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Yi FAN  
School of Material Science and Engineering, University of Jinan, Jinan 250022, China

Zhenxing WANG  
School of Material Science and Engineering, University of Jinan, Jinan 250022, China

Yu HUAN  
School of Material Science and Engineering, University of Jinan, Jinan 250022, China

Tao WEI  
School of Material Science and Engineering, University of Jinan, Jinan 250022, China

Xiaohui WANG  
State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

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Enhanced thermal and cycling reliabilities in (K,Na)(Nb,Sb)O₃–CaZrO₃–(Bi,Na)HfO₃ ceramics

Yi FANᵃ,†, Zhenxing WANGᵃ,†, Yu HUANᵃ,*, Tao WEIᵃ,*, Xiaohui WANGᵇ

ᵃSchool of Material Science and Engineering, University of Jinan, Jinan 250022, China
ᵇState Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

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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)(K₀.₄₈Na₀.₅₂)(Nb₀.₉₇₅Sb₀.₀₂₅)O₃–0.₀₁CaZrO₃–ₓ(Bi₀.₅Na₀.₅)HfO₃ ceramics are investigated. When x = 0.03, the ceramics exhibit the optimal electrical properties at room temperature and high Curie temperature (Tₐ = 253 °C). In addition, the ceramic has outstanding thermal stability (d₄₃ ≈ 301 pm/V at 160 °C) and fatigue resistance (variation of Pₑ and d₃₃ ~ 10% after 10⁴ 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 (Bi₀.₅Na₀.₅)HfO₃ 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(K₀.₄₈Na₀.₅₂)(Nb₀.₉₇₅Sb₀.₀₂₅)O₃–0.₀₁CaZrO₃–0.₀₃(Bi₀.₅Na₀.₅)HfO₃ ceramics.

Keywords: (Na,K)NbO₃ (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 (Na,K)NbO₃ (KNN) lead-free piezoelectric ceramics, as alternatives for lead-based piezoelectric ceramics, have attracted considerable attention due to their high Curie temperature (Tₐ ≈ 420 °C)
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 \( (d_{33} \approx 570 \text{ pC/N}) \) by construction of rhombohedral–tetragonal (R–T) phase boundary at room temperature. Besides, the superior piezoelectric properties with \( d_{33} \approx 550 \text{ pC/N} \) 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 \((0.99-x)(K_{0.48}Na_{0.52})(Nb_{0.975}Sb_{0.025})O_3-0.01CaZrO_3-x(Bi_{0.5}Na_{0.5})HfO_3\) ceramics by construction of PPB region and regulation of defect configuration. The excellent piezoelectric response \( (d_{33} = 352 \text{ pC/N}, d'_{33} = 379 \text{ pm/V}) \) 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 \( 10^6 \) cycles under driven electric field of 4 kV/mm. This study reveals that \( 0.96(K_{0.48}Na_{0.52})(Nb_{0.975}Sb_{0.025})O_3-0.01CaZrO_3-0.03(Bi_{0.5}Na_{0.5})HfO_3 \) ceramics are quite promising for practical applications.

2 Experimental

2 wt% Mn modified \((0.99-x)(K_{0.48}Na_{0.52})(Nb_{0.975}Sb_{0.025})O_3-0.01CaZrO_3-x(Bi_{0.5}Na_{0.5})HfO_3 \) ceramics were prepared using the conventional solid-state reaction method. All the raw powders of \( \text{Nb}_2\text{O}_5 \) (99.5%), \( \text{Na}_2\text{CO}_3 \) (99.8%), \( \text{K}_2\text{CO}_3 \) (99%), \( \text{Sb}_2\text{O}_3 \) (99.9%), \( \text{CaCO}_3 \) (99%), \( \text{ZrO}_2 \) (99%), \( \text{Bi}_2\text{O}_3 \) (99.8%), \( \text{HfO}_2 \) (99.9%), and \( \text{MnO} \) (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 butyral as 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 Cu Kα 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 \( (\varepsilon_r^T) \) and dielectric loss \( (\tan \delta) \) at 1 kHz were measured using a capacitance meter (Agilent 4294A, Agilent, Santa Clara, USA). Planar electromechanical 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).
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)KNNS–CZ–xBNH was determined by XRD and temperature dependence of dielectric constant (εr–T) curves. Figure 1 shows XRD patterns of the crushed ceramics. All the ceramics exhibit typical ABO3-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 wRp 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 Bi3+ (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 (Bi0.5Na0.5)HfO3 into KNN lattice. To clearly clarify the phase structure of (0.99–x)KNNS–CZ–xBNH ceramics, the εr–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 (TO–T), rhombohedral–orthorhombic phase transition (TR–O), rhombohedral–tetragonal phase transition (TR–T), and tetragonal–cubic transition (or TC). TR–O and TO–T 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. TO–T decreases and TR–O increases when x increases. For the ceramics with 0.03 ≤ x ≤ 0.04, the TO–T and TR–O merge into a single peak TR–T, indicating these ceramics located at rhombohedral–tetragonal phase boundary at room temperature [26]. The single peak TR–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)KNNS–CZ–xBNH 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.](www.springer.com/journal/40145)
Fig. 3 Temperature dependence of (a) \( \varepsilon_r \) 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.

