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Research Article

Energy storage behavior optimization of SBKT ceramics based on multi-sites charged defects synergistic regulation engineering

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Abstract: Lead-free relaxor ferroelectric ceramic is suitable for pulse energy storage. Achieving both high energy storage density and efficiency is crucial for the research. Herein, $(1-x)(0.5\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3-0.5\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3)-x\text{NaTaO}_3$ relaxor ferroelectric ceramic is fabricated to optimize microstructures and energy storage behavior based on multi-sites charged defects synergistic regulation engineering. Na^+ doping in A-site contributes to polymorphic polarization; Ta^{5+} doping in B-site refines grain and increases the electrical resistance; the formation and migration process of oxygen vacancy charged defects are significantly suppressed in O-site based on ion doping and the formation of $\text{Bi}_2\text{Ti}_2\text{O}_7$ -based insulating phase. The introduction and synergistic regulation of these charged defects enhance the ionic and charge disorder and configurational entropy, and induces more small-sized polar structure, resulting in the enhanced relaxor ferroelectricity and delayed polarization saturation. Meanwhile, the micromorphology is improved, resulting in the enhanced electrical insulation. Consequently, the polarization and breakdown behavior are optimized. $0.9(0.5\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3-0.5\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3)-0.1\text{NaTaO}_3$ exhibits low remnant polarization, high breakdown strength and maximum polarization, and achieves high energy storage density of 5.68 J/cm^3 with high efficiency of 88.1% at moderate operating electric fields 490 kV/cm, and excellent temperature ($-50\sim 150^\circ\text{C}$), frequency (10~500 Hz), and cycling stability. Meanwhile, the sample shows good pulsed charging-discharging properties with thermal stability and long cycle life (10^5 cycles at 25°C and 150°C). Therefore, this sample demonstrates promising potential for pulse energy storage, and this study offers a novel strategy and mechanism for the designing and optimization of advanced energy storage ceramics.

Keywords: Dielectric energy storage; Charged defects; Numerical simulations; Oxygen vacancy transport kinetics; First-principles calculations.

1 Introduction

Dielectric capacitors have significant advantages in pulsed power characteristics and a long cycle life coupled with excellent environmental stability, which play an irreplaceable role in pulsed power systems [1, 2]. Developing dielectric capacitors with outstanding energy storage behavior (high recoverable energy storage density (W_{rec}) and high energy storage efficiency (η)) is the key to the research. This requires the dielectric energy storage material to possess excellent polarization behavior (high maximum polarization (P_{max}), low hysteresis loss and weak polarization saturation) and breakdown behavior (high dielectric breakdown strength (BDS)).

Relaxor ferroelectrics $\text{Sr}_{0.7}\text{Bi}_{0.2}\square_{0.1}\text{TiO}_3$ (SBT, the symbol $\square$ represents the A-site structural vacancy in the perovskite structure.) have shown great potential in efficient pulse energy storage due to many advantages of low remnant polarization (P_r), low hysteresis loss, moderate BDS and high η . However, due to the limited size and content of polar structures in SBT, the P_{max} under the same electric field is still at a low level compared with other relaxor ferroelectrics, which limits W_{rec} [3]. $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (KBT) is a ferroelectric with high P_{max} . In previous studies, when KBT is introduced into SBT to form SBT-KBT (SBKT) ceramics, $\text{Bi}^{3+}\text{-K}^+$ defect dipole pairs are induced, which can optimize the polar structure and improve P_{max} of SBT [4]. An enhanced W_{rec} of 2.21 J/cm^3 with the η of 91.4% was achieved in 0.62SBT-0.38KBT. However, the formation of large-sized domain structures and insufficient electrical insulation led to the deterioration in P_r and BDS, limiting further improvements in energy storage performance. In recent years, various strategies (process optimization, insulation enhancement, defect engineering, etc.) have been adopted to improve the energy storage performance of SBKT ceramics. Li *et al.* prepared 0.7KBT-0.3SrTiO₃ ceramics and the energy storage performance

was enhanced via rolling technology [5]. A high W_{rec} of 2.31 J/cm³ with the η of 77.7% was achieved.

