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A New Method to Improve the Electrical Properties of KNN-based Ceramics: Tailoring Phase Fraction

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Abstract: Although both the phase type and fraction of multi-phase coexistence can affect the electrical properties of (K,Na)NbO₃ (KNN)-based ceramics, effects of phase fraction on their electrical properties were few concerned. In this work, through changing the calcination temperature of CaZrO₃ powders, we successfully developed the 0.96K_{0.5}Na_{0.5}Nb_{0.96}Sb_{0.04}O₃-0.01CaZrO₃-0.03Bi_{0.5}Na_{0.5}HfO₃ ceramics containing a wide rhombohedral-tetragonal (R-T) phase coexistence with the variations of T (or R) phase fractions. It was found that higher T phase fraction can warrant a larger piezoelectric constant (d_{33}) and d_{33} also showed a linear variation with respect to tetragonality ratio (c/a). More importantly, a number of domain patterns were observed due to high T phase fraction and large c/a ratio, greatly benefiting the piezoelectricity. In addition, the improved ferroelectric fatigue behavior and thermal

stability were also shown in the ceramics containing high T phase fraction. Therefore, this work can bring a new viewpoint into the physical mechanism of KNN-based ceramics behind R-T phase coexistence.

Keywords: Lead-free piezoceramics; Multiphase coexistence; Phase fraction; Electrical properties

1. Introduction

In the past several decades, extensive investigations have been concentrated on the lead zirconate titanate (PZT) -based materials due to the practical applications in electronic devices [1,2]. The results showed that the exceptionally piezoelectric properties can be observed in the compositions with morphotropic phase boundary (MPB), where both rhombohedral (R) and tetragonal (T) phases coexisted [3-5]. However, the recent works strongly demonstrated that not only the MPB but also the corresponding phase fraction affected piezoelectric properties of PZT-based ceramics [6-8]. For example, a leaping increase of d_{33} (from 685 pC/N to 825 pC/N) was achieved in $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3\text{-Pb}(\text{Sb}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Zr}_{0.39}\text{Ti}_{0.61})\text{O}_3$ ceramics with MPB by elevating the T phase contents from 0.445 to 0.80 [6]. In addition, a close relationship between phase fraction and piezoelectric properties was also observed in the CoCO_3 -modified PZN-PZT ceramics, that is, d_{33} value can be increased by increasing T phase fraction [7]. However, k_p was degraded in (Mn,Sb)-doped PZMnNS-PZT ceramics as T phase fraction decreased [8]. Therefore, it is meaningful to further explore the effects of phase fraction on piezoelectric properties of a material, especially for the lead-free piezoelectric materials due to the high toxicity of lead that goes against the sustainable development [9,10].

Among the lead-free piezoelectric materials, the potassium sodium-niobate (KNN)-based material is one of the most promising candidates [11]. In 2004, Saito *et al.* reported a large d_{33} of 416 pC/N in the highly textured KNN-based ceramics [12]. Since then, many attempts have been used to improve piezoelectric properties of KNN-based materials [11]. Among these methods, phase boundary is proved to effectively improve piezoelectric properties of KNN-based ceramics [11,13,14], and especially the giant d_{33} values (425 pC/N ~570 pC/N) were reported in KNN-based ceramics with a rhombohedral-tetragonal (R-T) phase coexistence [15-18]. It was thought that the enhanced piezoelectric properties originated from the easy polarization rotation and the occurrence of nano-domains [15-18]. However, there are few reports concerning the effects of phase fraction on electrical properties of KNN-based ceramics, especially for R-T phase boundary. Therefore, a work concerning the influences of phase fraction on the performance of KNN-based ceramics is highly expected.

Previously, it was reported that the phase fraction of the piezoceramics was closely related to the fabrication process [19]. In addition, the addition of Sb^{5+} , CaZrO_3 , and $\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ can effectively shift the rhombohedral-orthorhombic ($T_{\text{R-O}}$) and orthorhombic-tetragonal ($T_{\text{O-T}}$) phase transition temperature to the room temperature [20,21]. Thus, the material system of $0.96\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3-0.01\text{CaZrO}_3-0.03\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ was considered to investigate the effects of phase fraction of R-T phase coexistence on their electrical properties. We successfully tailored the phase fraction between R and T phases by means of changing the calcination temperatures of CaZrO_3 powders. The R-T phase

coexistence was fully supported by XRD patterns, ϵ - T curves, temperature-dependent Raman spectra & XRD patterns as well as Rietveld refinement. Subsequently, the effects of phase fraction on their piezoelectric, dielectric properties, ferroelectric fatigue behavior, and thermal stability were systematically studied, and the related physical mechanisms were analyzed in detail.

