Electrical Properties of Holmium doped (K,Na)(Nb,Sb)O₃-(Bi,Na)HfO₃ Ceramics with Wide Sintering and Poling Temperature Range

Hong Tao¹, Wenjuan Wu², and Jiagang Wu^{1,*}

¹*Department of Materials Science, Sichuan University, 610064, P. R. China*

²*Sichuan Province Key Laboratory of Information Materials and Devices Application, Chengdu University of Information Technology, Chengdu 610225, P. R. China*

Abstract: Here the electrical properties can be modified by the chemical compositions $\{0.965\text{K}_{0.45}\text{Na}_{0.55}\text{Nb}_{(1-x)}\text{Sb}_x\text{O}_3-0.035\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3, \text{KNNS}_x\text{-BNH}\}$, and moreover its temperature (i.e., sintering or poling temperatures) sensitivity of piezoelectricity can be further weakened by doping rare earth (i.e., Ho), which is beneficial to reproduction. Rhombohedral-tetragonal (R-T) phase boundary can be formed in the ceramics with a wide composition range of $x=0.04\sim 0.08$ by simultaneously increasing rhombohedral-orthorhombic (R-O) phase transition temperature ($T_{\text{R-O}}$) and decreasing orthorhombic-tetragonal (O-T) phase transition temperature ($T_{\text{O-T}}$). The R-T phase boundary warrants a large piezoelectric coefficient (d_{33}) of ~ 418 pC/N as well as a high Curie temperature (T_{C}) of ~ 242 °C in the ceramics with $x=0.04$, and a high electric field-induced strain of $\sim 0.33\%$ ($S_{\text{max}}/E_{\text{max}}=983$ pm V⁻¹) as well as a large d_{33} (~ 408 pC/N) can be attained in the ceramics with $x=0.07$. Especially, a high recoverable energy density ($W_{\text{rec}}\sim 0.54$ J/cm³) can be gained in the ceramics with $x=0.10$ under a low breakdown strength (~ 129 kV/cm). The piezoelectricity sensitive to sintering or poling temperatures can be weakened by introducing Ho element, that is, a high d_{33} of 400-458 pC/N can be attained in a wide range of sintering temperatures (1070-1120 °C) and poling temperatures (13~120 °C).

We believe that this investigation can be a significant promotion on the development of practical applications in (K, Na)NbO₃-based ceramics.

Keywords: Potassium-sodium niobate; Multiphase coexistence; Giant piezoelectricity; High strain; Rare earth (Ho)

***Corresponding author:** wujiagang0208@163.com and msewujg@scu.edu.cn

1. Introduction

High performance lead-free piezoelectric ceramics have been considered to be one of the most potential candidates to replace lead-based ones because a high Pb content in lead-based ceramics is harmful to environment and human health.^[1-13] In the past ten years, the potassium-sodium niobate [(K, Na)NbO₃, KNN] ceramics have drawn great attention with the aim of achieving high piezoelectric properties.^[1-13] For example, in 2004, a breakthrough in piezoelectric constant (d_{33} =416 pC/N) was realized in the (K, Na, Li)(Nb, Ta, Sb)O₃ ceramics by Saito *et al.*,^[9] and another great advance of a high piezoelectric constant (d_{33} =490 pC/N) was obtained in a new KNN-based ceramic in 2014,^[14] proving the progressive development of KNN-based ceramics by chemical modifications.

According to the developments of KNN-based ceramics, one can see that chemical modifications are one of the most effective ways to promote their electrical properties,^[3, 14-20] and moreover some typical progresses have been achieved in terms of the enhancement of electrical properties [See Table 1].^[9, 21-24] Obviously, it was found that the enhanced piezoelectricity of KNN-based ceramics is very related to the addition of Sb⁵⁺.^[17, 23-25] The KNN-based ceramics with R-T phase boundary

possessed a high d_{33} , but their piezoelectric response is strongly sensitive to the sintering and poling temperatures.^[3, 25, 26] The reproduction of KNN-based ceramics will be seriously affected due to the sensitivity to sintering and poling temperatures. Therefore, it is urgent to develop one way to solve this shortcoming. Here we hope to decrease the sensitivity to sintering and poling temperatures of KNN-based ceramics by introducing rare elements.

