Enhanced piezoelectric properties in potassium-sodium niobate-based ternary ceramics

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ABSTRACT: $(1-x)\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{1-y}\text{Sb}_y\text{O}_3-z\text{SrZrO}_3-x\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ (KNNS-SZ-BNH) lead-free ceramics were developed by the conventional solid-state reaction method. Effects of the additives ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$, SrZrO_3 and Sb^{5+}) on their phase structure, microstructure, and electrical properties were investigated. The rhombohedral-orthorhombic-tetragonal (R-O-T) phase boundary can be established in the ceramics with $0.03 \leq x \leq 0.05$, $0.04 \leq y \leq 0.06$, and $0.01 \leq z \leq 0.025$, and then their piezoelectric properties were improved. The ceramics with $x=0.03$, $y=0.04$ and $z=0.01$ possess the optimum piezoelectric properties ($d_{33}=470 \pm 5$ pC/N, $k_p=0.51 \pm 0.02$, and $T_C=244$ °C). We believe that R-O-T multiphase coexistence is mainly responsible for the enhancement of piezoelectric properties.

Keywords: (K,Na)NbO₃; Ternary System; Phase Boundary; Electrical Properties

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1. Introduction

Currently, lead zirconate titanate (PZT) and other lead-based counterparts play a predominant role in the electronic devices market because of their excellent electrical properties. However, high concentration lead over 60% in these materials harms people's health and contaminates the environment during fabrication process. Therefore, it is urgent to develop high-performance lead-free piezoceramics which are comparable to the lead-based ones [1-5].

Pure potassium-sodium niobate (KNN) ceramic possesses a high T_C of 415 °C, which is considered as one of the most promising lead-free materials to replace the lead-based ones. Unfortunately there is an inferior d_{33} (80~160 pC/N), which still cannot meet the demand of practical applications [2-5]. According to the previous reports, the excellent piezoelectric properties of lead-based ceramics were mainly attributed to the formation of morphotropic phase boundary (MPB), where multiphases (i. e., rhombohedral and tetragonal) can easily coexist [6-8]. Therefore, most researchers improved the piezoelectric properties of lead-free ceramics by designing and constructing multi-phases coexistence [2-5,9-11]. It is well known that a pure KNN ceramic often undergoes a paraelectric-ferroelectric phase transition and two ferroelectric-ferroelectric phase transitions with the decrease of ambient temperature, that is, cubic to tetragonal ($T_C \sim 415$ °C), tetragonal to orthorhombic ($T_{O-T} \sim 210$ °C), and orthorhombic to rhombohedral ($T_{R-O} \sim -150$ °C) [2,4,5]. Thus, in order to obtain multiphases coexistence in KNN ceramics at room temperature, it is

necessary to shift their T_{T-O} and/or T_{O-R} to room temperature.

In the past decades, numerous efforts have been used to construct phase boundaries in KNN-based ceramics [2,4,5,11-19]. These results show that T_{T-O} and/or T_{O-R} of KNN ceramics can be effectively shifted to room temperature by doping some additives (i. e., Li^+ , Sb^{5+} , Ta^{5+} , $Bi_{0.5}Na_{0.5}ZrO_3$ and so on) [3,12-15]. Previous results indicated the addition of Sb^{5+} can strongly affect the phase structure and electrical properties of KNN ceramics [13,14], that is, the addition of Sb^{5+} can effectively increase their T_{R-O} and decrease T_{O-T} . However, the improvement of piezoelectric properties is limited due to the finite solid solubility between KNN and Sb^{5+} . Therefore, new phase boundaries of KNN ceramics cannot be realized by only doping Sb^{5+} , and other additives must be doped if new phase boundaries are wanted. Recently, phase boundaries (i. e., orthorhombic-tetragonal (O-T) phase boundary, rhombohedral-tetragonal (R-T) phase boundary) of KNN ceramics have been established by doping $SrZrO_3$ or $Bi_{0.5}Na_{0.5}HfO_3$ or $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}ZrO_3$ [16-21]. Then, a series of d_{33} values (250~460 pC/N) were observed when the compositions locate at the region of phase boundaries. For example, a high d_{33} value of 419 pC/N was found in the region of R-T phase boundary through with the addition of both Sb^{5+} and $Bi_{0.5}Na_{0.5}HfO_3$ [20]. A large d_{33} value of 460 pC/N was also observed in the KNN ceramics modified by Sb^{5+} and $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}ZrO_3$ because of an R-T phase boundary [21]. In addition, the addition of $SrZrO_3$ improved the piezoelectric performance of KNN-based ceramics by constructing phase boundaries [16-19].

