Contribution of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ on Phase Boundary and Piezoelectricity in $\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-Bi}_{0.5}\text{Na}_{0.5}\text{SnO}_3\text{-}x\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ Ternary Ceramics

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Abstract: In this work, we have attained a large piezoelectricity ($d_{33} \sim 468 \text{ pC N}^{-1}$) in $(0.9925-x)\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-}0.0075\text{Bi}_{0.5}\text{Na}_{0.5}\text{SnO}_3\text{-}x\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ (abbreviation: KNNS-BNS- x BNZ) ternary ceramics, prepared by a conventional solid-state reaction method. We illuminated the role of BNZ on the phase boundary and piezoelectric properties of the ceramics. Rhombohedra-orthorhombic-tetragonal (R-O-T) phase coexistence can be developed by controlling BNZ content, and then a high d_{33} value of $\sim 468 \text{ pC N}^{-1}$ can be attained in the ceramics with $x=0.03$. This result indicates that a higher d_{33} value can be attained by forming a new phase boundary using the addition of BNZ with respect to those of $0.9925\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-}0.0075\text{Bi}_{0.5}\text{Na}_{0.5}\text{SnO}_3$ ceramics with an orthorhombic phase. In addition, the maximum value both strain and d_{33}^* are all obtained at $x = 0.04$ (strain $\sim 0.18\%$ and $d_{33}^* \sim 440 \text{ pm/V}$), which means that optimum BNZ content can enhance the strain and d_{33}^* of the ceramics. As a result, the ternary ceramic system may become one of the most promising candidates for the practical applications of KNN-based materials.

Keywords: (K,Na)NbO₃; Ternary system; Phase boundary; Piezoelectricity

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1. Introduction

It is well known that $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT)-based ceramics have drawn a lot of attention and then dominated most of the piezoelectric devices markets because of their excellent piezoelectricity. [1] However, the lead content (~ 60 wt %) of the ceramics exerts pressure on the surrounding environment during their preparation and processing. [2,3] So, this is a good chance to develop lead-free piezoelectric ceramics for the substitutions of PZT-based ceramics. To maintain social sustainable development, lead-free piezoelectric ceramics have attracted much attention. Among lots of candidates, $(\text{K},\text{Na})\text{NbO}_3$ (KNN) has become one of the most extensively investigated piezoelectric systems in the past decade owing to its large piezoelectric constant (d_{33}) and high Curie temperature (T_C). [4] However, it is difficult to obtain the dense KNN ceramics owing to the volatility of the alkaline components during sintering. [5]

In 2004, a breakthrough was achieved by Satio *et al.*, that is, a large d_{33} value (~ 416 pC/N) was attained in KNN-based ceramics doped with Li, Ta, and Sb, where they successfully used the reactive template grain growth (RTGG) methods to fabricate the dense ceramics and form a orthorhombic-tetragonal (O-T) phase boundary. [6] After that, the constructions of phase boundaries by the addition of ions or secondary members to obtain an enhanced piezoelectric property of KNN-based ceramics have become a hot button. In the past decade, a number of successful attempts have made to construct several kinds of phase boundaries (R-O, [7-9] O-T[10-13] and R-T[13-21]) in KNN-based ceramics in order to induce the enhancement of piezoelectric activity.

Previously, it was failed to establish a phase boundary by doping $\text{Bi}_{0.5}\text{Na}_{0.5}\text{SnO}_3$ into $\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3$, [22] and then a pure O phase was only observed at room temperature. In addition, a piezoelectric property of this material can't be fully improved, and then the maximum d_{33} value of $\sim 195 \text{ pC N}^{-1}$ can be found in the $0.9925\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-}0.0075\text{Bi}_{0.5}\text{Na}_{0.5}\text{SnO}_3$ ceramics. Recent research results also indicate that the addition of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$ could simultaneously increase $T_{\text{R-O}}$ and decrease $T_{\text{O-T}}$ of KNN materials. [23] As a result, the new phase boundary may be realized in $0.9925\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-}0.0075\text{Bi}_{0.5}\text{Na}_{0.5}\text{SnO}_3$ ceramics by introducing $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$. As a result, a new ternary material system consisting of $(0.9925\text{-}x)\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-}0.0075\text{Bi}_{0.5}\text{Na}_{0.5}\text{SnO}_3\text{-}x\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ was developed, and we hope to realize the enhancement of piezoelectric properties by controlling the BNZ compositions.

