Remarkably enhanced dielectric stability and energy storage properties in BNT–BST relaxor ceramics by A-site defect engineering for pulsed power applications

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Abstract: Lead-free bulk ceramics for advanced pulsed power capacitors show relatively low recoverable energy storage density (W_{rec}) especially at low electric field condition. To address this challenge, we propose an A-site defect engineering to optimize the electric polarization behavior by disrupting the orderly arrangement of A-site ions, in which $\text{Ba}_{0.105}\text{Na}_{0.325}\text{Sr}_{0.245-1.5x}\square_{0.5x}\text{Bi}_{0.325+x}\text{TiO}_3$ ($\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$, $x = 0, 0.02, 0.04, 0.06, \text{ and } 0.08$) lead-free ceramics are selected as the representative. The $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics are prepared by using pressureless solid-state sintering and achieve large W_{rec} (1.8 J/cm^3) at a low electric field ($@110 \text{ kV/cm}$) when $x = 0.06$. The value of 1.8 J/cm^3 is super high as compared to all other W_{rec} in lead-free bulk ceramics under a relatively low electric field ($< 160 \text{ kV/cm}$). Furthermore, a high dielectric constant of 2930 within 15% fluctuation in a wide temperature range of $40\text{--}350^\circ\text{C}$ is also obtained in $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ($x = 0.06$) ceramics. The excellent performances can be attributed to the A-site defect engineering, which can reduce remnant polarization (P_r) and improve the thermal evolution of polar nanoregions (PNRs). This work confirms that the $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ($x = 0.06$) ceramics are desirable for advanced pulsed power capacitors, and will push the development of a series of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT)-based ceramics with high W_{rec} and high-temperature stability.

Keywords: relaxor ferroelectrics; energy storage ceramics; ceramic capacitor; $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT); defect engineering

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1 Introduction

Dielectric capacitor is an indispensable component in contemporary electronic devices, which fulfills different functions such as direct current blocking, coupling, filtering, and pulse discharge [1–3]. Considering the complicated working environment, especially high temperatures (150–200 °C, even up to 300 °C), ceramic dielectrics would be more suitable for energy storage candidates than other polymer materials [4]. Generally, the energy storage properties of ceramic dielectrics can be evaluated by the following equations [5]:

$$W = \int_0^{P_{\max}} E dP \quad (1)$$

$$W_{\text{rec}} = \int_{P_r}^{P_{\max}} E dP \quad (2)$$

$$\eta = \frac{W_{\text{rec}}}{W} \times 100\% \quad (3)$$

where W , W_{rec} , η , E , dP , $P_{\max}$, and P_r denote total energy storage density, recoverable energy storage density, energy efficiency, applied external electric field, polarization increment at E , maximum polarization, and remnant polarization, respectively. Therefore, high $P_{\max}$, low P_r , and high breakdown strength E_b are important factors to achieve high W_{rec} [6,7]. However, high applied electric field may limit its application in integrated electronic circuits, as well as in wearable or implantable devices requiring low electric field. Pb-based relaxor ferroelectric and antiferroelectric ceramics had been considered as potential candidates, while the toxicity of Pb limits its application [8,9]. It is urgent to design and develop new Pb-free systems with high W_{rec} especially under relatively low electric field.

Bismuth sodium titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$, BNT) possesses characteristics of complicated phase structure with high $P_{\max}$, and hence is considered as a promising energy storage ferroelectric material [9–13]. Noted that a high P_r and poor sintering behavior of pure BNT ceramic result in a low W_{rec} . Different methods, therefore, are utilized to improve W_{rec} such as chemical doping, glass modification, multilayer structure design, and advanced sintering technology [14–22]. For chemical doping, it can be divided into chemical equivalent and aliovalent doping. Especially, the chemical aliovalent doping includes “donor” and “acceptor” doping, which can induce different types of defects and improve the properties of materials. For example, Cao

et al. [23] used Mn^{2+} as acceptor dopant to substitute B-site ions of $0.7[0.94\text{NBT}-0.06\text{BT}]-0.3\text{ST}$ ceramic, and acquired a high W_{rec} of 1.06 J/cm^3 . Xu *et al.* [24] found a pinched P – E loop behavior in Ta donor doped $\text{BNT}-0.06\text{BT}$ ferroelectric ceramic. It can be observed that defect engineering can effectively improve energy storage properties by forming different types of defect dipoles. For vacancy defect, on the one hand, it can influence internal electric field to reduce P_r , and on the other hand, it may pin domain wall to inhibit its switching. However, a few reports pointed out the chemical defects by adjusting the element ratio in composition to optimize the energy storage properties of BNT-based ceramics.