In this work, Sb^{5+} , SrZrO_3 , and $\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ were chosen as the additives, and then the $(1-x)\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{1-y}\text{Sb}_y\text{O}_3-z\text{SrZrO}_3-x\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ ceramics were fabricated by the conventional solid-state reaction method. Effects of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$, SrZrO_3 and Sb^{5+} on their phase structure, microstructure, and electrical properties were investigated. The results demonstrate that the electrical properties of KNN ceramics can be well improved by developing ternary material system.

2. Experimental procedure

In this work, $(1-x)\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{1-y}\text{Sb}_y\text{O}_3-z\text{SrZrO}_3-x\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ $\{(x=0\sim0.06$ with $y=0.04, z=0.01)$, $(y=0\sim0.08$ with $x=0.03, z=0.01)$ and $(z=0\sim0.03$ with $x=0.03, y=0.04)\}$ ceramics were fabricated by the conventional solid-state reaction method. Raw materials were K_2CO_3 (99%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), Sb_2O_3 (99.99%), SrCO_3 (99%), HfO_2 (99%), Bi_2O_3 (99.999%), and ZrO_2 (99%). The detailed fabrication processes can be easily found in our previous work [13,20]. In addition, the detailed measurement procedures for properties (e. g., crystal structure, dielectric, ferroelectric, and piezoelectric) can be also found in our previous references [13,20].

3. Results and discussions

Figs. 1(a), (c) and (e) show the composition dependence of phase structure of the ceramics. All ceramics display a pure perovskite structure without secondary phases, and the phase structure is also strongly dependent on the doping content. The expanded XRD patterns of the ceramics in the range of $44\text{-}47^\circ$ were also depicted [Figs. 1(b), (d) and (f)]. As shown in Fig. 1(b), the intensity ratio (2:1) between the

left peak and the right one was observed in the ceramics with $x=0$, indicating the involvement of an orthorhombic symmetry [14-19]. With an increase of x , the intensity of the left peak gradually reduces and the intensity of the right one increases, then a tetragonal-like symmetry was observed in the composition range of $0.02 \leq x \leq 0.05$. However, only one diffraction peak was observed in the ceramics with $x=0.06$, suggesting a rhombohedral phase [16,19]. There is a similar changing tendency in the ceramics with different y and z values, as shown in Figs. 1(d) and (f). In addition, an obvious peak shift (marked by the arrows) was observed in Fig. 1(f). After the addition of SrZrO_3 , the characteristic peaks are shifted to a lower angle. According to the Bragg's law, $2d \sin \theta = n\lambda$, where d is the interplanar spacing, θ is the angle of diffraction and λ is the wavelength of incident ray. Thus, this phenomenon could be caused by replacing A site (K: 0.138 nm, Na: 0.102 nm) with Sr^{2+} (0.118 nm). The difference of ion radius between Na^+ and Sr^{2+} (~ 0.016 nm) is inferior to the one between K^+ and Sr^{2+} (~ 0.02 nm), which means that Sr^{2+} prefers to replace Na^+ . After replacing Na^+ with Sr^{2+} , d increases, leading to the decrease of $\sin \theta$ or θ .

The temperature dependence of dielectric constant (ϵ_r - T) curves of the samples were conducted to judge their phase structure (Fig. 2). As shown in Figs. 2(a)-(d), there are two obvious abnormal dielectric peaks in the ceramics with $x=0$, which respectively correspond to their $T_{\text{R-O}}$ and $T_{\text{O-T}}$ [14-19]. With an increase of x , $T_{\text{R-O}}$ increases and $T_{\text{O-T}}$ decreases. Then, only one abnormal dielectric peak was observed in the ceramics with $x=0.03$, suggesting that both $T_{\text{R-O}}$ and $T_{\text{O-T}}$ were shifted to the same temperature. With the further increase of x , there is only one dielectric peak in the ceramics with $x=0.06$, representing the corresponding T_{C} . The similar representation could be found in the ceramics with ($x=0.03$, y , $z=0.01$) [Figs. 2(e)-(h)]. As for the ceramics with

$x=0.03$ and $y=0.04$, z), there is only one suppressed dielectric peak of T_{R-O} [Fig. 2(i)], while other ceramics showed a similar T_{R-O-T} [Figs. 2(j)-(l)]. According to their XRD patterns and ε_r vs. T curves, the ceramics with $0 \leq x \leq 0.01$, $y=0.04$, and $z=0.01$ possess an orthorhombic (O) phase structure, the ceramics with $0.02 \leq x < 0.03$, $0 \leq y \leq 0.03$, and $0 \leq z < 0.01$ possess an orthorhombic-tetragonal (O-T) phase boundary, the ceramics with $0.03 \leq x \leq 0.05$, $0.04 \leq y \leq 0.06$, and $0.01 \leq z \leq 0.025$ possess a coexistence phase involving rhombohedral (R), orthorhombic (O) and tetragonal (T) phases, and the ceramics with $x \geq 0.06$, $y \geq 0.07$, and $z \geq 0.03$ exhibit a rhombohedral (R) phase [16,19].

