Giant Piezoelectric Effect and High Strain Response in $(1-x)(\text{K}_{0.45}\text{Na}_{0.55})(\text{Nb}_{1-y}\text{Sb}_y)\text{O}_3$
 $-x\text{Bi}_{0.5}\text{Na}_{0.5}\text{Zr}_{1-z}\text{Hf}_z\text{O}_3$ Lead-free Ceramics

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Abstract: Here, we reported a high electric field-induced strain value of 0.34% ($S_{\text{max}}/E_{\text{max}}=901 \text{ pmV}^{-1}$) under a low electric field of 3.7 kV/mm as well as a large d_{33} ($\sim 418 \text{ pC/N}$) in the $(1-x)(\text{K}_{0.45}\text{Na}_{0.55})(\text{Nb}_{1-y}\text{Sb}_y)\text{O}_3-x\text{Bi}_{0.5}\text{Na}_{0.5}\text{Zr}_{1-z}\text{Hf}_z\text{O}_3$ ceramics with $x=0.035$, $y=0.04$, and $z=0.75$, which is mainly ascribed to the involvement of R-T phase boundary as well as optimized compositions (Hf/Zr). We investigated the relationships among composition, phase boundary, and electrical properties through $(1-x)(\text{K}_{0.45}\text{Na}_{0.55})(\text{Nb}_{1-y}\text{Sb}_y)\text{O}_3-x\text{Bi}_{0.5}\text{Na}_{0.5}\text{Zr}_{1-z}\text{Hf}_z\text{O}_3$ ceramics. The R-T phase boundary is constructed in the ceramics with $0.035 \leq x \leq 0.05$, $0.04 \leq y \leq 0.08$, and $0 \leq z \leq 1.0$. Meanwhile, the highest piezoelectric coefficient of $d_{33} \sim 442 \text{ pC/N}$ were obtained for $x=0.0375$, $y=0.04$, and $z=0.15$ due to the coexistence of R and T phases. Both dielectric constant and remanent polarization can gain the most excellent values for R-T, which is responsible for the enhanced piezoelectricity. We believe that such an investigation can promote the electrical properties of (K, Na)NbO₃-based ceramics and then provide practical applications.

Keywords: Potassium-sodium niobate; Multiphase coexistence; Large piezoelectricity; High strain; Physical mechanism

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1. Introduction

Piezoceramics are always one of the most important and widely used materials, and the related researches are becoming a forefront of high-technology advanced materials.^[1-9] Pb(Zr, Ti)O₃ (PZT) ceramics are currently used in many electric devices (e.g., sensors, actuators, ultrasound, transducers, etc.) because of their excellent piezoelectric effect and electric field-induced strain response.^[4-7, 10, 11] However, lots of researchers paid more attention to toxic Pb element instead of the everyday applications in the PZT ceramics. High lead content (~60%) of PZT caused some serious damages on environment and human during their preparation, process, and even disposal.^[4-7, 10, 11] As a result, some countries or regions pass the related laws or regulations including “waste of electrical and electronic equipment” (WEEE) and “restriction of the use of certain hazardous substance in electrical and electronic equipment” (RoHS) from the EU ^[5, 12, 13] for maintaining the sustainable developments. Therefore, considerable attention has been paid to the developments of lead-free piezoceramics to substitute lead-based ones.^[5, 14, 15]

Among these lead-free materials, (K,Na)NbO₃ (KNN) has become the most extensive investigations in the field of lead-free piezoceramics.^[5-7, 13-17] In the previous reports, some significant and typical breakthroughs have been achieved in KNN materials.^[6, 5-7, 18-21] For example, a remarkable achievement in d_{33} was obtained in 2004, that is, a high d_{33} (~416 pC N⁻¹) can be gained in the KNN ceramics doped by Ta, Sb, and Li via the complicated reaction template grain growth (RTGG) method.^[6] After that,

