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Enhanced piezoelectric, electrocaloric and energy storage properties at high temperature in lead-free $\text{Bi}_{0.5}(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{TiO}_3$ ceramics

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Abstract

The piezoelectric, electrocaloric and energy storage properties were systemically investigated in lead-free $\text{Bi}_{0.5}(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{TiO}_3$ ceramics from room temperature to high temperature region. These ceramics can be poled completely to obtain large piezoelectric coefficient (104-153 pC/N) at low electric field of ~30 kV/cm. The piezoelectric property shows good thermal stability due to high depolarization temperature (T_d). For BNKT_{20} , a large low electric field-induced strain of 0.36% is obtained at 120°C under 50 kV/cm, the corresponding normalized strain coefficient is up to 720 pm/V, which is larger than other BNT-based ceramics at high temperature region. The electrocaloric properties of these ceramics are studied via indirect and direct methods. Large EC value (~1.08 K) in BNKT_{20} ceramic is obtained at 50 kV/cm using indirect calculation. Above 100°C, the dielectric energy storage density and efficiency of BNKT_{20} is still up to ~0.85 J/cm³ and 0.75, respectively. The BNKT_x ceramics may become promising candidates in the fields of actuators,

electrocaloric cooling and energy storage at high temperature region.

Keywords: electrocaloric piezoelectric lead-free high temperature
application energy storage

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INTRODUCTION

Ferroelectric materials are widely studied due to their applications in actuators[1], piezoelectric sensors[2], ferroelectric memories[3], solid-states cooling[4] and energy storage devices[5, 6], etc. In the recent years, the growing concerns of the toxicity of lead and environmental protection, lead-free BaTiO_3 (BT)[7], $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN)[8], $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT)[9-13], BiFeO_3 (BFO)[14]-based materials are developed as alternatives for commercial Pb-based ceramics. Pure BNT ceramic exhibits rhombohedral R3c phase at room temperature with a high Curie temperature ($T_c \sim 320^\circ\text{C}$) and large remnant polarization ($P_r = 38 \mu\text{C}/\text{cm}^2$) as well as high coercive field ($E_c = 73 \text{ kV}/\text{cm}$)[15]. The high coercive fields hinder its promising application in the field of piezoelectric and dielectric energy storage.

The compositional modifications are highly desirable to decrease E_c and improve the dielectric, ferroelectric, piezoelectric and energy storage properties through the construction of morphotropic phase boundary (MPB) between the rhombohedral R3c (BNT) and tetragonal P4bm $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BKT)[15, 16]. For instance, a giant strain of 0.45% is obtained in BNT-BT-KNN ceramic under the electric field of 80 kV/cm by Zhang et al[10], which is even higher than that of commercial PZT ceramic. Classical $\text{Bi}_{0.5}(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{TiO}_3$ (BNKT_x) system exhibits excellent ferroelectric, piezoelectric and electromechanical response at MPB of 16-20% BKT content[15, 16]. Hiruma et al[16] have reported small-signal piezoelectric coefficient d_{33} of 168 pC/N in BNKT₂₀ and the normalized strain d_{33}^* of 291 pm/V for BNKT₂₂. For BNT-based ceramics, the large poling electric fields of 40-90 kV/cm were used to obtain large piezoelectric responses. The high poling electric fields can easily induce the physical flaws and even breakdown of piezoelectric ceramics, which is not beneficial for their piezoelectric application. Here, it is so desirable to investigate the relationship between the poling electric fields and piezoelectric coefficient of BNKT_x ceramics.