Figs. 3(a)-(c) display the temperature dependence of dielectric constant (ε_r - T) curves (25-400 °C) of the ceramics. The doping with Sb^{5+} , $SrZrO_3$ and $Bi_{0.5}Na_{0.5}HfO_3$ can reduce T_C of KNN ceramics [13,14,16-19]. It can be found from Fig. 3 that all ceramics show a decreasing T_C with the increase of doping content. It is worth noting that a relative high T_C (210~260 °C) as well as a good d_{33} (440~470±5 pC/N) were still observed in the range of $z = 0.01$ -0.025, although their T_C was reduced [Fig. 7(c)]. According to the phase transition temperature values (i. e., T_{R-O} , T_{O-T} , T_{R-O-T} and T_C) (Figs. 2 and 3), their phase diagrams were depicted (Fig. 4). All phase diagrams show a similar variation trend, that is, the area of orthorhombic gradually narrows and then disappears with the increase of the doping content, indicating the generation of multiphases coexistence (R, O and T). The phase structure of the ceramics becomes unclear with the further increase of doping content, which can be identified as pseudo-cubic or rhombohedral in other works [16,19].

Fig. 5 shows the scanning electron microscope (SEM) images of KNNS-SZ-BNH ceramics with x and z . For the ceramics varying with x values, it can be observed that the ceramics with $x=0$ show an inhomogeneous grain distribution, and a relatively homogeneous grain distribution is observed in the ceramics with $x=0.02$ and 0.03 , indicating that an appropriate amount of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ can promote the grain growth. However, the grain sizes of the ceramics with $x=0.05$ dramatically decrease [20]. As the amount of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ exceeds solid solubility, excess $\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ gathers at the grain boundaries and hinders the grain growth [20]. For the ceramics varying with z values, all ceramics show an inhomogeneous grain distribution, and their grain sizes gradually decrease as z increases [17]. Fig. 6 shows the element mapping of the ceramics with $x=0.03$, $y=0.04$, and $z=0.01$. It can be observed from Fig. 6 that all elements show a uniform distribution, suggesting a good chemical homogeneity.

Figs. 7(a)-(c) depict the piezoelectric properties (d_{33} and k_p) of the ceramics as a function of x , y , and z . A similar variation tendency can be observed in Figs. 7(a) and (b). With the increase of doping content, d_{33} first increases and then decreases sharply, while k_p firstly keeps unchanged and then decreases sharply. As for Fig. 7(c), both d_{33} and k_p first increase, then almost keep unchanged and finally decrease. The optimum piezoelectric properties ($d_{33}=440\sim 470\pm 5$ pC/N and $k_p=0.51\pm 0.02$) were obtained in the ceramics with the coexistence phases of R-O-T [Fig. 7(c)]. As compared with the KNN-based ceramics doped with SrZrO_3 or BNH, the present work shows a much larger d_{33} of 470 ± 5 pC/N than others' (where <350 pC/N for Refs [16-19], <420 pC/N

for Ref [20]), as well as a high T_C (~ 244 °C). It is well known that phase boundary plays an important role in enhanced piezoelectric properties of a material [2,4,5,22-25]. On the one hand, the rhombohedral symmetry has eight equivalent spontaneous polarization vectors, the orthorhombic symmetry has twelve equivalent ones, and the tetragonal symmetry has six equivalent ones, which means that multi-phases coexistence can provide more polarization vectors than the one with a single phase structure, especially for R-O-T coexistence phase. On the other hand, multiphases coexistence can decrease the polarization anisotropic energy of the ceramics and provide easy paths for polarization rotation in anisotropically flattened free energy profile [22-25].

Figs. 8(a)-(c) display the ferroelectric loops of the ceramics. All ceramics exhibit a typical ferroelectric loop, and the saturation degree of the loops was deteriorated by doping high content. Their P_r and E_C values are shown in Figs. 8(d)-(f). Their P_r value reduces as the doping content increases, indicating the deterioration of ferroelectricity. This phenomenon could be attributed to the change of phase structure in KNN-based ceramics. As we all know, the higher symmetry the material has, the worse ferroelectricity the material has [26]. As discussed above, all ceramics modified by a high content exhibit a rhombohedral or pseudo-cubic phase structure with a very high symmetry [16,19], which is the reason why ferroelectricity of the ceramics with high doping content was deteriorated [26].