In this work, the energy storage density, piezoelectric and strain properties can be improved in the $0.965\text{K}_{0.45}\text{Na}_{0.55}\text{Nb}_{(1-x)}\text{Sb}_x\text{O}_3\text{-}0.035\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ (KNNS_{*x*}-BNH) lead-free ceramics, and its sintering and poling temperatures sensitivity of piezoelectricity can be weakened by doping rare earth (i.e., Ho). Different phase boundary types can be tuned by changing the content of Sb^{5+} , and then a high d_{33} (~418 pC/N) and a large strain (~0.33%) were achieved in the R-T multiphase coexistence region. A high recoverable energy density ($W_{\text{rec}} \sim 0.54 \text{ J/cm}^3$) can be gained in the ceramics with $x=0.10$ under a low breakdown strength (~129 kV/cm). In addition, a weak dependence of piezoelectricity on sintering and poling temperatures can be realized by doping Ho, and importantly a large d_{33} (~458 pC/N) as well as a high T_C (~250 °C) can be well maintained. Especially, the recoverable energy density of the ceramics will be also investigated.

2. Experimental procedure

Lead-free ceramics including $0.965\text{K}_{0.45}\text{Na}_{0.55}\text{Nb}_{(1-x)}\text{Sb}_x\text{O}_3\text{-}0.035\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ (KNNS_{*x*}-BNH) and $0.965\text{K}_{0.45}\text{Na}_{0.55}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-}0.035(\text{Bi}_{0.90}\text{Ho}_{0.10})_{0.5}\text{Na}_{0.5}\text{HfO}_3$ {KNNS_{0.04}-B(Ho)_{0.10}NH} were fabricated by conventional solid-state method, and raw materials include K_2CO_3 (99.0%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), HfO_2

(99.0%), Sb_2O_3 (99.99%), Ho_2O_3 (99.99%), and Bi_2O_3 (99.999%). All raw materials were ball milled for 24 hours (h) with both ZrO_2 ball media and pure alcohol after weighed according to the corresponding formula. The powders 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 with the PVA as a binder after calcining at 850°C for 6 h. Finally, the pellets were sintered at $1065\sim 1100^\circ\text{C}$ for 3 h in air after removing PVA. In order to characterize their electrical properties, electrodes were placed on opposite sides of the ceramics using silver paste at 550°C for 10 min. All samples were poled in a silicon oil bath at room temperature by applying a direct current electric field of 3.0-4.0 kV/mm for 15 min.

The phase structure of the sintered samples was conducted by the X-ray diffraction (XRD) patterns with the machine of a CuK_α radiation in the θ - 2θ scan mode (Bruker D8 Advanced XRD, Bruker AXS Inc., Madison, WI, $\text{CuK}\alpha$) and the temperature (-120°C - 200°C) dependence of Raman spectra with HR LabRam Raman spectroscopy system where a 514 nm Ar laser was used for excitation. Their surface microstructure, energy dispersive X-ray (EDX) spectroscopy, and elements mapping were measured by a field-emission scanning electron microscope (FE-SEM) (JSM-7500, Japan). 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 $1^\circ\text{C}/\text{min}$ and at a frequency of 100 kHz. The relative permittivity (ϵ_r) and dielectric loss ($\tan \delta$) of the samples were measured by LCR analyzer (Tonghui 2816A, China and HP 4980, Agilent, U.S.A.). 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. 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. The strains that developed under the applied electric fields at 10 Hz and room temperature were measured with a MTI-2000 fotonic sensor.