Giant electric strain have been reported extensively via tuning the

depolarization temperature (T_d) of ferroelectric to ergodic relaxor phase transition to near room temperature in $(1-x)\text{Bi}_{0.5}(\text{Na}_{0.8}\text{K}_{0.2})_{0.5}\text{TiO}_3-x(\text{K}_y\text{Na}_{1-y})\text{NbO}_3$ (BNKT-KNN)(0.33-0.46% at 80 kV/cm) [13], $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\text{--}\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3\text{--}\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ (BNT-BKT-2BMN)(0.43% at 55 kV/cm) [17], $0.92\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.06\text{BaTiO}_3\text{--}0.02\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (BNT-BT-2KNN)(0.45% at 80 kV/cm) [10], $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.935}\text{Ba}_{0.065}\text{Ti}_{1-x}(\text{Al}_{0.5}\text{Sb}_{0.5})_x\text{O}_3$ (BNBT_{6.5-x}AS)(0.46% at 80 kV/cm) [18], $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.945-x}(\text{Bi}_{0.2}\text{Sr}_{0.7}\square_{0.1})_xBa_{0.055}\text{TiO}_3$ (BNBT-0.02BST) (0.428% at 60 kV/cm) [19] etc. Unfortunately, these large strains are significantly degrade with rising temperature due to their low depolarization temperatures. The electric-induced strain is only ~0.25% at high temperature of 120°C in BNBT-0.02BST [19]. For future promising application, their piezoelectric performances must be stable or degraded slightly to avoid the failure of the electronic devices at harsh environments, such as high temperatures. For instance, sensors and engines in automobiles can work at the temperature up to 150°C [20, 21].

Due to high energy storage density and intrinsic fast discharge-charge ability, dielectric capacitor is a promising candidate for energy storage application in hybrid electric vehicles and mobile devices [5, 6]. The ferroelectric materials for dielectric energy storage requires maximum polarization $P_{\max}$ and remnant polarization P_r as well as high breakdown fields. BNKT_x ceramics exhibit excellent ferroelectric properties at MPB and the temperature induced ergodic relaxor phase [16], suggesting that this ceramic owns good energy storage property. Dielectric energy storage has been studied extensively at room temperature [6, 22, 23]. The thermal stability of energy storage must be evaluated for their applications in automobiles and electronic devices [5, 24]. As an example of hybrid electric vehicles, the electric power systems work at the wide temperature range from -40°C to 140°C.

Solid-state cooling based on electrocaloric (EC) effect is a potential solution for cooling of computer chips and industrial refrigeration inspired by the discovery of giant EC temperature change in $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ (PZT) antiferroelectric thin films [4].

In the past decades, the indirect methods based on the thermodynamic Maxwell relation have been exploited to study the EC effect in various electrocalorics [4, 25-33]. The positive and negative EC temperature changes were observed in BNT [32, 34], BNT-BT [31], BKT-BNT [27, 31], BNBT6-0.5La₂O₃ [35], etc, using indirect methods based on Maxwell relation. Smaller negative EC value (-0.28 K) was reported only in unpoled BNT-18BKT at low electric field of 5 kV/cm via direct measurement [27]. The validity to study EC effect is still conversational in relaxor BNT-based ceramics using indirect methods [33, 34, 36]. The BNKT_x ceramics are a platform for the study the EC effect and the understanding of the physics mechanism due to the modulations of depolarization temperatures and ferroelectric properties as the BKT contents change.

In this work, we systematically investigate the temperature dependence of piezoelectric, electromechanical and electrocaloric properties as well as energy storage in Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO₃ (Abbreviated as BNKT_x; x=0.10,0.15,0.20,0.25) ceramics. Our studies offer some guidelines for promising applications of BNKT_x system for actuator, sensor, cooling and energy storage at high temperature environment.

Experimental procedures

The Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO₃ were fabricated using conventional solid state reaction method. Stoichiometric quantities of the raw materials, Bi₂O₃, K₂CO₃, Na₂CO₃, and TiO₂ were mixed in a planetary mill for 6 h with zirconia balls. After drying, the mixed powders were pre-sintered in covered alumina crucibles at 850°C for 4 h. After calcination, the ground power was ball-milled for 6 h, dried, and then pressed into the small disc of 10 mm and 1 mm thickness by uniaxial pressing and then a cold isostatic pressing treatment was used at 100 Mpa. The pellets were sintered in covered alumina crucibles at 1150 °C for 2 h in air atmosphere. To decrease the volatilization loss of bismuth and sodium elements, the pellets were buried into powders with the same composition. Silver electrodes were pasted and

fired on both sides of the sintered pellets at 600°C for 20 min for the electrical measurement.

