

Structure and properties of $(1-x)[(K_{0.5}Na_{0.5})NbO_3-LiSbO_3]-xBiFe_{0.8}Co_{0.2}O_3$ lead-free piezoelectric ceramics

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Abstract. Lead-free piezoelectric ceramics $(1-x)[0.95(K_{0.5}Na_{0.5})NbO_3-0.05LiSbO_3]-xBiFe_{0.8}Co_{0.2}O_3$ (KNN-LS- x BFC) were prepared by a conventional sintering technique. The effect of BFC content on the structure, piezoelectric and electrical properties of KNN-LS ceramics was investigated. The results reveal that the BFC is effective in promoting the sinterability and the electrical properties of the ceramics sintering at low temperature of 1030°C. The ceramics show a single perovskite structure, in which the tetragonal phase decreases while the orthorhombic phase increases with the increase of x . The more the BFC content is, the smaller and homogeneous grains were formed. With the increase of x , the d_{33} and the k_p increase to a maximum value and then slightly decrease, but the Q_m increases continuously. As BFC content increases, the Curie temperature T_c and remnant polarization P_r decrease, but the diffusivity of phase transition in KNN-LS ceramics will intensify and the coercive field E_c fluctuate between 1.16 and 1.51 kV mm⁻¹. The samples with $x = 0.004$ exhibit optimum electrical properties at room temperature ($d_{33} = 268$ pC N⁻¹, $k_p = 52\%$, $\epsilon_r = 1366$, $\tan \delta = 2.11\%$, $T_c = 325^\circ\text{C}$, $P_r = 20.4$ $\mu\text{C cm}^{-2}$, $E_c = 1.16$ kV mm⁻¹).

Keywords. Piezoelectric ceramics; KNN-LS; BFC-doping; properties.

1. Introduction

As important functional material, piezoelectric ceramics are mainly used in sensors, actuators and transducers. From many decades, lead-base piezoceramics play a dominant role in industrial production of piezoelectric applications owing to their excellent electrical properties [1,2]. However, PbO is a toxic oxide, which lead to environmental pollution and seriously threaten humans health [3,4]. More and more countries have restricted the use of lead-base ceramics by law [5,6]. Therefore, investigation in environment-friendly ceramics with excellent piezoelectric properties to replace the lead-base piezoceramics becomes an emergent work. Till now, the extensive investigation for lead-free piezoelectric ceramics mainly focus on three systems: $Na_{0.5}Bi_{0.5}TiO_3$ -based materials, $BaTiO_3$ -based ceramics and $K_{(1-x)}Na_xNbO_3$ -based ceramics [3–8].

Among the different alternatives, $K_{0.5}Na_{0.5}NbO_3$ -based (KNN) ceramics are considered as one of the promising substitutes for lead-base piezoceramics, due to their high Curie temperature and good piezoelectric properties [8,9]. However, dense and well-sintered pure KNN-base ceramics are difficult to obtain by conventional sintering method. It has been reported that $BiScO_3$ [10], $BiFeO_3$ [11], $BiCoO_3$ [12] are effective in improving the density and electrical properties of (KNa)NbO₃ ceramics. In preliminary works, we observed that the partial Co (20%) suitable for Fe is helpful to improve the properties of $(K_{0.5}Na_{0.5})NbO_3-LiSbO_3-BiFe_{1-x}Co_xO_3$ ceramics [13].

In this work, $BiFe_{0.8}Co_{0.2}O_3$ (BFC) was chosen as a sintering aid to add into $0.95(K_{0.5}Na_{0.5})NbO_3-0.05LiSbO_3$ (KNN-LS) basic composition, and the effect of BFC doping on the structure, piezoelectric and electrical properties of samples is investigated.