2. Experimental procedure

KNNS-BNS- x BNZ lead-free piezoelectric ceramics were prepared by the conventional solid-state method, and raw materials were highly pure carbonates and oxides [e.g., K_2CO_3 (99%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), Sb_2O_3 (99.99%), Bi_2O_3 (99.999%), SnO_2 (99.8%), ZrO_2 (99%)]. Those powders were weighed and ball mixed for 22 h with alcohol and dried to powders then. These powders were calcined at 850°C for 6 h in air, and then mixed with polyvinyl alcohol (PVA). After that, we pressed the powders into the disks of 10 mm diameter and 1 mm thickness under 10 MPa and burning off the PVA at 850°C in air. Then all samples were sintered at $1080\text{-}1120^\circ\text{C}$ for 3 h in air. Both sides of the disks were pasted with silver as electrodes and fired at 600°C for 10 min in air. Then, a direct current electric field of $2\text{-}4 \text{ kV mm}^{-1}$ was applied to the sample disks in the silicon oil bath at room temperature to induce the

piezoelectric properties.

Finally, we used series of methods to judge its properties. The phase structure was identified by X-ray diffraction (XRD) (Bruker D8 Advanced XRD, Bruker AXS Inc., Madison, WI, CuK α). The surface microstructure and element mapping of the samples was characterized by field emission-scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) (JSM-7500, Japan). The piezoelectric constant (d_{33}) was measured by piezo- d_{33} meter (ZJ-3 A, China) and the planar electromechanical coupling factor (k_p) was tested by impedance analyzer (HP 4194A). Their P - E hysteresis loops were measured using a Radiant Precision Workstation (USA) at 10 Hz and room temperature. By using a programmable furnace in connection with an LCR analyzer (HP 4980, Agilent, USA), we can get the curves of dielectric constant against temperatures (ϵ_r - T) of the ceramics.

3. Results and discussion

Figures 1(a)-(c) show the XRD patterns of the ceramics with different 2θ ranges. A pure perovskite structure without secondary phases was obtained in all samples, suggesting that BNZ can easily diffuse into the lattice. By combining both XRD patterns and ϵ_r - T curves [Figs. 1 and 2], it can be seen that an O phase is obviously appeared in the ceramics with $x=0$ and 0.01,²⁰ where their T_{R-O} (<-60 °C) and T_{O-T} (>95 °C) are far from room temperature. The O-T mixed phases are shown in the ceramics with $0.02 \leq x \leq 0.025$. However, the R-T phase coexistence can be formed in the ceramics with $0.035 \leq x \leq 0.04$, but their T_{R-T} (6-13 °C) is less than room temperature. The R phase can be observed in the ceramics with $0.05 \leq x \leq 0.06$, where the single peak can be exhibited. We simulated the XRD patterns ($2\theta=45-46^\circ$) of the

ceramics with $x=0.03$ by Lorentz method in order to identify the phase structure [See Fig. 1(d)]. It was found that the ceramics with $x=0.03$ possess multiphase coexistence of R, O, and T. As a result, the doping with BNZ can simultaneously raise T_{R-O} and reduce T_{O-T} of KNN, and finally results in the formation of new phase boundaries.

Figure 3(a) plots the ε_r - T curves of the ceramics in the temperature range from room temperature to 450 °C. As shown in Fig. 3(a), T_C of the ceramics gradually decreases with the increase of x , which means that the doping with BNZ cannot increase their T_C . In addition, we can find that the ε_r which locates at their T_C peaks, firstly increases and then decreases with increasing x , reaching a maximum value ($\varepsilon_r \sim 9920$) for $x=0.03$. This result also indicates the formation of new phase boundary. [24] Figure 3(b) is the phase diagram of the ceramics determined by both XRD patterns and ε_r - T curves. What can be seen is that phase boundary is very sensitive to the compositions of the materials. Both T_C and T_{O-T} decrease simultaneously with increasing BNZ contents, while T_{R-O} increases dramatically. What's more, the addition of BNZ shifts both T_{O-T} and T_{R-O} close to room temperature, and finally the multiphase coexistence can be achieved in the ceramics.

Figures 4(a)-(d) display the FE-SEM images of surface morphologies of the ceramics with $x=0, 0.02, 0.03$, and 0.05 . Figure 5 shows the statistics on the grain size distributions of the corresponding samples. The average grain sizes of the ceramics with $x=0, 0.02, 0.03$, and 0.05 are $3.45 \mu\text{m}$, $2.01 \mu\text{m}$, $2.49 \mu\text{m}$, and $0.21 \mu\text{m}$, respectively. More interestingly, the grain sizes drop dramatically for $x=0.05$ due to excess Bi^{3+} [25] and Zr^{4+} contents. [26]

Figure 6(a) shows the P - E loops of the ceramics as a function of BNZ content, measured at $f=10$ Hz and room temperature. We can observe a series of typical P - E loops in all samples. Figure 6(b) plots the remnant polarization (P_r) and coercive field (E_C) values of the ceramics as a function of BNZ content. It is obviously that E_C has a degrading trend with the increase of x , and P_r increases firstly with the addition of the BNZ and slightly decreases for $x>0.01$. In addition, P_r and E_C reduce slightly for the ceramics with $0.01 \leq x \leq 0.04$, and then dramatically decrease for $x>0.04$ owing to the decreased grain sizes.

