Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original Article

Ferroelectric P4mm to relaxor P4bm transition and temperature-insensitive large strains in $Bi(Mg_{0.5}Ti_{0.5})O_3$-modified tetragonal $0.875Bi_{0.5}Na_{0.5}TiO_3$-$0.125BaTiO_3$ lead-free ferroelectric ceramics

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ARTICLE INFO

Keywords:
$Bi_{0.5}Na_{0.5}TiO_3$
Tetragonal structure
Ferroelectrics
$Bi(Mg_{0.5}Ti_{0.5})O_3$
Field-induced strain

ABSTRACT

Tetragonal phase $(1–x)(0.875Bi_{0.5}Na_{0.5}TiO_3–0.125BaTiO_3)–xBi(Mg_{0.5}Ti_{0.5})O_3$ lead-free ferroelectrics were designed and fabricated by a conventional solid state route. All the specimens exhibit a tetragonal perovskite structure, and undergo a phase evolution from ferroelectric P4mm to antiferroelectric relaxor P4bm as the BMT addition increases. The critical composition $x = 0.04$ makes a bridge between the both tetragonal phases, and gives a large field-induced strain of 0.30% and an adequately-large electrostrictive coefficient Q_{33} of 0.0254 m^4/C^2. To be highlighted, the field-induce strain of the composition x = 0.04 shows an almost constant value over the temperature range of 18–100 °C, illustrating a temperature-insensitive behavior, which could be attributed to the widened gap between $T_{R–E}$ and $T_{F–R}$. The temperature-insensitive large strain of the tetragonal BNT–BT–BMT composition give a promising potential for application in precision position actuators.

1. Introduction

Lots of attention have been given to the field-induced strain behavior of a material for actuator applications. A large hysteresis-free electrostrictive strain up to ~0.1% has been reported in some lead-based relaxor ferroelectrics with a large Q_{33} value of ~0.02 m^4/C^2, among which $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is the typical one [1–3]. Because the toxicity of the lead would cause the environment pollution, great efforts have been devoted to probe the lead-free ferroelectrics with large strain, small hysteresis and high temperature stability.

$Bi_{0.5}Na_{0.5}TiO_3$–$BaTiO_3$ (BNT–BT) binary solid solution is a lead-free relaxor ferroelectric, and attracts much interest as a candidate alternative for PZT. Chiang, et al reported that rhombohedral-phase $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ crystals exhibit up to 0.25% strain with low hysteresis along the cubic < 001 > direction, which raised a boom about the electrostrictive strain behaviors of BNT–BT systems [4]. Zhang et al. observed a giant electrostrictive strain of 0.45% and a electrostrictive coefficient of (0.021–0.027) m^4/C^2 in the $0.94BNT–0.06BaTiO_3–0.02\,K_{0.5}Na_{0.5}NbO_3$ [5]. Researchers attributed the large field-induced strain emerging in BNT–based systems to the existence of non-ergodic polar nanoregions (PNRs) with R3c symmetry and ergodic PNRs with P4bm symmetry [6].

Most of researches on electrostrictive behaviors of BNT–BT were focused on compositions around its morphotropic phase boundary (MPB) compositions [7,8]. Except of the effect on the phase evolution and electric properties, the introduction of BT could significantly improve the sintering ability of BNT [9], which is important for industrial application. When BT content exceeds over 10 mol.%, the solid solution possesses tetragonal structure with P4mm space group at room temperature, and transforms into antiferroelectric relaxor and antiferroelectric with P4bm space group at temperatures $T_{F–R}$ and $T_{R–E}$ in sequence upon heating [10,11]. Especially, it is reported that tetragonal phase BNT–BT crystal exhibits free strains as high as 0.85% but with a great hysteresis characteristic of domain back-switching [4]. Hence, the modulation on tetragonal BNT–BT compositions with small-hysteresis field-induced strain behavior was of significance in science and application. Unfortunately, there was rare research reported on this issue until now.