some researchers gradually began to investigate the relationships between their phase boundary and electric properties in order to realize the further breakthroughs.^[5, 18-20] Through extensively exploring and positively investigating for more than 10 years, one can know that the phase boundaries types of KNN-based ceramics also seriously affect its piezoelectric activity, although the multiphase coexistence can further enhance their electrical properties.^[5-7,18-20] Before 2013, there are mainly two kinds of phase boundaries {rhombohedral-orthorhombic (R-O) and orthorhombic-tetragonal (O-T)} in the KNN-based ceramics, and an enhancement in piezoelectric property can be reached by shifting two phase transition temperatures to/near room temperature.^[5-7, 16-21] Recently, it has been found that rhombohedra-tetragonal (R-T) phase coexistence as one kind of new phase boundaries can be constructed in KNN-based ceramics by shifting their T_{R-O} and T_{O-T} to room temperature simultaneously,^[18, 21-23] and a dramatic enhancement of piezoelectricity can be achieved when the R-T phase boundary stays at/near room temperature. Since 2014, we have developed new KNN-based ceramics with a large piezoelectricity ($\sim 490 \text{ pC/N}^{-1}$) and got a T_C of 225°C by designing the R-T phase boundary using the refinement of the compositions,^[17] and however a relative low strain was achieved^[24]. More importantly, the investigation on the relationships among composition, phase boundary, and electrical properties in KNN-based materials are very critical to further understand the physical mechanisms and tailor their electrical properties. For example, the compositions (Zr, Ti, Sn or Hf) dependence of phase structure and electrical properties of KNN-based ceramics was investigated in detail, and the doped element types strongly affect the

piezoelectric effect by the change of phase structure.^[25] However, the effects of Hf/Zr on the phase structure and electrical properties of KNN-based ceramics were few reported.

In this work, we developed the $(1-x)(\text{K}_{0.45}\text{Na}_{0.55})(\text{Nb}_{1-y}\text{Sb}_y)\text{O}_3-x\text{Bi}_{0.5}\text{Na}_{0.5}\text{Zr}_{1-z}\text{Hf}_z\text{O}_3$ (abbreviation: KNNS-BNZH- x - y - z) material systems for simultaneously attaining a large d_{33} and a high strain, where x , y , and z are the following variations as shown below: x changed from 0 to 0.06 with $y=0.04$ and $z=0.15$, y changed from 0 to 0.10 with $x=0.035$ and $z=0.15$, z changed from 0 to 1.00 with $x=0.035$ and $y=0.04$. In this ceramics system, we investigated the composition dependence of their electric properties and phase boundary in detail, and the enhanced piezoelectricity was attained by constructing the R-T phase boundary. One can know that the doping with BNZ and Sb can greatly contribute to the formation of R-T phase boundary by increasing $T_{\text{R-O}}$ and decreasing $T_{\text{O-T}}$,^[26] and the addition of BNH and Sb also establishes a similar phase boundary.^[27] However, there were few reports on the influences of BNH, BNZ, and Sb content on the phase boundary and electrical properties of KNN ceramics. Finally, we realized the R-T phase boundary in the ceramics with $x=0.035\sim0.05$, $y=0.04\sim0.08$, and $z=0\sim1.00$ and then obtained a significant enhancement in their electric properties of this R-T regions. The specific relationships between R-T phase boundary and the enhanced electrical properties were also addressed.

2. Experimental procedure

The KNNS-BNZH- x - y - z piezoceramics were prepared by the conventional solid-state reaction method, and raw materials were carbonates or oxides including K_2CO_3 (99.0%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), HfO_2 (99.0%), Sb_2O_3 (99.99%), Bi_2O_3 (99.999%), and ZrO_2 (99%). All the raw materials were weighed according to the corresponding formula, and then were ball milled for 24 hours (h) with both ZrO_2 ball media and pure alcohol. The dried powders were calcined at 850 °C for 6 h and then were pressed into the disks with a diameter of ~1.0 cm and a thickness of ~1.0 mm under a pressure of 10 MPa after using the PVA as a binder. The specimens were sintered at 1070~1090 °C for 3 h in air after burning off the PVA. The silver paste covered on both sides of the samples at 600 °C for 10 min in order to characterize their electrical properties. All samples were polarized in a silicon oil bath of room temperature by applying a direct current electric field of 3-4 kV/mm for 30 min.

