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Influence of isovalent and aliovalent substitutions at Ti site on bismuth sodium titanate-based compositions on piezoelectric properties

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Abstract

The effect of isovalent and aliovalent substitutions in $Bi_{0.5}Na_{0.485}La_{0.005}TiO_3$ (BNLT) compounds were studied within the additive ranges of 0–2.5 at%. The Zr^{4+}, Nb^{5+} and Fe^{3+} ions were selected as the substituents. The modified BNLT compounds were prepared by conventionally mixed-oxide method. The calcination and sintering were performed at the temperatures of 750–850 °C and 1050–1150 °C, respectively. An increase in the substituents contents affected the physical and piezoelectric properties. The BNLT compositions with the addition of 1 at% Zr^{4+}, Nb^{5+} and Fe^{3+} ions exhibited high relative permittivities (ε_r) at 730, 735 and 660, respectively. The modified-BNLT with an addition of 1.0 at% Fe provided a piezoelectric coefficient (d_{33}) of 155 pC/N, Curie temperature (T_c) of 320 °C and electromechanical coupling factors in planar (k_p) and thickness (k_t) modes of 15 and 45%, respectively.

Keywords: C. Ferroelectric properties; C. Piezoelectric properties; D. Lead-free piezoelectrics; D. BNT

1. Introduction

The bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$: BNT) is one of excellent candidates for lead free piezoelectric ceramics with a high Curie temperature (T_c ~320 °C) [1,2]. BNT has two phase transformations which are cubic to tetragonal (515–525 °C) and tetragonal to rhombohedral phase (225–265 °C). Previous work [3] stated that the 0.5 at% La-doped BNT not only exhibited a decrease in high dielectric loss, but also presented a high piezoelectric coefficient (d_{33}) of 90–100 pC/N, superior to those obtained from modified $PbTiO_3$ (d_{33} of 56 pC/N). To further improve the piezoelectric properties, the modified BNT composition with 0.5 at% La ($Bi_{0.5}Na_{0.485}La_{0.005}TiO_3$: BNLT) was recently substituted by the Zr^{4+}, Nb^{5+} and Fe^{3+} ions at Ti-site in the range of 0.5–2.5 at%. The aim of this work is to present the effect of dopants on the physical, ferroelectric, dielectric and piezoelectric properties of modified BNLT system.

2. Experimental procedure

The modified BNLT powders were prepared by conventionally mixed-oxide method. The starting chemical substances were Bi_2O_3 (≥98%, Fluka), Na_2CO_3 (≥99.5%, Fluka), La_2O_3 (≥99.98%, Fluka), ZrO_2 (≥99%, Aldrish), Nb_2O_5 (>99.9%, Sigma–Aldrich), Fe_2O_3 (>99%, Aldrich) and TiO_2 (Alfa Aesar). Powders were weighed and ball-milled for 24 h in polypropylene bottles, utilized acetone as a mixture medium. All compositions were calcined at 800 °C for 2 h. The calcined ones were again ball-milled in the mixture medium absolute ethanol for 24 h. Disc-shaped specimens with 20 mm in diameter and 1.5 mm in thickness were fabricated using a hydraulic pressing, then cold isostatic pressed (CIP) at 2.5×10^8 N/m^2. Pellets of Zr- and Fe-BNLT compositions

