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Effect of HfO_2 content on the microstructure and piezoelectric properties of $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ lead-free ceramics

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Abstract

$(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$–$x$$HfO_2$ [BNBT–$x$$HfO_2$] lead-free ceramics were prepared using the conventional solid-state reaction method. Effects of HfO_2 content on their microstructures and electrical properties were systematically studied. A pure perovskite phase was observed in all the ceramics with $x=0$–0.07 wt%. Adding optimum HfO_2 content can induce dense microstructures and improve their piezoelectric properties, and a high depolarization temperature was also obtained. The ceramics with $x=0.03$ wt% possess optimum electrical properties (i.e., $d_{33}\sim168$ pC/N, $k_p\sim32.1\%$, $Q_m\sim130$, $\varepsilon_r\sim715$, tan $\delta\sim0.026$, and $T_d\sim106$ °C, showing that HfO_2-modified BNBT ceramics are promising materials for piezoelectric applications.

Keywords: Lead-free ceramics; $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$; HfO_2; Piezoelectricity

1. Introduction

Piezoelectric materials can achieve the transformation between mechanical and electrical energy, which are of great interest for various applications, such as actuators and sensors [1]. Conventional piezoelectric materials are lead zirconate titanate [Pb(Zr,Ti)O_3, PZT] lead-based ceramics [1], which contain the toxic lead substance that causes damage to the environment as well as the human health [1]. With the increasing awareness of environmental protection, much attention has been paid to the lead-free ceramics, and many countries have established related regularities to limit the use of lead-based ceramics [2–23]. Among these lead-free piezoceramics, bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$, BNT)-based ceramics attract much interest because of their excellent electrical performances, which are considered as a promising candidate materials for piezoelectric applications [14–23]. However, piezoelectric properties of the BNT-based ceramics need to be further improved in order to replace lead-based ceramics in a wider range of applications [14–23]. Recently, many researches with respect to BNT-based ceramics have been carried out, and some critical achievements have been attained through various doping or adding another ferroelectrics or nonferroelectrics to form uniform solutions [14–23]. Nevertheless, the enhancement of piezoelectric properties often raises the risk of the decrease of Curie temperature which also restricts the usage of the BNN-based piezoceramics to a large degree [14–23]. It was reported that $0.94(Bi_{0.5}Na_{0.5})TiO_3$–$0.06BaTiO_3$ ceramics exhibit improved piezoelectric properties on account of the coexistence of rhombohedral and tetragonal phase that induces more possible polarization states [21]. Moreover, the addition of some additives can improve the piezoelectric properties, but the depoling temperature (T_d) decreases [24,25], as shown in Table 1.

In this work, HfO_2-modified $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ (abbreviated as BNBT–$x$$HfO_2$) lead-free piezoelectric ceramics were prepared by the conventional solid-state reaction method, the influences of HfO_2 addition on their microstructures and

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Table 1
Piezoelectric properties of BNBT-based lead-free ceramics

Material system	d_{33} (pC/N)	k_p	T_d (°C)	Reference
BNBT	122	0.29	100	[21]
BNBT–CeO_2	152	0.34	~85	[24]
BNBT–La_2O_3–Nb_2O_5	135	0.19	~70	[25]
BNBT–HfO_2	168	0.321	~106	In this work

electrical properties were systematically studied, and the underlying physical mechanism was discussed in detail. These results indicate that HfO_2-modified $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ ceramics with $x=0.03$ wt% possess optimum electrical properties and no significant reduction of the depoling temperature (T_d) happens, suggesting that appropriate addition of HfO_2 is an effective way to enhance piezoelectric properties.

2. Experimental procedures

BNBT–$x$$HfO_2$ lead-free ceramics with $x=0$, 0.01, 0.03, 0.05, and 0.07 wt% were prepared using the conventional solid-state reaction method. Bi_2O_3 (99%), Na_2CO_3 (99.8%), $BaCO_3$ (99%), TiO_2 (98%), and HfO_2 (99.99%) were used as starting raw materials. They are ball milled for 24 h with agate media and alcohol. After calcination at 900 °C for 6 h, the calcined powders were milled for 12 h again, and then pressed into the disks of 10 mm in diameter and 1.2 mm in thickness under 10 MPa using polyvinyl alcohol (PVA) as a binder. After burning off PVA, the pellets were sintered at 1150 °C for 3 h in air. Silver pastes were fired on both sides of the pellets as the electrodes at 700 °C for 10 min. All samples were poled in the 30 °C silicon oil by applying the *dc* electric field of 3–4 kV/mm for 30 min. All the electrical properties of the specimens were measured after one more day.

