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Microstructure and electrical properties of $(1-x)[0.82Bi_{0.5}Na_{0.5}TiO_3–0.18Bi_{0.5}K_{0.5}TiO_3]–xBiFeO_3$ lead-free piezoelectric ceramics

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ABSTRACT

$(1-x)[0.82Bi_{0.5}Na_{0.5}TiO_3–0.18Bi_{0.5}K_{0.5}TiO_3]–xBiFeO_3$ lead-free piezoelectric ceramics (abbreviated as BNKT–BFx with x varying from 0 to 0.10 mol) were prepared by solid-state reaction process. Variation of the microstructure and piezoelectric properties of BNKT–BFx ceramics with BF content was investigated. The results indicated that the piezoelectric constant d_{33}, the planar electromechanical coupling factor k_p and mechanical quality factor Q_m varied with the BF amount. X-ray diffraction (XRD) analysis showed that the incorporated BF diffused into BNKT lattice to form a solid solution. Scanning electron microscope (SEM) also indicated that BF in high amount affected the microstructure. The morphotropic phase boundary (MPB) with rhombohedral and tetragonal coexistence for the ceramics lies in the range of $x = 0–0.06$ in $(1-x)$BNKT–xBF system. The optimum values of d_{33} and k_p are 122 pC/N and 0.317 at $x = 0.04$.

1. Introduction

Lead-free materials have recently been in demand owing to environmental protection concerns. The alternative materials are mainly focused on alkali niobates [1–3], bismuth layer structured [4] and tungsten bronze type oxide [5] and systems with perovskite structures in which a morphotropic phase boundary (MPB) occurs [6]. Like the perovskite type $Pb(Ti_{1-x}Zr_x)O_3$ (PZT) solid solution, where rhombohedral and tetragonal phases coexist, systems that include an MPB are especially interesting because their electromechanical properties are sharply enhanced at this boundary [7]. Bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (abbreviated as BNT), discovered by Smolensk and Aganovskaya [8] in 1960, has been considered to be a good candidate of lead-free piezoelectric ceramics because of its strong ferroelectricity at room temperature and high Curie temperature T_c of 320 °C [9–12]. However, BNT ceramics have high conductivity, causing some difficulty in the poling and their electromechanical properties are much lower than PZT ceramics. Furthermore, BNT ceramics depolarize above T_d. Some studies indicate that modifications of BNT ceramics can improve the poling process and the electrical properties. For examples, BNT-based compositions have been modified with $BaTiO_3$ [13], $Bi_{0.5}K_{0.5}TiO_3$ [14], $NaNbO_3$ [15], $BiFeO_3$ [16], La_2O_3 [17] and so on. Among the solid solutions that have been developed so far, $(1-x)Bi_{0.5}Na_{0.5}TiO_3–xBi_{0.5}K_{0.5}TiO_3$ (BNKT) system has attracted considerable attention because of the existence of rhombohedral–tetragonal morphotropic phase boundary (MPB) near $x = 0.18$ [18]. However, the electromechanical properties of the BNKT system are still too low to exceed their limits of practical use. In order to improve the piezoelectric properties of BNKT ceramics, in general, an approach to improve the electrical properties is compositional modification [19]. Because it has been demonstrated that a ternary system design is favorable to improve piezoelectric and ferroelectric properties [20]. Concerning bismuth ferrite, $BiFeO_3$(BF), has been of interest due to its simple perovskite structure with rhombohedral symmetry and high Curie temperature ($T_c = 836$ °C) [21].

In this article, $(1-x)$BNT–xBKT was selected as a representative of MPB compositions of $x = 0.18$ in the BNT–BKT system, and $BiFeO_3$ was selected as the modification component. $(1-x)[0.82Bi_{0.5}Na_{0.5}TiO_3–0.18Bi_{0.5}K_{0.5}TiO_3]–xBiFeO_3$ ceramics were prepared by solid-state process and the effect of $BiFeO_3$ addition on the microstructure and electrical properties was investigated.

