Enhanced thermal and cycling reliabilities in $(\text{K},\text{Na})(\text{Nb},\text{Sb})\text{O}_3\text{--CaZrO}_3\text{--}(\text{Bi},\text{Na})\text{HfO}_3$ ceramics

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Abstract: The thermal stability and fatigue resistance of piezoelectric ceramics are of great importance for industrialized application. In this study, the electrical properties of $(0.99-x)(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.975}\text{Sb}_{0.025})\text{O}_3\text{--}0.01\text{CaZrO}_3\text{--}x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{HfO}_3$ ceramics are investigated. When $x = 0.03$, the ceramics exhibit the optimal electrical properties at room temperature and high Curie temperature ($T_C = 253\text{ }^\circ\text{C}$). In addition, the ceramic has outstanding thermal stability ($d_{33}^* \approx 301\text{ pm/V}$ at $160\text{ }^\circ\text{C}$) and fatigue resistance (variation of P_r and $d_{33}^* \sim 10\%$ after 10^4 electrical cycles). Subsequently, the defect configuration and crystal structure of the ceramics are studied by X-ray diffraction, temperature–dielectric property curves and impedance analysis. On one hand, the doping $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{HfO}_3$ makes the dielectric constant peaks flatten. On the other hand, the defect concentration and migration are obviously depressed in the doped ceramics. Both of them can enhance the piezoelectrical properties and improve the temperature and cycling reliabilities. The present study reveals that the good piezoelectric properties can be obtained in $0.96(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.975}\text{Sb}_{0.025})\text{O}_3\text{--}0.01\text{CaZrO}_3\text{--}0.03(\text{Bi}_{0.5}\text{Na}_{0.5})\text{HfO}_3$ ceramics.

Keywords: $(\text{Na},\text{K})\text{NbO}_3$ (KNN)-based ceramics; thermal stability; fatigue resistance; crystal structure; defect structure

1 Introduction

Piezoelectric materials, due to the ability of direct conversion between mechanical and electrical energy, have been widely used as fuel injection, ultrasonic motors, printing machines, actuators, and high-accuracy positioning systems [1]. For the past decades,

lead zirconate titanate (PZT) family has dominated global piezoceramic market due to their excellent electrical performance and thermal stability [2,3]. Unfortunately, PZT-based ceramics contain more than 60 wt% lead element, which have an adverse effect on human health and environment [4,5]. To circumvent above issues, exploration of lead-free piezoelectric system is imperative. Over the last few decades, potassium sodium niobate $(\text{Na},\text{K})\text{NbO}_3$ (KNN) lead-free piezoelectric ceramics, as alternatives for lead-based piezoelectric ceramics, have attracted considerable attention due to their high Curie temperature ($T_C \approx 420\text{ }^\circ\text{C}$)

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and relatively good piezoelectric performance [6,7].

Although KNN-based materials are potential to be used in audio equipment, industrial electronics, as well as various pulsed-power applications [8], it should be noted that enhancing their piezoelectric properties is still the most important task now [9]. Fortunately, in recent years, series of prominent achievements have been reported. In particular, Xu *et al.* [10] successfully fabricated non-textured KNN-based lead-free ceramics with ultrahigh piezoelectric property ($d_{33} \approx 570$ pC/N) by construction of rhombohedral–tetragonal (R–T) phase boundary at room temperature. Besides, the superior piezoelectric properties with $d_{33} \approx 550$ pC/N were achieved in KNN-based ceramics by adjusting phase structure and domain configurations [11,12]. However, inferior thermal stability and fatigue resistance of KNN-based ceramics tremendously restrain their industrialized application [13–15]. Some researchers widen the working temperature range of KNN-based ceramics by constructing polymorphic phase transition (PPB) [14,16–18]. Meanwhile, acceptor dopants, such as Mn and La, are able to effectively improve the thermal stability [16,19,20]. Two common strategies were applied to improve the cycling reliability until now. Firstly, PPB temperature of the piezoelectric ceramics is shifted far below/above room temperature by doping, which has been achieved in PZT [21] and KNN [22,23] systems. However, it inevitably results in a tremendous decrease in the piezoelectric properties. The second case is to reduce defect concentration to prevent domain pinning [24].