Zhao *et al.* induced a high-resistivity second phase (Bi₂Ti₂O₇-based compounds) by combining SBKT ceramics with Er₂O₃, which enhanced the electrical insulation properties [6]. This results in an improvement of BDS and an enhanced W_{rec} of 2.17 J/cm³ with η of 83.9%. However, these works did not optimize the polar structure in SBKT main phase, resulting in high hysteresis loss and P_r . This limited the enhancement of BDS and W_{rec} , as well as low η . Zheng *et al.* introduced La(Mg_{2/3}Ta_{1/3})O₃ (LMT) into SBKT ceramics to construct heterogeneous structure using a multi-component optimization strategy [7]. Although the W_{rec} increased to 6.94 J/cm³, the η (80.6%) needs to be improved to reduce energy loss and maintain excellent service reliability. Therefore, the ionic doping strategy needs further optimization.

Aliovalent ion doping is an important and effective method for optimizing the performance of energy storage ceramics. The core essence of this method lies in the precise construction and control of charged defects. Zhao *et al.* doped Li⁺ and Bi³⁺ heterovalent ions into the A-site of the SBT, forming charged defects with positive and negative charge centers [3]. This induced Bi³⁺-Li⁺ defect dipoles, significantly improving the P_{max} of the SBT and achieving an enhanced W_{rec} of 3.44 J/cm³ and an η of 93.74%. Wang *et al.* introduced various heterovalent ions into Bi_{0.5}Na_{0.5}TiO₃-based ceramics, replacing the low-valent Ti⁴⁺ at the B site with high-valent Nb⁵⁺/Ta⁵⁺. This induced the formation of charged A-site cation vacancies to capture oxygen vacancies, reducing conductivity and effectively improving the BDS, resulting in an enhanced energy density of 2.1 J/cm³ and an energy storage efficiency of 92.9% [8]. However, systematic research is still lacking in the design of modification strategies and the elucidation of the mechanisms, especially the synergistic regulation mechanism of charged defects at multiple sites. In the ABO₃ type perovskite SBKT-based ceramics, the charged defects induced by aliovalent doping or the electricity valence imbalance can regulate the microstructure in multi-dimensions, while simultaneously optimizing carrier transport, polarization

behavior and breakdown characteristics. The regulation mechanism study is the key to improving the overall energy storage performance of SBKT ceramics.

The occupied sites (A, B and O-site), charge properties, concentration, and kinetic transport characteristics of charged defects significantly affect polarization and breakdown behavior. (1) A-site is an important site for regulating polarization because AO_{12} cages provide space for the ionic polar displacement, which induces spontaneous polarization and contributes to the polarity of the material [9]. Previous optimization strategies for energy storage ceramics with low polarization mostly adopted a single charged defect polar unit design, which easily leads to excessive growth and concentration of polar structures [4, 10]. Therefore, the introduction of multi-defect polar units is necessary. Na^+ exhibits obvious large off-center displacements and polar extension behaviors in many Bi-based perovskite system [9]. The introduction of Na^+ can form negative charge center, which interact with K^+ and Bi^{3+} to form various polarization displacements, contributing to the polymorphic polar structures. This unique multipolarity effect can break long-range ferroelectric order, and induce more small-sized polar structures with high polarization intensity, contributing to high P_{max} , low P_r and weak polarization saturation. (2) B-site is an important site for enhancing the electric insulation. Ta^{5+} in B-site can effectively decrease the grain size, and widen bandgap, contributing to enhancing electric resistance and suppressing breakdown behavior [8, 11, 12]. (3) The transport dynamics (concentration and migration) of oxygen vacancies, which are charge defects in O-site, significantly affect electrical insulation properties and BDS . Most existing reports focus on the regulation of oxygen vacancy concentration, neglecting the inhibition of oxygen vacancy migration. Furthermore, the mechanism study of oxygen vacancy regulation remains at the experimental characterization level, with few in-depth theoretical calculations and analyses. The substitution of Ta^{5+} in B-site can form charge defect with excess electrons, which can suppress the formation and migration of oxygen vacancy carriers [8]. Meanwhile, multi-aliovalent ions doping can form high ion and charge disorder. The induced high-

entropy lattice distortion and sluggish diffusion effect can further suppress oxygen vacancy migration and optimize microstructure [13-16]. These factors contribute to enhancing electric insulation and BDS.

