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Piezoelectric and dielectric properties of Dy_2O_3-doped $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ lead-free ceramics

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ABSTRACT

$(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3 + x$ wt% Dy_2O_3 with $x = 0–0.3$ ceramics were synthesized by conventional solid-state processes. The effects of Dy_2O_3 on the microstructure, the piezoelectric and dielectric properties were investigated. X-ray diffraction pattern confirmed that the coexistence of tetragonal and rhombohedral phases in the $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ composition was not changed by adding 0.05–0.3 wt% Dy_2O_3. SEM images indicate that all the ceramics have pore-free microstructures with high density, and that doping of Dy_2O_3 inhibits the grain growth of the ceramics. The addition of Dy_2O_3 shows the double effects on decreasing the piezoelectric and dielectric properties for $0 < x < 0.15$ when Dy^{3+} ions substitute B-site Ti^{4+} ions, and increasing the properties for $0.15 < x < 0.3$ when Dy^{3+} ions enters into A-site of the perovskite structure. The optimum electric properties of piezoelectric constant $d_{33} = 170$ pC/N and the dielectric constant $\varepsilon_r = 1900$ (at a frequency of 1 kHz) are obtained at $x = 0.3$.

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1. Introduction

$Bi_{0.5}Na_{0.5}TiO_3$ (BNT) as a promising candidate for lead-free piezoelectric ceramics has attracted considerable attention due to its strong ferro-electricity with a relative large remnant polarization ($Pr = 38\ \mu C/cm^2$) and relative high Curie temperature (320 °C) [1]. In spite of the high coercive field ($Ec = 7.3$ kV/mm) and the high conductivity of BNT ceramics, the microstructure and the electric properties can be tailored by suitable substitutions at the A and/or B sites of many perovskite compounds of a general formula ABO_3-type (A = mono or divalent ions, B = tri-pentavalent ions) of the compounds [2,3]. Among those modification research of BNT, the $(1-x)$ BNT–$x$$BaTiO_3$ (BNBT) system especially $0.94Bi_{0.5}Na_{0.5}TiO_3–0.06BaTiO_3$ (abbreviated as BNBT-6) shows improvement in the electric properties comparing with pure BNT ceramics owing to the existence of a rhombohedral–tetragonal morphotropic phase boundary (MPB) [4,5]. Further enhancement in the piezoelectric properties can be achieved by employing rare earth oxide such as CeO_2, Nd_2O_3, La_2O_3, Ga_2O_3 and Y_2O_3 [6–10]. Distinguished with the rare earth ions above, Dy^{3+} can substitute either A-site or B-site [11,12] which seemed to suggest an active role in densification, grain growth behavior and the electric properties of BNBT ceramics. In this study, Dy_2O_3 was selected as dopant of BNBT6 ceramics. A series of Dy_2O_3-doped (0–0.3 wt%) BNBT6 ceramics are prepared, and the dielectric constant and the piezoelectric constant were discussed as a function of Dy_2O_3 content.

2. Experiments

Reagent-grade Bi_2O_3, Na_2CO_3, TiO_2, $BaCO_3$ and Dy_2O_3 were used as starting materials. The stoichiometric amounts of oxides and carbonates were mixed for 1 h in ethanol medium according to the compositional formula $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3 + (0–0.3)$ wt% Dy_2O_3. The mixture was dried at 120 °C, and then calcined at 650 °C for 2 h. After calcining, the powders were granulated with polyvinyl alcohol (PVA) and pressed into disks with a diameter of 13 mm and thickness of 2 mm, which were subsequently sintered at 1150 °C for 2 h in a presence of the same composition in a covered crucible. The sintered pellets were ground and polished to obtain flat and parallel surfaces. Phase identification of the calcined products was characterized by X-ray diffraction analysis using a diffractometer (DMax-RA Japan Rigaku). The ceramic samples were then thermally etched at 950 °C for 1 h prior to microstructural investigation using a scanning electron microscope (SEM, HITACHI S-4300). For electrical property measurement, silver paste was fired on both surfaces of the well-polished pellets as electrodes. Specimens were immersed in silicon oil to prevent arcing. Piezoelectric properties were measured by a ZJ-3AN Berlincourt-type quasistatic d_{33} meter. For piezoelectric measurement, the specimens were poled under an electric field of 4–5 kV/mm for 15 min at 80 °C in silicon oil and then slowly cooled down to room temperature while maintaining half of the applied electric field.