The X-ray diffraction (XRD) machine with a Cu k_α radiation in the θ - 2θ scan mode (Bruker D8 Advanced XRD, Bruker AXS Inc., Madison, WI, CuK α) was used to analysis the phase structure of the ceramics. Their surface microstructures were measured by a field-emission scanning electron microscope (FE-SEM) (JSM-7500, Japan). And the dielectric against measured temperature (-150~200 °C, and 30~450 °C) of the samples were characterized with an *LCR* analyzer (Tonghui 2816A, China and HP 4980, Agilent, U.S.A.). The characterization of piezoelectric coefficient d_{33} was achieved by piezo-meter (ZJ-3A, China), and the planar electromechanical coupling factor k_p was measured by an impedance analyzer (HP 4294A). The polarization versus electric field (P - E) hysteresis loops of the samples were measured by a ferroelectric tester (radiant Technologies, Inc. Albuquerque, NM, USA) under a frequency of 10 Hz. And then the strain was measured by a MTI-2000 fonic sensor

under the applied electric fields at 10 Hz and room temperature.

3. Result and discussion

Figures 1(a), (c), and (e) show the XRD patterns of KNNS-BNZH- x - y - z ceramics, measured at $2\theta=20^\circ\sim60^\circ$ and room temperature. As shown in Figs. 1(a), (c), and (e), one can know that all samples show a typical perovskite structure, indicating that BNZH, Sb^{5+} , and Hf^{4+} can well diffuse into the KNN matrix successfully. However, the secondary phases still appear when a high Sb content was introduced, as indicated in Fig. 1(c). We preliminarily thought that this phenomenon mainly comes from the excessive Sb element [28] and then they can't completely diffuse into the matrix and generate the secondary phases. In order to further understand the phase evolutions, their amplified XRD patterns with $2\theta=44\text{--}47^\circ$ are shown in Figs. 1(b), (d), and (f). It can be found that their phase structure is strongly sensitive to the dopants contents, where the diffraction peak shapes change with various compositions. And we know that the judgment of phase structure needs more accurate measurement methods, and so the temperature-dependence of dielectric constant ($\epsilon_r\sim T$) curves and XRD patterns were jointly used to further confirm the phase transitions. It can be found from Fig. S1 that $T_{\text{R-O}}$ increases and $T_{\text{O-T}}$ decreases as x and y values increase, and then they are shifted to $T_{\text{R-T}}$ around room temperature by the compositions design. However, one can also know that Hf^{4+} and Zr^{4+} have a similar effect on their phase transition temperatures (See Fig. S1), where their $T_{\text{R-T}}$ does not show a similar trend as Zr^{4+} was replaced by Hf^{4+} . Therefore, by simultaneously considering both XRD patterns and

$\varepsilon_r \sim T$ curves, it can come to a conclusion, as shown below: O phase for $0 \leq x < 0.02$ and $y < 0.02$, O-T phase boundary for $0.02 \leq x \leq 0.03$ and $0.02 \leq y \leq 0.03$, R-T phase boundary for $0.035 \leq x \leq 0.05$ and $0.04 \leq y \leq 0.08$, and R phase for $x = 0.06$ and $y = 0.10$.

In addition, the Curie temperature (T_C) of the ceramics can be determined by the dielectric peak positions [Seen Figs. 2(a)-(c)], that is, their T_C values reduce as both BNZH and Sb^{5+} contents increased, and a stable T_C value can be observed for the addition of Hf^{4+} . Hence, both BNZH and Sb^{5+} can benefit the construction of R-T phase boundary, and Hf^{4+} and Zr^{4+} has a similar effect on the formation of phase boundaries.^[21] In order to further understand the phase transitions of the ceramics, we also plotted the phase diagram according to their $\varepsilon_r \sim T$ curves, as indicated in Figs. 2(d)-(f). We can observe from Figs. 2(d)-(f) that the phase structure gradually changed as the contents of BNZH and Sb^{5+} increased, while a phase coexistence can be found for the addition of different Hf^{4+} . As a result, O-T phase coexistence occurred for $0.02 \leq x \leq 0.03$ and $0.02 \leq y \leq 0.03$, and R-T phase boundary appeared for $0.035 \leq x \leq 0.05$, $0.04 \leq y \leq 0.08$, and $0 \leq z \leq 1$.

