Preparation and electrical properties of the new lead-free (1 − x)Bi0.5Na0.5TiO3−xBa(Ni1/3Nb2/3)O3 piezoelectric ceramics

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A new lead-free piezoelectric ceramics of (1 − x)Bi0.5Na0.5TiO3−xBa(Ni1/3Nb2/3)O3 (BNT−BNN) (x = 0.0−0.07) have been prepared by a conventional solid solution reaction method. Their structures and electric properties have been investigated systematically. A pure perovskite phase can be formed in x ≤ 0.06. By the introduction of Ba(Ni1/3Nb2/3)O3, the ceramics exhibit a lower coercive field $E_C$. Composition for x = 0.02 shows optimal piezoelectric properties, with the piezoelectric coefficient $d_{33} = 121$ pC/N. Temperature dependent $P(E)$ loops and $S(E)$ curves of 0.98BNT−0.02BNN indicate that the phase transition from the ferroelectric to antiferroelectric takes place over a very wide temperature range from 75 to 150°C.

Key-words : Perovskite, Dielectric, Ferroelectric, Antiferroelectric

1. Introduction

Lead-based piezoelectric ceramics with perovskite structure, represented by lead zirconate titanate (PZT) and its derivatives, are widely used for actuators, sensors, and many other applications due to their excellent piezoelectric properties in the morphotropic phase boundary (MPB). However, in consideration of the poisonous effect of lead oxide on environment and human health, it is necessary to develop lead-free piezoelectric ceramics for replacing them.

With the objective of developing potential advanced lead-free piezoelectric ceramics, much attention has been focused on Bi0.5Na0.5TiO3 (BNT), K0.5Na0.5NbO3 (KNN), BaTiO3 (BT) and mixed systems of these end members. Among the developed lead-free piezoelectric ceramics, BNT has some advantages due to its relative large remanent polarization ($P_r = 38\mu$C/cm$^2$). BNT is ferroelectric complex with rhombohedral symmetry at room temperature. It transforms from ferroelectric to antiferroelectric phase at ~200°C, and then into paraelectric phase at ~320°C. Nevertheless, pure BNT has a drawback of a high coercive field ($E_C = 7.3$ kV/mm) and a high conductivity, making the poling process of the ceramic extremely difficult. Thus, the pure BNT ceramic usually exhibits very poor piezoelectricity with the piezoelectric coefficient $d_{33} = 58$ pC/N. In order to further improve its piezoelectric properties, substantial efforts have been made to modify the property of BNT by forming BNT-based solid solutions, such as BNT−Bi0.5K0.5TiO3, BNT−NaNbO3, and BNT−SrTiO3 have been developed and studied intensively. Similar to pure BNT, the derivatives of BNT-based lead-free piezoelectric ceramics undergo a transition from the low-temperature ferroelectric (FE) phase to the high-temperature antiferroelectric (AFE) phase at a certain depolarization temperature ($T_d$). High piezoelectric strain could be obtained during the AFE–FE phase transition induced by the externally applied electric field, such as in BNT−BT−KNN lead-free system, an extremely high strain was observed in the piezoelectric ceramics especially with the composition of 0.92BNT−0.06BT−0.02KNN (0.45%). It needs to note that the performance of piezoelectric actuator is governed by the electric field-induced strain of the actuator material. Large achievable strain is desirable for actuator application.