2. Experimental procedure

In this work, the $0.96\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-}0.01\text{CaZrO}_3\text{-}0.03\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ (abbreviated as KNNS-CZ-BNH) ceramics were fabricated *via* the conventional solid-state reaction method. Raw materials were K_2CO_3 (99%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), Bi_2O_3 (99.999%), Sb_2O_3 (99.99%), HfO_2 (99.9%), CaCO_3 (99.5%) and ZrO_2 (99.5%). The KNNS-CZ-BNH ceramics were prepared by the two-step method, and the CaZrO_3 powders were synthesized in advance at the temperature range of 800-1200 °C for 2 h. In addition, the KNNS-CZ-BNH ceramics were also prepared by one-step method for the comparison. The detailed experimental procedure can be found in our previous publications [18,20]. The green disks were sintered at 1060~1100 °C for 3 h under corundum crucible in air. Silver paste was printed and fired on both sides of the samples at 600 °C for 30 min to form the electrodes for the electrical measurements. The samples were poled in a silicone oil bath by applying an electric field of 4kV/mm for 30 min at room temperature.

The X-ray diffraction (XRD) (Bruker D8 Advanced XRD, Brukeraxs Inc., Madison, WI, $\text{CuK}\alpha$) characterization was used to analyze the phase of the as-sintered samples. The density of the samples was measured using the Archimedes method, and then the relative density was calculated by the ratio of the measured density to theoretical

density. For the Rietveld refinement, a high resolution X-ray diffraction instrument (X'Pert Pro MPD (DY 120 PANalytical, Netherlands)) was used to collect the XRD data of the as-sintered samples. The Maud software package was used to perform the Rietveld refinement. For the cross-section morphology, the broken samples were polished and then thermally etched at 1000 °C for 10 minutes. Scanning electron microscopy (SEM, Quanta 600) was used to measure the cross-section morphologies of the ceramics. The piezoelectric constant (d_{33}) was tested by using a piezo- d_{33} meter (ZJ-3 A, China), and planar electromechanical coupling factor (k_p) was measured using an impedance analyzer (HP 4299A). The P - E hysteresis loops were measured at 10 Hz by a commercial ferroelectric analyzer (TF 2000, aixACCT Systems GmbH, Germany) with non-poled ceramics. The temperature dependence of dielectric constant (ϵ_r) of each sample was measured using a programmable furnace in connection with a LCR analyzer (HP 4980, Agilent, USA). The Raman spectra were measured by using a Horiba Aramis Raman spectrometer (Horiba Scientific) with excitation sources of 473 nm. The temperature was controlled by a connected temperature controller. The as-sintered samples were polished and etched by HF (50 wt%) acid for 5 min at room temperature, and then the domain patterns were observed by using the scanning electron microscopes (SEM, Quanta 600).

3. Results and discussion

Figure 1(a) displayed the XRD patterns of CaZrO_3 (abbreviated as CZ) powders synthesized at different temperatures. It was observed that all XRD patterns were partly consistent with the standard CZ patterns, which indicated that all pre-prepared CZ powders consisted of CZ and other ingredients (e.g., ZrO_2 and CaCO_3). It was reported that pure CZ powder can be synthesized at 1600 °C, which is responsible for

the secondary phases of this work [22]. Figure 1(b) exhibited the XRD patterns of KNNS-CZ-BNH ceramics with different CZ powders. A pure perovskite structure without secondary phases was observed in all the ceramics. Furthermore, the ratio of the $[200]_{\text{PC}}$ and $[002]_{\text{PC}}$ peak intensity (I_{200}/I_{002}) was strongly dependent on the calcination temperatures of CZ powders [Fig. 1(c)] [23]. It can be observed that the ceramics with CZ synthesized at 900 °C possessed the highest ratio of 2.1, whereas the lowest ratio of 1.76 was found in the ceramics with CZ synthesized at 1200 °C. It was believed that both the phase type and phase fraction simultaneously determined the intensity of $[hkl]_{\text{PC}}$ reflection of the as-sintered ceramics [24]. Here, all the ceramics were found to possess a rhombohedral-tetragonal (R-T) phase coexistence, which will be proved in the latter discussion. Therefore, the variations of I_{200}/I_{002} should be mainly attributed to the change of phase fraction.