In this study, good piezoelectric response, thermal stability, and cycling reliability are achieved in $(0.99-x)(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.975}\text{Sb}_{0.025})\text{O}_3-0.01\text{CaZrO}_3-x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{HfO}_3$ piezoelectric ceramics by construction of PPB region and regulation of defect configuration. The excellent piezoelectric response ($d_{33} = 352$ pC/N, $d_{33}^* = 379$ pm/V) and high T_C of 253 °C are obtained for the piezoelectric ceramics with $x = 0.03$. In addition, $x = 0.03$ ceramic exhibits excellent thermal stability under external electric field of 3 kV/mm. Furthermore, it is demonstrated that the ferroelectric performance (remnant polarization (P_r) and normalized strain (d_{33}^*)) of $x = 0.03$ ceramic undergoes a slight degradation within 10% after 10^4 cycles under driven electric field of 4 kV/mm. This study reveals that $0.96(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.975}\text{Sb}_{0.025})\text{O}_3-0.01\text{CaZrO}_3-0.03(\text{Bi}_{0.5}\text{Na}_{0.5})\text{HfO}_3$ ceramics are quite promising for practical applications.

2 Experimental

2 wt% Mn modified $(0.99-x)(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.975}\text{Sb}_{0.025})\text{O}_3-0.01\text{CaZrO}_3-x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{HfO}_3$ ($x = 0, 0.01, 0.02, 0.03, 0.04, 0.05$) (abbreviated as $(0.99-x)\text{KNNS}-\text{CZ}-x\text{BNH}$) ceramics were prepared using the conventional solid-state reaction method. All the raw powders of Nb_2O_5 (99.5%), Na_2CO_3 (99.8%), K_2CO_3 (99%), Sb_2O_3 (99.99%), CaCO_3 (99%), ZrO_2 (99%), Bi_2O_3 (99.8%), HfO_2 (99.9%), and MnO (99.9%) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., China. All the raw materials were weighed according to nominal stoichiometric composition and then homogenized in a planetary mill for 24 h using ethyl alcohol as medium. The mixed powders were calcined twice at 850 °C for 4 h with intermediate milling to enhance the compositional homogenization. Subsequently, the powder mixtures were milled, dried, and sieved. The powders were then compacted into pellets with diameter of ~10 mm and thickness of ~1 mm by uniaxial pressing in a stainless-steel die using polyvinyl butyralas binder. The green pellets were sintered in air at 1040–1100 °C for 2 h. For electric measurement, the two main surfaces of the sintered disk samples were coated with silver paste and then heat-treated at 550 °C for 30 min. The disk samples were poled in silicon oil under a direct current electric field of 3 kV/mm at 70 °C for 30 min.

After mechanical polishing and thermally etching at 1040–1090 °C for 0.5 h, the microstructure of the sintered ceramics was checked by the scanning electron microscope (SEM; SU8010, Hitachi Company, Japan). Crystalline structure of the crushed sintered ceramics was determined by X-ray diffraction (XRD; D8 Advance, Bruker, Germany) with $\text{Cu K}\alpha$ radiation. XRD results were analyzed using Rietveld refinements with general structure analysis system (GSAS) software. Quasistatic piezoelectric coefficient (d_{33}) of the poled ceramics was measured using a quasistatic piezoelectric coefficient meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). Dielectric permittivity (ϵ_{33}^T) and dielectric loss ($\tan\delta$) at 1 kHz were measured using a capacitance meter (Agilent 4294A, Agilent, Santa Clara, USA). Planar electro-mechanical coupling factor (k_p) was determined by an impedance analyzer (Agilent 4294A, Agilent, Santa Clara, USA). Insulation resistance (IR) under a fixed applied electric field of 1 kV/mm was measured by an insulation resistance tester (TH2683A, Tonghui, Jiangsu,

China). Temperature-dependent dielectric properties at 1 kHz were measured using a capacitance meter (HP4278A, Hewlett-Packard, Santa Clara, USA) with an automated temperature controller. Ferroelectric polarization hysteresis (P – E) loops and electric-field-induced strain (S – E) with a frequency of 1 Hz were obtained by TF Analyzer 2000E ferroelectric measuring system (aixACCT Systems GmbH, Aachen, Germany). Impedance spectrum over frequencies from 40 Hz to 1 MHz under a root-mean-square voltage (V_{rms}) of 1 V AC signal was measured by dielectric impedance spectrometer (Precision impedance analyzer 4294A, Agilent, USA) equipped with a cryostat. The impedance spectra were fitted with an assumed equivalent circuit assisted by Z-View software (Version 3.0; Scribner Associates, Inc.) to evaluate the equivalent direct current (DC) resistance (R) and capacitance (C) component values.