$Bi(Mg_{0.5}Ti_{0.5})O_3$ (BMT) has an orthorhombic symmetry with antiferroelectric feature, which is analogous to $PbZrO_3$ [12,13]. Due to its antiferroelectric characteristic, BMT can effectively disrupt the long-range ferroelectric order of BNT–BT compositions around MPB, and transforms the nonergodic PNRs into ergodic ones [14,15]. Besides, incorporating BMT into MPB composition 0.92BNT–0.08BT ceramics expands the temperature range between the $T_{F–R}$ and the maximum dielectric temperature T_m [16], which may be beneficial to the temperature stability of field-induced strains.

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https://doi.org/10.1016/j.jeurceramsoc.2017.12.022
Received 18 November 2017; Received in revised form 14 December 2017; Accepted 15 December 2017

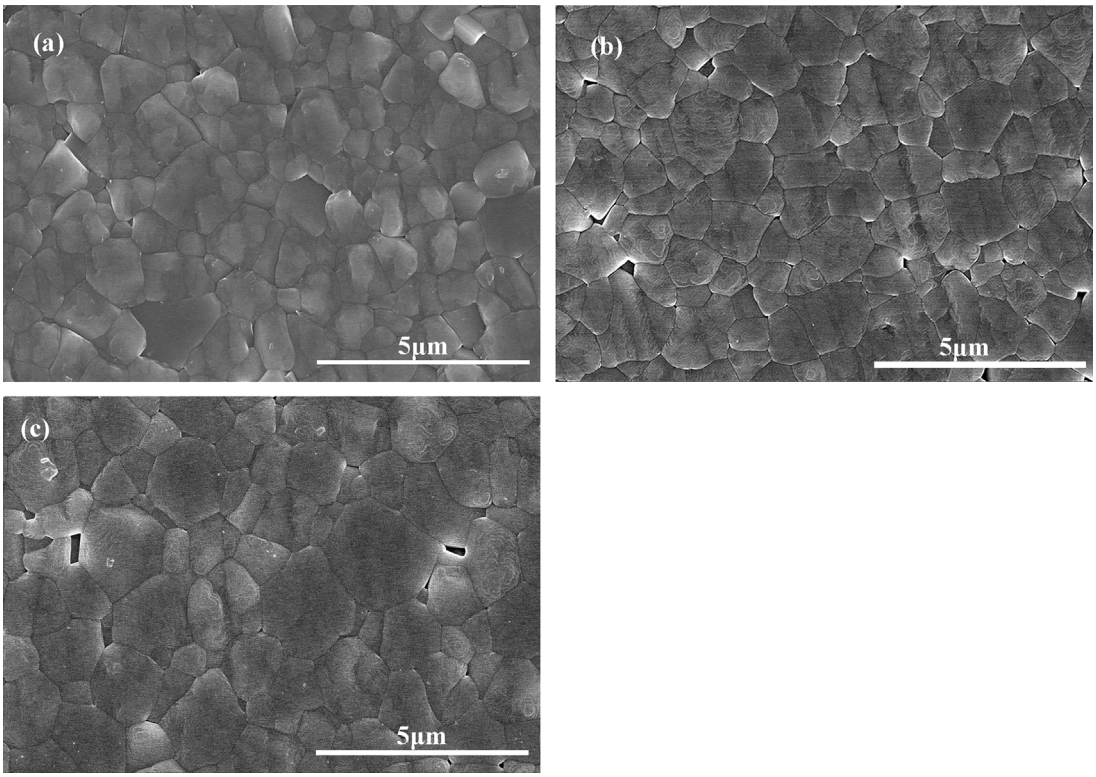

Fig. 1. Typical SEM micrographs of BNBMT100x ceramics: (a) x = 0, (b) x = 0.04 and (c) x = 0.08.