Figures 2(a) and (b) showed the temperature dependence of dielectric constant (ϵ_r - T) in the temperature range of -150-200 °C and 25-400 °C, respectively. It was found that one anomaly was only observed in Fig. 2(a), which was widely regarded as the rhombohedral-tetragonal (R-T) phase coexistence with $T_{\text{R-T}}=45\pm10$ °C [14-18,24]. Furthermore, T_{C} of the ceramics was almost independent on the calcination temperatures of CZ powders, accompanying with an unchanged T_{C} value of 262 ± 5 °C. Thus, the variations of calcination temperatures of CZ powders did not substantially affected the types of phase structure, providing the basis of analyzing the effects of phase fraction on electrical properties of this work. Additionally, the addition of Sb^{5+} and/or CZ and/or BNH reduced T_{C} of KNN-based ceramics, which accounted for the decreased T_{C} in this work [20,21].

Previously, the Raman technique was extensively used to identify the phase transition evolution in KNN-based materials [25]. To further demonstrate the R-T phase coexistence, thus we performed the temperature-dependent Raman spectra of the ceramics with CZ synthesized at 900 °C, as shown in Fig. 3(a). Generally, the NbO_6 vibration consists of six modes, $1A_{1g}(\nu_1)+1E_g(\nu_2)+2F_{1u}(\nu_3,\nu_4)+F_{2g}(\nu_5)+F_{2u}(\nu_6)$, where $1A_{1g}(\nu_1)+1E_g(\nu_2)+1F_{1u}(\nu_3)$ are stretching modes and the rest are bending modes [25]. Furthermore, the A_{1g} mode represents a double-degenerate symmetric O-Nb-O stretching vibration, which can determine the phase transition evolution [25]. Therefore, the Raman spectra in the range of $500\text{-}700\text{ cm}^{-1}$ were analyzed via the Lorentz fitting, as shown in Fig. 3(b). Fig. 3(c) showed the Raman shift of A_{1g} mode as a function of temperatures. Here, the position of A_{1g} mode was obtained using the Lorentz fitting method. With the increasing temperatures, the A_{1g} peaks gradually shifted to a lower wavenumber. As the temperatures increased up to $45\pm 10\text{ }^\circ\text{C}$ ($\sim T_{\text{R-T}}$), the A_{1g} peaks almost kept unchanged, resulting in the formation of a plateau region. Such a plateau region strongly confirmed a stable multi-phases coexistence, which corresponded to the rhombohedral-tetragonal (R-T) phase coexistence of this work [25,26]. With the further increase of temperatures, the A_{1g} mode continued to shift to a lower wavenumber. As a result, the temperature-dependent Raman spectra also testified the R-T phase coexistence of this work.

To show the structural evolution of R-T as a function of temperatures, the *in situ* temperature-dependent XRD patterns were measured, as shown in Figure 4(a). The enlarged patterns with $2\theta=45\text{-}46^\circ$ were showed in Fig. 4(b). It was found that the splitting $\{200\}_{\text{PC}}$ peaks were observed at $T=25\text{ }^\circ\text{C}\text{-}200\text{ }^\circ\text{C}$. With the increasing temperatures, the peak intensity of $[002]_{\text{PC}}$ decreased, while the increased intensity

can be found in $[200]_{\text{PC}}$ peak. When the temperatures increased from 50 °C to 100 °C, an apparent shifting to higher angle was observed, as marked by the red arrows in Fig. 4(b). According to the ε_r - T curves [Fig. 2], a pure T phase should be observed at $T > T_{\text{R-T}}$ ($\sim 45 \pm 10$ °C). Thus, the shifting of diffraction peaks was due to the phase transition from R-T to T. As $T = 250$ °C approached to $T_{\text{C}} = 262 \pm 5$ °C, a single $\{200\}_{\text{PC}}$ peak was observed, suggesting the formation of paraelectric phase (Cubic phase). Figure 4(c) showed the simulation of enlarged XRD patterns with $2\theta = 45$ - 46° . The R-T phase coexistence remained before the temperatures reached to 100 °C, after which the phase structure totally transformed to single T phase and then C phase, consistent with the ε_r - T curves [Figs. 2(a) and (b)].