3 Results and discussion

Phase structure of $(0.99-x)\text{KNNS}-\text{CZ}-x\text{BNH}$ was determined by XRD and temperature dependence of dielectric constant (ε_r – T) curves. Figure 1 shows XRD patterns of the crushed ceramics. All the ceramics exhibit typical ABO_3 -type perovskite structure without any impurity phases. The XRD results were analyzed using Rietveld refinements with GSAS software to confirm the phase structure and lattice parameters. The refinement parameters are summarized in Table 1. All the wR_p values are less than 15%, demonstrating the reliability of refinement results. With the increase of x , the phase structure transforms obviously. When x is less than

0.02, the ceramics exhibit a pure orthorhombic structure. For $x = 0.03$ and $x = 0.04$ samples, the rhombohedral and tetragonal phases coexist in the ceramics. When x increases to 0.05, the ceramics show a pure tetragonal phase. In addition, the lattice parameters are summarized in Table 1. It can be found the lattice shrinks with the increase of x for the compositions with the same crystal structure, which should be ascribed the smaller ionic radius of Bi^{3+} (1.39 Å) with 12 coordination number (CN) than that of K^+ (1.64 Å) with 12 CN [25]. The shrunken unit cell also confirms the diffusion of the doping $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{HfO}_3$ into KNN lattice. To clearly clarify the phase structure of $(0.99-x)\text{KNNS}-\text{CZ}-x\text{BNH}$ ceramics, the ε_r – T curves from -110 to 200 °C measured at 100 kHz were performed as shown in Fig. 2. The anomalies in the curves correspond to the orthorhombic–tetragonal phase transition ($T_{\text{O-T}}$), rhombohedral–orthorhombic phase transition ($T_{\text{R-O}}$), rhombohedral–tetragonal phase transition ($T_{\text{R-T}}$), and tetragonal–cubic transition (or T_{C}). $T_{\text{O-T}}$ and $T_{\text{R-O}}$ of $x = 0$ ceramic are at about 180 and -60 °C, respectively. Therefore, $x = 0$ ceramic exhibits orthorhombic phase structure at room temperature, in accordance with the XRD results in Fig. 1. $T_{\text{O-T}}$ decreases and $T_{\text{R-O}}$ increases when x increases. For the ceramics with $0.03 \leq x \leq 0.04$, the $T_{\text{O-T}}$ and $T_{\text{R-O}}$ merge into a single peak $T_{\text{R-T}}$, indicating these ceramics located at rhombohedral–tetragonal phase boundary at room temperature [26]. The single peak $T_{\text{R-T}}$ of $x = 0.05$ ceramic is severely suppressed as shown in Fig. 2(f), demonstrating that $x = 0.05$ sample possesses a tetragonal phase structure [27,28].

Fig. 1 XRD patterns and Rietveld refinement of $(0.99-x)\text{KNNS}-\text{CZ}-x\text{BNH}$ ceramics: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.03$, (e) $x = 0.04$, and (f) $x = 0.05$.

Fig. 2 Temperature dependence of ϵ_r measured at 100 kHz of (0.99- x)KNNS-CZ- x BNH ceramics.

Table 1 Lattice parameters and refinement parameters of the KNN-based ceramics

x	R_p	wRp	Space group	Fraction	a (Å)	b (Å)	c (Å)	α (°)	V (Å ³)
0	0.0819	0.1068	<i>Amm2</i>	100	3.960	5.639	5.667	90	126.546
0.01	0.0923	0.1211	<i>Amm2</i>	100	3.965	5.636	5.654	90	126.348
0.02	0.0914	0.1190	<i>Amm2</i>	100	3.963	5.626	5.650	90	125.971
0.03	0.0907	0.1152	<i>P4mm</i>	58	3.983	3.983	3.986	90	63.235
			<i>R3m</i>	42	3.973	3.973	3.973	89.91	63.323
0.04	0.0979	0.1293	<i>P4mm</i>	82	3.976	3.976	3.993	90	63.123
			<i>R3m</i>	18	3.988	3.988	3.988	89.88	63.217
0.05	0.0929	0.1211	<i>P4mm</i>	100	3.973	3.973	3.980	90	62.823

Figures 3(a) and 3(b) display the temperature dependence of ϵ_r and $\tan\delta$ from -100 to 400 °C, respectively. It can be found that T_C decreases rapidly with the increase of doping content, in coincidence with Refs. [27,29]. It is notable that the dielectric abnormal peaks become broader as the increase of doping content, which could enhance the thermal stability of piezoelectric properties and widen the working temperature range. According to Figs. 2 and 3(a), phase diagram is depicted in Fig. 3(c). The relatively high T_C of 253 °C is obtained in $x = 0.03$

sample.