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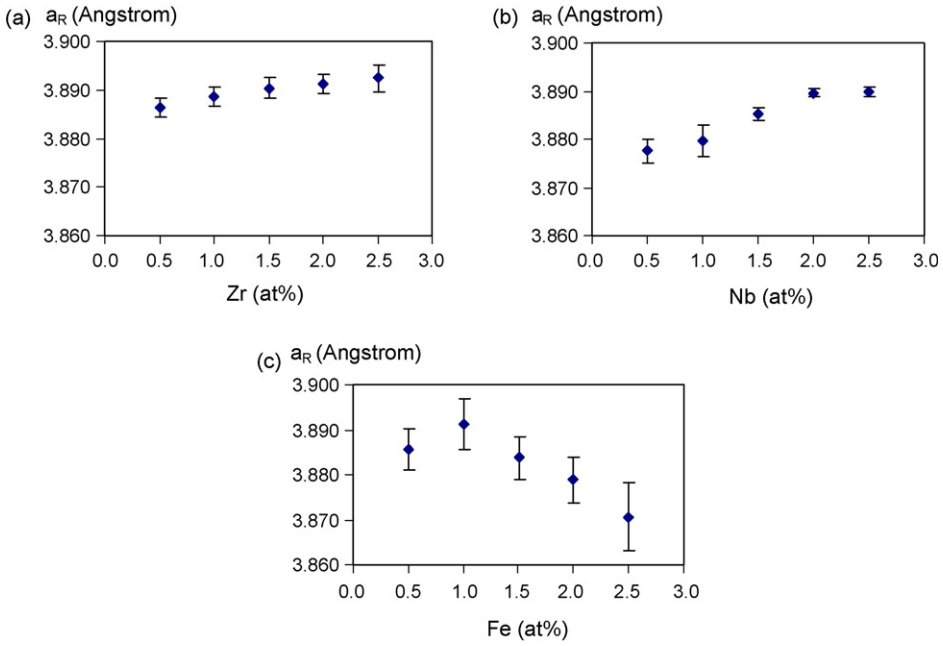

Fig. 1. Lattice distances of modified BNLT; (a) Zn-modified BNLT (Zr-BNLT), (b) Nb-modified BNLT (Nb-BNLT) and (c) Fe-modified BNLT (Fe-BNLT).

were sintered in air atmosphere at 1100 °C, while those of Nb-BNLT were sintered at 1050 °C with soaking time at 2 h.

Phase development and lattice refinement of all compositions were studied by XRD analytical technique (XRD: JEOL, JDX-3530). Silicon powders (NIST SRM 640C) were added and utilized as an internal standard. The relative permittivity (K) was measured at various frequencies using the 4194A Impedance Gain/Phase analyzer (Hewlett Packard). The temperature dependence of relative permittivity of BNLT-based specimens was investigated using broad band system (BDS systems in combination with the QUATRO Cryosystem). The volume resistivity of BNLT-based specimens was determined using a resisitivity chamber (Keithley: 6150). Ferroelectric properties were measured using RT66A standardized ferroelectric test system (Radiant Technology). The optimum poling condition was achieved at 45 kV/cm 5 min at room temperature. Piezoelectric charge coefficient (d_{33}) was measured using a piezo d_{33}-m (Piezometer system PM25). Thickness (k_t) and planar coupling coefficient (k_p) were determined using the resonance method [9].

3. Results and discussion

3.1. Lattice parameter of modified BNLT

XRD results confirmed the existing of a single perovskite structure in all calcined powders. The lattice distances (a_R) of the Zr- and Nb-BNLT compounds increased with an increase in the addition of substituents and tended to be constant with the Zr^{4+} and Nb^{5+} contents at 1 and 2 at%, respectively (Fig. 1(a) and (b)). Increasing in lattice distance might result from the radii difference of the subsituents. The Zr^{4+} and Nb^{5+} ions had larger ionic radii (0.72 Å for $Zr^{4+}$and 0.64 Å for Nb^{5+}) than that of Ti^{4+} (0.61 Å) causing the distortion in the lattice parameters

Table 1
The physical, dielectric and piezoelectric properties of Fe and Nb modified BNLT system

