Modification of Strain and Piezoelectricity in (K,Na)NbO₃-(Bi,Na)HfO₃ Lead-free Ceramics with High Curie Temperature

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Abstract: In this work, the $(1-x)\text{K}_{0.45}\text{Na}_{0.55}\text{NbO}_3-x\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ lead-free ceramics with a high Curie temperature were prepared by the normal sintering, and the enhancement in strain and piezoelectricity can be attained by tailoring the corresponding compositions. The orthorhombic-tetragonal (O-T) phase coexistence was observed in the ceramics with $0.03 < x < 0.055$, and then such a phase boundary was reasonably identified by X-ray diffraction patterns as well as temperature-dependent Raman spectra and dielectric constant. A large piezoelectric constant (d_{33}) of ~ 385 pC/N and a high Curie temperature (T_C) of ~ 315 °C can be simultaneously induced in the ceramics with $x=0.05$. More interestingly, a high unipolar strain of $\sim 0.187\%$ was shown in the ceramics with $x=0.04$. It was found that the enhanced piezoelectric properties should be attributed to the two phase coexistence as well as enhanced dielectric and ferroelectric properties. We believe that this material is one of the most promising candidates in the field of high-temperature piezoelectrics.

Keywords: (K,Na)NbO₃; Bi_{0.5}Na_{0.5}HfO₃; High Curie temperature; Piezoelectricity; Strain

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I. INTRODUCTION

With the development of science and technology, piezoelectric ceramics play a really important role in the society, which are widely used for sensors, actuators, transducers, buzzers, and other electronic devices.^[1,2] $(1-x)\text{PbZrO}_3\text{-}x\text{PbTiO}_3$ (PZT) has been considered to be one of the most important piezoceramics because of its excellent piezoelectric coefficient.^[1,2] However, lead is a heavy metal and its toxicity is well known, and PZT will be prohibited in the near future because more than 60 wt % lead is contained. Some of the symptoms of lead poisoning are headaches, constipation, nausea, and reduced fertility. Therefore, it is urgent to develop lead-free piezoelectric materials substituting for the widely used PZT systems.^[3]

$(1-x)\text{KNbO}_3\text{-}x\text{NaNbO}_3$ (KNN) is one of the most promising lead-free piezoceramics for replacing PZT ones, and good electrical properties were extensively reported.^[3-20] In 2004, a breakthrough was made by Saito *et al.*, that is, a high piezoelectric constant (d_{33}) of ~ 416 pC/N was achieved in the textured KNN -based ceramics, which intrigues great interest in the field of lead-free piezoelectrics.^[4] Since then, KNN ceramics has been regarded as the most promising candidate to replace the lead-based ceramics.^[3] However, the strain of this material is lower with respect to that of PZT ceramics.^[5] In addition, the d_{33} of KNN -based ceramics is promoted mostly by sacrificing the corresponding Curie temperature (T_C).^[3] As a result, it is highly expected to achieve large piezoelectricity, high strain, and high T_C in the same KNN -based ceramics.

In the past, we have observed a high d_{33} (~ 419 pC/N) in $(1-x)\text{K}_{0.45}\text{Na}_{0.55}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-}x\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ ceramics,^[21] and unfortunately a low T_C (~ 242 °C) can be only

attained due to the involvement of antimony.^[3,17] In addition, antimony (Sb) is considered as toxic material. In this work, a new $(1-x)\text{K}_{0.45}\text{Na}_{0.55}\text{NbO}_3$ - $x\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ [(1- x)KNN- x BNH] ceramic system has been fabricated via normal sintering in order to attain both a large d_{33} and a high T_C . $\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ (BNH) could quickly decrease the orthorhombic-tetragonal phase transition temperature ($T_{\text{O-T}}$) and gradually rise the rhombohedral-orthorhombic phase transition temperature ($T_{\text{R-O}}$), and a high T_C can be well maintained. The phase boundaries concerning O-T were reasonably established in this quasi-binary system. The d_{33} of ~385 pC/N and strain of ~0.187% were observed respectively at $x=0.05$ and $x=0.04$, and a high T_C of >315 °C is also attained. In this work, the comprehensive performance of d_{33} , strain, and T_C is superior to the previous reported results of KNN -based ceramics. The related physical mechanisms were also given.

