Journal of the European Ceramic Society xxx (2015) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Electric field-induced ultrahigh strain and large piezoelectric effect in $Bi_{1/2}Na_{1/2}TiO_3$-based lead-free piezoceramics

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ARTICLE INFO

Article history:
Received 16 May 2015
Received in revised form
27 September 2015
Accepted 30 September 2015
Available online xxx

Keywords:
Lead-free piezoelectrics
Electrical properties
Microstructure

ABSTRACT

Lead-free piezoelectric ceramics, $(Bi_{1/2}Na_{1/2})_{0.935}Ba_{0.065}Ti_{1-x}(Fe_{1/2}Nb_{1/2})_xO_3$, were prepared by the conventional solid-state reaction method. The room temperature ferroelectric *P*–*E* loops illustrated the transition of ferroelectric domains. The composition and electric field dependent strain behavior of this system were investigated. A highest unipolar strain of ~0.422% and corresponding normalized strain, d^*_{33} $(=S_{max}/E_{max})$ of 844 pm/V under an applied field of 50 kV/cm were observed at $x = 0.020$, due to the destabilization of the ferroelectric order. It is observed that the unipolar strain of BNBT-0.02FN is temperature insensitive, and the d^*_{33} maintains a high value of ~600 pm/V at 90 °C. The observed large strain behavior can be attributed to the transformation from the ferroelectric phase at zero electric field into a relaxor ferroelectric phase under an applied electric field. The large strain response with good temperature stability would be quite suitable for environmental-friendly solid-state actuator applications.

1. Introduction

Lead-based ferroelectric materials such as lead zirconate titanate (PZT) have been widely utilized for piezoelectric or dielectric components and other electromechanical devices [1–3]. Nevertheless, the large amounts of hazardous lead in these materials have spurred enormous efforts to search for new alternate lead-free materials [4,5].

Since the bismuth-based perovskite ceramics, $Bi_{1/2}Na_{1/2}TiO_3$ (BNT) was found to possess promising piezoelectric and ferroelectric properties, various promising BNT-based solid solutions have been proposed: examples including the binary $Bi_{1/2}Na_{1/2}TiO_3$-$BaTiO_3$ (BNT-BT) [6], $Bi_{1/2}Na_{1/2}TiO_3$-$K_{0.5}Na_{0.5}NbO_3$ (BNT-KNN) [7], the ternary $Bi_{1/2}Na_{1/2}TiO_3$-$Bi_{1/2}K_{1/2}TiO_3$-$BaTiO_3$ (BNT-BKT-BT) [8], $Bi_{1/2}Na_{1/2}TiO_3$-$BaTiO_3$-$(K_{0.5}Na_{0.5})NbO_3$ (BNT-BT-KNN) [9] and $Bi_{1/2}Na_{1/2}TiO_3$-$BaTiO_3$-$BiAlO_3$ (BNT-BT-BA) [10]. Although extensive efforts have been done in lead-free alternatives, the lead-free counterparts still cannot compete with the lead-based ones in terms of the global electrical properties [11]. There is an urgent demand to develop new piezoelectric lead-free materials with desired properties. Zhang et al. [9] reported a $Bi_{1/2}Na_{1/2}TiO_3$-$BaTiO_3$-$K_{0.5}Na_{0.5}NbO_3$ (BNT-BT-KNN) ceramics having a giant strain response of 0.45% at 80 kV/cm driving field equivalently 560 pm/V. Pham et al. [12] studied a Nb-doped $Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}TiO_3$ (BNKTN) ceramics near the morphotropic phase boundary (MPB) and reported a large unipolar strain of 0.448% at 70 kV/cm. The subsequent researches on the mechanism of the giant strain in BNT-based systems, as well as new BNT-based compositions further accelerated studies on BNT-based ceramics. However, the practical application of BNT-based ceramics is hindered due to the fact that large strain response needs a high electric field to trigger.