Figure 7(a) shows the ε_r & $\tan \delta$ curves of the ceramics as a function of BNZ content, measured at 10 kHz and room temperature. We can see from Fig. 7(a) that ε_r gradually increases and then drops with the increase of x , and getting a maximum value for $x=0.03$. As for the $\tan \delta$ value, the ceramics shows a slight fluctuation. Figure 7(b) shows the composition dependence of d_{33} and k_p in KNNS-BNS- x BNZ ceramics. This result indicates that d_{33} is strongly dependent on the phase boundaries types. As shown in Fig. 7(b), one can find that d_{33} increases quickly and then decreases with the addition of x , a peak d_{33} value (~ 468 pC/N) can be clearly observed in the ceramics with $x=0.03$. In the past, it was thought that the R-T phase boundary can greatly promote the piezoelectric response of KNN-based ceramics. [16-21,24,27-28] However, it is difficult to form the R-T phase boundary at room temperature of this work, and their T_{R-T} is below room temperature. As a result, a high piezoelectricity cannot be observed in the ceramics with $0.035 \leq x \leq 0.04$. One can find that the R-O-T phase boundary can be formed in the ceramics with $x=0.03$, and then the enhanced piezoelectric properties can be clearly demonstrated [Fig. 7(b)]. Different from the piezoelectric constant, the k_p value keeps a high value for $x \leq 0.04$ and then

dramatically drops with further increasing x .

Figures 8(a)-(b) show the d_{33} and $\Delta d_{33}/d_{33}$ against annealing temperatures of the ceramics as function of BNZ. For the ceramics with $x < 0.05$, both d_{33} and $\Delta d_{33}/d_{33}$ slightly decrease with the increase of annealing temperatures (T_a) and then drop dramatically when T_a is near their corresponding T_C . As for the best composition, the d_{33} remains a higher value ~ 340 pC/N at $T_a \sim 250$ °C ($T_C \sim 240$ °C). That is to say, the ceramics has a good thermal stability of d_{33} , which is very important for practical applications. Figures 9(a)-(b) plot the electric-field-induced strain and converse piezoelectric coefficient ($d_{33}^* = S_{\max}/E_{\max}$) of the ceramics. The maximum value both strain and d_{33}^* are all obtained at $x = 0.04$ (strain $\sim 0.18\%$ and $d_{33}^* \sim 440$ pm/V), which means that optimum BNZ content can enhance the strain and d_{33}^* of the ceramics.

4. Conclusion

We obtained a large d_{33} value of ~ 468 pC N⁻¹ in the KNNS-BNS- x BNZ ternary ceramics with $x=0.03$ by constructing multiphase coexistence. In addition, the enhancement of the piezoelectricity is mainly attributing to the formation of R-O-T phase boundary. The ceramics with R-O-T phase boundary show the optimum electrical properties (i.e., $\epsilon_r \sim 2682$, $\tan \delta \sim 0.038$, $E_c \sim 8.17$ kV/mm, $P_r \sim 16.7$ $\mu\text{C}/\text{cm}^2$, $d_{33} \sim 468$ pC N⁻¹, $T_C \sim 240$ °C). As a result, it may be a feasible way to promote the piezoelectricity of KNN-based ceramics by constructing the ternary system.

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Figure captions

Figure 1. (a)- (c) XRD patterns of the ceramics as a function of BNZ, and (d) XRD patterns simulated by the Lorentz method of the ceramics with $x=0.03$

Figure 2. ε_r - T (-160~200 °C) curves of the ceramics as a function of x .

Figure 3. (a) ε_r - T (30~450 °C) curves of the ceramics as a function of x , and (b) phase diagram.

Figure 4. FE-SEM images of the ceramics with (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.03$, and (d) $x = 0.05$.

Figure 5 Grain size distribution of the ceramics with (a) $x=0$, (b) $x=0.02$, (c) $x=0.03$, and (d) $x=0.05$.

Figure 6. (a) P - E loops and (b) P_r and E_C values of the ceramics as a function of BNZ content.

Figure 7. Composition dependence of (a) ε_r and $\tan \delta$ and (b) d_{33} and k_p in KNNS-BNS- x BNZ ceramics.

Figure 8 (a) Thermal stability of the ceramics as a function of x and (b) their corresponding $\Delta d_{33}/d_{33}$ versus T_a .

Figure 9(a). (a) S - E curves and (b) strain and d_{33}^* values of the ceramics as a function of BNZ content.

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