x	Density (% of theoretical density)	Volume resistivity (Ω cm)	T_c (°C)	K (1 kHz) after poling	d_{33} (pC/N)	k_t (%)	k_p (%)	Grain size (μm)
$Bi_{0.5}Na_{0.485}La_{0.005}Fe_xTi_{(1-(3/4)x)}O_3$								
0.005	98	1.96×10^{11}	325	274	133	45	15	1.13 ± 0.11
0.010	98	5.25×10^{11}	320	464	155	46	17	1.46 ± 0.19
0.015	97	7.05×10^{10}	325	515	142	49	12	2.21 ± 0.22
0.020	97	1.99×10^{10}	330	475	146	48	12	3.41 ± 0.38
0.025	96	1.62×10^{10}	–	377	135	48	15	4.23 ± 0.24
$(Bi_{0.55}Na_{0.485}La_{0.005})Nb_xTi_{(1-x)}O_3$								
0.005	91	4.58×10^{8}	–	715	39	45	12	0.44 ± 0.03
0.010	94	1.43×10^{10}	–	452	43	46	13	0.34 ± 0.01
0.015	94	8.67×10^{9}	–	528	31	49	12	0.33 ± 0.03
0.020	93	9.26×10^{9}	–	573	29	48	11	0.32 ± 0.03
0.025	90	4.51×10^{8}	–	752	40	48	12	0.30 ± 0.03

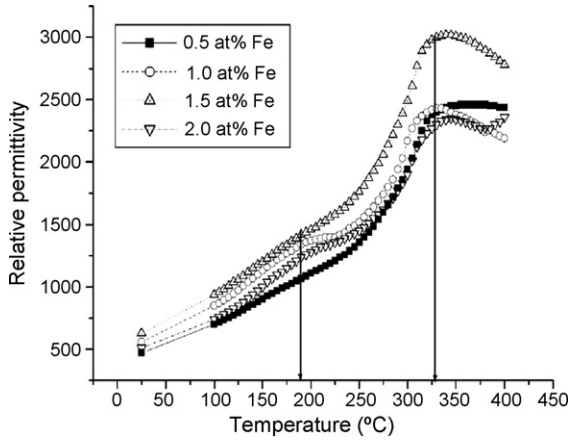

Fig. 2. Temperature dependence of relative permittivity of Fe-BNLT specimen.

[4,5]. However, an increase in Fe contents presented a shorter lattice distance (Fig. 1(c)). It may come from not only the smaller atomic radius of Fe ions but also a lower positive valency of Fe ions. This lower valency of Fe ions created oxygen vacancies causing the movement of the neighboring ions. The movement of ions possibly affected the distortion of lattice distance in Fe-modified BNLT composition, and, reduced the lattice distance.

3.2. Physical, dielectric and piezoelectric properties of modified BNLT

Table 1 shows the physical, dielectric and piezoelectric properties of Fe-modified BNLT. The densities of Fe-BNLT specimens exhibited more than 95% of theoretical densities. The relative permittivities of Fe-BNLT decreased with an increase in Fe content. It might result from the larger grain size with an addition of Fe contents in modified BNLT composition [7]. Temperature dependence of relative permittivity of Fe-BNLT specimens exhibited two phase transitions (Fig. 2) which was similar to the pure BNT [2]. The first phase transition presented at approximately 160–200 °C whereas the second phase transition (T_c) has occurred at the maximum relative permittivity, presented at approximately 320–330 °C. The modified BNLT with an addition of 0.1 at% Fe exhibited a piezoelectric charge coefficient (d_{33}) at 155 pC/N and electromechanical coupling factors in planar (k_p) and thickness (k_t) modes at 15 and 45%, respectively. With reference to the BNT composition, the Fe-modified BNLT one gave doubly increasing in terms of piezoelectric properties.

3.3. Microstructures of modified BNLT

The microstructures of modified BNLT were investigated by SEM. The surface polished pellets of all samples were thermally etched at the 100 °C below their sintering temperatures [6]. The average grain size of BNLT and modified BNLT was performed using the line-intercept method (Table 1). The addition of a small amount of Zr^{4+} in BNLT compounds did not affect any change in microstructure and the average grain size of Zr-BNLT was approximately 1 μm. For Nb-BNLT, the grain size was decreased by an addition of a small amount of Nb. The doping of the Nb^{5+} ions were suppressed the growth of grain, yielding grain size of about three times smaller than those of the undoped BNLT ceramics (from 1 to 0.3 μm). For Fe-BNLT, the average grain size of Fe-BNLT increased with an increase in Fe content (Fig. 3). The average grain size of 0.5, 1.0, 1.5, 2.0 and 2.5 at% Fe in BNLT are 1.13, 1.46, 2.21, 3.41 and 4.23 μm, respectively. The Fe ions in BNLT system behave as a grain size promoter.