In previous work, most of the studies were focused on the A-site substitution or B-site single-ion replacement, while little attention has been paid to the effect of B-site complex ions substitution. Jin et al. [13] introduced $(Al_{0.5}Nb_{0.5})^{4+}$ into the B-site of BNT and found a large strain S_{max}/E_{max} of 575 pm/V and high piezoelectric constant d_{33} of 210 pC/N. Li et al. [14] prepared Fe-modified $0.875Bi_{0.5}Na_{0.5}TiO_3$-$0.06Bi_{0.5}Li_{0.5}TiO_3$-$0.065BaTiO_3$-0.005Mn ceramic with a large unipolar strain of 0.4% under 40 kV/cm. In light of these observations, a new ternary solid solution was designed and characterized through introducing B-site complex-ion $(Fe_{1/2}Nb_{1/2})^{4+}$ into the MPB solid solution $(Bi_{1/2}Na_{1/2})_{0.935}Ba_{0.065}TiO_3$ (BNBT). It is expected that $(Fe_{1/2}Nb_{1/2})^{4+}$ modification in BNBT ceramics can enhance the electromechanical properties. In this work, we fabricated BNBT-based

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http://dx.doi.org/10.1016/j.jeurceramsoc.2015.09.043
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ceramics with $(\mathrm{Fe}_{1/2}\mathrm{Nb}_{1/2})^{4+}$ addition using a conventional solid-state reaction method and systematically studied the influence of compositional modification on the crystal structure, ferroelectric and piezoelectric properties and field-induced strain behaviors.

2. Experimental procedure

The $(\mathrm{Bi}_{1/2}\mathrm{Na}_{1/2})_{0.935}\mathrm{Ba}_{0.065}\mathrm{Ti}_{1-x}(\mathrm{Fe}_{1/2}\mathrm{Nb}_{1/2})x\mathrm{O}3$ (BNBT-x FN)($x = 0.000$, 0.005, 0.010, 0.015, 0.020, 0.030) ceramics were prepared by the conventional solid-state reaction method using reagent-grade metal oxides or carbonate powders of $\mathrm{Bi_2O_3}$ (99%), $\mathrm{TiO_2}$ (99.5%), $\mathrm{Na_2CO_3}$ (99.8%), $\mathrm{BaCO_3}$ (99%), $\mathrm{Fe_2O_3}$ (99.49%) and $\mathrm{Nb_2O_5}$ (99.96%) as starting materials. All raw materials were purchased from Sinopharm Chemical Reagent Co., Ltd. The raw materials were weighed at stoichiometric proportion and then mixed homogenised by planetary ball milling in a polyethylene with stabilized zirconia balls for 12 h, using anhydrous ethanol as liquid medium. After drying, the mixed powders were calcined at 850 °C for 2 h and then milled again for 6 h. Then the powders were mixed with an appropriate amount of polyvinyl butyral (PVB) binder, and pressed into pallets having a diameter of 12 mm and a thickness of 1.0 mm under the pressure of about 200 MPa. After burning off PVB, the ceramics were sintered in an alumina crucible at 1100–1180 °C for 2 h in air. To avoid the loss of bismuth and sodium oxides during sintering, the pellets were embedded into preprepared powder with the same composition.

The crystal structure of the ceramics was determined by X-ray diffraction (XRD) using a Cu Kα radiation ($\lambda = 1.54178$ Å) (D8 Advance, Bruker Inc., Germany). The microstructure of the ceramics was observed by scanning electron microscopy (SEM) (JSM-6380, Japan) on polished and thermally etched cross-sections as well as on fracture surfaces. The density of the ceramics was analyzed using electronic densimeter (MatsuHaku, QL-300C, Taiwan). Silver electrodes were coated on the top and bottom surfaces of the ceramics for the subsequent electrical measurements. The ferroelectric hysteresis loops, bipolar and unipolar strain curves were measured, at 10 Hz in silicon oil with the aid of a Sawyer–Tower circuit to apply an electric field with sinusoidal waveform, with ferroelectric analyzer (TF2000 analyzer, Aixacct, Germany) along with the laser interferometer (SIOS Meßtechnik GmbH, Germany) under an electric field of 50 kV/cm. The samples were poled in silicon oil at room temperature under 50–70 kV/cm for 20 min, and piezoelectric measurements were then carried out using a quasi-static d_{33}-meter YE2730 (SINOCERA, China). The temperature dependence of dielectric properties was measured by a broadband dielectric spectrometer (Novocontrol Germany) at temperatures ranging from room temperature to 500 °C with a heating rate of 3 °C/min.