X-ray diffraction (XRD Shimadzu 7000) was used to detect the phase structure of the ceramics. The surface morphology of the BNKT₂₀ was characterized using field emission scanning electron microscopy (FEI QUANTA FEG 250). The temperature dependence of dielectric constants and loss tangents were collected in the temperature range of 30-450°C at three frequencies of 1k Hz, 10k Hz and 100k Hz and 1V using LCR meter (HP 4980, Agilent, USA). The ferroelectric hysteresis loops were recorded at 10 Hz using a Radiant ferroelectric workstation. For piezoelectric characterization, the ceramics were poled using different DC electric fields for 20 min at room temperature. The *in situ* piezoelectric coefficient (d_{33}) was measured with a commercial Berlincourt-type d_{33} meter (ZJ-3A, China) equipped with heater. The electric-induced strain was measured by a MTI-2000 Photonic sensor at 10 Hz. The modified differential scanning calorimeter (DSC, TA Instruments Q200) was used to measure directly electrocaloric temperature change.

Results and discussions

The XRD patterns of BNKT_x ceramics are presented in Figure 1. The perovskite phase is observed in these ceramics. The split (111) peaks at 40° and single (200) peaks at 46° can be observed at low BKT content ($x=0.10$, and 0.15), which indicates that these ceramics exist rhombohedral (R3c) symmetry. The BNKT₂₅ ceramic shows tetragonal (P4bm) symmetry, as indicated by the split (200) peaks at 46° and singlet (111) peak at 40°. The tetragonal and rhombohedral phases coexist in the BNKT₂₀ ceramic due to the presence of split (111) and (200) peaks, indicating that this ceramic is located at the morphotropic phase boundary (MPB). The SEM microstructures of BNKT₂₀ ceramics are displayed in the inset of Figure 1. It was observed that all ceramics exist similar morphologies with regular rectangular-shape grains and clear grain boundaries [37].

Dielectric spectroscopy can offer the information of relaxor property and the phase transition temperatures of the ceramics. We measured the temperature dependence of dielectric constants and losses of poled BNKT_x ceramics upon the heating process at the frequencies of 10 kHz, 100 kHz and 1000 kHz, as shown in Figure 2. Two dielectric anomaly peaks are observed for all the ceramics within the temperature range of 25-450°C. The first peak is the depolarization temperature (T_d), which is occurred at the phase transition from ferroelectric to ergodic relaxor phase [17]. The sharp anomaly of dielectric loss confirms further T_d . The T_d is 203 °C, 142 °C, 92°C, and 141°C, respectively, as the BKT content increases. The latter abnormal peak is the temperature of the maximum of dielectric constants T_m . The ceramics exhibit paraelectric cubic phase above T_m . T_m increases successively from 301°C ($x=0.10$) to 323°C ($x=0.25$) with increasing of BKT content. It is observed that the strong frequency-dependent dielectric constant at T_d and T_m is due to the presence of local polar nanoregions at higher content BKT, which indicates that the doping BKT induces strong ferroelectric relaxor behavior, which may be related to the lattice distortion due to larger ionic difference between K^+ (1.64 Å) and Na^+ (1.39 Å) [38]. The doping BKT disturbs the ferroelectric order and lead to the evolution from the long-order ferroelectric phase to short-range ergodic relaxor phase. The dielectric constants of BNKT₂₀ ceramic (~5800) at T_m are larger than other three ceramics, it is expected that the ceramic owns excellent ferroelectric, piezoelectric and electrocaloric properties.

The ferroelectric hysteresis loops of BNKT_x ceramics at different electric fields are displayed in Figure 3. The polarization increases with increasing of electric fields in these ceramics. These ceramics exhibit the ferroelectric feature at 70 kV/cm. The maximum polarization (P_m) at 70 kV/cm is 30.2 $\mu C/cm^2$ for BNKT₁₀, 34.5 $\mu C/cm^2$ for BNKT₁₅, 40.1 $\mu C/cm^2$ for BNKT₂₀ and 35.7 $\mu C/cm^2$ for BNKT₂₅, respectively, as shown in Figure 4. The BNKT₂₀ ceramic has largest polarization value, which can be explained by the facilitation of polarization rotation due to fatten free energy profile between rhomboheral and tetragonal phase [39]. The coercive field (E_c) decreases

monotonously from 52 kV/cm to 20 kV/cm as the BKT content increases, as shown in Figure 4.