Figs. 9(a)-(c) show ε_r and $\tan \delta$ of the ceramics. Both ε_r and $\tan \delta$ are closely related with the kind and content of the additives. The addition of both BNH and SrZrO_3 shows a similar effect on their ε_r and $\tan \delta$, that is, ε_r first increases and then reduces, and $\tan \delta$ almost keeps unchanged as the doping content increases. However, for with the addition of Sb^{5+} , both ε_r and $\tan \delta$ increase as the doping content increases. Generally, both dielectric properties and ferroelectric properties are closely related with piezoelectric properties of a material, according to an equation of $d_{33} \sim \alpha \varepsilon_r P_r$ (α is the electrostrictive coefficient) [26-28]. The equation suggests that d_{33} should exhibit a similar changing trend with respect to $\varepsilon_r P_r$. Here, the composition dependence of $\varepsilon_r P_r$ and d_{33} is shown in Figs. 10(a)-(c). From the figures, there is a similar changing trend for the composition dependence of d_{33} and $\varepsilon_r P_r$. Therefore, except for R-O-T coexistence phase, $\varepsilon_r P_r$ also plays a part role in the improvement of piezoelectric properties [26-28].

4. Conclusions

The KNNS-SZ-BNH ceramics were developed by the conventional solid-state reaction method. Both XRD patterns and ε_r - T curves confirmed the involvement of an R-O-T coexistence phase in the composition region of $0.03 \leq x \leq 0.05$, $0.04 \leq y \leq 0.06$, and $0.01 \leq z \leq 0.025$. The ceramics with $x=0.03$, $y=0.04$ and $z=0.01$ exhibit the highest piezoelectric coefficient ($d_{33}=470 \pm 5$ pC/N), the highest planar coupling factor ($k_p=0.51 \pm 0.02$) as well as a relatively high Curie temperature ($T_C=244$ °C). Multiphases coexistence as well as the enhancement of ferroelectric and dielectric

properties are responsible for the improved piezoelectric properties. We believe that this work can promote the understanding how to design high-performance KNN-based ceramics.

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Figure captions

Fig. 1. XRD patterns of the ceramics as a function of (a) (x , $y=0.04$, $z=0.01$), (c) ($x=0.03$, y , $z=0.01$), and (e) ($x=0.03$, $y=0.04$, z); Amplified patterns in the range of $44\sim 47^\circ$ as a function of (b) (x , $y=0.04$, $z=0.01$), (d) ($x=0.03$, y , $z=0.01$) and (f) ($x=0.03$, $y=0.04$, z).

Fig. 2. ϵ_r vs. T ($-150\sim 200^\circ\text{C}$) curves of the ceramics as a function of x (a), y (b) and z (c).

Fig. 3. ϵ_r vs. T ($25\sim 400^\circ\text{C}$) curves of the ceramics as a function of x (a), y (b) and z (c).

Fig. 4. Phase diagrams of the ceramics as a function of x (a), y (b) and z (c).

Fig. 5. SEM images of surfaces for KNNS-SZ-BNH ceramics: (a)-(d) $x=0, 0.01, 0.03$, and 0.05 ; (e)-(h) $z=0, 0.015, 0.025$, and 0.03 .

Fig. 6. Element mappings of the ceramics with $x=0.03$, $y=0.04$, $z=0.01$ in the scale of $5\ \mu\text{m}$.

Fig. 7. d_{33} and k_p of the ceramics as a function of x (a), y (b), and z (c).

Fig. 8. Ferroelectric loops of the ceramics as a function of x (a), y (b) and z (c); P_r and E_C as a function of x (d), y (e) and z (f).

Fig. 9. ϵ_r and $\tan \delta$ of the ceramics as a function of x (a), y (b) and z (c), measured at room temperature.

Fig. 10. $\epsilon_r P_r$ and d_{33} curves of the ceramics as a function of x (a), y (b) and z (c).

Fig. 1

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Fig. 10

Graphical Abstract

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Enhanced piezoelectric properties ($d_{33}=470\pm 5 \text{ pC/N}$, $k_p=0.51\pm 0.02$, $T_C=244 \text{ }^\circ\text{C}$) were obtained in the KNN-based ceramics with an R-O-T phase boundary driven by Sb^{5+} , $\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ and SrZrO_3 .