3. Results and discussion

Fig. 1a shows the X-ray diffraction patterns of the BNBT6 + (0–0.3) wt% Dy_2O_3 samples sintered at 1150 °C for

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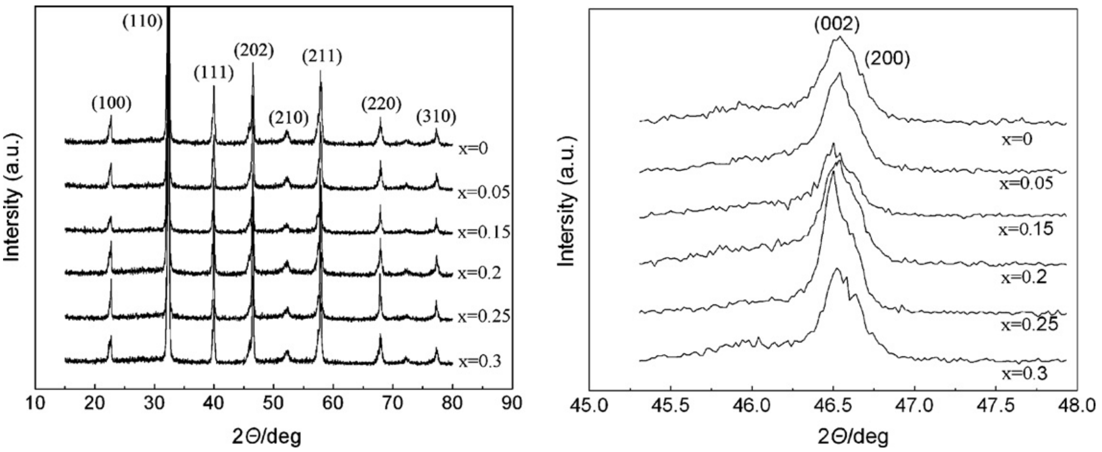


Fig. 1. XRD patterns of the BNBT6–xDy$_2$O$_3$ (x = 0–0.3) specimens sintered at 1150 °C for 2 h.

2 h. With the addition of Dy_2O_3 (0.05–0.3 wt%), all the specimens exhibit typical ABO_3 perovskite structure without any detectable secondary phases, implying that Dy^{3+} ions mainly diffused into the BNBT lattices during sintering, and did not lead to an obvious change in the phase structure of BNBT6. To examine the influence of Dy_2O_3 addition on the structure of BNBT6, further XRD analysis was performed in the range of 45–48° shown in Fig. 1b. Clearly splitting of (2 0 0) and (0 0 2) peaks from (2 0 2) can be observed at about 46.5°, signifying a phase transformation from rhombohedral to tetragonal phase, and suggesting the existence of a MPB with rhombohedral and tetragonal phases in all the specimens.

According to Tsur et al. [13], the ion with ionic radius being between 0.087 nm and 0.094 nm was called amphoteric ion, which could occupy both A-site and B-site with different partitioning for each ion. The dysprosium ionic radius (Dy^{3+}) is 0.091 nm [14] that means it might occupy both A-site and B-site of the perovskite BNBT6 structure. As the atomic radius of Dy^{3+} is larger than that of Ti^{4+}(0.068 nm), the lattice constants will increase continuously if Dy^{3+} occupies B-site. Similarly, as the atomic radius of Dy^{3+} is smaller than that of A-site ions ($R_{[Bi]} = 0.117$ nm, $R_{[Na]} = 0.139$ nm, $R_{[Ba]} = 0.134$ nm), a slight decrease in the lattice parameters of BNBT6 will be occurred with Dy^{3+} on A-sites. The lattice parameter a axis of the perovskite determined by XRD results and unit cell volume of the BNBT6 ceramics doped with Dy_2O_3 as a function of dopant concentration were shown in Fig. 2. Both of them increase with increasing Dy^{3+} concentration until they reach maximum value at $x = 0.15$ respectively, then decreases with further increase of Dy^{3+} concentration. It proves that Dy^{3+} occupies the B-site at lower substitution content until $x = 0.15$, then enters A-site at higher substitution content.