2. Experimental

A series of $(1-x)[0.95(K_{0.5}Na_{0.5})NbO_3-0.05LiSbO_3]-xBiFe_{0.8}Co_{0.2}O_3$ (KNN-LS- x BFC) ($x = 0.000, 0.002, 0.004, 0.006, 0.008$) samples were prepared by the conventional solid-state reaction method using analytical-grade metal oxides and carbonates powders: Na_2CO_3 (99.5%), K_2CO_3 (99.5%), Li_2CO_3 (99.8%), Sb_2O_3 (99.5%), Nb_2O_5 (99.5%), Bi_2O_3 (99.9%), Fe_2O_3 (99.9%) and Co_2O_3 (99.5%). The stoichiometric powders were mixed by ball-milling in alcohol for 24 h, then, the mixed powders were calcined at 880°C for 6 h. The calcined mixture was ball-milled again for 12 h, then dried, sifted and mixed with 5 wt% poly vinyl alcohol (PVA) solution. The obtained powders were pressed into pellet disk of 15 mm diameter and 1.2–1.5 mm thickness. After burning off PVA, pellets were sintered at 1030°C for 3 h. Silver paste electrodes were formed on top and bottom surfaces of the samples after firing at 600°C for 10 min. For electrical measurements, the samples were poled at 80°C in a silicon oil bath at 3.5 kV mm⁻¹ for 15 min.

Phase purity and crystal structure of sintered ceramics were characterized using X-ray diffraction (XRD) (D8-2-Advanced, Bruker Inc. Germany) with $CuK\alpha$ radiation. The microstructure was observed by a scanning electron

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microscope (SEM) (JSM-5610LV). The piezoelectric constant (d_{33}) was measured using a quasi-static piezoelectric meter (ZJ-3A). The planar electromechanical coupling coefficient (k_p), mechanical quality factor (Q_m), dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) were measured by impedance analyzer (Agilent4294A). Ferroelectric hysteresis (P - E) loops were measured at room temperature using a ferroelectric tester (Radiant Precision Workstation, USA).

3. Results and discussion

Figure 1a shows the X-ray diffraction (XRD) patterns of KNN-LS- x BFC ceramics with various x sintered at 1030°C. It is seen that all the specimens show a pure perovskite phase at room temperature, and no secondary phase is observed in the investigated range. From figure 1a, it is observed that the specimens with $x \leq 0.002$ show a typical structure of tetragonal phase, in agreement with JCPDS card no. 71-0945 for KNN, but the double peaks at 22 and 45° are gradually

weakened and amalgamated into a single peak with the increase of BFC content, which indicated that the phase structure changes from tetragonal phase to orthorhombic phase, in agreement with JCPDS card no. 71-2171 for KNN. The XRD pattern around $x = 0.002$ – 0.008 shows mixed phases. This result indicates that the BFC has completely diffused into the KNN lattice to form a new solid solution in the investigated range and the transition point for the structural change is confirmed to be around $x = 0.002$ – 0.008 . Figure 1b shows the magnified XRD of KNN-LS- x BFC ceramics in the range of 44–47°. It also found that the (200) and (020) peaks positions shift slightly towards higher angles with $x \leq 0.004$, but while $x > 0.004$, the diffraction peaks positions shift towards lower angles. This may be due to the Co^{2+} ions enter into A- and B-sites of the perovskite structure and lead to a variation of lattice parameter. The smaller ionic radius of Co^{2+} (0.72 Å) substituted A-site ion (Na^+ : 0.97 Å) while $x \leq 0.004$, the lattice parameter decreases; when BFC content further increases, the Co^{2+} begin to diffuse into B-site ions (Nb^{5+} : 0.69 Å), and the lattice parameter increases.

SEM micrographs of the microstructure of KNN-LS- x BFC ceramics with various BFC contents sintered at 1030°C are shown in figure 2a–d. From figure 2, it can be seen that the microstructures of BFC doped KNN-LS ceramics are dense, and the crystalline grains show cubic shape, but the grain size becomes smaller and homogeneous with increase in the BFC content, which indicated that the addition of BFC is effective to crystalline refinement. Some larger grains and holes have been observed in KNN-LS without doping BFC shown in figure 2a, but the size of grain and number of holes decrease with increasing the BFC content as shown in figure 2b. However, no abnormal larger grains are observed in the samples when $x \geq 0.004$, as shown in figure 2c–d, the grains are relatively homogeneous and the size of grain decreases.