II. EXPERIMENTAL PROCEDURE

The ceramics with a formula of $(1-x)\text{K}_{0.45}\text{Na}_{0.55}\text{NbO}_3$ - $x\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ [(1- x)KNN- x BNH] were synthesized by the conventional solid-state sintering method. Raw materials including K_2CO_3 (99%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), Bi_2O_3 (99.999%), and HfO_2 (99%) were weighed with an electric balance and then were ball milled for 24 h with alcohol. The dried powders were calcined at 850 °C for 6 h and were mixed with a binder of 8 wt% poly vinyl alcohol (PVA). After that, the calcined powders were pressed into the disks with a diameter of 10 mm and a thickness of 1 mm under a pressure of 10 MPa. After PVA was burned off, the pellets were sintered at 1065-1115 °C for 3 h in air. Then the sintered samples were pasted with silver and then fired at 600 °C for 10 min. At last, the direct current electric field of 2-4 kV/mm was applied to pole each sample in a silicon oil bath.

The phase purity and crystal structure of the samples were analyzed by the X-ray diffraction (XRD) machine with a PANalytical X'Pert PRO X-ray diffractometer with a $\text{CuK}\alpha$ radiation ($\lambda=1.54187 \text{ \AA}$) operating at 40 kV and 40 mA. HR LabRam Raman spectroscopy system was used to measure the temperature (-120°C-200°C) dependence of the Raman spectra, where a 514 nm Ar laser was used for excitation. Field emission-scanning electron microscopy (FE-SEM) (JSM-7500, Japan) was used to characterize the microstructure. Temperature dependence of dielectric properties of the samples was conducted upon heating from -150 to 200 °C and room temperature to 450 °C respectively at 1 °C/min and a frequency of 100 kHz. The relative permittivity and dielectric loss of the samples were measured using an *LCR* meter (HP 4980, Agilent, U.S.A.) in the poled state. Their polarization against electric field (*P-E*) hysteresis loops were conducted using a standardized ferroelectric test system at room temperature and a frequency of 10 Hz. The strains that developed under the applied electric fields at 10 Hz and room temperature were measured with a MTI-2000 fonic sensor. Finally, the piezoelectric constant d_{33} and the planar electromechanical coupling factor k_p were measured by a piezo- d_{33} meter (ZJ-3 A, China) and impedance analyzer (HP 4194A) respectively.

III. RESULTS AND DISCUSSION

In this work, we tried to investigate the effects of BNH contents on the phase structure (room temperature) of the ceramics by analyzing their XRD patterns as well as temperature-dependent dielectric constant (ϵ_r vs T) and Raman spectra. Firstly, we characterized the composition dependence of XRD patterns of the ceramics, as shown in Figure 1. By analyzing the peaks of the XRD patterns, one can find that typical

perovskite structure was constructed in the ceramics. However, we also found the weak peaks in the amplification XRD patterns, and then these peaks can be identified as $\text{K}_4\text{Nb}_2\text{O}_7$.^[22,23] To address their phase evolutions, the expanded XRD patterns at $2\theta=21\text{-}23^\circ$ and $2\theta=44\text{-}47^\circ$ are respectively shown in Figs. 1(b) and (c). For the ceramics with $x\leq 0.03$, their XRD peaks shapes are similar to a pure KNN, showing the involvement of an O phase.^[3] However, the diffraction peak shapes gradually change as x increases, which will be further discussed by considering both their XRD patterns and ε_r vs T curves. As shown in Fig. 2(b), it could be found that $T_{\text{R-O}}$ is gradually moved to a higher temperature with the increase of BNH content, while $T_{\text{O-T}}$ is quickly shifted to a lower temperature and even disappears for $x=0.055$. In addition, it is well known that the R phase can be identified due to the $\{111\}$ peak in XRD patterns.^[12-14] One can see that the $\{111\}$ peaks of this work match the typical peak shapes of R phase for $x>0.06$, and then we can also find that the $\{200\}$ peaks gradually become a single peak, further illustrating the existence of R phase.^[13,14] By considering Figs. 1 and 2(b), we may get the conclusion that the phase boundary appears for $0.04\leq x\leq 0.05$ and disappears for $x\geq 0.055$, a tetragonal phase can be observed at room temperature in the ceramics with $0.055\leq x\leq 0.06$, and finally a rhombohedral phase structure is reasonably established for $x>0.06$.

Figure 2(a) plots the ε_r vs T ($T=25\text{-}450^\circ\text{C}$) curves of the ceramics. From this figure, T_C declines from 387°C to 150°C when the compositions change from 0.01 to 0.08. ε_r of the ceramics with $x=0.05$ reaches a maximum value due to the involvement of phase boundaries.^[3] In addition, the ε_r - T curves become broadened for $x\geq 0.07$ because of the greatly decreased grain sizes. Their $T_{\text{O-T}}$ and $T_{\text{R-O}}$ simultaneously shift to room temperature as x increases [See Fig. 2(b)]. Figure 2(c) addresses the phase diagram of

the ceramics determined by their corresponding ε_r - T curves (-150~450 °C) [Figs. 2(a) and (b)]. It could be found from Fig. 2(c) that both T_{O-T} and T_{R-O} are very sensitive to the compositions in this ceramics system, while T_C slightly changes ($x \leq 0.06$). In this material, T_{O-T} can be shifted to near room temperature by changing the BNH contents. It is well known that the O-T phase boundary can be constructed when their phase transition temperatures are limited to a temperature range.^[3, 24, 25,26] Therefore, the O-T phase coexistence may be formed when the compositions are located at $0.04 \leq x \leq 0.05$. Generally speaking, a high T_C (315~340 °C) means that the ceramics could be well used in high-temperature piezoelectric devices.