In this work (Fig. 1), based on multi-sites charged defects synergistic regulation engineering, Na^+ and Ta^{5+} are introduced into the A-site and B-site of SBKT ceramics, respectively. $(1-x)(0.5\text{SBT}-0.5\text{KBT})-x\text{NaTaO}_3$ (abbreviated as SBKT-100xNT, $x=0, 0.05, 0.1, 0.15, 0.2$) ceramics was fabricated to regulate the microstructure in multiple dimensions and optimize polarization and breakdown behavior, thereby improving the energy storage performance of SBKT. With appropriate doping, the multi-state polarization effect at A-site is enhanced; the ferroelectric instability at B-site is improved; and the ion and charge disorder effect based on the introduced multiple charged defects is enhanced. These factors result in the disruption of long-range orders, the reduction in ferroelectric microdomains, and the increase in smaller-sized polar structures, contributing to high $P_{\max}$ and low P_r . Benefiting from the high-valent substitution of Ta^{5+} in B-site, the high-entropy effect and the formation of $\text{Bi}_2\text{Ti}_2\text{O}_7$ -based insulating phase, oxygen vacancy dynamics transport is suppressed, and the electrical insulation improves. Meanwhile, the grain size decreases and the secondary phase remain at low level. These factors contribute to high BDS. Ultimately, the $x = 0.1$ sample exhibits high energy storage density of 5.68 J/cm^3 with high efficiency of 88.1% at moderate operating electric fields 490 kV/cm, and excellent pulsed charging-discharging performance. The energy storage performance possesses excellent stability of temperature ($-50\sim 150^\circ\text{C}$), frequency (10 Hz $\sim$ 500 Hz) and fatigue resistance. The pulsed charging-discharging performance possesses excellent thermal stability and long cycle life (10^5 cycles at 25°C and 150°C). The synergistic regulation mechanism is investigated in depth through first-principles calculations, numerical simulation, fine microstructural characterization, first-order reversal curves (FORC) and so on.

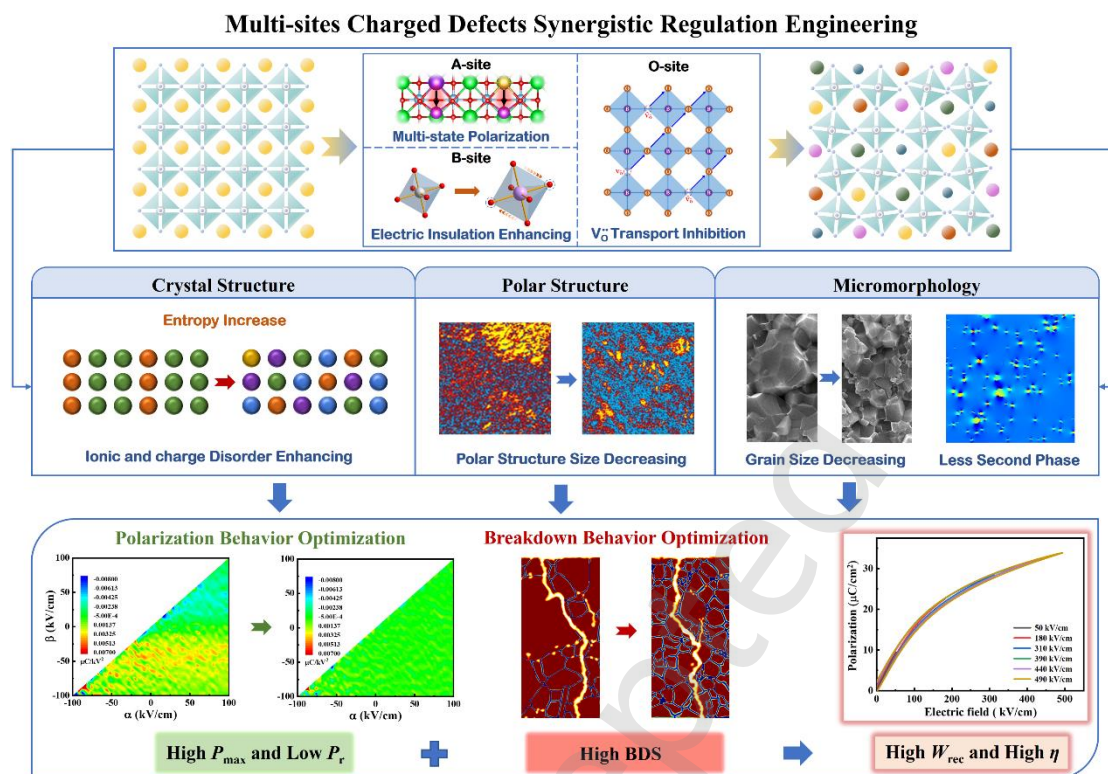


Fig. 1 Schematic diagram of the strategy to improve the energy storage properties in this work.