Figure 3 shows the piezoelectric properties of KNN-LS- x BFC ceramics with various BFC contents. From figure 3a, it can be seen that the piezoelectric constant d_{33} and planar electromechanical coupling coefficient k_p exhibit the similar transformational trend with increase in the BFC contents, i.e., d_{33} and k_p increases with the increase of x reaches a maximum value of $d_{33} = 276 \text{ pC N}^{-1}$ when $x = 0.002$ and $k_p = 52\%$ when $x = 0.004$, respectively, and then slightly decreases. Similar phenomenon was also observed in non-stoichiometric NKNT ceramics reported by Lee [14], and the increase of k_p is attributed to the increase of density and uniformity of the grain size. In addition, the value of mechanical quality factor Q_m for the ceramics initially increases slightly with increase of the BFC contents when $x < 0.002$, following a sharp increase from 31 ($x = 0.002$) to 56 ($x = 0.004$), then again to a slow increase, indicating that the addition of BFC is effective to increase the Q_m . The main reason for the phenomenon is attributed to the ion substitution. When BFC was doped into KNN-LS ceramics, most of the Co^{2+} substituted for Nb^{5+} to produce the oxygen vacancies, which result in a pinning effect on the domain walls, and as the amount of BFC is increased, the oxygen vacancies are also increased.

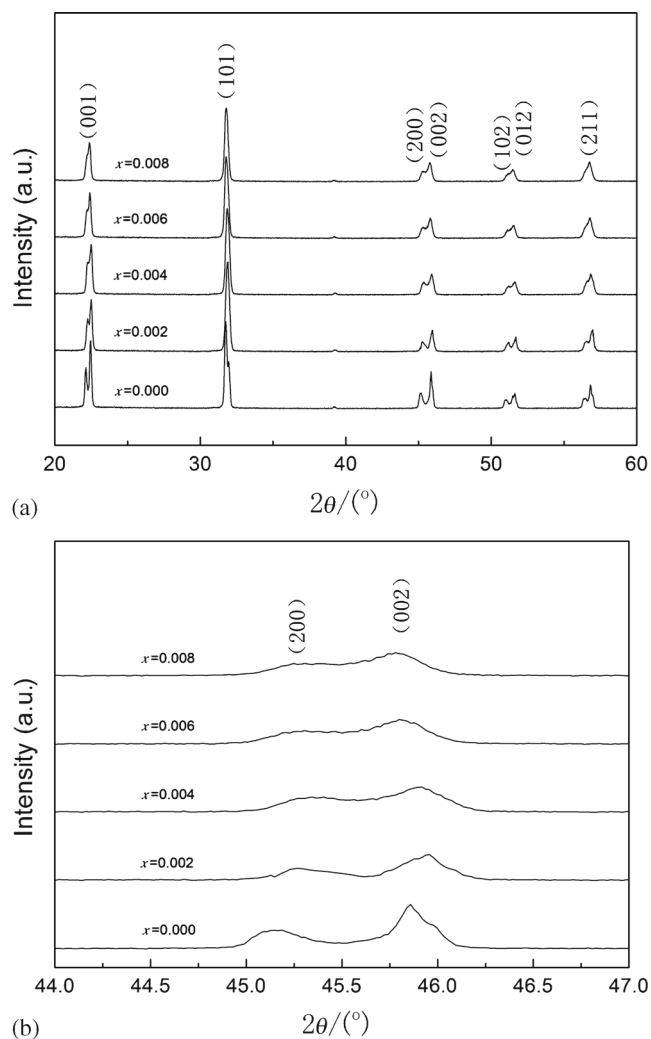


Figure 1. XRD patterns of KNN-LS- x BFC ceramics sintered at 1030°C.