To further clarify their phase structure, we measured the temperature (-120°C to 200 °C) dependence of Raman spectra of the ceramics with $x=0.05$, measured in 50~1000 cm^{-1} , as shown in Fig. 3. It can be seen that there are three vibrational modes for BO_6 (i.e., ν_1 , ν_2 , and ν_5).^[6] The peak around 600 cm^{-1} is ν_1 , which is stronger than the left one. However, a weaker peak is named as ν_2 . Interestingly, the ν_1 peak shifts to a lower wavenumber slightly, and then becomes more broadened and weaker with increasing measurement temperatures. And then, we also magnified the Raman spectra with the wavenumbers from 450 cm^{-1} to 700 cm^{-1} as a function of $T=-120$ °C, -80 °C, 40 °C, and 200 °C, as shown in Fig. 4. According to the data of Fig. 4, one can see that ν_1 shifts and gets weaker as the temperatures increase again, indicating that the phase transition can be induced by varied temperatures. In addition, we also plotted the temperature dependence of both ν_1 modes and dielectric constant of the ceramics with $x=0.05$, as shown in Fig. 5. More interestingly, one can find that the anomalous Raman peaks are obtained when the measurement temperatures locate at T_{O-T} regions, confirming the O-T phase coexistence. This result indicates that the

Raman peak frequencies increased because of the phase transitions from O to T.^[27] As a result, the O-T phase boundary should exist in the ceramics by discussing the XRD patterns as well as temperature dependence of Raman spectra and dielectric constant.

Figure 6 shows the FE-SEM images of the ceramics with different x values at their optimum sintering temperatures. The dense microstructure can be developed in all the ceramics. In addition, one can know that their grain sizes increase first and then decrease as the BNH contents continue increasing. According to the previous reports,^[3] the microstructure evolution may be due to the incorporation of Bi^{3+} and Hf^{4+} . When the Bi^{3+} and Hf^{4+} contents keep a small value ($x \leq 0.05$), the grain growths can be promoted by the existence of more vacancies because two kinds of ions can well enter into crystal lattice. Figure 7 shows the FE-SEM images of the ceramics with different compositions under the same sintering temperature of 1108 °C. From the images, we can find the same change tendency of grain sizes in the ceramics [See Fig. 6]. In addition, it can be noted that the grain sizes can be changed when the sintering temperatures of the ceramics with $x=0.01$ and 0.03 are away from the most optimum values, as shown in Figs. 6 and 7.

Figure 8(a) shows the composition dependence of both d_{33} and k_p in the ceramics. One can know that d_{33} increases first and then decreases with the increase of x , reaching a peak value of ~385 pC/N for $x=0.05$. As a result, a higher d_{33} is obtained in the ceramics with both R-O and O-T phase boundary regions. As known to all, d_{33} of the ceramics is related to not only the compositions but also polarization conditions (e.g., poling temperatures, poling electric fields, and dwell time).^[3,16,17] For KNN ceramics, the poling temperature (T_p) becomes very important due to the intrinsic characteristics

of O-T phase boundary with a PPT.^[3,16,17] Therefore, we plot the curves of d_{33} and k_p against T_p in the ceramics with $x=0.05$, as shown in the inset of Fig. 8(a). As seen in it, the d_{33} rises first and then drops with the changed temperatures from 10 °C to 140 °C, reaching a peak value of ~385 pC/N at 40 °C. The previous studies show that the phase boundary is one of the most important reasons for enhancing d_{33} .^[3, 16,17]

Figure 8(b) shows ε_r and $\tan \delta$ of the ceramics, measured at $f=100$ kHz. ε_r increases continuously with increasing x from 0.01 to 0.05, and then keeps a high value for $x \geq 0.05$. On the other hand, the $\tan \delta$ increases first and then decreases for $x < 0.05$, and $\tan \delta$ keeps a low value for $x \geq 0.05$, reaching a peak value for $x=0.03$. As a result, the dielectric property can also be enhanced due to the formation of phase boundary. In addition, the equation of $d_{33} \sim \varepsilon_r P_r$ is available for illuminating the physical mechanisms of the promotion of d_{33} .^[3,9] Therefore, the curve of $\varepsilon_r P_r$ against x is shown in the inset of Fig.8(b). $\varepsilon_r P_r$ has a similar changing trend with d_{33} , getting a highest value in the phase boundary region. So, the promotion of ε_r and P_r can also lead to the enhancement of d_{33} except for the involvement of phase boundaries.