We study the relation between piezoelectric coefficient d_{33} and poling electric fields in BNKT_x ceramics at room temperature, as shown in Figure 5 (a). It is found that BNKT_x ceramics is poled completely to obtain the large piezoelectric coefficient d_{33} under the low driving field of 30 kV/cm, which is even lower than that of coercive field. Under the electric field of 70 kV/cm, the corresponding coercive fields (E_c) are 52 kV/cm, 42 kV/cm, 30 kV/cm, 20 kV/cm for $x=10, 15, 20, 25$, respectively, as shown in Figure 4. The d_{33} is 104 pC/ N for BNKT_{10} , 113 pC/ N for BNKT_{15} , 153 pC/ N for BNKT_{20} and 111 pC/ N for BNKT_{25} , respectively, see Figure 5 (a). Such values are comparable to previous results, such as 105 pC/ N [40], 168 pC/ N [16] for BNKT_{20} . The non-180° ferroelectric domain switching leads to the piezoelectric response below 30 kV/cm in BNKT_x ceramics. The remnant polarization and coercive field of BNKT_{20} ceramic were shown in Figure 6 at different fields and temperatures. The sudden increment of remnant polarizations and coercive fields are attributed to ferroelectric domain switching [41], see Figure 6 (a) and (b). It is indicated that the ferroelectric domain can be switched completely above the coercive field of 30 kV/cm to obtain large piezoelectric coefficient. In addition, similar low field poling behavior in BNT-BT ceramics is related to low electric field-induced irreversible nanodomains coalescence into thin lamellar domains via *in situ* transmission electron microscopy [42]. Recent work suggested that large piezoelectric coefficient can be obtained under low electric field of 30 kV/cm in BNKT_{20} , which is attributed to the electric-induced ergodic relaxor-to-ferroelectric phase transition [43]. For BNKT_{25} ceramic, the decreased d_{33} is related to the increment of ergodic relaxor phase due to the doping of BKT compared to that in BNKT_{20} .

Previous studies [13, 37] indicated that the piezoelectric and electromechanical responses are severely upgraded with rising temperatures in BNT-based ceramics due to low T_d . Here, the *in situ* piezoelectric coefficients d_{33} of these ceramics are

measured at the temperature range from 20°C to 200°C, as displayed in Figure 5 (b). For BNKT_x, the d_{33} decreases drastically at 170 °C ($x=0.15$), at 100 °C ($x=0.20$), at 130 °C ($x=0.25$), which is attributed to the temperature-induced phase transition from long-range ferroelectric order to short-range ergodic relaxor. These depolarization temperatures are also corroborated via temperature dependence of dielectric constants and loss measurement, see in Figure 2. Interestingly, the d_{33} increased slightly with increasing of temperatures. For BNKT₁₀, the d_{33} is increased from 100 pC/N at 20°C to 125 pC/N at 165°C, see in Figure 5 (b). Similar phenomena of increased d_{33} have been observed in BiFeO₃-based ceramic [14, 44] and PZT5 ceramic [45]. The increased d_{33} may be related to the non-180 domain switching induced by internal bias field due to low activation energy at rising temperature. For BNKT₂₀, the E_c^+ is 52 kV/cm, and the E_c^- is 45 kV/cm. For BNKT₁₀ and BNKT₁₅, the piezoelectric coefficient d_{33} is still ~120 pC/N at higher temperature up 165°C, which can be beneficial for piezoelectric application at higher temperature, compared to low T_c (~90°C) of BZT-BCT system[7].