3. Result and Discussion

3.1 Phase structure

It is well known that phase structure can strongly affect electrical properties of KNN materials, especially in the region of phase boundaries.^[3, 9, 14, 20, 25, 27, 28] Here the XRD patterns, temperature dependent of dielectric constant (ϵ_r - T), and Raman spectra were used to analyze the phase structure of the ceramics. Figures 1(a)-(c) show the room-temperature XRD patterns of the ceramics with different Sb^{5+} content, measured at $2\theta=20^\circ$ - 60° , 21° - 63° , and 45° - 47° . One can see from Fig. 1(a) that pure perovskite phases were observed in the ceramics with $x \leq 0.10$. According to the previous references, the doping with Sb^{5+} can induce the phase transition in KNN-based ceramics,^[23-25] which may be due to the position of Sb^{5+} as they enter into crystal lattice. Hence, the expanded XRD patterns were provided to further analyze their phase structure, as shown in Figs. 1(b) and (c). Obviously, the shapes of diffraction peaks gradually change with the increase of Sb^{5+} content. In addition, Figure 2 gives the ϵ_r - T curves of the ceramics, measured at -150°C ~ 200°C and 100 kHz. The phase transition of the ceramics can be analyzed preliminarily by both their XRD patterns and ϵ_r - T curves. It is worth noting that the temperature dependence of phase transitions changes with varied compositions, that is, $T_{\text{R-O}}$ increases and $T_{\text{O-T}}$ decreases when x changes from 0.01 to 0.03, and their $T_{\text{R-T}}$ appears for $x=0.04$ - 0.08 and the two characteristic peaks disappear for $x=0.09$ and 0.10 replaced by the peaks

of T_C . More importantly, their T_{O-T} and T_{R-T} always stay around room temperature, which can clearly explain the occurrence of the phase transitions including O-T and R-T in the ceramics. As a result, the composition dependence of phase structure of the ceramics can be defined as the following: $0.01 \leq x \leq 0.03$ for O-T, $0.04 \leq x \leq 0.08$ for R-T, and $0.09 \leq x \leq 0.10$ for pseudocubic.

To investigate the relationship between Sb^{5+} content and T_C , their ϵ_r-T curves were plotted in Fig. 3(a), measured at 30 °C~450 °C and 100 kHz. From the curves, the T_C of different composition can be gained except for $x=0.09$ because the peaks are a little broaden. To further analysis ϵ_r-T curve for $x=0.09$, the frequency dependence of dielectric constant is obtained, as shown in the insert of Fig. 3(a). One can see that the peak value decreases gradually and the temperature increases as the frequency increases from 10Hz to 100kHz.^[29, 30] Therefore, the temperature of the peak values cannot be used as T_C because the ceramics with $x=0.09$ can be relaxor. And then the phase diagram of the ceramics were established according to the data of ϵ_r-T curves, as shown in Fig. 3(b). As shown in this diagram, their T_C values decrease gradually when the content of Sb^{5+} increases. In addition, T_{R-O} increases and T_{O-T} decreases simultaneously, and then T_{R-T} can be kept around room temperature for $x=0.04-0.08$. As a result, the phase evolution of the ceramics can be defined as below: O-T for $0.01 \leq x \leq 0.03$, R-T for $0.04 \leq x \leq 0.08$, and pseudocubic for $x=0.09$ and 0.10.