Based on our previous work, a binary solid solution of $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.65}(\text{Ba}_{0.3}\text{Sr}_{0.7})_{0.35}\text{TiO}_3$ (BNT–BST) is considered as a good energy storage material due to “clamped” behavior in P – E loop and high dielectric constant ϵ_r (~4000) at room temperature [25,26]. However, its relatively high P_r and poor dielectric temperature stability make it hard to obtain high W_{rec} . Based on the above considerations, we propose an A-site defect engineering, i.e., adjusting the Bi/Sr ratio by generating different concentrations of Sr^{2+} vacancy to enhance W_{rec} in this work. Consequently, the phase structure, micrograph, dielectric temperature stability, and energy storage properties of $\text{Ba}_{0.105}\text{Na}_{0.325}\text{Sr}_{0.245-1.5x}\square_{0.5x}\text{Bi}_{0.325+x}\text{TiO}_3$ ceramics are investigated.

2 Experimental

$\text{Ba}_{0.105}\text{Na}_{0.325}\text{Sr}_{0.245-1.5x}\square_{0.5x}\text{Bi}_{0.325+x}\text{TiO}_3$ ($\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$, $x = 0, 0.02, 0.04, 0.06$, and 0.08) ceramics were fabricated using a solid-state process. Raw materials Bi_2O_3 (99.9%), Na_2CO_3 (99.8%), TiO_2 (99.9%), BaCO_3 (99.0%), and SrCO_3 (99.9%) (purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were weighted according to stoichiometric formula and mixed in planetary ball mill for 24 h with zirconia balls in ethanol. After separating the balls, the mixtures were dried, calcined at 800 °C for 3 h, and then milled again for 24 h. The powder was compacted into pellets of 13 mm in diameter and about 1 mm in thickness under the pressure of $120 \pm 10 \text{ MPa}$ after granulated by adding polyvinyl alcohol solution (PVA, 5 wt%). The disks were preheated at 650 °C for 2 h to remove PVA binder, and finally sintered at 1180–1240 °C for 2 h in air followed by furnace cooling.

The phase structure evolution was identified using the X-ray diffraction (XRD, D8-Advance, Bruker, Germany) with Cu K α radiation and the Raman spectroscopy (in Via, Renishaw, UK). The microstructure features of the ceramic sample were observed by a scanning electron microscope (SEM, JSM-6700F, JEOL, Japan) after polishing and thermally etching. For electrical performance testing, ceramic samples were polished to smooth and parallel in both surfaces and then painted Ag electrode on both sides. The dielectric properties of ceramics were measured using a precision impedance analyzer (HP4294A, Agilent, USA) over a temperature range from -100 to 400 °C. For P – E loop and charge–discharge measurements, the ceramic samples were polished to 0.3 – 0.35 mm and covered a central electrode with margin blank on both sides. The P – E hysteresis loops and I – E curves were examined using a ferroelectric analyzer at 10 Hz (Trek model 609B, USA) based on a standard sawyer-tower circuit. The temperature dependent charge–discharge capability was tested using a designed RLC circuit (CFD-003, Tongguo Technology, Shanghai, China) being connected to a temperature controlled chamber.