Figure 7 shows the room temperature electric-induced bipolar strain (a) and unipolar strain (b) of BNKT_x at 60 kV/cm and 10 Hz. The bipolar butterfly-shaped S-E curve is asymmetric in nature, which is related to the internal bias field induced by defect dipoles [9]. The internal bias field is larger; the asymmetric curve is more obvious, which is consistent with the observation of ferroelectric loops, as shown in Figure 3. The asymmetric feature of bipolar strain is not obvious in BNKT₂₅, the defect dipoles can be suppressed by the doping of BKT. The negative strain shows also the existence of ferroelectric order; see in Figure 7(a), which is ascribed to the large electric field induces reversibly the relaxor to long-range ferroelectric phase transition at room temperature. The corresponding room temperature bipolar strain of BNKT_x at 60 kV/cm is 0.07%, 0.11%, 0.15% and 0.14%, for BNKT_x of $x=0.10, 0.15, 0.20$ and 0.25 , respectively. The largest electric-induced strain is obtained in BNKT₂₀, which is related to the existence of the morphotropic phase boundary region [16]. The corresponding normalized strain d_{33}^* ($d_{33}^*=S_{\max}/E_{\max}$) is 250 pm/V

in this ceramic, as displayed in the inset of Figure 5(b). The strain ($\sim 0.19\%$) of BNKT_{20} was obtained at 80 kV/cm by Hiruma et al[16]. Figure 7 (c) shows the unipolar strain of BNKT_{20} ceramic at the different electric fields. At 20 kV/cm, the unipolar strain is only $\sim 0.027\%$, the corresponding normalized strain d^*_{33} is about 135 pm/V. The unipolar strain and corresponding normalized strain d^*_{33} increase linearly as the electric field increases. The unipolar strains of BNKT_{20} ceramic are measured at 50 kV/cm at five different frequencies, as displayed in Figure 7 (d). At 100 Hz, the unipolar strain is only 0.069%. The maximum of the unipolar strain was observed at the frequency of 10 Hz. It is evident that the electric-induced strain strongly depends on the frequency of applied electric field. In the case of the frequency of 100 Hz, smaller strain with large hysteresis is related to the incompleteness of domain wall motion due to short timescale. The phenomenon of time-dependent strain and hysteresis is further confirmed that electric strain is originated from the reversible ergodic relaxor to ferroelectric phase transition.

The temperature-dependent ferroelectric and electromechanical properties of BNKT_{20} and BNKT_{25} are investigated in details. At room temperature, the square-like ferroelectric loops and negative strain exhibit ferroelectric order. The values of polarization and strain become larger with increasing of temperatures. Above 75°C , the pinched ferroelectric loops were observed in both ceramics, as shown in Figure 8 (a) and (d), indicating that the temperatures induce the ferroelectric-ergodic relaxor phase transition. At 120°C , the disappearance of negative strain indicates the nature of relaxor at high temperature. The largest electric strain is $\sim 0.36\%$ in BNKT_{20} , and 0.32% in BNKT_{25} at 120°C , under the low electric field of 50 kV/cm. The corresponding normalized strain d^*_{33} is 720 pm/V for BNKT_{20} and 640 pm/V for BNKT_{25} , respectively, see the inset of Figure 5 (b) and Figure 8. Large strains are better than those in BNT-based ceramics, such as BNBTFN [54] (d^*_{33} of 500 pm/V at 120°C), BNKTN-ST [37] (d^*_{33} of 570 pm/V at 110°C), BNKT-BA [56] (d^*_{33} of 415 pm/V at 120°C), BNKT-KNN [13] (d^*_{33} of 400 pm/V at 120°C), et al. see Table 2. At high temperatures, the large reversible strains are attributed to the synergic effect of the

temperature-induced structural phase transition and the occurrence of short-range ergodic relaxor phase as well as non-180° domain switching induced by external electric fields [37].