To obtain the phase fraction of R-T, we performed the Rietveld refinement for each composition using KNbO_3 mode [27] and the ceramics with CZ synthesized at 900 °C was chosen as an example, as shown in Figure 5. It was found that the simulated data well matched the original one, indicating an appropriate refinement process. Table 1 listed the detailed refinement results. Firstly, the low R_w ($< 12\%$) and Sig (≤ 1.2) values indicated a good refinement process. Then, it is interesting to note that the phase fraction strongly depended on the calcination temperatures of CZ powders. The ceramics with CZ powder synthesized at 900 °C possessed the highest T phase fraction (~ 0.80), whereas the ones with CZ synthesized at 1200 °C exhibited the lowest T phase fraction (~ 0.528) [14,28]. As a result, through changing the calcination temperatures of CZ powder, the phase fraction of R-T phase coexistence was successfully tailored.

Figure 6(a) showed the d_{33} values of the ceramics sintered at different temperatures. The high d_{33} of each composition can be attained at an optimum sintering temperature, that is, d_{33} firstly increased and then decreased as the sintering temperatures increased. F. Bortolani *et al.* systematically investigated the sintering mechanism of KNN-based ceramics by an EDS analysis [29]. The results showed that too low sintering temperatures cannot guarantee a well-developed phase structure and too high sintering temperature can cause lots of volatilization of K/Na, both of which cannot warrant a good piezoelectricity [29]. Here, it is interesting to note that the ceramics with CZ synthesized at 900 °C simultaneously possessed a higher d_{33} of 445-455 pC/N and a wide sintering temperature range of 1070-1095 °C as compared with others. Fig. 6(b) showed the d_{33} values and phase fraction between T and R phases of the ceramics with CZ synthesized at different temperatures. It was noted that both d_{33} and γ (γ was the ratio of T_{fraction} to R_{fraction}) displayed a very similar variation. A high γ value corresponded to a large d_{33} value and vice versa, demonstrating that piezoelectric properties were strongly dependent on the fraction of T phase. The similar phenomenon was also observed in PZT-based and KNN-based ceramics with O-T phase coexistence, which might be attributed to the large lattice distortion and the induced internal stress in T phase [30]. Except for the phase fraction, the tetragonality ratio (c/a) also correlated with the piezoelectricity to some extent [31]. Therefore, the relationship between d_{33} and tetragonality ratio (c/a) was plotted in Fig. 6(c). d_{33} showed a linear variation with respect to tetragonality ratio (c/a), revealing a direct relationship between crystalline symmetry and piezoelectric properties [31]. Therefore, both the fraction of T phase and tetragonality ratio (c/a) can strongly affect the piezoelectric properties of this work, and thus the piezoelectric properties can be effectively enhanced by these two methods.

To further explain the difference of piezoelectricity among the ceramics containing different CZ powders, we observed the domain configurations by chemical etching method [32]. Figures 7(a) and (b) showed the typical SEM images of domain configurations in the ceramics with CZ synthesized at 900 °C. It was clearly showed that the complicated domain configurations were observed. As shown in Figs. 7(a) and (b), a considerable amount of short domain segments [marked by the yellow arrow] were observed, which was often found in KNN-based ceramics with O-T and/or R-T [33]. The formation of short domain segments was mainly attributed to the R-T phase boundary and the existence of 180° ferroelectric domain walls [33]. In addition, many sets of parallel striped domains [marked by the red arrow] were also found, as indicated in tetragonal KNN-based ceramics and PZT ceramics with high T phase content [33]. It was inferred that these parallel striped domain patterns mainly originated from large c/a ratio [33,34]. In addition, some watermark domains [marked by the dashed line] were due to the existence of 180° ferroelectric domain walls [Fig. 7(b)] [33,34]. For the ceramics with CZ synthesized at 1200 °C, only some short segment domains were observed in Figs. 7(c) and (d), which were much shorter than the ones [Figs. 7(a) and (b)]. Therefore, the domain configurations also supported the high T phase fraction and large c/a ratio in the ceramics with CZ synthesized at 900 °C, and meanwhile the vast domain patterns greatly benefited the piezoelectricity under the simulation of electric fields.