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

| \( x \) | \( R_p \) | \( wR_p \) | Space   | Fraction | \( a (\text{Å}) \) | \( b (\text{Å}) \) | \( c (\text{Å}) \) | \( \alpha (^\circ) \) | \( V (\text{Å}^3) \) |
|-----|-----|-----|--------|----------|----------------|----------------|----------------|----------------|----------------|
| 0   | 0.0819 | 0.1068 | Amm2  | 100     | 3.960 | 5.639 | 5.667 | 90          | 126.546       |
| 0.01 | 0.0923 | 0.1211 | Amm2  | 100     | 3.965 | 5.636 | 5.654 | 90          | 126.348       |
| 0.02 | 0.0914 | 0.1190 | Amm2  | 100     | 3.963 | 5.626 | 5.650 | 90          | 125.971       |
| 0.03 | 0.0907 | 0.1152 | \( P_{4nm} \) | 58   | 3.983 | 3.983 | 3.986 | 90          | 63.235        |
| 0.04 | 0.0979 | 0.1293 | \( R_{3m} \) | 42   | 3.973 | 3.973 | 3.973 | 89.91       | 63.323        |
| 0.05 | 0.0929 | 0.1211 | \( P_{4nm} \) | 82   | 3.976 | 3.976 | 3.993 | 90          | 63.123        |

Figures 3(a) and 3(b) display the temperature dependence of \( \varepsilon_r \) 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. 4 SEM surface images of (0.99–x)KNNS–CZ–xBNH 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–xBNH ceramics

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

\[
C = \left( R^{1/n} Q \right)^{1/n}
\]  

The fitting \( R, Q, n, \) and \( C \) parameters are listed in Table 3. It is noted that the capacitance values are \( 10^{-10} \text{--} 10^{-9} \text{ F} \), 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 resistance can be used to evaluate the defect mobility becomes difficult in high defect concentration in the ceramics. The low defect concentration and migration would enhance the electrical properties of \( x = 0.03 \) ceramic. Therefore, the defect mobility becomes difficult in high defect concentration in the ceramics. The low defect concentration and migration would enhance the electrical properties of \( x = 0.03 \) ceramic.

where conductivity \( (\sigma) \) is calculated by DC \( R \), \( \sigma_0 \) 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 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

| \( x \) | \( T \) \(^{\circ}\text{C} \) | \( DC \ R \) \( (\Omega) \) | \( Q \) | \( n \) | \( C \) \( (nF) \) |
|-------|------|------|-----|-----|-------|
| 0.05  | 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 | 1.63E-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–xBNH 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–xBNH 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–xBNH ceramics are summarized in Table 2. Dielectric constant $\varepsilon_r$ increases monotonously with the increase of (Bi$_{0.5}$Na$_{0.5}$)HfO$_3$ 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 ($P_s$) 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 $\varepsilon_r \times P_s$ 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]:

$$d_{33} = 2Q_{11} \varepsilon_0 \varepsilon_3 P_3$$

(6)

where $\varepsilon_3$ and $P_3$ are the relative permittivity and polarization along the polar axis, $\varepsilon_0 = 8.854 \times 10^{-12}$ 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 m$^4$/C$^2$ for different materials. In this case, $Q_{11}$ could be constant because of the low concentration of doped elements. For poled piezoceramics, $P_s$ and $\varepsilon_s$ were equal.
to $P_3$ and $\varepsilon_{33}$, respectively. Therefore, $d_{33}$ is in proportion to $\varepsilon_1 \times P_3$. It can be found that $d_{33}$ shows a similar tendency with $\varepsilon_1 \times P_3$, 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 ($S_{\text{max}}$) and $d'_{33}$ ($d'_{33} = S_{\text{max}}/E_{\text{max}}$) is plotted in Fig. 8(f). It can be found that $S_{\text{max}}$ 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 electromechanical 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; $k_p = 40.9\%$; $\varepsilon_1 = 2016$; tan$\delta_1 = 0.019$; $IR = 4.82 \times 10^{11} \Omega \cdot \text{cm}$) are obtained in $x = 0.03$ ceramic.

Thermal and cycling reliabilities of $(0.99-x)$KNNS–CZ–xBNH 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 $^\circ$C (65 pm/V), indicating the thermal stability of $x = 0$ ceramic is inferior. The increasing unipolar $S_{\text{max}}$ from 160 to 200 $^\circ$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 $^\circ$C and shows excellent thermal stability. When the measurement temperature reaches 120 and 160 $^\circ$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. $P_t$ 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–c1) $x = 0$ and (a2–c2) $x = 0.03$ 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)KNNS–CZ–xBNH 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 (Bi0.5Na0.5)HfO3 makes the dielectric constant peaks flatten, which can enhance the temperature and cycling reliability of (0.99–x)KNNS–CZ–xBNH ceramics. When x = 0.03, the ceramics exhibit the optimal electrical properties ($d_{33}^p = 352 \text{ pC/N}$; $d_{33}^s = 379 \text{ pm/V}$; $k_p = 40.9\%$; $\varepsilon_t = 2016$; $\tan \delta = 0.019$; IR = $4.82 \times 10^{13} \text{ W/cm}$) and high $T_c$ of 253 °C. In addition, x = 0.03 ceramic exhibits excellent thermal stability ($d_{33}^s \approx 301 \text{ pm/V}$ at 160 °C) and fatigue resistance (variation of $P_x$ and $d_{33}^s$ ~10% after $10^8$ electrical cycles). The study demonstrates that (0.99–x)KNNS–CZ–xBNH piezoelectric ceramics are expected to replace part of lead-based piezoelectric ceramics in the future.

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