The coexistence of multi-phases in ferroelectric ceramics can strongly improve their electrocaloric properties [27, 28, 46]. First, the electrocaloric effect of BNKT_x ceramics at 50 kV/cm is estimated using indirect method based on Maxwell relation [4]. As follows: $\Delta T = -\frac{T}{\rho C_p} \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T} \right)_E dE$, where ρ is the density and C_p is heat capacity of the ceramic. E_1 ($E_1=0$ kV/cm) and E_2 are the initial and final applied electric field, respectively. The ferroelectric loops of BNKT_x ceramic at 50 kV/cm at different temperatures are depicted in Figure 9. Except BNKT₁₀, the pinched P-E loops start to occur during increasing temperature, which implies that the temperatures lead to the ferroelectric to ergodic relaxor phase transition, see Figure 9 (b),(c) and (d). At 120°C, the strong pinched ferroelectric loops were observed in the three ceramics, suggesting that the ergodic relaxor state is occurred above T_d . It is consistent with the observation of dielectric measurements. In these ceramics, the coercive fields decreases obviously with increasing of temperatures, see in Figure 9 and 6 (b). The values of polarization increases at measured temperatures for BNKT₁₀, BNKT₁₅ and BNKT₂₅, their corresponding depolarization temperatures are 203°C, 142°C and 141°C, respectively. Below T_d , the increment of polarizations are related to the domain switching at both driving fields such as electric and temperature fields. Using the thermodynamics Maxwell relation, the negative electrocaloric temperature changes are obtained below T_d . The validity of the relation in relaxor ferroelectric are still controversial to calculate the electrocaloric effect [29]. For BNKT_x ($x=0.10$, 0.15 and 0.25) compositions, the EC temperature changes are calculated as a function of temperatures at 50 kV/cm, as shown in Figure 10. The maximum negative EC values are obtained -2.6 K at 70°C in BNKT₁₀, -2.2 K at 42°C in BNKT₁₅ and -1.03 K at 48°C in BNKT₂₅, respectively. The large negative EC effect was also reported in BNT-6BT (-2.4 K at 122°C) [47], BNBT6-0.5La₂O₃ (-2.61 K at 87°C) [35], and

BNT-6BT (-1.0 K at 75 °C) [48] as shown in Table 1. The discrepancies using indirect and direct methods have been reported in the pure BNT ceramic [34], BNT-6BT ceramic [34, 49], BNT-18BKT [27]. Noted that the large negative EC temperature change (-1.0 K at 75 °C) is obtained using the direct DSC measurement in BNT-6BT system [48].

The mechanisms of negative EC effect have been suggested in La-PZT[26], $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ [50], BTO with defect dipoles [51]. In BNT-based materials, the giant negative EC values obtained may be artifacts via the indirect method due to the nonergodic state below T_d [36]. In BNT-based ceramics, it should be cautious to calculate the electrocaloric temperature change in relaxor BNT-based ceramics, especially at the temperature range below T_d . Direct measurement of EC temperature changes are convincing in various electrocalorics [49, 52, 53]. For BNKT_{20} and BNKT_{25} ceramic, the EC values are directly measured at relatively low electric fields using the modified DSC devices. The EC temperature changes were collected at three low electric fields, i.e. 20 kV/cm, 25 kV/cm, 30 kV/cm. At room temperature, the ferroelectric loops are unsaturated at low electric fields of 30 kV/cm, see Figure 3 (c) and (d). The thermodynamics Maxwell relation is invalid at such non-equilibrium state [27]. The indirect method is not useful to utilize to calculate the EC temperature change at low electric fields and/or below T_d . Due to the complexity of phase transition induced by the temperature and electric fields, direct measurement of EC temperature changes is strongly suggested to study the EC effect in BNT-based ceramics.

At room temperature, the EC values are only 0.023-0.03K at 30 kV/cm via direct measurement. The small EC effect is originated from the ferroelectric order induced by external electric fields. Although the ferroelectric loops are unsaturated at such low electric fields. The EC temperatures increases rapidly above 80°C, which can be explained by temperature-induced the long-range ferroelectric to short-range ergodic relaxor phase transition. At 30 kV/cm, the EC value is about 0.29 K in BNKT_{20}

ceramic at ~85 °C; 0.18 K in BNKT₂₅ ceramic at ~105°C ,as shown in Figure 11. Using indirect calculations, the positive EC value of 1.08 K at ~107°C is observed at 50 kV/cm for BNKT₂₀, see Figure 10. In the case of BNKT₂₀, the largest EC temperature changes are existed near T_d using both direct and indirect methods. Similar observations have been reported in BNT-6BT [49], NBT-18KBT [27] ceramics. The enhancement EC effect is attributed to the flattened free energy profile between nonergodic and ergodic states [49].The EC efficiency ($\Delta T/\Delta E$) is suggested to compare to the EC effect of different materials [52]. The EC efficiency in BNKT₂₀ is 0.216 K mm/kV at 50 kV/cm, which is comparable and even larger than some BNT-based ceramics [37, 54-56], as shown in Table 1.