It is very necessary to identify phase structure of the ceramics in order to unveil the origin of the enhanced electrical properties. In this work, the composition dependence of Raman spectra were also provided, measured at room temperature and in the frequency range of 100 to 1600 cm^{-1} , as shown in Fig. 4. One can see from Fig. 4(a)

that typical Raman spectra are obtained in the ceramics with different Sb contents, indicating the formation of a typical perovskite structure.^[24, 31-33] In addition, in order to analyze their phase transitions, the expanded Raman spectra in the wavenumber range of 450~700 cm^{-1} after background subtraction and simulated by Lorentzian method with $x=0.01, 0.03, 0.05$, and 0.08 were obtained, as shown in Figs. 4(b)~(e). According to these spectra, there are two peaks involved, which correspond to ν_1 (600 cm^{-1}) and ν_2 (550 cm^{-1}), respectively. More importantly, ν_1 mode shifts gradually as the content of Sb^{5+} increases, illustrating the phase transition-induced by the compositions. As a result, O-T phase boundary is formed in the ceramics with $x=0.01$ and 0.03 , and R-T phase boundary appears as O phase is submerged for $x=0.05$ and 0.08 , which matches the conclusion of XRD patterns and ε_r - T curves.

3.2 Microstructure

Figures 5(a)-(d) show the FE-SEM surface images of the ceramics with different Sb^{5+} content sintered at the same temperature (1075 °C). Their grain sizes firstly increase and then decrease as x increases from 0.01 to 0.08 . In addition, the grain size distribution of the ceramics with $x=0.01, 0.03, 0.05$, and 0.08 was presented, as shown in Figs. 6(a)~(d). One can see that there are larger grains in the ceramics with $x=0.03$ and 0.05 , while the grain sizes become smaller for $x=0.01$ and 0.08 . Furthermore, the average grain sizes of the ceramics as a function of x were plotted, as shown in Fig. 6(e). Their grain sizes firstly increase and then decrease, reaching a maximum value for $x=0.05$. The grain refinement happens in the ceramics with $x=0.08$ maybe due to the low sintering temperature.^[34, 35] High sintering temperature is necessary for the ceramics with high concentration, which were illustrated in previous reports.^[34, 35]

Moreover, the amount of holes firstly decrease and then increase with the increase of Sb^{5+} [See Fig. 5(a)-(d)], indicating that the addition of Sb^{5+} also improves the bulk density.^[36, 37] Therefore, the ceramics with large grain sizes and fewer holes can be achieved in the ceramics with $x=0.05$, which is in favour of the enhancement of electrical properties.^[38] Moreover, Sb is homogeneously distributed in all samples [Fig. 5(e)-(h)], indicating the well homogeneity in this ceramics.

3.3 Properties

In this work, the composition dependence of d_{33} and k_p in the ceramics were also characterized, as shown in Fig. 7(a). Both d_{33} and k_p firstly increase for $x=0.01-0.03$ and decline rapidly for $x \geq 0.08$, reaching a large value for $x=0.04-0.07$. In particular, one can see that the ceramics can stay high d_{33} values (>400 pC/N) for $x=0.04\sim 0.07$, and the largest d_{33} value (~ 418 pC/N) is gained for $x=0.04$. This result indicates that a giant piezoelectricity can be realized in KNN-based ceramics with a wide compositional range, which benefits the practical applications. More importantly, the formation of phase boundaries always makes a determined influence on the enhancement of d_{33} , especially the involvement of R-T phase boundary.^[13-20] For example, a high d_{33} of 416 pC/N was achieved in the textured (K, Na, Li)(Nb, Ta, Sb)O₃ ceramics with O-T phase boundary by Saito *et al.*,^[9] and another breakthrough of $d_{33}\sim 490$ pC/N was realized in the KNN-based ceramics with R-T phase boundary by Wu *et al.*^[14] The enhanced d_{33} mostly comes from the construction of phase boundaries, and the giant d_{33} in a wide composition range can effectively promote the development of their practical applications. However, the decreased d_{33} of the ceramics with $x=0.08$ may be due to the suppressed R-T phase boundary, which is characterized according to the subdued R-T peak and XRD patterns [Figs. 1 and 2].