After mechanical polishing and thermal etching at 1040 – 1090 °C for 0.5 h, the microstructure of (0.99- x)KNNS-CZ- x BNH ceramics is detected by SEM as shown in Fig. 4. More than 100 random grains from SEM images were counted to figure out the average grain sizes, which is summarized in Table 2. All the ceramics show a relatively homogeneous grain distribution. It is noted that the doping ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$) can immensely suppress the grain growth, in accordance with some previous reports [29,30]. To further analyze element distribution and confirm the existence of the elements involved, element mappings of $x = 0.05$ ceramic are carried out as displayed in Fig. 5. All the elements (e.g., K, Na, Nb, Sb, Ca, Zr, Bi, and Hf) are found in the ceramics. The element mapping data show that all the elements are homogeneously distributed in the ceramics. In addition, the densities of the ceramics are measured by Archimedes method and the relative densities are calculated and summarized in Table 2. It can be found that relative density of the doping ceramics is higher than the undoped ceramics, which can improve the electrical properties.

Fig. 3 Temperature dependence of (a) ϵ_r and (b) $\tan\delta$ measured at 100 kHz of (0.99- x)KNNS-CZ- x BNH ceramics. (c) Phase diagram of (0.99- x)KNNS-CZ- x BNH ceramics.

Fig. 4 SEM surface images of (0.99- x)KNNS-CZ- x BNH ceramics: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.03$, (e) $x = 0.04$, and (f) $x = 0.05$.

Fig. 5 Element mappings of the rectangular region in Fig. 4(f).

Table 2 Electrical properties and physical properties of (0.99- x)KNNS-CZ- x BNH ceramics

x	d_{33} (pC/N)	k_p (%)	ε_r	$\tan\delta$	IR ($\Omega\cdot\text{cm}$)	Relative density	Average grain size (μm)
0	145	25.5	577	0.028	1.90×10^{11}	95.5	9.2
0.01	187	38.0	631	0.022	3.13×10^{11}	96.8	7.6
0.02	226	30.3	1018	0.021	3.83×10^{11}	97.2	5.2
0.03	352	40.9	2016	0.019	4.82×10^{11}	97.6	3.6
0.04	345	37.1	2433	0.026	2.43×10^{11}	97.5	2.3
0.05	249	27.3	2393	0.024	9.95×10^{10}	97.5	1.5

The defect configuration has a great influence on the structure and properties of the KNN-based ceramics [31]. To explore the defect configuration of (0.99- x)KNNS-CZ- x BNH ceramics, impedance spectroscopy analysis is performed in frequency range from 40 Hz to 1 MHz at different temperatures. Nyquist plots of all samples at a series of temperatures (450–650 °C) are exhibited in Fig. 6, where Z' and Z'' refer to the real and imaginary parts of the complex impedance (Z^*),

respectively. It is evident that only one semicircle is observed in the $Z'-Z''$ plots. Accordingly, an equivalent electrical circuit comprising one RC circuit (R is parallel to C) is used to fit the experimental impedance spectra [32]. All the complex plane plots are not perfect semicircles, which are slightly depressed instead of being centered on the abscissa axis (known as Debye's model). Therefore, a constant phase element, CPE, replaces the standard capacitance element in

practice to provide a better fit to the experimental data [33]. The capacitance value of CPE is calculated by Q and relaxation distribution parameter (n) with respect to the following equation [34]:

$$C = (R^{1-n}Q)^{1/n} \quad (1)$$

The fitting R , Q , n , and C parameters are listed in Table 3. It is noted that the capacitance values are 10^{-10} – 10^{-9} F, which is consistent with the bulk ferroelectric ceramics [35]. It demonstrates that the proposed equivalent electrical circuit and fitting process are reasonable in this study. The extracted direct current (DC) resistance can be used to evaluate the defect concentration. It can be found that the DC R of $x = 0.03$ ceramic is much smaller than the other sample, which implies that the defect concentration of $x = 0.03$ ceramic is relatively lower than the other samples. According to Rietveld refinements, the doping Bi and Hf elements would substitute into A-site and B-site, respectively. The reactions are expressed by the following equations:

Besides, the oxygen ions in the lattice ($\text{O}_\text{O}^\times$) would turn into oxygen gas, accompanied by the formation of an ionized oxygen vacancy ($\text{V}_\text{O}^{\bullet\bullet}$) and two electrons (e') when the perovskite-type piezoelectric ceramics are sintered at high temperature. The reaction can be given by

It has been verified that the dominant defect is oxygen vacancy in the KNN-based ceramics [36,37]. In the doped ceramics, the defect dipoles of ($2\text{V}_\text{A}' - \text{V}_\text{O}^{\bullet\bullet}$) and ($2\text{Hf}'_\text{Nb} - \text{V}_\text{O}^{\bullet\bullet}$) form, restraining the oxygen vacancies migration. Therefore, with the increase of doping ($\text{Bi}_{0.5}\text{Na}_{0.5}$) HfO_3 , the mobile oxygen vacancy concentration decreases for $0 < x < 0.03$. With the further increase of doping content, the content of these defect dipole increases and reaches saturation point, leading to the separation of defect dipoles. Hence, the oxygen vacancy concentration increases when $x > 0.03$.

In order to analyse the defect migration of (0.99– x) KNNS–CZ– x BNH ceramics, the activation energy for conduction is calculated by Arrhenius equation as follows:

$$\sigma = \sigma_0 \exp(-E_a / k_B T) \quad (5)$$

where conductivity (σ) is calculated by DC R , σ_0 is pre-exponential term, k_B is Boltzmann constant, and T is measuring temperature. E_a is activation energy for conduction, which is the formation energy of the charge carriers and migration/hopping energy of charge carriers over a long distance [32,38,39]. E_a values are calculated and shown in Fig. 7. All the coefficient of determinations R^2 are close to 1, indicating the linear fitting is reliable. It can be seen that E_a firstly increases and then decreases, which reaches the maximum for $x = 0.03$ ceramic. Therefore, the defect mobility becomes difficult in $x = 0.03$ ceramic. The low E_a of highly doped ($\text{Bi}_{0.5}\text{Na}_{0.5}$) HfO_3 ceramics ($x = 0.05$ sample) should be ascribed to the high defect concentration in the ceramics. The low defect concentration and migration would enhance the electrical properties of $x = 0.03$ ceramic.

Table 3 Fitting parameters obtained from impedance spectroscopy

x	T (°C)	DC R (Ω)	Q	n	C (nF)
0	450	17,799	7.67E-10	0.96946	5.39E-10
	500	6098	2.27E-9	0.96368	1.49E-09
	550	2763	1.55E-9	0.93140	6.24E-10
	600	1315	1.65E-9	0.93023	6.20E-10
	650	687	1.39E-9	0.91521	3.85E-10
0.01	450	24,849	2.10E-9	0.96666	1.49E-09
	500	9305	1.61E-9	0.93042	7.02E-10
	550	4507	1.55E-9	0.93478	6.77E-10
	600	2107	1.32E-9	0.92202	4.47E-10
	650	1012	1.60E-9	0.89345	3.26E-10
0.02	450	40,880	2.64E-9	0.92164	1.21E-09
	500	13,163	1.90E-9	0.92331	7.88E-10
	550	5877	1.00E-9	0.90009	2.63E-10
	600	2492	1.49E-9	0.90472	3.99E-10
	650	1263	1.02E-9	0.91428	2.86E-10
0.03	450	58,084	1.21E-9	0.95141	7.42E-10
	500	23,118	9.51E-10	0.95187	5.53E-10
	550	10,734	8.43E-10	0.94894	4.51E-10
	600	4262	8.67E-10	0.95781	5.00E-10
	650	2047	8.52E-10	0.90452	2.10E-10
0.04	450	49,516	1.23E-9	0.99722	1.20E-09
	500	20,461	9.26E-10	0.96282	6.08E-10
	550	8152	8.46E-10	0.95780	5.01E-10
	600	3854	9.65E-10	0.91789	3.15E-10
	650	1781	8.10E-10	0.98435	6.54E-10
0.05	450	41,700	1.53E-9	0.98462	1.32E-09
	500	25,161	1.33E-9	0.92808	5.98E-10
	550	10,031	1.16E-9	0.91228	3.89E-10
	600	4103	1.63E-9	0.92074	5.84E-10
	650	1907	7.37E-9	0.91742	2.70E-09

Fig. 6 Impedance spectra at a series of temperatures for (0.99- x)KNNS-CZ- x BNH ceramics: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.03$, (e) $x = 0.04$, and (f) $x = 0.05$.