Relaxor ferroelectrics exist small P_r and E_c and large P_{max}, it can be expected to obtain high energy density for energy storage devices. The BNKT₂₀ ceramic of large polarization (P_{max}=40.1μC/cm²) demonstrates the temperature-induced ergodic relaxor behavior, see Figure 9(c). Here, the energy storage properties of BNKT₂₀ ceramic have been investigated at broad temperature range from 20 °C to 180 °C under the electric field of 60 kV/cm. The energy storage density W_{total} is calculated by the applied electric field E and the polarization: $W_{total} = \int_0^{P_m} E dP$. The recoverable energy storage density is calculated by the equation: $W_{rec} = \int_{P_r}^{P_m} E dP$, where P_m and P_r are the maximum polarization and remnant polarization, respectively, E is the applied electric field. The efficiency (η) is calculated by $\eta = \frac{W_{rec}}{W_{total}}$. Figure 12 shows the energy storage density and the energy storage efficiency at the temperature range from 20°C to 180°C. At room temperature, the density and efficiency of BNKT₂₀ is only about 0.136 J/cm³ and 0.16, respectively, due to larger P_r in the ferroelectric phase. With the increasing of temperatures, the ergodic relaxor phase starts to occur and the ferroelectric order becomes weak, which is accordance with the observation with ferroelectric loops, see in Figure 8 (a) and Figure 9 (c). The calculated energy density and efficiency are dramatically enhanced at the temperature range from 50°C to 120°C. Above 120°C, the density is stable at ~0.79-0.83 J/cm³ and the

corresponding efficiency is ~0.72 to 0.83. Such values are larger or comparable to that in BNBTFN [54], BNKTT-ST [37], BLNKTZ [57], BNT-7KN [58] et al, as shown in Table 2. We believe that the BNKT₂₀ ceramic show its superiority for high temperature energy storage at relative low electric field.

CONCLUSIONS

Lead-free Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO₃ ceramics are studied systemically for their piezoelectric, electromechanical, electrocaloric properties as well as energy storage from room temperature to high temperature region. It is found that the low electric field (~30 kV/cm) can pole completely these ceramics to obtain large d_{33} . The d_{33} are constant or increased below depolarization temperature, which displays excellent thermal stability at broad temperature range. The increased d_{33} of BNKT₁₅ ceramic may be related to non-180 domain switching induced by internal bias field during increasing temperatures. Large strain of 0.35% in BNKT₂₀ is obtained under the low field of 50 kV/cm at 120°C, the corresponding normalized strain d^*_{33} is 720 pm/V. Such value is higher than that in other BNT-based ceramics at high temperature region. The positive large EC effect are observed around T_d both indirect and direct methods. Large EC efficiency of 0.216 K mm/kV in BNKT₂₀ is obtained at 50 kV/cm. This value is comparable or higher than some lead-free based ceramics. Above 100°C, the energy storage density and efficiency of BNKT₂₀ are 0.8 J/cm³ and 0.75, respectively, at low fields of 60 kV/cm. Our studies suggest that the BNKT_x ceramics may be a promising candidate for applications in high temperature actuator, hybrid electric vehicles and nuclear fuel plant.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

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Figure 1. The XRD patterns of BNKT_x ceramics, the inset: SEM microstructure of BNKT₂₀ ceramics

Figure 2. Temperature dependence of poled dielectric constants and loss tangents of BNKT_x ceramics (a) $x=0.10$, (b) $x=0.15$, (c) $x=0.20$, (d) $x=0.25$

Figure 3. The ferroelectric loops of BNKT_x ceramics (a) $x=0.10$, (ab) $x=0.15$, (c) $x=0.20$, (d) $x=0.25$ at room temperature and 10 Hz

Figure 4. Polarization (P_m and P_r) and coercive field (E_c) of BNKT_x ceramics at 70 kV/cm.