2. Experimental procedure

$(1-x)[Bi_{0.5}Na_{0.5}TiO_3–Bi_{0.5}K_{0.5}TiO_3]–xBiFeO_3$ ceramics ($x = 0$, 0.02, 0.04, 0.06, 0.08 and 0.10) were prepared by a conventional ceramics technique. Reagent grade oxide or carbonate powders of Bi_2O_3, Na_2CO_3, K_2CO_3, TiO_2 and Fe_2O_3 were used as starting materials. BNT, BKT, and BF were prepared at first separately. BNT was calcined at 850 °C for 2 h and BKT and BF were calcined in the pressed pellet form

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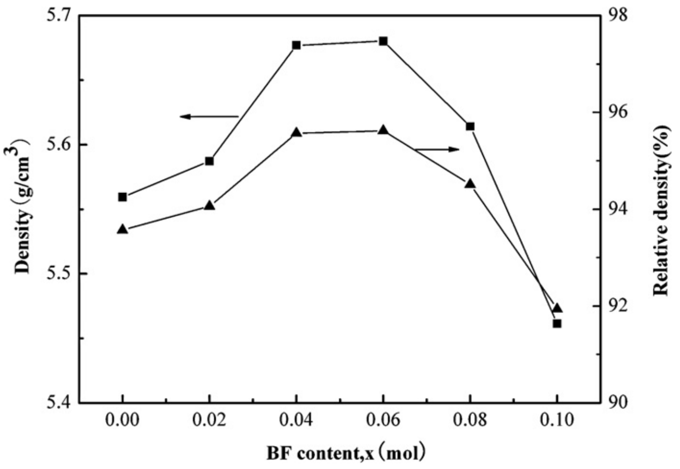

Fig. 1. Dependences of measured density and relative density on BF content for BNKT–BF*x* ceramics.

at 800 °C for 3 h. Then, they were weighted according to the above-mentioned formula. The powders were wet ball-milled with alcohol as media for 24 h. The dried mixtures were added with polyvinyl alcohol as a binder. The granulated powders were pressed into discs with diameter 12 mm and thickness 1.2 mm under a uniaxial pressure of 200 MPa. The compacted discs were sintered from 1140 to 1200 °C for 2 h.

The sintered density of the ceramic samples was measured by the Archimedes' technique. The crystalline phase of sintered ceramics was identified by X-ray diffraction (XRD) analysis with Cu Kα radiation (λ = 1.5418 Å). The microstructure of sintered samples was observed by means of scanning electron microscope (SEM).

The sintered discs were polished for electrical property measurements. Silver paste was fired on both faces of the discs at 850 °C as electrodes. The specimens for measurement of piezoelectric properties were poled in silicone oil at 30–40 °C under 3–4 kV/mm for 30 min.

Piezoelectric constant d_{33} was measured by means of a quasi-static d_{33} meter (ZJ-4A, China) based on the Berlincourt method at 110 Hz. Planar electromechanical coupling factor k_p and mechanical quality factor Q_m were measured using an impedance analyzer (Agilent 4294A) by a resonant and anti-resonant method.

3. Results and discussion

Fig. 1 shows the dependences of the measured density and relative density of the BNKT–BF*x* ceramics as a function of BF content. The measured densities of the BNKT–BF*x* bulk samples increase with increasing BF content and then decrease. As shown in Fig. 1, although the measured and relative densities have decreased with BF content above 0.06, the relative density was still above 92%. This fact suggests that all the BNKT–BF*x* ceramics are well sintered.

The similar XRD patterns for all the BNKT–BF*x* ceramics sintered at 1150 °C for 2 h in air were observed. Fig. 2 shows the XRD patterns of $(1-x)$BNKT–xBF ceramics in the 2θ range of 20–90°. It can be seen that BNKT–xBF ceramics possess a single-phase perovskite structure, which indicates that K^+, Bi^{3+} and Fe^{3+} ions diffuse into BNKT lattices to form solid solutions. As the BF addition increases, the (1 1 0) peak of these BNKT–BF*x* ceramics gradually shift to the lower 2θ angles because Fe^{3+} (0.65 Å) has a larger radius than Ti^{4+} (0.61 Å). The XRD patterns in the 2θ range of 38–48 ° for the ceramics samples with various amounts of $BiFeO_3$ are shown in Fig. 3. Splitting of XRD peaks was detected for the samples with $x = 0$. They can be assigned to a (0 0 3)/(0 2 1) peak splitting and a (0 0 2)/(2 0 0) peak splitting according to the rhombohedral symmetry and tetragonal symmetry, respectively. This characterizes the coexistence of rhombohedral and tetragonal phases, which is consistent with the nature of the specimen with an MPB composition. When the $BiFeO_3$ content $x \leq 0.06$, the ceramics samples maintained the coexistence of the two phases. However, the (0 0 3)/(0 2 1) peak splitting is slight and (0 0 2)/(2 0 0) peak merges into a single (2 0 2) peak at $x \geq 0.08$ and when $x = 0.10$, the phenomenon is obvious, which indicates that the crystalline structure varies from the coexistence of rhombohedral and tetragonal phases to a rhombohedral phase.