Recently, in the case of BNT-based lead-free systems, attentions have been attracted by the Bi0.5Na0.5TiO3−Ba(Me)O3 solid solutions, where Me can be a single cation of valence +4 (e.g., Ti4+ and Zr4+), or a mixture of cations with an average valence of +4 (e.g., Cu1/3Nb2/3 and Al1/2Nb1/2). Analogous to the traditional PZT, an MPB composition could be formed in the Bi0.5Na0.5TiO3−Ba(Me)O3 solid solutions, and enhanced piezoelectric properties compared to pure BNT were obtained as expected. In particularly, Bi0.5Na0.5TiO3−Ba(Me)O3 solid solutions of 0.94BNT−0.06BaTiO3, 0.9525BNT−0.0475BaCu1/3Nb2/3O3, and 0.9045BNT−0.0955BaAl1/2Nb1/2O3, respectively produced superior $d_{33}$ values of 125, 125 and 133 pC/N in their MPB compositions. It is supposed that Ba(Me)O3 have positive effect in enhancing the piezoelectric properties of BNT. Furthermore, complex perovskite ceramics with the general formula BaB′2B″(ix), where B′ = Mg, Ni, or Zn and B″ = Nb or Ta, were found to have an extremely high quality factors in the microwave region. To make full use of the merits of both materials of BaB4B2(0.6)xO9 and BNT, the cubic Ba(Ni1/3Nb2/3)O3 was substituted into BNT to form a binary system of (1 − x)Bi0.5Na0.5TiO3−xB at(Ni1/3Nb2/3)O3 (BNT−BNN) to improve the...
piezoelectric properties.\(^{(20)}\) Lead-free ceramics of BNT-BNN were fabricated by an ordinary sintering method, and their structures, electric properties, and temperature dependent electric properties have been studied systematically.

2. Experimental procedure

\((1 - x)\text{BNT-}x\text{BNN} (x = 0.0-0.07)\) samples were prepared by a conventional solid-state method. Bi\(_2\)O\(_3\) (99%), Na\(_2\)CO\(_3\) (99%), TiO\(_2\) (99%), Ba\(_2\)CO\(_3\) (99%), Nb\(_2\)O\(_5\) (99.99%) were chosen as starting raw materials and weighted according to the stoichiometric formula. The powders were ball-milled in alcohol for 12 h. The dried slurries were calcined at 850°C for 5 h. After calcination, the powders were re-milled again for another 12 h and dried. Subsequently, the powders were pressed into green disks with a diameter of 10 mm and thickness of ~2 mm at 200 MPa, then sintered at 1150°C for 2 h in a covered alumina crucible. To reduce the volatilization of Bi and Na during sintering, the green compacts were embedded by the calcined alumina powder.

The crystal structure was characterized by X-ray diffraction (XRD, X’Pert PRO, PANalytical, Almelo, Netherlands) using Cu Kα radiation. For electrical measurements, sintered disks were ground and polished to a thickness of ~0.6 mm. The samples were electroded with silver paste and then fired at 550°C for 30 min. A triangular waveform at a frequency of 1 Hz was applied to detect electric field-induced polarization \(P(E)\) and longitudinal strain \(\varepsilon(E)\) curves in a silicone oil bath by a ferroelectric analyzer (aixACCT, TF Analyzer 1000, Aachen, Germany, Laser type: Sios Mi-60). The temperature dependence of polarization curves, bipolar and unipolar strains were all explored from room temperature to 150°C with intervals of 25°C. Before collecting data for each temperature, samples were held at each specified temperature for 30 min to minimize thermal fluctuations. Temperature dependent dielectric constant and loss were determined by an impedance analyzer (HP4294A, Hewlett-Packard, Palo Alto, CA) in the frequency range of \(10^2-10^8\) Hz from room temperature to 600°C. For piezoelectric measurements, samples were poled at room temperature under an electric field of 8 kV/mm for a dwell time of 15 min. After 24 h aging of the poled samples, the \(d_{33}\) values were measured using a quasi-static meter (Chinese Academy of Acoustics, ZJ-3, Beijing, China).

3. Results and discussion

The room temperature XRD patterns of \((1 - x)\text{BNT-}x\text{BNN}\) \((x = 0.0-0.07)\) are shown in Fig. 1(a). All the investigated compositions exhibit a pure perovskite structure except for \(x = 0.07\), where a tiny trace of impurity appears approximately at \(2θ = 30°\) due to the limitation of the solid solubility. One can see that the peaks, such as \((111)\) [Fig. 1(b)], shift to lower diffraction angles with increasing the BNN content, suggesting that there is a lattice expansion. This is probably due to the relatively large ionic radii of Ba\(^{2+}\) compared with Bi\(^{3+}\) and Na\(^{+}\) at the A-site (coordination number (CN) = 12, \(R_{Bi} = 1.61\) Å > \(R_{Na} = 1.45\) Å > \(R_{Ba} = 1.39\) Å).\(^{(21)}\) The corresponding lattice parameter \(a\) was calculated based on a rhombohedral structure. The lattice parameter of \((1 - x)\text{BNT-}x\text{BNN}\) increases from \(a = 3.8735(8)\) Å for \(x = 0.0\) to \(a = 3.9059(6)\) Å for \(x = 0.06\). It could be concluded that the BNN has been diffused into BNT and leads to the lattice expansion. The asterisk around \((111)\) peak indicates a superstructure peak [Fig. 1(b)], which characterizes the space group of \(R3C\).\(^{(22)}\) It disappears when \(x\) reaches 0.04 because of the reduced lattice distortion.\(^{(23)}\)