To investigate the effects of phase fraction on their ferroelectric properties, we performed the ferroelectric loops measurement, as shown in Figure 8(a). All the ceramics possessed the saturated ferroelectric loops and the saturability was related to

the calcination temperatures of CZ. Fig. 8(b) plotted the variations of remnant polarization (P_r) and coercive field (E_C) of the ceramics. Both P_r and E_C were strongly dependent on the calcination temperatures of CZ. Considering above-mentioned refinement results of phase contents, the more T phase fraction the ceramics possessed, the higher P_r and E_C value the ceramics possessed. The variations of P_r were consistent with the results of previous works, while E_C showed a controversial variation [6-8]. It is believed that the degree of lattice distortion and the induced internal stress are larger for the tetragonal phase than the rhombohedral phase, and thus the clamping effect during the motion of domain walls is greater in tetragonal phase [32]. The enhanced clamping effect on the domain wall motion can make it need higher electric fields to fully achieve a saturated polarization situation, accounting for the increase of E_C in the ceramics with high T phase content observed in this work.

Subsequently, the effects of phase fraction on the ferroelectric fatigue behavior were studied, as shown in Figs. 9(a)-(c). All the samples exhibited a saturated ferroelectric loop and slightly fluctuated even after 10^7 cycles, suggesting a good fatigue behavior. A subtle contrast can be observed among these ceramics, that is, the loops' saturation of the ceramics synthesized by one-step method almost kept unchanged, the loops of the ceramics with CZ synthesized at 900 °C were slightly improved and the degraded loops were found in the ceramics with CZ synthesized at 1200 °C after 10^7 cycles. Here, we also recorded the d_{33} values of the ceramics after 10^0 and 10^7 cycles, as shown in Fig. 9(d). One can see that all the samples showed a slight reduction in d_{33} after 10^0 and 10^7 cycles, suggesting an endurable fatigue behavior.

Deriving P_r values from P - E loops, the comparison concerning fatigue behavior among several representative lead-free material systems (e.g., KNN-, BT-, and BNT-based ceramics) was shown in Fig. 9(e) [35-39]. Consistent with the above-mentioned variation, normalized P_r of the ceramics synthesized by one-step method remained unchanged under fatigue cycles, whereas the ceramics with CZ synthesized at 900 °C and 1200 °C showed an increasing and a decreasing variation, respectively [Fig. 9(e)]. In addition, comparing with other results, our results showed an obvious improvement in fatigue behavior [Fig. 9(e)] [35-39]. According to the previous references, some factors can influence the fatigue behavior of a material, such as measurement conditions (e.g., temperature, voltage amplitude, frequency, electrodes and so on) and material itself (e.g., grain size, porosity, crystal structure and so on) [40]. In addition, some models were also proposed to explain the fatigue behavior, such as domain-wall pinning models, dead/blocking layer model, nucleation inhibition model and so on [40]. It is worth noting that the fatigue scenarios are usually explained by combining with two or more models instead of only one model [40]. In addition, the space charge is also widely recognized to exist in the bulk piezoceramics, which could accumulate at the grain boundary and reduce the ferroelectricity during electric cycles [35,40]. Here, due to the same measurement conditions, we reasonably attributed the fatigue behavior to the combination of phase fraction, space charge accumulation, grain size and porosity [40].

As discussed above, the higher T phase fraction, the more difficult the domain wall motion is. For the ceramics synthesized by one-step method and the ceramics with CZ synthesized at 900 °C, a high T phase fraction was observed [Table 1]. At the beginning of electric cycles, the domain walls were slightly pinned. After