The microstructures of the sintered ceramics were observed by SEM shown in Fig. 3. The homogeneous grain and pore-free microstructures are in good agreement with the high density of the ceramics (above 95.5% of the theoretical density) determined by Archimedes method. Slightly decrease in the grain size can be observed in the micrographs of the samples with 0, 0.15, 0.2, and 0.3 wt% Dy_2O_3, indicating that Dy_2O_3 addition inhibits the grain growth. It is because Dy_2O_3 dopant is easily to concentrate at grain boundaries without any energy, therefore to restrain abnormal grain growth during sintering.

Fig. 4 presents the piezoelectric constant d_{33} as a function of the amount of Dy_2O_3. The d_{33} first decrease with the addition of Dy_2O_3 until $x = 0.15$, then increase with further addition of Dy_2O_3. This is consistent with the Dy^{3+} occupation analysis above. For $0 < x < 0.15$, Dy^{3+} ions substitute for B-site Ti^{4+} ions with the increasing content of Dy^{3+}. Under this condition, Dy^{3+} ions exhibit some properties of acceptor type additives. For $0.15 < x < 0.3$, Dy^{3+} enters into the A-site of BNBT6 ceramics, In this case, Dy^{3+} ions acts as a donor leading to some vacancies of A-site in the lattice, which facilitates the ferroelectric domains reorientation and thus improves the piezoelectric properties significantly [6]. At 0.3 wt% Dy_2O_3, the piezoelectric constant of the ceramics increases obviously from 157 pC/N of pure BNBT6 to 170 pC/N. Both of the d_{33} values are larger than the values of pure BNBT6 ceramics and BNBT-based lead-free piezoelectric ceramics prepared by conventional solid-state method reported in the literature [15–17].

The room temperature dielectric constant and the dielectric loss tan δ of the BNBT6 based ceramics as a function of frequency for different x are given in Figs. 5 and 6 respectively. The dielectric constant slightly decreased with the addition of Dy_2O_3 till $x = 0.15$, then greatly increased with increasing x up to 0.3, and reached a maximum value of 1900 at $x = 0.3$ (1.0 kHz frequency). It can also be seen that ε_r decreases with increasing frequency especially at relatively low frequency, showing a diffuse phase transition behavior. With the addition of Dy_2O_3, the dielectric loss tan δ decreased until $x = 0.15$. Although the dielectric loss increased with more Dy_2O_3 content, resulted from the defect in lattice formed during the process of Dy^{3+} occupation into the A-