Figure 5. (a) The piezoelectric coefficient d_{33} of BNKT_x ceramics as a function of poling DC electric field, (b) The thermal stability of d_{33} and the normalized strain d_{33}^* of BNKT_x ceramics at different temperatures.

Figure 6. (a) The remnant polarizations (a) and coercive fields (b) of BNKT₂₀ ceramic at different electric fields at elevated temperatures.

Figure 7. Field-induced bipolar strain (a) and unipolar strain (b) of BNKT_x ceramics at room temperature and 10 Hz (c) unipolar strain of BNKT₂₀ ceramics at different electric field. (d) unipolar strain of BNKT₂₀ ceramics at different frequencies under external electric field of 50 kV/cm.

Figure 8. The ferroelectric loops and bipolar strain and unipolar strain (a), (b), (c) of BNKT_{20} and (d), (e), (f) of BNKT_{25} at different temperature.

Figure 9. The P-E loops of BNKT_x ceramic (a) $x=0.10$, (b) $x=0.15$, (c) $x=0.20$, (d) $x=0.25$ at different temperatures at 50 kV/cm. The inset: The polarization as a function of temperatures at 50 kV/cm.

Figure 10. The electrocaloric temperature change of BNKT_x ceramic at 50 kV/cm.

Figure 11. The electrocaloric temperature change of BNKT_x (a) $x=0.20$, (b) $x=0.25$ at different electric fields using direct measurement.

Figure 12. The energy storage density and efficiency of BNKT₂₀ as a function of temperature under the electric field of 60 kV/cm.

Table 1 Comparison of the electrocaloric temperature change of various ceramic
electrocalorics

Materials	T(°C)	T _d (°C)	E (kV/cm)	EC values	EC efficiency (Kmm/kV)	Methods	Ref.
BNKT ₂₀	85°C	92°C	30	0.29	0.10	Direct	Our works
BNKT ₂₀	107 °C	92°C	50	1.08	0.216	Indirect	Our works
BNKT ₂₅	100 °C	141°C	30	0.17	0.055	Direct	Our works
BNT-7KN	75°C	40°C	55	0.80	0.145	Direct	Ref. 57
BNT-18BK T	80°C	67°C	50	1.06	0.212	Indirect	Ref.31
0.94BNT-0. 06BT	185 °C	122 °C	70	1.2	0.17	Indirect	Ref.47
BNBT6-0.5 La ₂ O ₃	138 °C	87 °C	50	1.5	0.30	Indirect	Ref.35
BNT-6KN	75 °C	40 °C	70	1.7	0.24	Indirect	Ref.31
BNT-6BT	110°C	101°C	50	0.86	0.17	Direct	Ref.49
BNKT ₁₀	70°C	203°C	50	-2.6		Indirect	Our works
BNKT ₁₅	42 °C	142°C	50	-2.2		Indirect	Our works
BNT-6BT	50 °C	122 °C	70	-2.4		Indirect	Ref.47
BNBT6-0.5 La ₂ O ₃	64 °C	87 °C	50	-2.61		Indirect	Ref.35

Table 2 comparison of the electromechanical strain and energy storage density of other ceramics at high temperature

Materials	T(°C)	E (kV/cm)	d_{33}^* (pm/V)	Energy storage (J/cm ³)	Efficiency	Ref.
BNKT ₂₀	120 °C	50	720			Our works
		60		0.83	0.72	
BNKT ₂₀	180 °C	60	-	0.79	0.83	Our works
BNKT ₂₅	120 °C	50	640	0.42	0.63	Our works
BNBTFN	120 °C	50	500			Ref.54
BNKTN-ST	110 °C	60	570	1.18	0.81	Ref.37
		50	300	0.62	0.90	
BNT-BT-KN N	130 °C	60	333			Ref.55
BNKT-BA	130 °C	60	415			Ref.56
BLNKTZ	125 °C	60		0.8	0.75	Ref.57
BNKT-0.01 KNN	120°C	70	400			Ref.13