experiencing the full cycles, the clamping domain walls were slightly loosened and then the ferroelectricity can be improved [35]. Meanwhile, the space charge could accumulate at grain boundaries during electric cycles, which would clamp the domain wall motion and deteriorate the ferroelectricity [35]. Furthermore, we took the cross-section morphologies of the samples into account. As shown in Figs. 10(a), the ceramics synthesized by one-step method, exhibited the considerable holes among grains, indicating a relatively porous microstructure. However, the other two compositions displayed the dense cross-section morphology with few holes [see Figs. 10(b) and (c)]. As we know, the fatigue behavior is closely related to the microstructure of the piezoceramic samples [40]. The porous microstructure will deteriorate the ferroelectricity of KNN-based ceramics during electric cycles due to the existence of pores and microcracks [40]. In addition, the corresponding grain size statistics were listed in Figs. 10 (d-f). The ceramics with CZ synthesized at 900 °C exhibited the maximum average grain size ($\sim 1.66 \mu\text{m}$), while the ones with CZ synthesized at 1200 °C displayed the minimum average grain size of ($1.33 \mu\text{m}$). Recently, Rubio-Macros *et al.* reported that the increased grain size could enhance the ferro/piezoelectric properties, and the decreased grain size could enhance the coupling effect between grains and grain boundaries, which hindered the domains switching [28]. Considering the complicated factors, a brief graphic chart was proposed to visually show the effect of these factors on the fatigue behavior of KNNS-CZ-BNH ceramics, as shown in Fig. 10(g). With the increasing degree, size or content, the space charge accumulation and porosity could deteriorate the ferroelectricity, while the T phase fraction and grain size improved the ferroelectricity after experiencing electric cycles. Thus, the slightly improved ferroelectricity of the ceramics with CZ synthesized at 900 °C after electric cycles was mainly attributed to the high T phase

fraction (~ 0.80), dense microstructure and large grain size, which surpassed the negative effect of space charge accumulation. The deteriorated ferroelectricity of the ceramics with CZ synthesized at 1200 °C after electric cycles was due to the low T phase fraction and fine grain size. The fatigue behavior of the ceramics synthesized by one-step method should lie between them because of the relatively high T phase fraction (~ 0.726) and moderate grain size, resulting in a fatigue-free behavior.

It was reported that the thermal stability of KNN-based ceramics can be effectively improved by doping CZ [21]. Here, we measured P - E loops of the ceramics as a function of temperatures, as shown in Figs. 11(a)-(c). It was observed that P - E loops of all samples became slim with increasing temperatures, resulting in the reduction in both P_r and E_C [Figs. 11(c) and (d)]. It is well known that the long-range ordered ferroelectric polarization and domain structures can be gradually destroyed with increasing temperatures, and finally a paraelectric phase was observed. Therefore, the decreased P_r was mainly attributed to the gradually vanished long-range ordered ferroelectric polarization and domain structures. On the other hand, E_C characterizes the difficulty to achieve a full domain wall motion and domain switching. With increasing temperatures, the domain structures gradually vanished, consequentially resulting in the decreased E_C . Furthermore, the ceramics with CZ synthesized at 900 °C exhibited the smallest variation of P - E loops as compared with other two ceramics, indicating that a high T phase fraction can effectively improve the thermal stability.

Here, we also compared the thermal stability of our work with other lead-free ceramics, as shown in Fig. 11(d). Previously, the addition of CaZrO_3 improved the temperature stability of KNN-based [see the green line in Fig. 11(d)] [21]. The

improvement of thermal stability and piezoelectricity was achieved by constructing KNN:ZnO composite ceramics [see the purple line in Fig. 11(d)] [41]. In this work, the enhanced thermal stability was observed in the ceramics with CZ powder synthesized at 900 °C possessing a high T phase fraction [see the red line in Fig. 11(d)], which was superior to the above-mentioned two ceramic systems and even comparable to KNLN6+CT ceramics that were previously considered to possess a good thermal stability [see the orange line in Fig. 11(d)] [42,43]. When the measurement temperatures reached as high as 200 °C, a high normalized P_r value of 0.61 was still observed in the ceramics with CZ synthesized at 900 °C [see the red line in Fig. 11(d)]. Fig. 11(f) displayed the comparison of d_{33} values among these ceramic systems. The ceramics of this work possessed a high d_{33} value of 375-450 pC/N, whereas a moderate or inferior d_{33} lower than 350 pC/N was observed in other ceramic systems. Therefore, tailoring the phase fraction can substantially improve the ferroelectric properties, fatigue behavior as well as thermal stability of KNN-based ceramics.

4. Conclusions

In this work, the $0.96\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-}0.01\text{CaZrO}_3\text{-}0.03\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ ceramics were prepared by the conventional sintering method. By tailoring the calcination temperatures of CaZrO_3 powders, the T (or R) phase fraction of R-T phase coexistence was successfully tailored. A higher T phase fraction can warrant a larger d_{33} value and d_{33} exhibited a linear variation with respect to tetragonality ratio value. More importantly, the substantial domain patterns were observed due to high T phase fraction and large c/a ratio, which greatly benefited the piezoelectricity. In addition, the improved ferroelectric fatigue behavior and thermal stability were also shown in

the ceramics containing high T phase ratio. We believe that our work can promote the design and understanding of high-performance KNN-based ceramics.