Fig. 7 Arrhenius plots of conductivity versus $1000/T$ for (0.99- x)KNNS-CZ- x BNH ceramics: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.03$, (e) $x = 0.04$, and (f) $x = 0.05$.

The electrical properties of (0.99- x)KNNS-CZ- x BNH ceramics are summarized in Table 2. Dielectric constant ϵ_r increases monotonously with the increase of (Bi_{0.5}Na_{0.5})HfO₃ doping content, which is consistent with Ref. [40]. Polarization–electric field (P – E) hysteresis loops are displayed in Figs. 8(a) and 8(b). It can be seen that all the ceramics exhibit the well-saturated P – E hysteresis loops, indicating the good ferroelectricity. It can be observed that the spontaneous polarization (P_r) reaches the highest value near the PPB region ($0.03 \leq x \leq 0.04$), which should be ascribed to the abundant polarization direction and low free energy [41,42]. In addition, composition dependence of d_{33} and $\epsilon_r \times P_r$ are shown in Fig. 8(c). In

ferroelectric materials, the piezoelectric coefficients were proportional to the product of polarization and permittivity. The longitudinal piezoelectric coefficient d_{33} can be expressed as follows [43]:

$$d_{33} = 2Q_{11}\epsilon_0\epsilon_{33}P_3 \quad (6)$$

where ϵ_{33} and P_3 are the relative permittivity and polarization along the polar axis, $\epsilon_0 = 8.854 \times 10^{-12}$ F/m is the permittivity of the vacuum, and Q_{11} is the electrostrictive coefficient of the paraelectric phase, which typically varies between 0.05 and 0.1 m⁴/C² for different materials. In this case, Q_{11} could be constant because of the low concentration of doped elements. For poled piezoceramics, P_r and ϵ_r were equal

Fig. 8 (a, b) P - E hysteresis loops of $(0.99-x)\text{KNNS-CZ-}x\text{BNH}$ ceramics. (c) d_{33} and $\varepsilon_r \times P_r$ values as a function of x . (d, e) Unipolar S - E curves of $(0.99-x)\text{KNNS-CZ-}x\text{BNH}$ ceramics. (f) d_{33}^* and $S_{\max}$ values as a function of x .

to P_3 and ε_{33} , respectively. Therefore, d_{33} is in proportion to $\varepsilon_r \times P_r$. It can be found that d_{33} shows a similar tendency with $\varepsilon_r \times P_r$, which both reach the highest values near the PPB region ($0.03 \leq x \leq 0.04$). Besides, unipolar electric field-induced strain (S - E) curves for all samples are shown in Figs. 8(d) and 8(e). The electric field-induced maximum strain ($S_{\max}$) and d_{33}^* ($d_{33}^* = S_{\max}/E_{\max}$) is plotted in Fig. 8(f). It can be found that $S_{\max}$ and d_{33}^* reach the maximum in $x = 0.03$ ceramics. The enhanced P_r and low defect concentration should be responsible for the high piezoelectric properties for $x = 0.03$ sample [23]. As summarized in Table 2, the other piezoelectric properties, such as electro-mechanical coupling factor k_p , exhibit the similar trend with d_{33} . The IR reaches maximum and dielectric loss $\tan\delta$ is lowest for $x = 0.03$ sample, in accordance with the DC R obtained from impedance analysis. It should be ascribed to the low defect concentration and mobility. The optimal electrical properties ($d_{33} = 352$ pC/N; $d_{33}^* = 379$ pm/V; $k_p = 40.9\%$; $\varepsilon_r = 2016$; $\tan\delta = 0.019$; $IR = 4.82 \times 10^{11} \Omega\cdot\text{cm}$) are obtained in $x = 0.03$ ceramic.