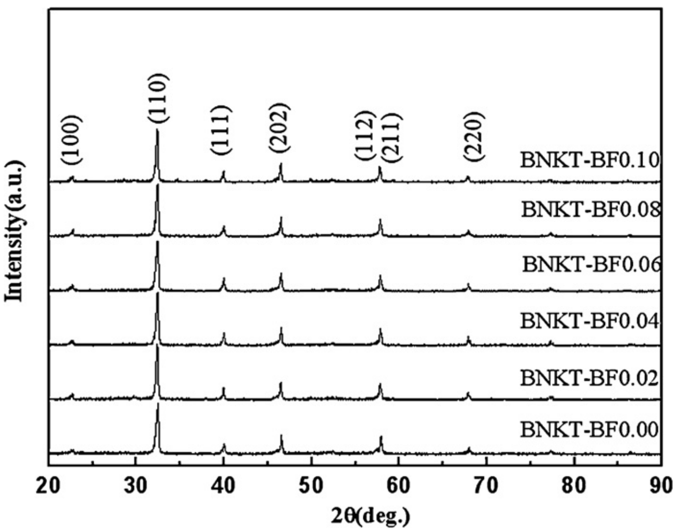

Fig. 2. XRD patterns of $(1-x)$BNKT–xBF ceramics sintered at 1150 °C for 2 h.

Fig. 4 shows the microstructures of the sintered BNKT–BF*x* ceramics containing 0, 0.02, 0.04, 0.06, 0.08 and 0.10 mol BF observed using SEM. Almost no pores are found on the surface and all specimens are dense. From Fig. 4, it shows that the incorporation of BF causes denser in the microstructure and a slight increase in the grain size. It is because that Fe^{3+} enters into the sixfold coordinated B-site of the perovskite structure to substitute for Ti^{4+} because of radius matching. When the content of BF is above 0.08 mol, there is obviously liquid state in the BNKT–BF*x* ceramics samples. It causes the density and relative density of BNKT–BF*x* ceramics decrease, as shown in Fig. 1.

Fig. 5 reveals the piezoelectric constant d_{33} and the planar electromechanical coupling factor k_p of $(1-x)$BNKT–xBF ceramics as a function of BKT and BF content. d_{33} and k_p increase with the amount of BF up to 0.04, and then decrease with further increase with the BF amount in $(1-x)$BNKT–xBF systems. The samples near the MPB composition show the optimal piezoelectric properties. The maximum values of d_{33} = 122 pC/N and k_p = 0.317 are obtained at x = 0.04.

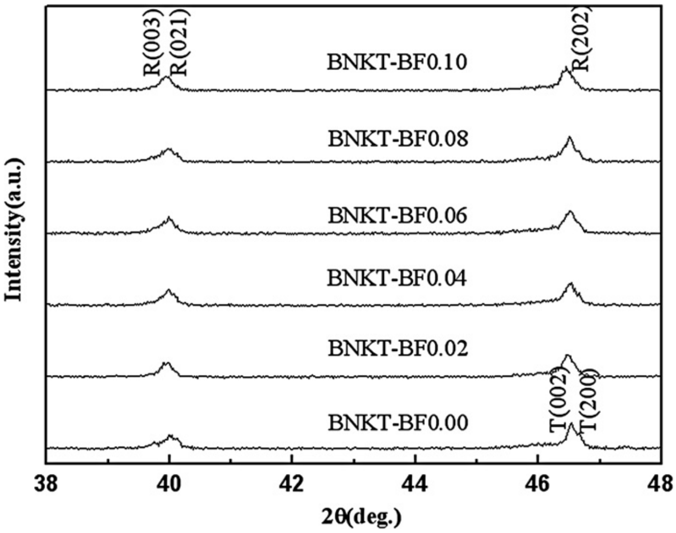

Fig. 3. XRD patterns of $(1-x)$BNKT–xBF ceramics in the 2θ range of 38–48°.