Figure 7(b) shows the composition dependence of ε_r and $\tan \delta$ of the ceramics, measured at room temperature and 100 kHz. One can see that both ε_r and $\tan \delta$ show a similar changed tendency, that is, both of them increase gradually as the content of Sb^{5+} changes from 0.01 to 0.09 and then decrease for $x \geq 0.10$, which matches the previous relevant reports.^[17, 39] From this analysis, it is proved that the dielectric properties can be well enhanced when Sb^{5+} was added to KNN.^[40] It should be found that the electrical properties of KNN-based ceramics are very sensitive to preparation conditions.

To further analyze the influence of preparation condition on their electrical properties, rare earth element holmium (Ho) was doped to the ceramics $[0.965\text{K}_{0.45}\text{Na}_{0.55}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3-0.035(\text{Bi}_{0.90}\text{Ho}_{0.10})_{0.5}\text{Na}_{0.5}\text{HfO}_3]$. The sintering and poling temperatures dependence of d_{33} in the Ho-doped ceramics was presented, and piezoelectric response of the ceramics without rare earth element was also addressed for comparison, as shown in Figs. 7(c) and (d). One can see from Fig. 7(c) that the ceramics doped by Ho can stay a higher d_{33} (~458 pC/N) when the sintering temperatures change from 1080 °C to 1120 °C. However, there is a big fluctuation in d_{33} for the ceramics without Ho when the sintering temperatures were slightly changed. In addition, d_{33} of the Ho-modified ceramics increases firstly and then decrease with increasing poling temperature (T_p) as the same as the ones without Ho [See Fig. 7(d)], and all the values can stay above 400 pC/N for all poling temperatures. Moreover, the electrical properties (e.g., d_{33} , ε_r , T_C , P_r , E_c) of the ceramics with $x=0.04$ and the one modified by Ho were listed in Table 2. Both d_{33} and T_C can be slightly increased by introducing the rare earth of Ho. As a result, the addition of Ho can effectively attain a high d_{33} value in a wide sintering or poling temperature.

The P - E curves of the ceramics as a function of x was plotted in Fig. 8(a), measured at room temperature and 10 Hz. One can see from Fig. 8(a) that typical and saturated ferroelectric hysteresis were obtained in the ceramics with $x=0.01$ - 0.08 , indicating the formation of good ferroelectricity, and slim P - E loops were found in the ceramics with $x=0.09$ and 0.10 due to the phase transition (pseudocubic). In addition, the composition dependence of residual polarization (P_r) and coercive field (E_c) of the ceramics were provided to study the effects of Sb^{5+} on their ferroelectricity, as shown in Fig. 8(b). P_r decreases for $x=0.01$ - 0.03 , slightly fluctuates for $x=0.04$ - 0.07 , and then decreases quickly for $x \geq 0.08$. This phenomenon may be due to the combined effects of phase structure and grain size.^[41, 42] As for E_c , it shows a decreasing tendency as x increases gradually. Combined with previous reports,^[37, 43] the addition of Sb^{5+} can decrease the ferroelectricity in KNN ceramics.

It is well-known that the lead-free ceramics set the seal on high power energy storage applications because of relaxor ferroelectric phenomenon due to their high polarization saturation (P_s) and low remnant polarization (P_r).^[29, 30] Interestingly, the energy storage property of the ceramics with $x=0.10$ was attended as its appearance of relaxor. Therefore, the P - E hysteresis loop at different electric fields (11~129 kV/cm) were shown in Figs. 9(a)~(g), measured at 10 kHz and room temperature. One can get the values of high P_s ($23.47 \mu\text{C}/\text{cm}^2$) and low P_r ($4.86 \mu\text{C}/\text{cm}^2$) under the highest electric field (~129 kV/cm). For further analyzing the energy storage property, the recoverable energy density (W_{rec}) of the ceramic was provided according to the relative equation: $W_{\text{rec}} = \int_{P_r}^{P_s} E dp$, as shown in Fig. 9(h). A high recoverable energy

density value of 0.54 J/cm^3 is possessed under a low electric field as there were some reports on a high energy storage density of KNN-based ceramics, but unfortunately a high electric field of $>200 \text{ kV/cm}$ is often used in the past. [30,44]