3 Results and discussion

Figure 1(a) shows XRD patterns of $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics at $2\theta = 20^\circ$ – 80° . All samples are pure pseudocubic perovskite structure without trace of any other secondary phases. As seen from Fig. 1(b), the diffraction peak (200) slightly shifts toward a high angle with the increase of x value, indicating that the cell volume gradually decreases. This phenomenon

Fig. 1 XRD patterns of $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics: (a) $2\theta = 20^\circ$ – 80° and (b) $2\theta = 46^\circ$ – 47° .

should be attributed to the following reasons: One is the replacement of Bi^{3+} ions with a smaller ionic radius ($r_i = 1.35$ Å, coordination number = 12) to Sr^{2+} ($r_i = 1.44$ Å, CN = 12) with a larger one; and the other is that Sr vacancy content gradually increases with x value, while the existence of vacancy provides a space for lattice contraction.

It is well known that the Raman spectroscopy is an effective tool to investigate the crystalline structure information and phase transition. Figure 2(a) shows Raman spectra of $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics at room temperature. Generally, BNT material possesses 16 active phonon modes, and the irreducible representation is $\Gamma_{\text{Raman}} = 4A_1 + 1B_1 + 3B_2 + 8E$ based on the group theory [27,28]. Figure 2(b) displays the fitted Raman pattern only including eight modes for pure BNT–BST ceramics at room temperature, which should be attributed to disorder occupation of ions at A-site and polycrystalline feature of ceramics. In order to better illustrate the results, four main regions can be classified into the Raman spectra: (1) The modes below 200 cm^{-1} (ν_1, ν_2) are related to A-site cation vibration, including Bi^{3+} , Na^+ , Ba^{2+} , and Sr^{2+} ions; (2) the modes around 200 – 400 cm^{-1} (ν_3, ν_4) should be associated with the vibration of Ti–O bond; (3) the modes from 400 to 700 cm^{-1} (ν_5, ν_6) are related to $[\text{TiO}_6]$ vibrations, namely the breathing and stretching of the oxygen octahedron; (4) the modes above 700 cm^{-1} (ν_7, ν_8) are ascribed to the super-position of vibration A_1 (longitudinal optical) and E (longitudinal optical) overlapping bands [28–31]. The Raman patterns are decomposed by Lorentz peak fitting to investigate the effect of x value on the vibration modes. The fitted Raman patterns for the represented $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics with $x = 0$ and $x = 0.06$ are shown in Figs. 2(b) and 2(c), respectively. With the increase of x value, the ν_2 phonon mode's wavenumber presents an obvious shifting upward tendency, and signal intensity enhances as shown in Fig. 2(d). Meanwhile, the ν_3 phonon mode's wavenumber also shows a similar tendency. The results may be ascribed to the enhancement of the polarity of unit cell by the increase of Sr vacancy [32,33]. Furthermore, it can be seen that the gap of wavenumber between ν_5 and ν_6 gradually increases, and the intensity of the ν_6 phonon mode has a slight enhancement, which should be related to the strengthening of the TiO_6 octahedral distortion, as shown in Fig. 2(d).

Figure 3 displays the micrograph feature of polished and thermally-etched $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics.

It can be seen from Figs. 3(a)–3(e) that $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics possess uniform grains and extremely high density. As x value increases, the grain size gradually increases (Fig. 3(f)), which should be attributed to the following two reasons: One is that Bi^{3+} replaces the A-site ion, and the lattice shrinkage will cause stress; and the other is that Bi^{3+} replaces Sr^{2+} ,

in order to maintain charge balance, defects such as Sr vacancy and empty lattices will be formed, and stress will also be generated, which accelerates the mass transfer rate between particles and weakens the competition with the adjacent grains, leading to accelerated grain growth and densification promotion of ceramics during the sintering process [34].

Fig. 2 (a) Raman patterns of $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics at room temperature. Lorentz peak fitting of Raman pattern for represented $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics with (b) $x = 0$ and (c) $x = 0.06$. (d) Wavenumbers of Raman peaks from v_1 to v_8 of $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics as a function of x value.

Fig. 3 SEM images of polished and thermally-etched surface of BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics: (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.04$, (d) $x = 0.06$, and (e) $x = 0.08$; and (f) average grain size of BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics as a function of x value.