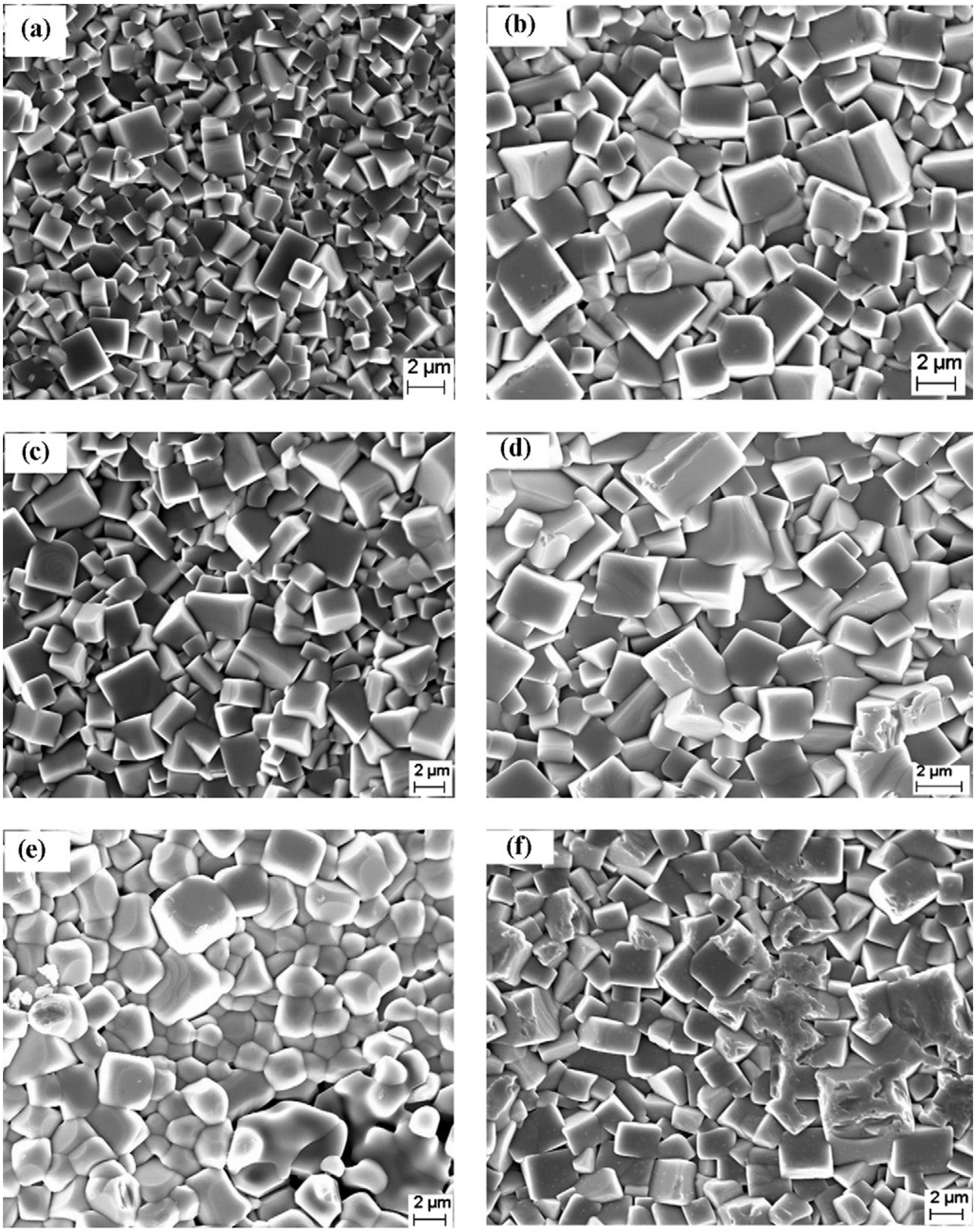

Fig. 4. SEM images of BNKT–BFx ceramics sintered at 1150 °C for 2 h: (a) $x = 0$; (b) $x = 0.02$; (c) $x = 0.04$; (d) $x = 0.06$; (e) $x = 0.08$; and (f) $x = 0.10$ mol.