For analyzing the microstructure evolution, we measured the FE-SEM images of the ceramics with different compositions, as shown in Fig. 3. From these images, it can be found that all sintered samples can form a stable solid solution and their grain sizes increase firstly and then decrease as the doping contents increase. More interestingly, the grain size distribution was obtained to analyze the microstructure evolution of the

ceramics, as shown in Fig. 4. One can see from Figs. 4(a)~(l) that the grain sizes show a strongly compositional dependence, and their average grain sizes increase firstly and then decrease with increasing x , y or z [See Figs. 4(m)~(o)]. The reason can be explained as followed: when the x , y , and z stay a lower value, Bi^{3+} , Sb^{5+} , Zr^{4+} , and Hf^{4+} can well enter into the KNN lattice and provide more oxygen vacancies that always promote the grain growths.^[22] We can also see that a higher x , y or z value results in the smaller grain sizes due to the excessively doped elements,^[29] and then the stable solid solutions together with a dense microstructure can be formed as smaller grains gather into the gaps among larger ones.^[22,23] Therefore, the doping with BNZH, Sb^{5+} , Zr^{4+} , and Hf^{4+} has a significant influence on their grain growths.

Figures 5(a)-(c) show the composition dependence of piezoelectric coefficient (d_{33}) and electromechanical coupling factor (k_p) of the ceramics with different additives, measured at room temperature. We can know from Fig. 5 that the d_{33} is strongly dependent on the BNZH and Sb^{5+} contents and is almost independent on the ratio of $\text{Zr}^{4+}/\text{Hf}^{4+}$. However, there is a similar changing trend of d_{33} and k_p , that is, the values of d_{33} and k_p increase firstly and then decrease as both x and y increase. In particular, d_{33} and k_p respectively reach maximum values of ~ 442 pC/N and $\sim 49\%$ with the composition of $x=0.0375$, $y=0.04$, and $z=0.15$. This value is much higher than that ($d_{33}\sim 80$ pC/N and $k_p\sim 23.2\%$) of a pure KNN one,^[15-23, 30] and is even much larger with respect to some typical KNN-based ceramics with different additives,^[6, 13, 21, 25,26, 31] as shown in Table 1. It can persuasively indicate that BNZH and Sb^{5+} can significantly enhance piezoelectric property of KNN ceramics. Interestingly, it must

be put forward that the most excellent d_{33} and k_p values are always obtained in the ceramics with the multiphase coexistence regions, and especially the obvious improvement in piezoelectricity can be gained as the ceramics possess a R-T phase boundary rather than the O-T one. As a result, this phenomenon further proved the close relationships between piezoelectric property and multiphase coexistence in KNN-based ceramics again.^[5, 6, 13, 17-23,30,32] In addition, the highest $d_{33} \sim 442$ pC/N can be well established in the ceramics with $z=0.15$, although all samples attained relatively high d_{33} and stayed R-T phase boundary with increasing z . Hence, the enhanced piezoelectric response can be achieved by constructing R-T phase boundary using the composition modification of these additives.^[5, 6, 13, 17-23, 30,32]

In addition, one can see from Fig. S2(a) that ϵ_r increases for $0 \leq x \leq 0.035$ and then slightly decreases for $0.035 \leq x \leq 0.06$, reaching a maximum value (~ 2250) for $x=0.035$ which belong to R-T phase boundary region. It should be well known that phase boundary and defects can be responsible for the increasing of dielectric, and be proved in this ceramics again.^[33] For illuminating the physical mechanisms of the enhanced d_{33} , the curves of $\epsilon_r P_r$ and d_{33} against the compositions are shown in Figs. 6(a)-(c). As shown in Figs. 6(a)-(c), the composition dependence of d_{33} and $\epsilon_r P_r$ curves presented a similar tendency, that is, both d_{33} and $\epsilon_r P_r$ firstly increase and then decrease as the x , y , and z contents increase. More interestingly, the peak values of d_{33} and $\epsilon_r P_r$ are always obtained at the same x , y , and z values, and both of them belong to the phase boundary regions.^[32] Based on the equation of $d_{33} \sim \epsilon_r P_r$, one can know that the improvement of ϵ_r and P_r can also lead to the enhanced d_{33} except for the involvement of phase boundaries.^[5, 17]