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Figure Captions

Figure 1: (a) XRD patterns of CaZrO_3 powders synthesized at different temperatures; (b) XRD patterns of the ceramics containing different CaZrO_3 powders and correspondingly enlarged XRD patterns in the 2θ range of $44-47^\circ$; (c) Intensity ratio between $[200]_{\text{PC}}$ and $[002]_{\text{PC}}$ peaks of the ceramics modified by CaZrO_3 powders synthesized at different temperatures. The XRD patterns were indexed according to the pseudo-cubic structure axes.

Figure 2: ε_r - T curves of the ceramics in the measurement temperature range of (a) $-150-200^\circ\text{C}$ and (b) $25-400^\circ\text{C}$.

Figure 3: (a) Raman spectra of the ceramics with CZ synthesized at 900°C as a function of temperatures ($-100-100^\circ\text{C}$). (b) Lorentz fitting of the Raman spectrum ($T=-150^\circ\text{C}$) in the wavenumber range of $500-700\text{ cm}^{-1}$. (c) Raman shift of ν_1 mode and relative permittivity with the variation of temperatures.

Figure 4: Temperature-dependent XRD patterns of the ceramic powder with CZ synthesized at 900°C in the 2θ range of (a) $20-60^\circ$ and (b) $45-46^\circ$. (c) Enlarged XRD patterns with $2\theta=45-46^\circ$ simulated by Lorentz fitting. The XRD patterns were indexed according to the pseudo-cubic structure axes.

Figure 5: Enlarged Rietveld refinement of the ceramics with CZ synthesized at 900°C .

Figure 6: (a) d_{33} values of the ceramics as a function of sintering temperatures. (b) d_{33} and γ ($\gamma=T_{\text{fraction}}/R_{\text{fraction}}$) and (c) d_{33} vs c/a of the ceramics with CZ synthesized at different temperatures.

Figure 7: SEM images of domain configurations in the ceramics with CZ synthesized at (a-b) 900°C and (c-d) 1200°C .

Figure 8: (a) P - E loops and (b) P_r & E_c values of the ceramics containing different

CZ powders.

Figure 9: P - E loops of the ceramics with CZ synthesized at (a) one-step method, (b) 900 °C, (c) 1200 °C as a function of electric cycles. (d) d_{33} value of the ceramics before and after 10^7 cycles. (e) Comparison of normalized P_r among different lead-free piezoceramic systems after electric cycles.

Figure 10: Cross-sections of the ceramics containing CaZrO_3 powder calcined at (a) 900 °C, (b) one-step method, and (c) 1200 °C. (d-f) The corresponding grain size statistics of the three compositions. (g) Effect of different factors on the ferroelectricity of KNNS-CZ-BNH ceramics after electric cycles.

Figure 11: Thermal stability of P - E loops of the ceramics with CZ synthesized at (a) one-step method, (b) 900 °C, and (c) 1200 °C. (d) P_r/P_{r-T} and (e) E_C/E_{C-T} values of several representative KNN-based ceramic systems as a function of temperature. (f) Corresponding comparison of d_{33} values among these ceramic systems.

Figure 1

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Figure 11

Table 1: Refinement results, sintering temperature and relative density of the ceramics containing CZ synthesized at different temperatures.

CaZrO ₃ powder synthesized @	R_w (%)	Sig	R		T		Phase fraction R/T	T_s^* (°C)	Relative density (%)
			a (Å)	α (°)	$a=b$ (Å)	c (Å)			
one-step	11.03	1.19	3.9682	89.93	3.9589	4.0109	0.274/0.726	1085	96.3
800 °C	11.06	1.18	3.9685	89.87	3.9634	4.0022	0.29/0.71		96.7
900 °C	11.07	1.16	3.9799	89.88	3.9651	4.0011	0.20/0.80		96.7
1000 °C	11.03	1.18	3.9795	89.86	3.9641	3.9985	0.377/0.623		96.6
1100 °C	10.01	1.20	3.9682	89.79	3.9636	3.9899	0.408/0.592	1090	96.9
1200 °C	10.95	1.18	3.9786	89.84	3.9663	3.9876	0.472/0.528	1090	96.9

* T_s represents the sintering temperature of each composition.