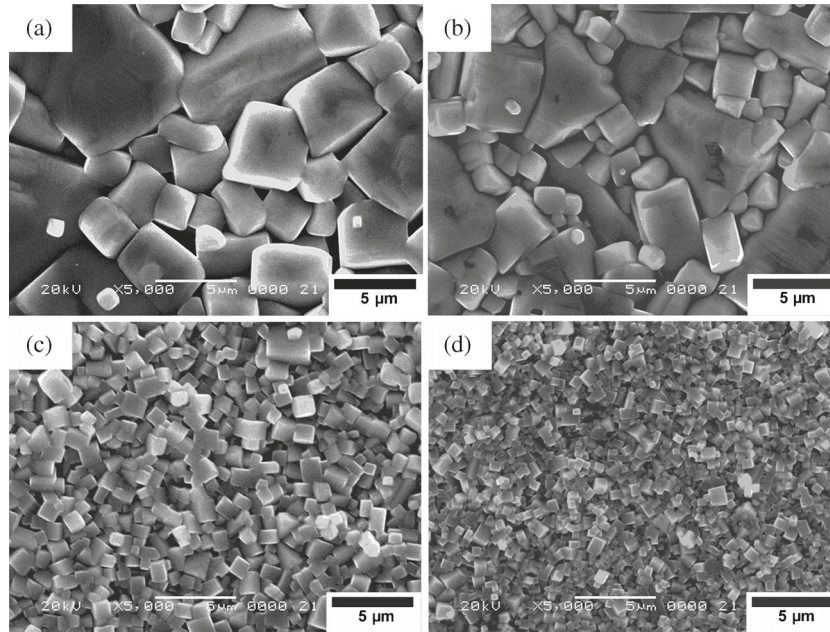


Figure 2. SEM micrographs of KNN-LS- x BFC ceramics with various x : (a) $x = 0$; (b) $x = 0.002$; (c) $x = 0.004$ and (d) $x = 0.006$.

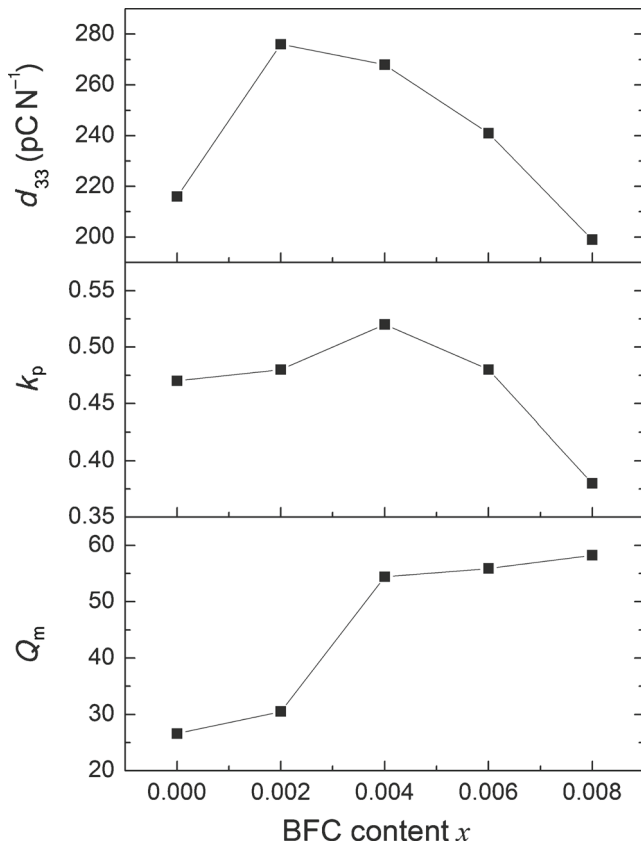


Figure 3. Compositional dependence of piezoelectric properties of KNN-LS- x BFC ceramics.

The result indicates that the doping of BFC cause ‘hard doping’ effect in the KNN-LS- x BFC ceramics. Through contrast, it is easy to find that the value of d_{33} (276 pC N^{-1})

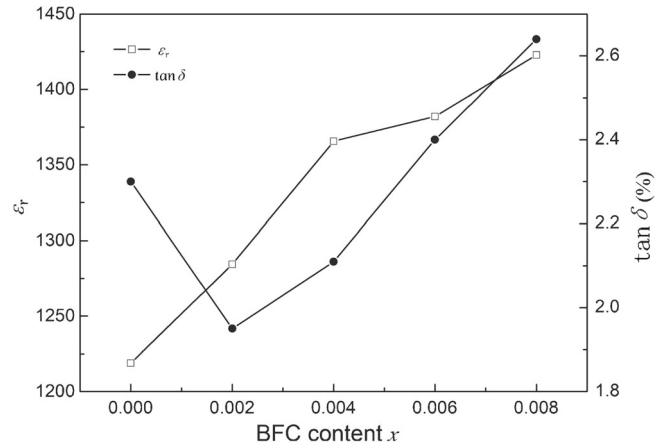


Figure 4. ϵ_r and $\tan \delta$ of KNN-LS- x BFC ceramics as a function of x .

for KNN-LS- x BFC ceramics with $x = 0.004$ is higher than that of 231 pC N^{-1} for KNN-LS-BF ceramics sintering at 1100°C [15], but in the k_p and Q_m only tiny changes occur.