Figure 8(c) shows the P - E loops of the ceramics as a function of BNH, measured at $f=10$ kHz and room temperature. All ceramics have typical P - E loops except for $x < 0.07$, and a slimmer P - E loop is shown for $x \geq 0.07$. To analyze the influences of BNH content on ferroelectrics, we plotted remnant polarization (P_r) and coercive field (E_c) against x , as shown in Fig. 8(d). The P_r and E_c have a similar changing trend with the composition. Both of them increase first and then decrease with increasing x from 0.01 to 0.08. As a result, a high P_r value can be achieved in phase boundary region. One can know that P_r can represent the ferroelectric property of KNN ceramics, and

therefore the addition of BNH to KNN can enhance the ferroelectric properties by forming the phase boundaries.^[3,18,28,29] However, the increased E_c values in the multiphase coexistence region may come from the lattice distortion and the clamped domain walls as the phase structure changed.^[28] To further check E_c of the ceramics with a poor ferroelectricity, we provided the I - E curves of the samples with $x \geq 0.07$, as shown in Fig. 9. It was reported that the coercive field of a ferroelectric material is an electric field corresponding to its current peak,^[19,20,30] and then E_c of the ceramics with $x=0.07$ and 0.08 can be attained.

In this work, we also pay attention to the strain investigation of the ceramics. Figure 10(a) plots the strain curves of the ceramics as a function of x , measured at $f=10$ kHz and room temperature. Typical unipolar strain curves can be attained in this kind of ceramics. Figure 10(b) shows the unipolar strain values of this ceramics against the compositions. The strain value firstly increases and then decreases as the composition changes from 0.01 to 0.08, reaching a peak value at $x=0.04$ due to the multiphase coexistence. More interestingly, a higher strain value can be found in the phase boundary region. According to the previous reports, the same phenomenon also appeared in other KNN ceramics.^[21,31,32] As a result, a high strain may be attained due to existence of multiphase regions.^[21,32]

IV. CONCLUSION

In this work, our purpose is to attain large d_{33} , high strain, and high T_C in $\text{K}_{0.45}\text{Na}_{0.55}\text{NbO}_3\text{-Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ lead-free ceramics without antimony. According to the results, we have realized our established goal, that is, a large d_{33} of ~ 385 pC/N, a high T_C of ~ 315 °C, and a high unipolar strain of $\sim 0.187\%$ have been observed in the

ceramics by forming the O-T phase boundary. As a result, we believe that this ceramics will play an important role in the further research of potassium-sodium niobate lead-free piezoceramics.

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Figure captions

Fig. 1: XRD patterns of the ceramics with different x values, measured at (a) $2\theta=20-70^\circ$, (b) $2\theta=21-23^\circ$, (c) $2\theta=44-47^\circ$, measured at 20°C .

Fig. 2: (a) ϵ_r vs. T ($25\sim 450^\circ\text{C}$) curves and (b) ϵ_r vs. T ($-140\sim 200^\circ\text{C}$) of the ceramics with different x values, and (c) is their phase diagram.

Fig. 3: Raman spectra in the wavenumber ranges from 50 cm^{-1} to 1000 cm^{-1} of the ceramics with $x=0.05$, measured at -120°C to 200°C .

Fig. 4: Raman spectra simulated by Lorenz method in the ceramics with $x=0.05$ as a function of $T=-120^\circ\text{C}$, -80°C , 40°C , and 200°C .

Fig. 5: Evolutions of ν_1 modes and dielectric constant of the ceramics with $x=0.05$ as a function of $T=-150^\circ\text{C}\sim 200^\circ\text{C}$.

Fig. 6: FE-SEM images of the ceramics with different x values.

Fig. 7: FE-SEM images of the ceramics with different x values at 1108°C .

Fig.8: (a) d_{33} and k_p , (b) ϵ_r and $\tan \delta$, (c) P - E loops, and (d) P_r and E_C of the ceramics with different x values.

Fig.9: Polarization-electric field loop (P - E) and current-electric field loop (I - E) of the ceramics with (a) $x=0.07$ and (b) $x=0.08$, measured at room temperature and 10 kHz .

Fig.10. (a) strain hysteresis and (b) strain values against x of the ceramics with different x values.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10