The temperature dependence of d_{33} and normalized d_{33} in the ceramics with different x was used to show the thermal stability of the ceramics, as shown in Figs. 10(a) and (b). It can be obtained in Fig. 10(a) that d_{33} decreases as the annealing temperatures (T_a) increase. The curves of their normalized d_{33} vs temperatures were plotted in Fig. 10(b). It should be obviously noted that d_{33} of the ceramics with $x=0.01-0.07$ can stay a high value as T_a increases ($<T_C$) and drops quickly to zero for $T_a>T_C$ as it declines gradually for $x=0.08\sim 0.09$. As a result, d_{33} of the ceramics can stay a well thermal stability for $x\leq 0.07$ and shows a poor stability for $x\geq 0.08$ due to the R phase.

In recent years, some researchers have paid great attention to the strain of KNN-based ceramics. [3, 17, 24, 27] And some typical results have been reported in KNN-based ceramics. For example, a high unipolar strain of 0.18% was obtained in the KNN-based ceramics with O-T phase boundary by Li and Wang *et al.* [45] In this work, the unipolar electric field-induced strain curves of the ceramics as a function of x were also supplied, measured at $f=10 \text{ kHz}$ and room temperature, as shown in Figs. 11(a) and (b). One can see from Fig. 11(a) that all samples show the typical strain curves of the ceramics with different compositions. In order to further analyze the composition dependence of strain values, both strain and d_{33}^* against x of the ceramics were plotted, as shown in Fig. 11(b). One can see that strain and d_{33}^* show a similar changed tendency as x increases, that is, both of them increase for $x\leq 0.07$ and then decrease for $x>0.07$, and the maximum values (a high strain $\sim 0.33\%$ and $d_{33}^* \sim 983$

pmV-1) are obtained for $x=0.07$ due to the formation of R-T multiphase coexistence. What was proved in previous reports is that phase boundaries can make great influence on strain and piezoelectricity.^[3, 12, 14, 24, 27, 45] However, this result can well indicate that the strain of this work is greatly affected by not only phase boundaries but also compositions.^[24, 45] One can see that a high strain and a large d_{33}^* can be obtained in the ceramics with appropriate compositions, which is higher than those of the reported KNN-based ceramics.

4. Conclusion

The energy storage density, piezoelectricity, and strain properties of KNN-based ceramics can be well modified by chemical modifications, and importantly a high d_{33} can be attained in a wide sintering and poling temperature by introducing Ho. Phase boundaries (O-T and R-T) were successfully formed by shifting the content of Sb^{5+} , and then the enhanced electrical properties can be achieved. Due to the R-T phase boundary, a giant d_{33} of ~ 418 pC/N as well as a large $k_p \sim 45\%$ were obtained in the ceramics with $x=0.04$, together with a high $T_C \sim 242$ °C. Then, an enhanced strain value of 0.33% ($S_{\max}/E_{\max}=983$ pm V⁻¹) was provided in the ceramics with $x=0.07$ together with a high $d_{33} \sim 408$ pC/N, which is also belong to R-T multiphase coexistence region. A high recoverable energy density ($W_{\text{rec}} \sim 0.54$ J/cm³) can be gained in the ceramics with $x=0.10$ under a low breakdown strength (~ 129 kV/cm). Interestingly, the sintering or poling temperature sensitivity of piezoelectricity can be effectively decreased by introducing Ho, and moreover a larger d_{33} can be well attained (~ 458 pC/N). As a result, the Ho-modified ceramics with enhanced electrical properties and less sensitivity in preparation condition are prosperously achieved with

the formation of R-T phase boundary, which can be significant in the practical applications as a new KNN-based ceramics in the future.