X-ray diffraction (XRD) characterization of the ceramics was performed using Cu $K\alpha$ radiation ($\lambda=1.54178$ Å) in the θ–2θ scan mode (DX1000, Dandong, China). The surface morphology of the samples was observed by a scanning emission microscope (SEM) (JSM-5900, Japan). The temperature dependence of the dielectric constant of the ceramics was examined using a programmable furnace with an *LCR* analyzer (HP4294, Hewlett-Packard 4294 Impedance Analyzer, Palo Alto, CA).The piezoelectric constant was measured using a piezo-d_{33} meter (ZJ-3A, Institute of Acoustics Academic Sinica, Beijing, China). The relative permittivity ε_r, dielectric loss tan δ, electromechanical coupling coefficient k_p, and mechanical quality factor Q_m of the ceramics were determined by the resonance method using an impedance analyzer (HP 4294A, Hewlett-Packard 4294A Impedance Analyzer).

3. Results and discussion

The XRD patterns of the HfO_2-modified BNBT lead-free ceramics with $x=0$, 0.01, 0.03, 0.05, and 0.07 wt% are shown in Fig. 1. Single perovskite structures were observed in all the compositional range, and no impurity phase can be detected, confirming the formation of a stable solution between HfO_2 and BNBT, as shown in Fig. 1(a). Fig. 1(b) is correspondingly expanded XRD patterns of the ceramics in the range of 2θ from 46.0 to 47.5. It is found that the diffraction peaks shift to lower angles initially and conversely to higher ones with $x>0.05$ wt%. It is because of the fact that Hf ions enter onto A-site firstly that decrease the lattice parameters due to smaller radius than that of $(Bi_{0.5}Na_{0.5})^{2+}$, and then the displacement of Ti^{4+} by Hf^{4+} with the increasing of Hf content conversely induces the increase of lattice parameters on account of the larger radius of Hf compared with Ti^{4+}. These results show that Hf^{4+} diffuses into the lattice of BNBT ceramics, considerably affecting the piezoelectric properties.

Fig. 2(a)–(c) shows the SEM micrographs of the BNBT–$x$$HfO_2$ ceramics with $x=0$, 0.03, and 0.07 wt%. As shown in Fig. 2, the addition of Hf can promote the grain growth of these ceramics, and dense microstructures as well as clear grain boundaries can be obversed. It is also found that the ceramics of $x=0.03$ wt% possess relatively fine and well-distributed grains, which is helpful to improve electrical performances.

The temperature dependence of dielectric constant and dielectric loss over the range of temperatures from room temperature to 500 °C at different frequencies is shown in Fig. 3. There are two apparent peaks, which one is corresponding to T_c, while the other is accordance with T_d [14–25]. Negligible change of these two phase transition temperatures could be investigated and the ceramics with x=0 and 0.03 wt% possess similar values of T_d and T_c, nearly equal to 106 °C and 280 °C, respectively. This result confirms that the addition of HfO_2 cannot decrease their T_d and T_c of BNBT ceramics. It is well known that the improvement of d_{33} value in BNT-based ceramics often causes the decrease of their T_d and T_c [24,25]. As a result, the introduction of HfO_2 not only improves the d_{33} but also keeps high T_d and T_c values of this work. Moreover, it is also found in Fig. 3(b) that the BNBT–$x$$HfO_2$ ceramics with $x=0.03$ wt% exhibit broader peaks of dielectric constants over the measuring frequency range, as compared with the ceramics with $x=0$ shown in Fig. 3(a). It can be explained that the appropriate addition of HfO_2 results in more randomly compositional distribution at A-site, which enhances the relaxor behaviors.

In order to analyze dielectric properties of the HfO_2-modified BNBT lead-free ceramics, the variation of relative permittivity and dielectric loss with different contents of HfO_2 is measured at 100 kHz, as shown in Fig. 4. It can be seen that the ceramics over all compositional range exhibit moderate dielectric performances. Furthermore, the dielectric constant