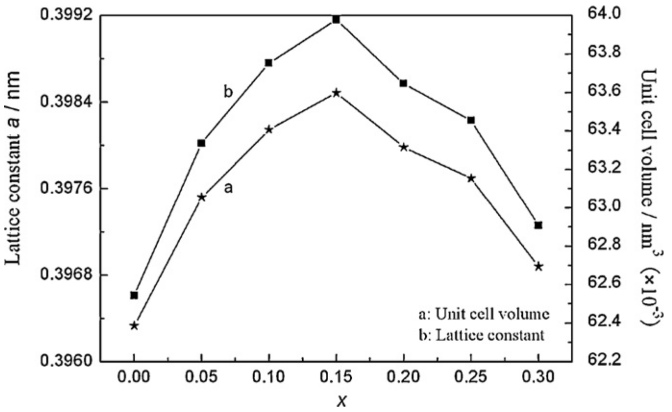
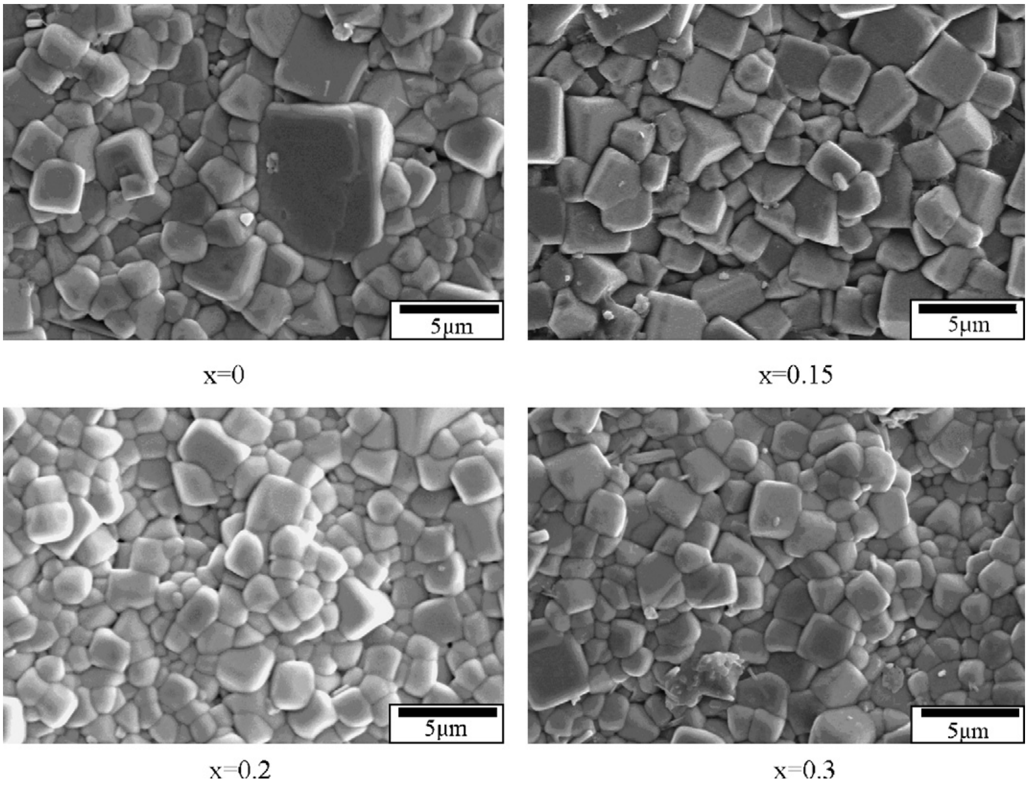


Fig. 2. The lattice parameter a axis of the perovskite and unit cell volume of the BNBT6 ceramics doped with Dy_2O_3 as a function of dopant concentration.



x=0 x=0.15

x=0.2 x=0.3

Fig. 3. SEM micrographs of the BNBT6–xDy$_2$O$_3$ (x = 0–0.3) specimens (a) x = 0, (b) x = 0.15, (c) x =0.2, and (d) x = 0.3.

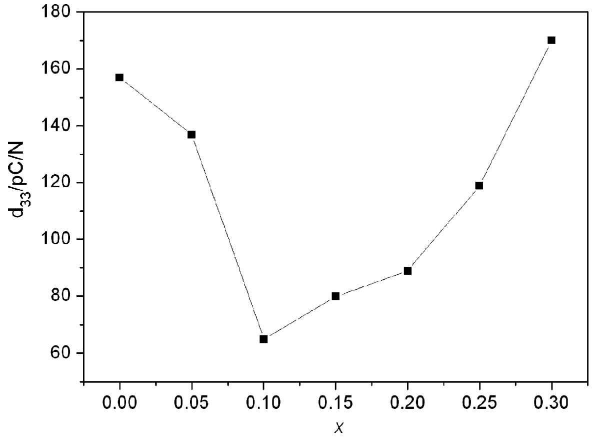


Fig. 4. The piezoelectric constant d_{33} of the specimens changing with the amount of Dy$_2$O$_3$.