Figure 4 shows the variation in dielectric properties ϵ_r and dielectric loss $\tan \delta$ values of the KNN-LS- x BFC ceramics measured at room temperature. It can be seen that the dielectric constant ϵ_r increase with the increase of BFC contents x from 0 to 0.008, but the dielectric loss $\tan \delta$ decreases to a lowest value of 1.95% with the increase of BFC contents x from 0 to 0.002, then increase with the further increase of BFC contents x . It is considered that the variety of dielectric constants and dielectric loss may be ascribe to the change of grain size and density of the ceramic. Similar to the d_{33} , the electrical properties ($\epsilon_r = 1284\text{--}1366$, $\tan \delta = 1.95\text{--}2.11\%$) of KNN-LS- x BFC ceramics with $x = 0.002\text{--}0.004$

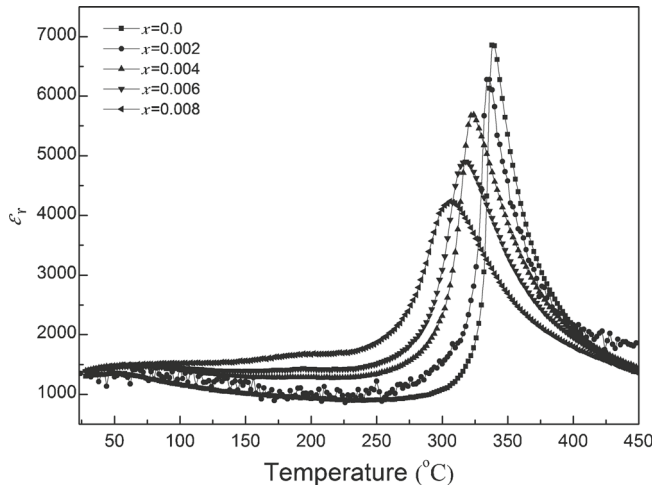


Figure 5. Temperature dependence of ϵ_r for KNN-LS- x BFC ceramics measured at 1 kHz.

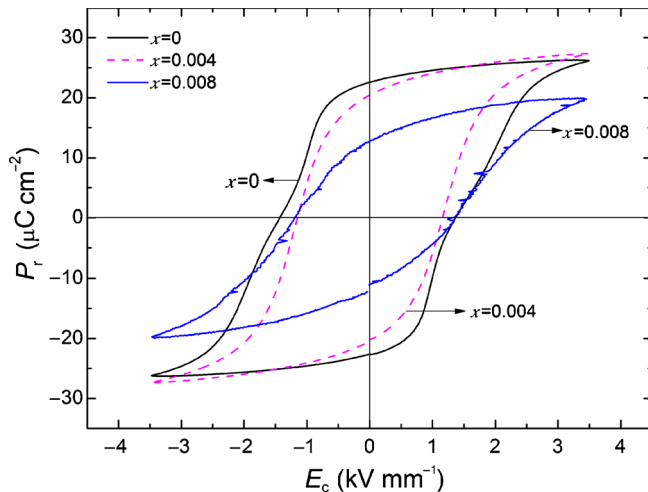


Figure 6. P - E hysteresis loops of the KNN-LS- x BFC ceramics.

are also better than that ($\epsilon_r = 1041$, $\tan \delta = 3.15\%$) of KNN-LS-BF ceramics [15], these results indicated that the suitable amounts of BFC can improve the electrical properties of KNN-LS- x BFC ceramics.