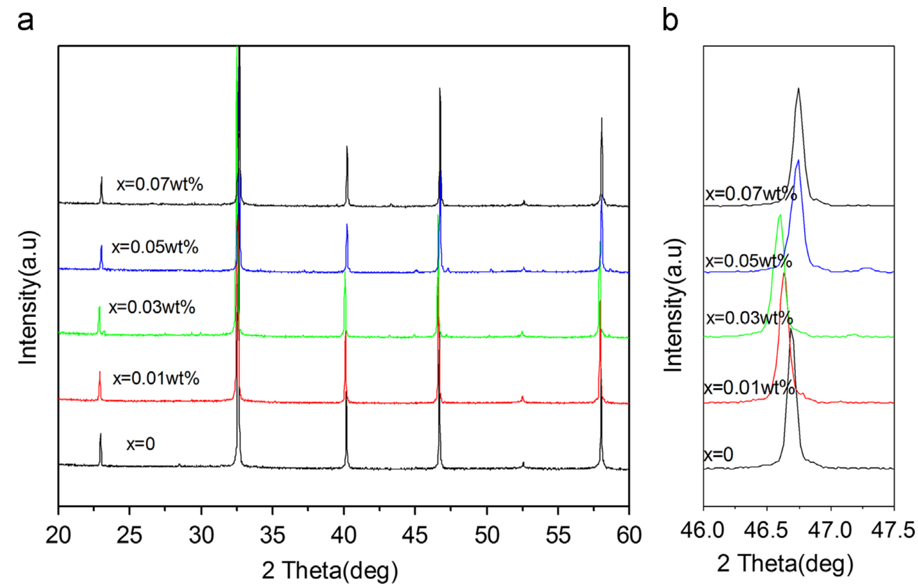

Fig. 1. (a) XRD patterns of BNBT–xHfO$_2$ lead-free ceramics, and (b) corresponding expanded XRD patterns of the ceramics in the range of 2θ from 46.0° to 47.5°.

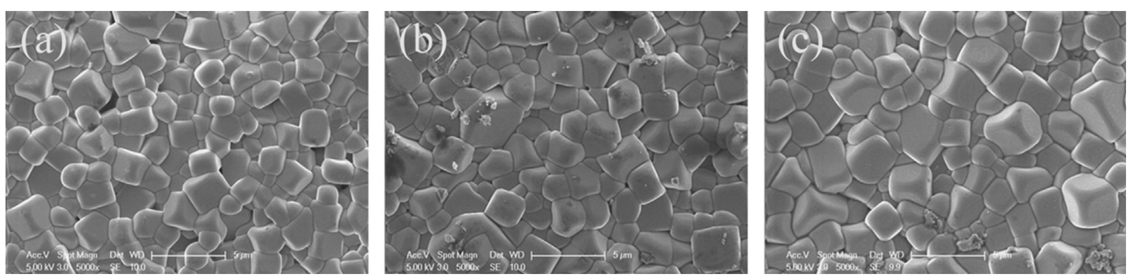

Fig. 2. SEM micrographs of BNBT–xHfO$_2$ lead-free ceramics with (a) $x=0$ wt%, (b) $x=0.03$ wt%, and (c) $x=0.07$ wt%.

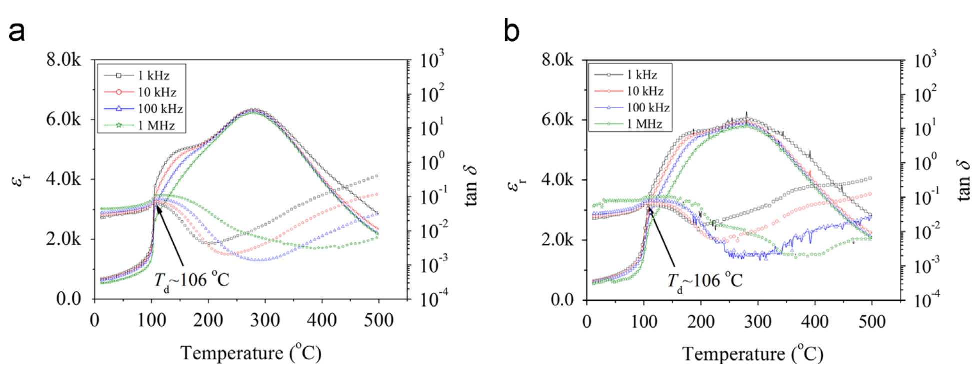

Fig. 3. Temperature dependence of dielectric constant and dielectric loss for BNBT–xHfO$_2$ lead-free ceramics with (a) $x=0$ wt% and (b) $x=0.03$ wt% as a function of measuring frequencies.

slightly decreases, and a lowest dielectric loss is observed in the ceramic with $x=0.03$ wt%. As a result, the ceramics with $x=0.03$ wt% possess relatively optimum dielectric properties of $\varepsilon_r=715$ and tan $\delta=0.026$.