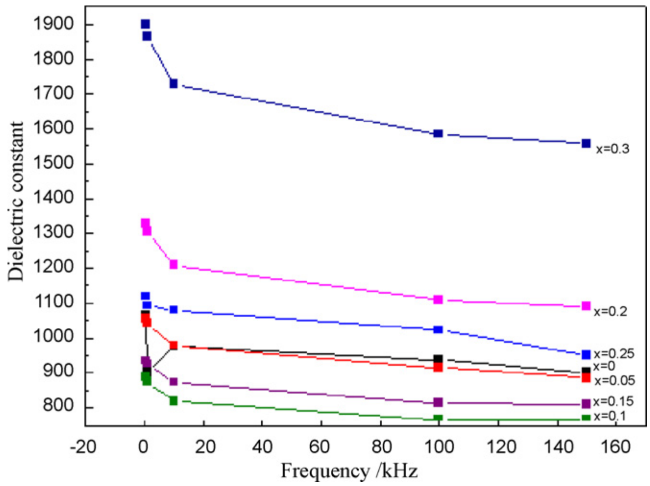


Fig. 5. The dielectric constant ε_r of BNBT6–xDy$_2$O$_3$ (x = 0–0.3) system (x = 0–0.3) at room temperature.

site of BNBT6 ceramics, all the ceramics exhibit a relative lower dielectric loss value ranging from 0.047 to 0.053. Table 1 presents the grain size, substitution sites and the electrical properties for BNBT6 + xDy$_2$O$_3$ ceramics. As is reported in the literature [18], grain size and microstructures more on less influence the electrical properties of the ceramics. For Dy$_2$O$_3$ doped BNBT6 ceramics as is shown in Table 1, the substitution site seems to play a more important role on the electrical properties than grain size does.

Table 1
Grain size, substitution sites and the electrical properties for BNBT6 + xDy$_2$O$_3$ ceramics.

Dy concentration	Grain size (μm)	Substitution sites	d_{33} (pC/N)	ε_r (1 kHz)	Tan δ (1 kHz)
x = 0	1.67	B	157	1012	0.047
x = 0.15	1.53	B	80	876	0.053
x = 0.2	1.30	A	89	1327	0.049
x = 0.3	1.25	A	170	1900	0.048

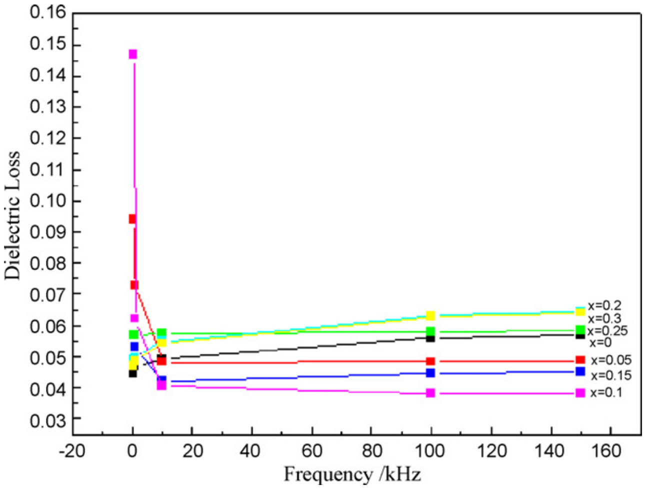


Fig. 6. The loss tangent of BNBT6–xDy$_2$O$_3$ (x = 0–0.3) system at room temperature.

4. Conclusion

$(Bi_{1/2}Na_{1/2})_{0.94}Ba_{0.06}TiO_3$ (BNBT6) ceramics with 0–0.3 wt% Dy_2O_3 has been synthesized by conventional solid-state reaction sintering method. XRD research indicates that the Dy_2O_3-doped BNBT6 ceramics remain single-phase perovskite structure with the coexistence of rhombohedral and tetragonal phases. SEM examination reveals that doping of Dy_2O_3 inhibits the grain growth of the ceramics. The addition of Dy_2O_3 shows the double effects on decreasing the piezoelectric and dielectric properties for $0 < x < 0.15$ when Dy^{3+} ions substitute B-site Ti^{4+} ions, and increasing the properties for $0.15 < x < 0.3$ when Dy^{3+} ions enter into A-site of the perovskite structure. The BNBT6 ceramics doped with 0.3 wt% Dy_2O_3 gave an obvious increase of the dielectric constant and a remarkable increase of piezoelectric constant: $d_{33} = 170$ pC/N, $\varepsilon_r = 1900$ (at a frequency of 1 kHz). All the BNBT6 ceramics with Dy_2O_3 added exhibit a relative lower dielectric loss value ranging from 0.047 to 0.053.

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