The P - E curves of the ceramics as a function of x , y , and z were shown in Figs. 7(a)-(c), measured at room temperature and 10 Hz. We can see from Figs. 9(a) and (b) that the ceramics with $0 \leq x < 0.04$ and $0 \leq y < 0.08$ exhibit typical ferroelectric hysteresis loops, while there is a slim P - E loop for $x \geq 0.04$ and $y \geq 0.08$. In addition, all the ceramics with different Hf^{4+} contents can obtain the saturated P - E loops [See Fig. 7(c)]. In order to further understand the ferroelectric property, we plotted the composition dependence of their remnant polarization (P_r) and coercive field (E_C), as shown in Figs. 7(d)-(f). As the BNZH contents increase, one can see that P_r reduces dramatically and a light increase still appeared for the phase boundary regions [See Figs. 7(d) and (e)]. However, E_C still increases firstly and then decreases as x increases. It is well known that P_r can represent the ferroelectric property of KNN ceramics, and then the doping with BNZH will degrade the ferroelectric property with respect to a pure KNN ceramic.^[34, 35] On the other hand, E_C has a close relationship with microstructure, indicating the changed tendency comes from the change of grain size,^[31] that is, E_C decreases gradually with decreasing grain sizes.^[36] This phenomenon may be due to the clamping effect by the neighboring grains, which can make the domain wall motion difficult.^[37] For the ceramics containing Sb^{5+} , we can learn from Fig. 7(b) that both P_r and E_C decrease as y increases, which conforms to the previously reports about Sb^{5+} -modified KNN ceramics.^[38,39] In addition, P_r increases for $0 \leq z \leq 0.25$ and decreases for $0.25 < z \leq 0.5$, then slightly increase for $0.5 < z \leq 0.75$, and finally decreases again. Nevertheless, their E_C values almost keep unchanged as the z values increase except for a light decrease for $z=0.25$. As a result, the change of Hf^{4+}

contents may slightly affect the ferroelectric property of the ceramics system, indicating that Hf^{4+} and Zr^{4+} have a similar effect on their ferroelectric properties.

Figures 8(a)-(c) show the composition dependence of the normalized d_{33} against annealing temperatures (T_a) of the ceramics. From these figures, the normalized d_{33} reduces slowly and stays relatively high values in all samples before T_a reaches their corresponding T_C . However, apparent reductions in d_{33} occur when T_a is above T_C , and then the normalized d_{33} drops to zero eventually. As a result, this ceramics system possesses a good thermal stability of d_{33} for $T_a < T_C$.

Figures 9(a)-(c) show the unipolar electric field -induced strain curves of the ceramics as a function of x , y , and z , measured at $f=10$ kHz and room temperature. As shown in Fig. 9, typical unipolar strain curves can be attained in this ceramics. In order to further analyze the composition dependence of strain values, we plotted both strain and d_{33}^* against the x , y , and z contents of the ceramics, as shown in Figs. 9(d)-(f). The maximum strain and d_{33}^* obtain a similar changed trend as the contents of BNZH, Sb^{5+} , and Hf^{4+} increase. Maximum strain and d_{33}^* increase for $0 \leq x \leq 0.03$ and drop for $0.03 \leq x \leq 0.06$ ($y=0.04$, $z=0.15$), as shown in Fig. 9(d). And they increase for $0 \leq y \leq 0.02$ and reduce for $0.06 \leq y \leq 0.10$, and stay high values for $0.02 < y < 0.6$ ($x=0.035$ and $z=0.15$) [See Fig. 9(e)]. It can be found that the enhancement of strain always happened in the ceramics with multiphase coexistence.^[25,40-45] For example, Li *et al.* reported a high unipolar strain of 0.18% in $0.92(\text{Na}_{0.535}\text{K}_{0.48})\text{NbO}_3\text{-}0.08\text{LiNbO}_3$ ceramics with the O-T phase coexistence,^[43,44] and a high strain of 0.14% was observed in the