3.4. Effect of the substituents in BNLT system

3.4.1. Isovalent substitution

The substitution of Zr ion at Ti-site of BNLT system exhibited high relative permittivity (700–730). It might result from the fine grain of Zr modified BNLT [7]. The resistivity of Zr-modified BNT specimens drastically decreased with an addition of Zr contents, causing a difficulty in poling. As a result, the piezoelectric properties of Zr-modified BNLT specimens could not be determined.

3.4.2. The aliovalent substitution

With reference to the Fe substitution in BNLT system, the Fe ion in BNLT system acted as an acceptor dopant. Additionally, the Fe ion can be formed as either Fe^{3+} or Fe^{2+}, then the Fe ion could be substituted at either A-site (Bi- or Na-site) or B-site (Ti-site) in the BNLT structure. The modification of Fe ion in BNLT system is a rather complex issue and required further study. The relative permittivities of Fe-BNLT decreased with an increase in Fe content, which corresponded with its microstructure. The finer grain size of Fe-BNLT resulted in higher

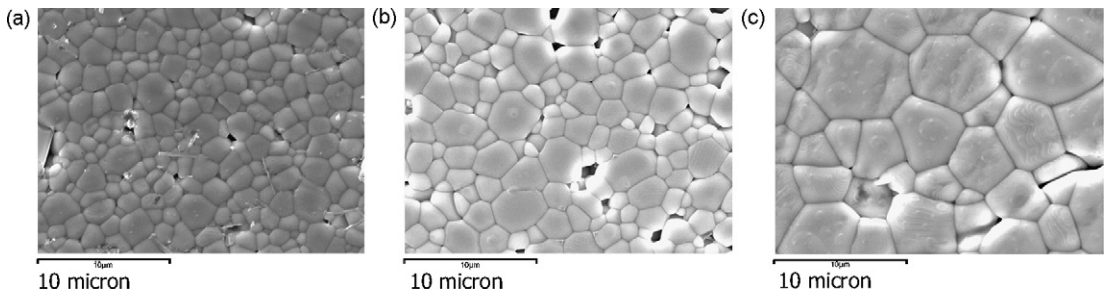

Fig. 3. Microstructures of the sintered Fe-BNLT specimens, sintered at 1100 °C for 2 h and thermally etched at 1000 °C for 5 min; (a) 0 at% Fe, (b) 1 at% Fe and (c) 2 at% Fe.

relative permittivity. The modification by Fe in BNLT system could improve the piezoelectric properties and exhibited a piezoelectric charge coefficient (d_{33}) at 155 pC/N.

The aliovalent substitution of Nb ions at Ti-site in BNLT system behaves as a donor dopant. Generally, in lead-based piezoelectric system, Pb vacancies were created during sintering process. The coexistence of Pb vacancies in the Pb-based system can be compensated for electrons created by the donor dopant [8]. However, the BNLT-based system could not create A-site vacancies as lead-based piezoelectrics did, causing a slight decrease in volume resistivity of the system with Nb substitution. The decrease in resistivity accompanying with very fine grains in the microstructure of Nb modified BNLT specimens resulted in difficulty in poling, leading to poor piezoelectric properties.

4. Conclusions

The modified BNLT compounds were prepared by conventionally mixed-oxide method. An increase of the substituents affected the lattice distortion and the microstructure of modified BNLT. The small amount of some particular substituents, i.e., the Zr and Nb ions, diminished the volume resistivity and grain sizes as well. Based on the experiment, the aliovalent substitution with the acceptor dopant, i.e., Fe, could enhance the piezoelectric properties. The 1 at% Fe in modified BNT exhibited a piezoelectric coefficient (d_{33}) value of 155 pC/N and the electromechanical coupling factor in thickness mode (k_t) of 46% and planar mode (k_p) of 17%.

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