Figure 5 shows the temperature dependence of the dielectric constant ϵ_r for KNN-LS- x BFC ceramic measured at 1 kHz. From figure 5, it can be seen that all samples of KNN-LS- x BFC ceramics exist as a single peak in the curve, corresponding to the Curie temperature (T_c) of tetragonal-cubic ferroelectric phase transition, and the orthorhombic-tetragonal phase transition temperatures are all lower than room temperature. From the illustration, it also can be seen that the T_c peak shift continually towards lower temperature with the increase of BFC content x , indicating that the T_c decreases with the increase of BFC content x . When BFC content x increased from 0 to 0.008, the T_c decreased from 340 to 305°C. Besides, it can be observed that the T_c peak broaden with the increase of BFC content x , which indicated

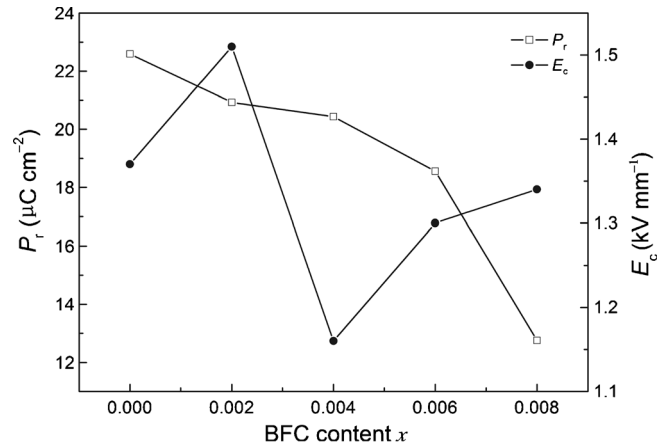


Figure 7. P_r and E_c of KNN-LS- x BFC ceramics as a function of x .

that the introduction of BFC would conduce the diffusivity of phase transition in KNN-LS ceramics.

Figure 6 shows the P - E hysteresis loops of the KNN-LS- x BFC ceramics. All the samples show a hysteresis loop of P - E when an electric field of 3.5 kV mm^{-1} is applied. From figure 6, it can be seen that the shapes of P - E loop for samples with various BFC contents x are different. The P - E loops for KNN-LS- x BFC ceramics with $x \leq 0.004$ are more saturated, suggesting better ferroelectric properties. Variations of the remnant polarization (P_r) and the coercive field (E_c) of the KNN-LS- x BFC ceramics are showed in figure 7. As can be seen, P_r decreases from 22.59 to $12.75 \text{ } \mu\text{C cm}^{-2}$ as BFC content x increase from 0 to 0.008, but the E_c of the ceramics initially increases to a maximum value of 1.51 kV mm^{-1} with the increase of BFC content before $x = 0.002$, then decrease sharply to the minimum value of 1.16 kV mm^{-1} when $x = 0.004$, finally increases again when $x > 0.004$. The decrease in P_r is due to the reduced grain amount in tetragonal phase. As for the variety of E_c , further work needs to be carried out to understand the reasons behind it.

4. Conclusions

BFC can be completely diffused into the KNN lattice to form a new solid solution in the investigated range, and good piezoelectric properties of the ceramics can be obtained with proper BFC content at low sintering temperature of 1030°C . The ceramics contain a single perovskite structure with tetragonal phase and orthorhombic phase, but the tetragonal phase decreases while the orthorhombic phase increases with the increase of x . The grain size KNN-LS- x BFC ceramics becomes smaller and homogeneous with increase in the BFC content, which indicated that the addition of BFC is an effective method to crystalline refinement. With the increase of BFC content x , the Curie temperature T_c decreases, but the T_c peak broadens, which indicated that the introduction of BFC would conduce the diffusivity of phase

transition in KNN–LS ceramics. The d_{33} and k_p increase with the increase of x to a maximum value of $d_{33} = 276 \text{ pC N}^{-1}$ when $x = 0.002$ and $k_p = 52\%$ when $x = 0.004$, respectively, and then slightly decreases, but the Q_m increases continuously. The P – E loops for KNN–LS– x BFC ceramics with $x \leq 0.004$ are more saturated, suggesting better ferroelectric properties. With the increase of BFC content x , remnant polarization P_r decreases continually, but the coercive field E_c fluctuate between 1.16 and 1.51 kV mm⁻¹. For the compositions of $x = 0.004$, the samples exhibit optimum piezoelectric and ferroelectric properties at room temperature.

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