(K_{1-x}Na_x)_{0.92}Li_{0.08}NbO₃ ceramics due to the involvement of O-T phase boundary.^[45]

Then it can be conclusion that the formation of phase boundaries can result in high strain and d_{33}^* of this work, and the R-T phase boundary may be responsible for the enhanced unipolar strain of this work. However, we can notice from Fig. 9(c) that the two values drop slightly for $0 \leq z \leq 0.15$, increase dramatically for $0.15 < z < 0.75$, and then decrease again for $0.75 \leq z \leq 1.00$ ($x=0.035$, $y=0.04$), as shown in Fig. 9(f). More importantly, the maximum strain ($\sim 0.34\%$) and d_{33}^* ($\sim 901 \text{ pmV}^{-1}$) values can be attained in the ceramics with $x=0.035$, $y=0.04$, and $z=0.75$. Such a result indicates that the co-addition of Hf and Zr can further enhance the strain behavior of KNN-based ceramics, and the strain behavior is sensitive to not only the phase boundary but also the doped composition.^[25,40-45] Table 1 lists the strain values of the samples in this work and the available data of other KNN -based ceramics.^[6, 13, 21, 25,26,31] One can know that both of strain and d_{33}^* values of this work are obviously larger than those of reported KNN-based ceramics.

4. Conclusion

KNNS-BNZH- x - y - z ceramics was fabricated by a conventional solid-state reaction method, and BNZH, Sb⁵⁺, and Hf⁴⁺ significantly affect their phase structure and electric properties. Enhanced electrical properties were achieved due to the formation of R-T phase boundary by adjusting the x , y , and z values. Due to R-T phase coexistence region, a large d_{33} value of $\sim 442 \text{ pC/N}$ as well as a high k_p value of $\sim 49\%$ were obtained in the ceramics with $x=0.0375$, $y=0.04$, and $z=0.15$, together with a

high T_C of 250 °C. In addition, there are both higher strain value of 0.34% ($S_{\max}/E_{\max}=901 \text{ pmV}^{-1}$) under a low electric field of 3.7 kV/mm and large d_{33} of 418 pC/N in the ceramics with $x=0.035$, $y=0.04$, and $z=0.75$, which is superior to those of the previously reported KNN-based ceramics. In consequence, the additives of BNZH, Sb^{5+} , and Hf^{4+} can apparently benefit the enhancement of electrical properties by constructing R-T phase boundary using the suitable compositions, providing a new method to obtain high-performance potassium-sodium-niobate materials.

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Table 1. Electrical properties of KNN -based ceramics

Composition	d_{33} pC/N	Strain %	d_{33}^* pmV ⁻¹	T_c °C	Ref.
$(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.10}Sb_{0.06})O_3$	416	—	750/2.0kV/mm	253	6
$0.96[(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}Nb_{1-x}Sb_xO_3]-0.04[BaZrO_3]$	400	—	—	175	42
$(K,Na)(Nb,Sb)O_3-Bi_{0.5}Na_{0.5}AO_3$ (Hf, Zr, Ti, Sn)	450	0.25/3.0kV/mm	834/3.0kV/mm	242	41
$(1-x)(K_{0.48}Na_{0.52})(Nb_{0.95-y-z}Ta_zSb_y)O_3-xBi_{0.5}(Na_{0.82}K_{0.18})_{0.5}ZrO_3$	400	0.18/2.5kV/mm	706/2.5kV/mm	240	13
$(1-x)(K_{0.4}Na_{0.6})(Nb_{0.96}Sb_{0.04})O_3-xBi_{0.5}K_{0.5}Zr_{1-y}Sn_yO_3$	427	0.22/2.5kV/mm	880/2.5kV/mm	268	21
$(1-x)K_{0.45}Na_{0.55}Nb_{0.96}Sb_{0.04}O_3-xBi_{0.5}Na_{0.5}HfO_3$	419	0.31/5.1kV/mm	608/5.1kV/mm	242	26
$(1-x)(K_{0.45}Na_{0.55})(Nb_{1-y}Sb_y)O_3-xBi_{0.5}Na_{0.5}Zr_{1-z}Hf_zO_3$	442	0.34/3.7kV/mm	901/3.7kV/mm	250	This work