3. Results

The XRD patterns with a 2θ ranging from 20° to 70° for BNBT-x FN samples are demonstrated in Fig. 1(a). All ceramics exhibited a pure perovskite structure and no second phases or impurities can be observed. This implied that the doped $(\mathrm{Fe}_{1/2}\mathrm{Nb}_{1/2})^{4+}$ have diffused into the crystal lattice and formed a stable solid solution with BNBT. Fig. 1(b) shows the expanded XRD patterns in the 2θ range of 45–48°. The positions of (2 0 2) peak shift slightly to the lower angle with the increase of $(\mathrm{Fe}_{1/2}\mathrm{Nb}_{1/2})^{4+}$ content, suggesting the expansion of lattice constant [15]. This was attributed to the differences in ionic radii of Fe^{3+} (0.645 Å, CN = 6), Nb^{5+} (0.64 Å, CN = 6) and Ti^{4+} (0.605 Å, CN = 6) [16], The results indicated that the $(\mathrm{Fe}_{1/2}\mathrm{Nb}_{1/2})^{4+}$ is entered into the B-site of BNT to substitute Ti^{4+} for the radius matching, while the differences in ionic radii resulting in the lattice deformation at the same time. The similar observations were also reported in previous studies [15,17,18].

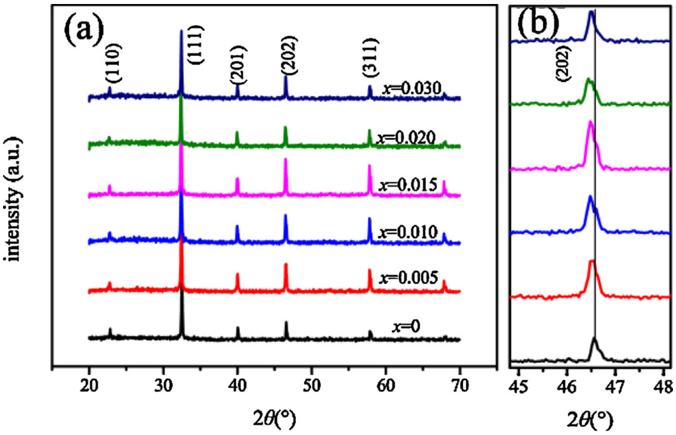

Fig. 1. XRD patterns of BNBT-x FN ceramics in the 2θ range: (a) 20–70°and (b) 45–48°.

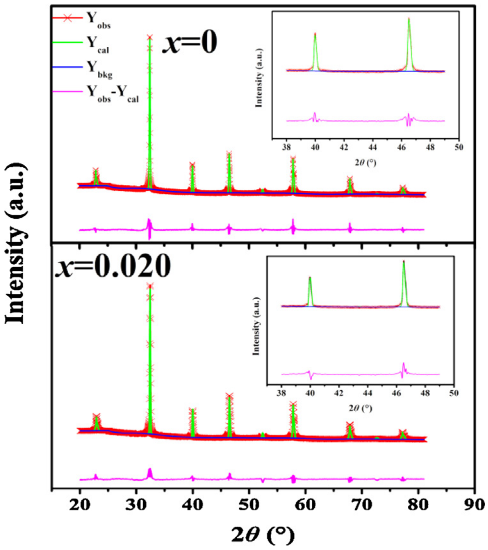

Fig. 2. Rietveld refinement for the samples of $x = 0$ and $x = 0.020$ at room temperature, the inset enlarges the fit in 2θ range from 38° to 50°.

Table 1
Structure parameters of $x = 0$ and $x = 0.020$ obtained from rietveld refinement.

Parameters		$x = 0$	$x = 0.020$
Lattice parameters (Å)	$a = b$	5.517339	5.519778
	c	3.905571	3.907389
Angle (°)	$\alpha = \beta = \gamma$	90	90
Space group		P4 bm	P4 bm
Rwp (%)		8.68	8.47
Rp (%)		4.97	4.83
χ^2		3.12	2.68

In order to determine the crystal structures of BNBT-x FN ceramics more accurately, the XRD Rietveld refinements for BNBT and BNBT-0.020FN were carried out with P4bm space group at room temperature by using the GSAS-EXPGUI program [19]. The XRD data were collected in a 2θ range of 20–80° with a step size of 0.02°. The final refined profiles for BNBT and BNBT-0.020FN are presented in Fig. 2. Inspection from Fig. 2, the refined profile fits well with the experimental data. The final factors, Rwp, Rp, chi-squared values (χ^2) are 8.68%, 4.97%, 3.12 for BNBT, and 8.47%, 4.83%, 2.68 for BNBT-0.020FN, respectively. The Rietveld refined parameters are listed in Table 1. The observed lattice parameters are in close agreement to the already published reports on BNT [20,21].

Please cite this article in press as: R. Cheng, et al., Electric field-induced ultrahigh strain and large piezoelectric effect in $\mathrm{Bi}_{1/2}\mathrm{Na}_{1/2}\mathrm{TiO}_3$-based lead-free piezoceramics, *J Eur Ceram Soc* (2015), http://dx.doi.org/10.1016/j.jeurceramsoc.2015.09.043