig. 2(c1)–(c8). The structural symmetry of the samples can be well established from the peak splitting and the relative intensity of these reflection lines. The $(002)_T/(200)_T$ and $(200)_{PC}$ peaks could be simultaneously detected in the $x = 0.325-0.385$ samples, indicating that there existed an MPB between T and PC phases.

The microstructure of the selected samples is shown in Fig. 3. It is evident that the introduction of PMN had an obvious influence on the evolution of the microstructure. Pure BNT-PT ($x=0$) showed relatively large grains and a relatively low density (~95%). With the introduction of PMN, the grain size decreased and the sample density slightly increased (>97% as $x \geq 0.3$). The average grain size, as estimated with a linear interception method, increased from ~6 μm for the $x=0$ sample to ~3–4 μm for the $x=0.3$, $x=0.375$ and $x=0.425$ samples. It is worthy of note that the grain morphology significantly changed from polyhedra to irregular shapes with adding PMN into BNT-PT. Two kinds of grains with different contrasts were observed in samples with $x > 0$ probably as a result of different crystalline surfaces they have. There were no traces of secondary phases as identified by the XRD results in Fig. 2.

Fig. 4(a)–(g) shows the temperature and frequency dependence of dielectric permittivity (ϵ_r) of BNT-PT- $x\text{PMN}$ ceramics before and after poling. It can be seen that a spontaneous relaxor to ferroelectric transformation occurred at temperatures T_{fr} in virgin samples with $x \leq 0.3$ in terms of clearly observed frequency-independent

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