Figure captions

Fig. 1: XRD patterns of KNNS-BNZH- x - y - z ceramics as a function of (a) x ($y=0.04$, $z=0.15$), (c) y ($x=0.035$, $z=0.15$), and (e) z ($x=0.035$, $y=0.04$) measured at $2\theta=20-60^\circ$. (b), (d), and (f) are the magnified XRD patterns at $2\theta=44-47^\circ$.

Fig. 2: $\varepsilon_r \sim T$ curves of KNNS-BNZH- x - y - z ceramics as a function of (a) x ($y=0.04$, $z=0.15$), (b) y ($x=0.035$, $z=0.15$), and (c) z ($x=0.035$, $y=0.04$), measured at 30-450 °C. Phase diagram of KNNS-BNZH- x - y - z ceramics with (a) x ($y=0.04$, $z=0.15$), (b) y ($x=0.035$, $z=0.15$), and (c) z ($x=0.035$, $y=0.04$).

Fig. 3: FE-SEM images of the ceramics with different compositions: (a)~(h) $x=0$, 0.01, 0.02, 0.03, 0.035, 0.04, 0.05 and 0.06 ($y=0.04$, $z=0.15$); (i)~(l) $y=0$, 0.04, 0.06 and 0.10 ($x=0.035$, $z=0.15$); (m)~(p) $z=0$, 0.15, 0.50 and 1.00 ($x=0.035$, $y=0.04$).

Fig. 4: Grain size of the ceramics with different compositions: (a)~(d) $x=0$, 0.02, 0.035, 0.05 ($y=0.04$, $z=0.15$); (e)~(h) $y=0$, 0.04, 0.06 and 0.10 ($x=0.035$, $z=0.15$); (i)~(l) $z=0$, 0.15, 0.50 and 1.00 ($x=0.035$, $y=0.04$). And composition dependence of grain sizes as a function of (m) x ($y=0.04$, $z=0.15$), (n) y ($x=0.035$, $z=0.15$), and (o) z ($x=0.035$, $y=0.04$).

Fig. 5: Composition dependence of d_{33} and k_p of the ceramics with (a) x ($y=0.04$, $z=0.15$), (b) y ($x=0.035$, $z=0.15$), and (c) z ($x=0.035$, $y=0.04$).

Fig. 6: Composition dependence of d_{33} and $\varepsilon_r P_r$ of the ceramics with (a) x ($y=0.04$, $z=0.15$), (b) y ($x=0.035$, $z=0.15$), and (c) z ($x=0.035$, $y=0.04$).

Fig. 7: P - E curves of KNNS-BNZH- x - y - z ceramics as a function of (a) x ($y=0.04$, $z=0.15$), (b) y ($x=0.035$, $z=0.15$) and (c) z ($x=0.035$, $y=0.04$). (b), (e) and (f) are their corresponding P_r and E_c values.

Fig. 8: Thermal stability of KNNS-BNZH- x - y - z ceramics as a function of (a) x ($y=0.04$, $z=0.15$), (b) y ($x=0.035$, $z=0.15$), and (c) z ($x=0.035$, $y=0.04$).

Fig. 9: unipolar strain curves of KNNS-BNZH- x - y - z ceramics as a function of (a) x ($y=0.04, z=0.15$), (b) y ($x=0.035, z=0.15$) and (c) z ($x=0.035, y=0.04$). Maximum value of the strain and d_{33}^* of the ceramics with the composition of (d) x ($y=0.04, z=0.15$), (e) y ($x=0.035, z=0.15$) and (f) z ($x=0.035, y=0.04$).

Fig. 1

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