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Table 1. Electrical properties of some typical ceramics

Composition	d_{33} pC/N	Strain %	d_{33}^* pm V ⁻¹	T_C °C	Ref.
PZT-2	152	—	—	370	21
PZT-4	410	—	700	250	22
(K _{0.44} Na _{0.52} Li _{0.04})(Nb _{0.84} Ta _{0.10} Sb _{0.06})O ₃	416	0.15	750	253	9
0.96(K _{0.48} Na _{0.52}) _{0.95} Li _{0.05} Nb _{1-x} Sb _x O ₃ -0.04BaZrO ₃	400	—	—	175	23
(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 _y O ₃	427	0.22	880	268	24
0.965K_{0.45}Na_{0.55}Nb_(1-x)Sb_xO₃-0.035Bi_{0.5}Na_{0.5}HfO₃	418	0.33	983	242	This work

Table 2. Electrical properties of $\text{KNNS}_{0.04}\text{-BNH}$ and $\text{KNNS}_{0.04}\text{-B(Ho)}_{0.10}\text{NH}$ ceramics.

Composition	d_{33}	T_C	P_r
	pC/N	$^{\circ}\text{C}$	$\mu\text{C}/\text{cm}^2$
$0.965\text{K}_{0.45}\text{Na}_{0.55}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-}0.035\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$	418	242	16.08
$0.965\text{K}_{0.45}\text{Na}_{0.55}\text{Nb}_{0.96}\text{Sb}_{0.04}\text{O}_3\text{-}0.035(\text{Bi}_{0.90}\text{Ho}_{0.10})_{0.5}\text{Na}_{0.5}\text{HfO}_3$	458	250	16.03

Figure captions

Figure 1: (a) XRD patterns and (b)-(c) expanded XRD patterns of $\text{KNNS}_x\text{-BNH}$ ceramics.

Figure 2: (a)-(m) Temperature dependence of dielectric constant of the ceramics, measured at $-150\text{ }^{\circ}\text{C} \sim 200\text{ }^{\circ}\text{C}$ and 100 kHz.

Figure 3: (a) Temperature ($30\text{ }^{\circ}\text{C} \sim 450\text{ }^{\circ}\text{C}$) dependence of dielectric constant and frequency dependence of dielectric constant for $x=0.09$, (b) phase diagram of the ceramics.

Figure 4: (a) Raman spectra (100 to 1600 cm^{-1}) of the ceramics, and their magnified and fitted Raman spectra with (b) $x=0.01$, (c) $x=0.03$, (d) $x=0.05$, and (e) $x=0.08$.

Figure 5: FE-SEM surface images and Sb^{5+} element mapping of the ceramics with (a) and (e) $x=0.01$, (b) and (f) $x=0.03$, (c) and (g) $x=0.05$, (d) and (h) $x=0.08$

Figure 6: Grain size distribution of the ceramics with (a) $x=0.01$, (b) $x=0.03$, (c) $x=0.05$, (d) $x=0.08$, and (e) average grain sizes of the ceramics as a function of x .

Figure 7: (a) d_{33} and k_p and (b) ε_r and $\tan \delta$ of the ceramics as a function of x , and (c) d_{33} vs sintering temperature (T_s) and (d) d_{33} vs poling temperature (T_p) of $\text{KNNS}_{0.04}\text{-BNH}$ and $\text{KNNS}_{0.04}\text{-B(Ho)}_{0.10}\text{NH}$ ceramics.

Figure 8: (a) P - E curves and (b) P_r and E_c of the ceramics as a function of x .

Figure 9: (a)~(g) P - E curves of the ceramics with $x=0.10$ measured at different electric fields ($11 \sim 129\text{ kV/cm}$) and (h) recoverable energy density of the samples measured at 129 kV/cm and room temperature.

Figure 10: (a) d_{33} and (b) normalized d_{33} vs. temperatures of the ceramics with different x .

Figure 11: (a) S - E curves and (b) maximum strain (%) and d_{33}^* of the ceramics as a function of x

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11