Thermal and cycling reliabilities of $(0.99-x)\text{KNNS-CZ-}x\text{BNH}$ ceramics are very important for industrialized application. Figures 9(a) and 9(b) exhibit the temperature dependence of unipolar S - E curves of $x = 0$ and $x = 0.03$ ceramics measured at 4 kV/mm, respectively. d_{33}^*

of $x = 0$ and $x = 0.03$ ceramics are depicted in Fig. 9. It can be observed that d_{33}^* reduces sharply from 20 (163 pm/V) to 160 °C (65 pm/V), indicating the thermal stability of $x = 0$ ceramic is inferior. The increasing unipolar $S_{\max}$ from 160 to 200 °C is attributed to the coexistence of orthorhombic and tetragonal as shown in Fig. 3(a). For $x = 0.03$ ceramic, d_{33}^* reduces slowly from 20 to 120 °C and shows excellent thermal stability. When the measurement temperature reaches 120 and 160 °C, the normalized d_{33}^* can attain 95% and 79%, respectively. The excellent thermal stability of $x = 0.03$ ceramic should be attributed to the depressed rhombohedral and tetragonal phase boundary near room temperature [14,44,45]. Figures 10 and 11 show the evolution of P - E hysteresis loops and unipolar S - E curves of $x = 0$ and $x = 0.03$ ceramics with electrical cycling up to 10^4 cycles under a fixed driven electric field of 3 kV/mm. An obvious degradation of P_r and d_{33}^* can be observed with the increase of cycle for $x = 0$ ceramic. The cycling results in the reduction in P_r and d_{33}^* by about 20% after 10^4 cycles. Nevertheless, P_r and d_{33}^* hardly degrade up to 10^3 cycles for $x = 0.03$ ceramic. After 10^4 cycles, only approximately 10% loss of P_r and d_{33}^* occurs. The fatigue resistance of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{HfO}_3$ doped ceramics is much better than that of undoped ceramics, which should be ascribed to the low defect concentration [18,46].

Fig. 9 Temperature dependence of unipolar S - E curves at a fixed electric field of 4 kV/mm for (a) $x = 0$ and (b) $x = 0.03$ ceramics.

Fig. 10 P - E hysteresis loops measured after 10^0 , 10^1 , 10^2 , 10^3 , and 10^4 fatigue cycles of (a1–e1) $x = 0$ and (a2–e2) $x = 0.03$ ceramics. P_r as a function of fatigue cycle for (f1) $x = 0$ and (f2) $x = 0.03$ ceramics.

Fig. 11 Unipolar S - E curves measured after 10^0 , 10^1 , 10^2 , 10^3 , and 10^4 fatigue cycles of (a1–e1) $x = 0$ and (a2–e2) $x = 0.03$ ceramics. d_{33}^* values as a function of fatigue cycle for (f1) $x = 0$ and (f2) $x = 0.03$ ceramics.

4 Conclusions

In summary, the piezoelectric response, thermal stability, and fatigue resistance of $(0.99-x)\text{KNNS}-\text{CZ}-x\text{BNH}$ piezoelectric ceramics are systematically investigated in the study. $x = 0$ ceramic exhibits a pure orthorhombic structure at room temperature and high defect concentration, which results in the inferior electrical properties, thermal stability, and cycling reliability. The doping $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{HfO}_3$ makes the dielectric constant peaks flatten, which can enhance the temperature and cycling reliability of $(0.99-x)\text{KNNS}-\text{CZ}-x\text{BNH}$ ceramics. When $x = 0.03$, the ceramics exhibit the optimal electrical properties ($d_{33} = 352 \text{ pC/N}$; $d_{33}^* = 379 \text{ pm/V}$; $k_p = 40.9\%$; $\varepsilon_r = 2016$; $\tan\delta = 0.019$; $IR = 4.82 \times 10^{11} \Omega\cdot\text{cm}$) and high T_C of 253°C . In addition, $x = 0.03$ ceramic exhibits excellent thermal stability ($d_{33}^* \approx 301 \text{ pm/V}$ at 160°C) and fatigue resistance (variation of P_r and $d_{33}^* \sim 10\%$ after 10^4 electrical cycles). The study demonstrates that $(0.99-x)\text{KNNS}-\text{CZ}-x\text{BNH}$ piezoelectric ceramics are expected to replace part of lead-based piezoelectric ceramics in the future.

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