The temperature dependence of dielectric constant and loss on poled samples have been tested from room temperature to 600°C under various frequencies. Take the composition of \(x = 0.02\) for example [Fig. 2(a)], since it exhibits preferable piezoelectric properties as discussed below. Similar to the pure BNT and other BNT-based solid solutions, the ceramics exhibit two dielectric anomalies at \(T_d\) and \(T_{m95}^{\pm}\).\(^{(5)}\)\(^{(6)}\) \(T_d\) is the depolarization temperature which corresponds to the phase transition from the ferroelectric state to the antiferroelectric one. While \(T_{m95}\) is the maximum temperature at which \(ε_r\) reaches a maximum value and corresponds...
to the phase transition from the antiferroelectric state to the paraelectric one.\(^{24}\) For all the investigated compositions, an apparent relaxor character with frequency-dependent slight above room temperature and the broadening of the peak of \(e_1\) at \(T_m\) is observed, which is attributed to the structural disordering and the compositional fluctuation.\(^{23}\) Similar phenomenon has also been observed in other BNT-based lead-free ceramics.\(^{25}\) The variations of \(T_m\) and \(T_d\) are shown in Fig. 2(b). It can be seen that for the \((1-x)\)BNT–xBNN \((x = 0.01-0.06)\) ceramics, \(T_m\) decreases from 323 to 272°C as \(x\) increases from 0.01 to 0.04, and then increases to 298°C with \(x\) further increases to 0.06. Different from \(T_m\), \(T_d\) decreases continuously as the increase of \(x\) without any high fluctuation. For \(x = 0.02, T_m\) and \(T_d\) are 285 and 143°C, respectively.

The evolution of polarization loops \(P(E)\) and bipolar strain curves \(S(E)\) versus electric field of \((1-x)\)BNT–xBNN \((x = 0.01-0.06)\) were measured at room temperature (Fig. 3). For the compositions with \(x \leq 0.04\), samples exhibit well saturated \(P(E)\) hysteresis loops [Fig. 3(a)]. While \(x\) increases to 0.05, the loop becomes seriously constricted, exhibiting an antiferroelectric characteristic.\(^{25}\) The remnant polarization \(P_r\) decreases slightly within the range of \(x \leq 0.04\). With further increasing \(x\) to 0.05, there is a sharp decrease of \(P_r\). The drastically decreased \(P_r\) and thinned hysteresis loops indicates the phase transition from FE to AFE state.\(^{26}\) Agreeing to the above \(P(E)\) hysteresis loops, the compositions of \((1-x)\)BNT–xBNN with \(x \leq 0.04\) exhibit an archetypical butterfly shape curve [Fig. 3(b)]. However, the \((S(E)\) curves of 0.95BNT–0.05BNN and 0.94BNT–0.06BNN are different from that of the ferroelectric one. The strain disappears on removal of the electric field, and no negative strain is observed when the polarization orientation is reversed. This behavior is similar to that of ceramics with a dominated antiferroelectric order.\(^{26,27}\) According to the non-zero \(P_r\) and \(E_C\) for the compositions of \(x \geq 0.05\), it could be supposed that these compositions simultaneously possess both ferroelectric and antiferroelectric orders at room temperature.