Figures 4(a)–4(e) show temperature dependence of dielectric properties for BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics with different x values at frequencies of 1 kHz, 10 kHz, 100 kHz, and 1 MHz. It should be mentioned that relaxor ferroelectric has two obvious characteristics: One is that T_m , the absolute temperature corresponding to the maximum dielectric constant ϵ_m , shifts toward high temperature with increasing frequency, and the other one is that dielectric constant at T_m decreases with the increase of frequency whereas that of loss tangent follows the reverse order. Meanwhile, a modified Curie–Weiss law is applied to evaluate the relaxor characteristic [35]:

$$\frac{1}{\epsilon_r} - \frac{1}{\epsilon_m} = \frac{(T - T_m)^\gamma}{C} \quad (4)$$

where ϵ_r and C are the relative dielectric constant T is the measured actual temperature and the Curie constant, respectively. The diffuseness factor γ decreases with decreasing relaxor degree and varies between 1 (for normal ferroelectric) and 2 (for ideal relaxor ferroelectric) [36]. With increasing x value, γ value increases from 1.71 to 2.00, indicating that relaxor characteristic is effectively enhanced. For pure BNT–BST ceramics, one dielectric peak at T_m and obvious relaxor behavior below T_m can be observed. After composition modification, wave-like double peaks can be found in dielectric spectra, and corresponding temperatures are named as T_{m1} and T_{m2} . Noted that dielectric relaxor behavior only exists at a temperature below T_{m1} , and

thus dielectric peak at T_{m1} is similar to that at T_m . Thus, a new dielectric peak at T_{m2} should be induced by the Bi–Sr ratio change. In addition, it can be seen that T_{m1} and T_{m2} correspond to the transition from relaxor to ferroelectric phase and ferroelectric to paraelectric phase, respectively. Actually, a similar phenomenon can also be observed in other BNT-based systems while the related reason is still controversial [32,37–40].

Temperature coefficient of capacitance (TCC) is a crucial factor to influence its application scenes. In general, it can be calculated by Eq. (5):

$$TCC = \frac{\epsilon - \epsilon_{base}}{\epsilon_{base}} \quad (5)$$

where ϵ_{base} denotes dielectric constant at a based temperature. As x value increases, the dielectric peak at T_{m1} is suppressed, while the temperature difference $\Delta T = T_{m2} - T_{m1}$ is gradually enhanced, which is beneficial for enhancing temperature stability. Figure 4(f) shows TCC of BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics with different x values by choosing 150 °C as the based temperature. With increasing x value, dielectric temperature stability is effectively enhanced especially at high temperatures, which is attributed to the appearance of a new dielectric peak at T_{m2} . For $x = 0.06$ composition, a wide temperature range of $TCC \leq \pm 15\%$ at the temperature range of 40–350 °C.

In order to further explore the reason for generating dielectric peak at T_{m2} , a variable Raman spectrum is used. Figure 5 shows Raman spectra and wavenumber

Fig. 4 Temperature dependent dielectric constants and loss of BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics at typical frequencies: (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.04$, (d) $x = 0.06$, and (e) $x = 0.08$; and (f) TCC for BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics with different x values by choosing 150 °C as the based temperature.

of Raman peaks of BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics with $x = 0.06$ over a temperature range from room temperature to 275 °C. As temperature increases, the signals of modes ν_2 and ν_6 gradually present a disappeared tendency, while other modes change slightly, as shown in Fig. 5(a). All modes display a decreased tendency, with no abrupt change in wavenumber (Fig. 5(b)). The result illustrates that modes ν_2 and ν_6 are sensitive to phase structure of BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics with $x = 0.06$. The slow transitions of modes ν_2 and ν_6 both demonstrate that phase structure of $x = 0.06$ composition has a

slight change. Therefore, it can be concluded that the new dielectric peak at T_{m2} should be attributed to the thermal evolution of polar nanoregions (PNRs) affected by the concentration of Sr vacancy [40]. Furthermore, it should be noted that T_{m2} has a slowly increased tendency as x increases, and this may due to the decrease of structural stability by increasing Sr vacancy. And then higher temperature is needed to adjust the structural stability because T_{m2} corresponds to ferroelectric–paraelectric phase transition temperature.