In this study, a binary solid solution $0.875Bi_{0.5}Na_{0.5}TiO_3$–$0.125BaTiO_3$ with P4mm structure was selected as matrix, and BMT was introduced to modulate the phase structure and field-induced strain behavior. The results showed that the composition $x = 0.04$ gives a large field-induced strain of 0.30% and an adequately-large electrostrictive coefficient Q_{33} of 0.0254 m^4/C^2. To be highlighted, the field-induce strain of the composition $x = 0.04$ presents a temperature-insensitive behavior. The correlation of the field-induced strain with the phase structure were discussed in details in this paper.

2. Experimental procedure

The ceramic specimens with composition (1–x)(0.875BNT–0.125BT)–xBMT ($0 \le x \le 0.08$) were prepared by a conventional solid-state reaction method. The high-purity raw materials, including Na_2CO_3 (≥99.0%), $BaCO_3$ (≥99.0%), Bi_2O_3 (≥99.0%), $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ (≥99.0%) and TiO_2 (≥99.0%), were weighed according to the chemical formula. The mixed powders were ball-milled in nylon jugs using partially-stabilized zirconia as media in alcohol for 12 h. After drying, the powder mixtures were calcined at 850 °C for 4 h with an increasing ramp rate of 3 °C min^{-1} and then milled again for 12 h. The calcined powders were uniaxially pressed into pellets with 11.5 mm in diameter under 400 MPa. Sintering was carried out at 1150 °C for 2 h with a heating rate of 3 °C min^{-1} in covered alumina crucibles. To minimize the volatilization of Bi and Na during the sintering, the green compacts were fully embedded in the BNT powders. For electrical measurements, the sintered disks were ground and polished to a thickness of about 0.6 mm, and electroded with silver pastes on two sides. To realize the Ohmic contact between silver pastes and ceramics, the electroded disks were fired at 560 °C for 1 h. According to the different content of BMT, the specimens are labelled as BNBMT100x ($0 \le x \le 0.08$), respectively.

The relative density was evaluated by the Archimedes method. The crystal structure was characterized by X-ray diffraction (XRD, Bruker, D8 Advance, Karlsruhe, Germany) using Cu Kα radiation source ($\lambda = 1.54178$ Å) in the 2θ range of 20–70°. The micromorphology was detected on the cross-sections of the specimens by a field emission scanning electron microscope (SEM, FEI Quanta 450, US). Before the SEM observation, the specimens were polished and thermally etched at 1000 °C for 40 min. Domain images and selected-area electron diffraction (SAED) pattern were carried out using a transmission electron microscopy (TEM, JEM-2000F, JEOL, Tokyo, Japan) at an accelerating voltage of 200 kV. Specimens for TEM observation were prepared by mechanical polishing, followed by a dimple grinder thinning process, and finally by argon ion thinning. To explore the depolarization behavior, the specimens were poled at 70 °C for 30 min in silicone oil and cooled to room temperature under a dc field of 4–5 kV/mm. The temperature-dependent dielectric responses were measured by precision inductance-capacitance-resistance meter (E4980A, Agilent, USA) in a frequency range of 0.1–1000 kHz for unpoled and poled specimens. The electric field induced polarization (P–E) and strain (S–E) measurements were carried out at 1 Hz in bipolar and unipolar modes using a ferroelectric tester (Premier II, Radiant Technologies, USA) equipped with a photonic sensor (2100, MTI, USA) and a temperature chamber.

3. Results and discussion

Fig. 1 shows the typical SEM micrographs of specimens BNBMT0, BNBMT4 and BNBMT8, showing their dense and homogenous microstructures. Other specimens give similar micro-morphologies. All specimens have relatively high densities (ρ ≥ 97.5% of theoretical density), implying that these tetragonal BNT–based compositions possess an excellent sintering ability. Good densification behavior would provide an additional advantage as compared to other alkaline–containing lead-free compositions. Besides, the average grain size for all specimens keeps at about 1.1 μm, showing a weak composition dependence. The weak composition dependence of the grain size in this study will not make an obvious effect on the corresponding dielectric and ferroelectric properties.

Fig. 2a shows the XRD patterns of unpoled specimens BNBMT100x.