Note that the \((1-x)\)BNT–xBNN ceramics exhibit enhanced piezoelectric properties. The piezoelectric coefficient \(d_{33}\) increases from 58 pC/N for pure BNT to 121 pC/N for \(x = 0.02\). The piezoelectric property \(f\) 0.98BNT–0.02BNN ceramics are comparable to the other BNT-based lead-free piezoelectric materials, such as 0.94(Bi0.5Na0.5)TiO3–0.06BaTiO3 and 0.92(Bi0.5Na0.5)TiO3–0.08BiAlO3.\(^{28}\) The improved piezoelectric properties could be attributed to the decreased \(E_C\), which makes it easier to get the ceramics full poled during the poling process. Furthermore, the enhanced piezoelectric properties may also associate with the decrease in the depolarization temperature \(T_d\) from \(\sim 200°C\) for pure BNT to 143°C for \(x = 0.02\). The similar relationship between the piezoelectric coefficient and the depolarization temperature could also be observed in the \((1-x)-(Bi_0.5Na_0.5)TiO_3-xBaTiO_3\) ceramics.\(^{29}\) It is well-known that the loss of macro-ordering and decay back to a disordered microdomain texture takes place at the depolarization temperature, thus the depolarization temperature can be seen as an indication of the stability of ferroelectric domains.\(^{30}\) The decreased depolarization temperature suggests that the addition of BNN makes the ferroelectric domains less stable, and as a result, the reorientation of the 90° domains becomes easier. Therefore, the piezoelectric properties are improved in the BNT–BNN ceramics.

In order to detect the detail phase transition of FE–AFE, temperature dependence of piezoelectric properties were investigated from RT to 150°C with intervals of 25°C. The \(P(E)\) loops of 0.98BNT–0.02BNN exhibit a typical hysteresis curve below 75°C [Fig. 4(a)]. Similar to the composition dependence of \(P(E)\) loops, the \(E_C\) decreases with increasing temperature, resulted from the reduction of the crystal lattice distortion. Both \(P_t\) and \(P_r\) decrease with increasing temperature [Fig. 4(b)]. Once the temperature is increased to 75°C, the hysteresis loop becomes slightly constrained, and the constriction becomes more and more serious with increasing temperature. The negative strain of \(S(E)\) curves decreases with the increase of temperature, and it completely disappears at 150°C [Fig. 4(c)], indicating a characteristic of antiferroelectric state.\(^{31}\) This is consistent with the \(T_d\) evaluated from temperature-dependent relative permittivity measurement as mentioned before. Although the \(P_t\) decreases obviously, it is still non-zero even at 150°C. Corresponding to the broad dielectric peak, the antiferroelectric phase arises below 150°C and coexists with the ferroelectric phase in a wide temperature range.

Temperature dependence of unipolar \(S(E)\) curves are also utilized for the analysis of the phase transition of FE–AFE [Fig. 4(d)]. The electric field induced unipolar strain increases gradually from RT to 50°C, followed by a sharp increase from 50 to 75°C, then the growth trend of strain turns to be slow and reaches the highest value at 125°C. Further increasing the temperature up to 150°C, the strain, however, decreases. Below 50°C, there is no AFE order, thus no contribution of field induced.
FE–AFE transition to strain. Therefore, the increase in strain below 50°C is attributed to the piezoelectric effect and the non-180° domain switching. When the temperature reaches up to 75°C, the BNT–BNN has mixed FE–AFE orders, evidenced by the constricted FE loops. The strain accounts for both contributions from the onset of FE–AFE phase transition and the strain from the domain reorientation of the FE phase. At the same time, it is also corresponding to the dielectric loss where it gets the highest value at around 75°C.

4. Conclusions

In conclusion, the pure pervoskite phase of \((1-x)\)BNT–xBNN \((x \leq 0.06)\) can be formed by the conventional solid solution method. The introduction of BNN can successfully decrease the \(E_C\) of pure BNT and improve the piezoelectric properties. Composition for 0.98BNT–0.02BNN exhibits enhanced piezoelectric coefficient \(d_{33} = 121\) pC/N, which is about twice of that of pure BNT. Temperature dependence of \(P(E)\) loops and \(S(E)\) curves suggest that the phase transition from FE to AFE of 0.98BNT–0.02BNN occurs in a wide temperature range from 75 to 150°C. Temperature dependent dielectric constant and loss show that it exhibits \(T_m = 285°C\), and \(T_d = 143°C\), respectively.

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