The "soft" and "hard" additive model is a successful one that reveals the variation of piezoelectric properties [22]. According to "soft" and "hard" additive model, Bi^{3+} ionic of $BiFeO_3$ should enter into A-site of BNKT–BF ceramics to compensate the vapor of Bi in the sintering process, which does not cause obvious variation of piezoelectric properties. According to Shannon's effective ionic radius with a coordination number of six [23], Fe^{3+} ionic has a radius of 0.65 Å, which is close to that of Ti^{4+} ionic (0.61 Å). Therefore, Fe^{3+} ionic should enter into the sixfold coordinated-site of the perovskite structure to substitute for Ti^{4+} because of radius matching. Due to a lower valence state compared with Ti^{4+}, the incorporation of Fe^{3+} ionic into the octahedral site of the structure produced excess negative charges and oxygen vacancies are created. The clamping effect association with oxygen vacancies hinders sufficient reorientation of ferroelectric domains during electrical poling and leads to a decrease of d_{33}, k_p. Therefore, the "soft" and "hard"

Table 1
The properties of BNKT–BF ceramics as a function of BF content.

Composition	Sintering temperature (°C)	Density (g/cm^3)	tan δ	k_p	Q_m	d_{33} (pC/N)
BNKT–BF0.00	1150	5.559	0.050	0.263	110	100
BNKT–BF0.02	1150	5.587	0.046	0.285	100	104
BNKT–BF0.04	1150	5.677	0.045	0.317	94	122
BNKT–BF0.06	1150	5.680	0.051	0.302	89	113
BNKT–BF0.08	1150	5.614	0.053	0.296	83	110
BNKT–BF0.10	1150	5.461	0.054	0.275	80	103

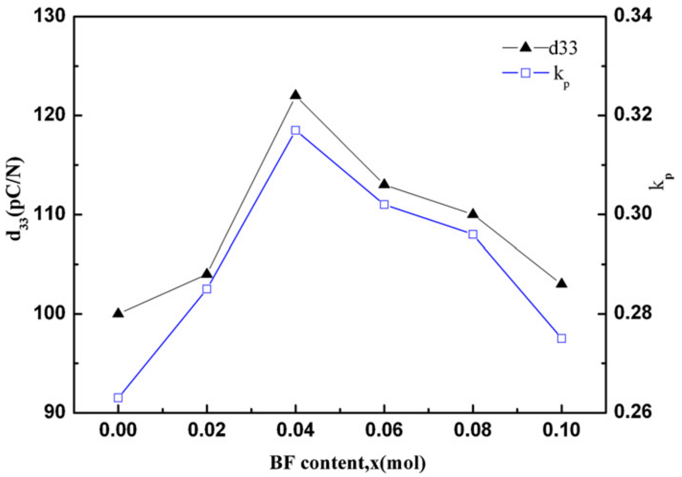

Fig. 5. Piezoelectric constant d_{33} and planar electromechanical coupling factor k_p of $(1-x)$BNKT–xBF ceramics as a function of the content of BF.

additive theory well explains the change of piezoelectric properties such as d_{33}, k_p in BNKT–BF ceramics. At the same time, Q_m should increase with the increasing of $BiFeO_3$ content. However, Q_m variation of BNKT–BF ceramics cannot be used in the "soft" and "hard" additive theory analysis to explain.

In a polycrystalline system, dielectric and piezoelectric properties are dependent on both intrinsic and extrinsic mechanisms [24,25]. Intrinsic contributions are from the relative ion or cation shift that preserves the ferroelectric crystal structure. The extrinsic contributions are from the domain wall motion. The extrinsic mechanisms are thermally activated processes and can be frozen out at very low temperature. The intrinsic mechanisms are due to MPB missing in BNKT–BF system with the BF content increasing. Thus, the mechanical quality factor Q_m decreases with the BF content increasing. The properties of BNKT–BF ceramics as a function of BF content are shown in Table 1, in which most electrical properties vary with a similar tendency.

4. Conclusion

A study on the microstructure and electrical characterization of $BiFeO_3$-doped $0.82Bi_{0.5}Na_{0.5}TiO_3$–$0.18Bi_{0.5}K_{0.5}TiO_3$ lead-free piezoelectric ceramics was conducted. Dense ceramics were successfully obtained by the ordinary sintering method in air. The addition of $BiFeO_3$ caused a promoted grain growth in the BNKT system. The morphotropic phase boundary (MPB) with rhombohedral and tetragonal coexistence for the ceramics lies in the range of $x = 0$–0.06 in $(1-x)$BNKT–xBF systems. It shifts from the coexistence of rhombohedral and tetragonal phases to a rhombohedral phase at $x \geq 0.08$. The optimum values of d_{33} and k_p are 122 pC/N and 0.317 at $x = 0.04$.

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