Figure 6(a) shows P – E loops of BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics at 60 kV/cm and room temperature. As x

Fig. 5 (a) Raman spectra and (b) wavenumbers of Raman peaks from ν_1 to ν_8 of BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics with $x = 0.06$ at different temperatures.

Fig. 6 (a) Measurement of P - E loops at 60 kV/cm for $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics with different x values, and corresponding I - E loops are shown in the inset; (b) P_{max} , P_r , and $P_{\text{max}} - P_r$ versus x value for $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics at 60 kV/cm; (c) recoverable energy density W_{rec} and (d) energy efficiency η as a function of applied electric field for $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics.

value increases, P - E loops gradually go slim, which is beneficial for improving energy storage property, and the maximum polarization at a given electric field slightly decreases with the increase of x value. Combined with I - E loops at the same conditions, current peaks gradually diffuse, and corresponding intensity decreases, indicating the relaxor characteristic is enhanced [41]. In addition, P_{max} , P_r , and $P_{\text{max}} - P_r$ versus x value for $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics at 60 kV/cm are exhibited in Fig. 6(b). A relatively high $P_{\text{max}} - P_r$ of $27.52 \mu\text{C}/\text{cm}^2$ can be obtained at $x = 0.06$ composition due to a rapid decrease in P_r , because the PNRs are dynamic sensitive to external electric field stimuli. Figures 6(c) and 6(d) show energy efficiency η and recoverable energy density W_{rec} of $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics at different electric fields, respectively. As x value increases, η presents an increased tendency obtaining a high value for $x = 0.06$ composition, and then decreases again with further increasing x value. Meanwhile, $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics with $x =$

0.06 possess a maximum W_{rec} of $1.8 \text{ J}/\text{cm}^3$ only at a low electric field of 110 kV/cm, as shown in Fig. 6(d).

In order to investigate the working stability at different external fields, temperature, frequency, and electric fatigue dependent energy storage properties of $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics with $x = 0.06$ have been examined. Figure 7(a) shows P - E loops of $x = 0.06$ ceramics over a temperature range of 30–150 °C at 60 kV/cm and 10 Hz. As temperature increases, P - E loops gradually go slim, and keep a high P_s and low P_r . Therefore, W_{rec} and η of $x = 0.06$ ceramics possess good temperature stability, as exhibited in Fig. 7(b). Meanwhile, frequency dependent P - E loops of $x = 0.06$ ceramics at 60 kV/cm are displayed in Fig. 7(c). It can be seen that energy loss has a slight increase tendency during discharge process, which may be related to vacancy defect pin domain wall. W_{rec} and η of $x = 0.06$ ceramics, therefore, show a slight decrease at frequencies of 1–100 Hz, as shown in Fig. 7(d). Finally, P - E loops as a function of cycle number and

Fig. 7 P – E loops as a function of (a) temperature, (c) frequency, and (e) cycle number for BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics with $x = 0.06$. W_{rec} and η as functions of (b) temperature, (d) frequency, and (f) cycle number for BNS_{0.245-1.5x}□_{0.5x}B_{0.325+x}T ceramics with $x = 0.06$.

corresponding W_{rec} and η for $x = 0.06$ ceramics are illustrated in Figs. 7(e) and 7(f), respectively. Noted that polarization of $x = 0.06$ ceramics keeps a stable value at 10 Hz after 10^5 electric cycles. Obviously, $x = 0.06$ ceramics possess a good fatigue endurance, and W_{rec} and η as functions of cycles are illustrated in Fig. 7(f).