Fig. 5 shows the piezoelectric constant d_{33}, electromechanical coupling coefficient k_p, and mechanical quality factor Q_m of the BNBT–xHfO$_2$ ceramics as a function of x. It is found that piezoelectric constant d_{33} increases firstly, then decreases with the further increase of HfO$_2$ content, and reaches its maximum value of 168 pC/N at $x=0.03$ wt%. The variation of planar electromechanical coupling coefficient k_p with x performs analogous trend compared to d_{33}, and attains the maximum of 32.1% at the same compositional point. In contrast, the mechanical quality factor Q_m slightly increases with the increase of HfO$_2$ content. It is concluded that the ceramics with $x=0.03$ wt% possess optimum piezoelectric properties of $d_{33}=168$ pC/N and $k_p=32.1$%, which is larger than those of BNBT ceramics with other additives [24,25], as

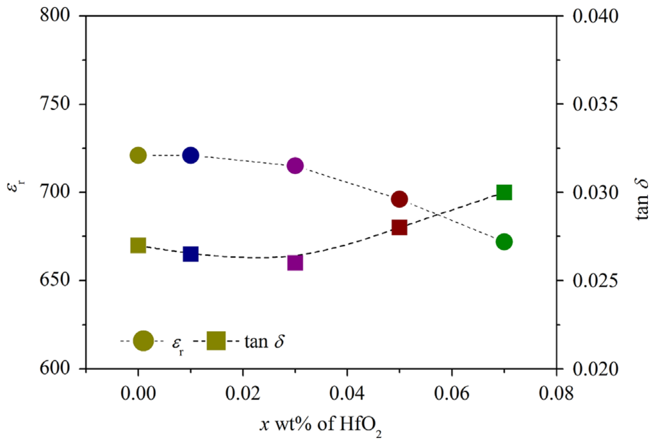

Fig. 4. Relative permittivity ε_r and dielectric loss tan δ of the ceramics as a function of x.

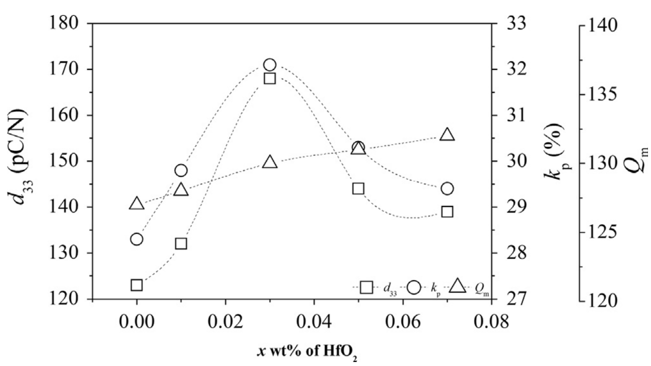

Fig. 5. Piezoelectric constant d_{33}, planar electromechanical coupling coefficient k_p, and mechanical quality factor Q_m of the ceramics as a function of x.

shown in Table 1. The explanation of the change may be that the appropriate addition of HfO_2 entering onto A-site gives rise to the donor dopants due to the larger valences compared with $(Bi_{0.5}Na_{0.5})^{2+}$, which generates cation vacancies to compensating the charge defects. The A-site vacancies are proposed to release the stress build-up associated with motion of non-180° domain walls and result in their easier displacement [26], which is contributed to the improvement of piezoelectric properties like soft-PZT ceramics. However, no effective contribution to the enhancement but sharp degradation of piezoelectric properties has conversely been made by excess addition of HfO_2 that occupied the B-site which has been confirmed by XRD patterns as shown in Fig. 1(b). It is possible because of the fact that there has been no cation vacancies yielded on B-site owing to the same valences of Hf^{4+} and Ti^{4+}; at the same time, a high concentration of cation vacancies on A-site also make piezoelectric properties deteriorate so that the softening effect is lost [26].

4. Conclusion

HfO_2-modified $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ lead-free ceramics were prepared using the conventional solid-state reaction method, and their microstructures and electrical properties were systematically studied. The appropriate addition of HfO_2 results in dense microstructures and enhanced piezoelectric properties, while maintaining relatively high Curie temperature. HfO_2-modified BNBT lead-free ceramics with $x=0.03$ wt % exhibit optimum properties of $d_{33}=168$ pC/N, $k_p=32.1\%$, $Q_m=130$, $\varepsilon_r=715$, tan $\delta=0.026$. These results suggest that HfO_2-modified BNBT lead-free ceramics are one of the foremost potential lead-free materials for piezoelectric applications.

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