Charge–discharge characteristic is an essential factor for dielectric materials to evaluate its energy storage

capabilities, and thus charge–discharge measurement is fulfilled at a specified circuit. Generally, discharge energy density W_d can be calculated by the equation as Eq.(6) [42]:

$$W_d = \frac{R \int i^2 dt}{V} \quad (6)$$

where R is the load resistance (100 Ω), i is the maximum discharge current, and V is the effective volume of

Fig. 8 (a) Overdamped discharge current curves and (b) corresponding discharge density W_d as a function of electric field for $x = 0.06$ ceramics at room temperature, (c) overdamped discharge current curves, and (d) corresponding discharge density W_d as a function of temperature for $x = 0.06$ ceramics at 80 kV/cm.

ceramic between two electrodes. Figures 8(a) and 8(b) show room-temperature underdamped discharge waveform and corresponding W_d of $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics with $x = 0.06$ ceramics at different electric fields. As the electric field increases, the maximum discharge current $I_{\max}$ and W_d both gradually enhance. It should be mentioned that W_d is less than W_{rec} at the same electric field for $x = 0.06$ composition. This may be attributed to the following two reasons [43]: One is that the domain cannot switch quickly to respond to the external electric field; and the other is that equivalent series resistance (ESR) generates Joule heat during charge–discharge process. The discharge rate is characterized by evaluating factor $t_{0.9}$ (the dashed line in Fig. 8(b)), which represents the time needed for releasing 90% of all stored energy [44]. Figure 8(b) shows that $t_{0.9}$ is about 0.1 μs for $x = 0.06$ ceramics at room temperature, which illustrates that energy can be released by a pulse current way in a short time. Variable temperature discharge current curves as a function of time for $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics with $x = 0.06$ ceramics are displayed in Fig. 8(c). As temperature

increases, the maximum discharge current $I_{\max}$ basically keeps a stable value while W_d possesses an obvious enhancement as shown in Fig. 8(d). The discharge capability of $x = 0.06$ ceramics possesses good temperature stability, which is beneficial for the application in high-temperature environment.

To better evaluate the energy storage properties of $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics, we compared W_{rec} and $E_{\max}$ of $x = 0.06$ and 0.08 compositions with some lead-free ceramic bulks reported previously [45–55]. It can be seen from Fig. 9(a) that a large W_{rec} ($> 1.5 \text{ J/cm}^3$) usually requires a high E_b ($> 160 \text{ kV/cm}$) to produce high polarization, especially for some BT-based and $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ -based materials. In this work, a high W_{rec} can be achieved under a relatively low electric field, which exceeds other BNT-based energy storage ceramics at the same electric field, even in other lead-free systems. With further comparing W_{rec} and η of different compositions, it could be noted that high W_{rec} and η are hard to obtain simultaneously in one system influenced by heat loss at electric field, as shown in Fig. 9(b). Noted that $\text{BNS}_{0.1555}\square_{0.03}\text{B}_{0.385}\text{T}$ ($x = 0.06$)

Fig. 9 A comparison of energy storage properties (W_{rec} and η) between some reported lead-free ferroelectric ceramics and this work. Note that 1 and 2 in the red ball denote the $x = 0.06$ and $x = 0.08$ compositions in this work, respectively.

ceramics possess a relatively high W_{rec} ($> 1.5 \text{ J/cm}^3$), together with a high η ($> 70\%$) under relatively low electric field ($< 160 \text{ kV/cm}$), demonstrating that it is potential to obtain both high W_{rec} and η , which should be a promising candidate for power ceramic capacitor application.

4 Conclusions

In this work, an A-site defect engineering is proposed to improve the energy storage performance of $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ lead-free ceramics. High recoverable energy density of 1.8 J/cm^3 under low electric field ($@110 \text{ kV/cm}$) and energy efficiency of 72% are achieved simultaneously in the sample with $x = 0.06$. This good energy storage performance is attributed to the A-site defect engineering that can reduce P_r . The ceramic also exhibits satisfactory temperature, frequency, and cycling stabilities as well as a high charge–discharge rate. $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ($x = 0.06$) ceramics show a high dielectric constant of 2930 within 15% fluctuation in a wide temperature range of 40–350 °C. This high-temperature stability is attributed to the A-site defect engineering, which can improve the thermal evolution of PNRs. All these advantages indicate that $\text{BNS}_{0.245-1.5x}\square_{0.5x}\text{B}_{0.325+x}\text{T}$ ceramics are suitable for solid-state pulse power ceramic capacitors, and the A-site defect engineering is a robust strategy to improve the W_{rec} and high-temperature stability of lead-free ceramics.

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