2 Experimental

SBKT-100xNT ($x = 0, 0.05, 0.1, 0.15, 0.2$) ceramics were fabricated by the solid-state reaction method. The raw powders are SrCO_3 (Chengdu Kelong Chemical Co., Ltd., Chengdu, China), Bi_2O_3 (Chengdu Shudu Nanomaterials Technology Development Co., Ltd., Chengdu, China), K_2CO_3 (Chengdu Kelong Chemical Co., Ltd., Chengdu, China), TiO_2 (Xiantao Zhongxing Electronic Materials Co., Ltd., Xiantao, China), Na_2CO_3 (Chengdu Kelong Chemical Co., Ltd., Chengdu, China) and Ta_2O_5 (Chengdu Kelong Chemical Co., Ltd., Chengdu, China). The purity of all raw powders is above 99%. SrCO_3 , Bi_2O_3 , and TiO_2 are weighted according to the related stoichiometric ratios (Sr excess 3% to obtain pure SBT) to fabricate SBT. Then, these powders are ball milled for 8 h in ethyl alcohol and zirconia balls. After that, the ceramic slurry was dried and pre-sintered at 950 °C for 3 h in air atmosphere to synthesize SBT. In a similar way, Bi_2O_3 , K_2CO_3 and TiO_2 powders were used to fabricate KBT, and Na_2CO_3 and Ta_2O_5 powders were used to fabricate NT. The pre-sintering temperatures of KBT and

NT are 800 °C and 950 °C, respectively. For the fabrication of SBKT-NT, the SBT, KBT and NT powders which have been pre-sintered were weighted according to the related stoichiometric ratios and ball milled 6 h in ethyl alcohol and zirconia balls. The mixture was dried and mixed with 10 wt.% solution of PVA (polyvinyl alcohol), and the solvent used in the 10% PVA binder solution is deionized water. After that, the powder was pressed into disks under 10 MPa. The size of green bodies is about 10 mm of diameter and about 1 mm of thickness. Finally, the disks buried with the stabilized ZrO₂ powders were sintered at 600 °C for 2 h to remove PVA, and then sintered at 1140 ~ 1175 °C for 3 h in air atmosphere.

3 Results and discussion

3.1 Crystal structure and micro-morphology analyses of SBKT-NT

All samples exhibited a perovskite main phase structure that could be indexed as SrTiO₃ (PDF#98-005-6092) (Fig. 2(a)). With the increasing x , the diffraction peaks shift to lower angles, indicating that the lattice constant and cell volume are gradually increasing. This is due to the replacement of Ti⁴⁺ (0.605 Å, 6 C.N.) with smaller equivalent ionic radius by larger Ta⁵⁺ (0.64 Å, 6 C.N.) [17]. When $x > 0$, the second phase of Bi₂Ti₂O₇ appears, and the content of the second phase gradually increases with the increase of doping content. This can be attributed to the introduction of NT and elements volatilization, and the formation mechanism is related to the interaction between SrBi₄Ti₄O₁₅ and the intermediate phase formed by doping elements during ceramic sintering [6]. All samples show broadened and diffused Raman peaks (Fig.2(b)), which is ascribed to the high ionic disorder induced by NT doping and the overlap of adjacent Raman vibrational modes [18]. The modes around 118 cm⁻¹ and 146 cm⁻¹ represent the vibrations of K-O/Na-O bonds. When $x \geq 0.05$, the 118 cm⁻¹ Raman mode appears and the 146 cm⁻¹ Raman mode with a gradually decreasing FWHM trend becomes more obvious (Fig. S1(a)), which is mainly due to the introduction of Na⁺. As x increases, the Raman peak around 146 cm⁻¹ shows a redshift trend (Fig. 2(c)), which is related to the weakening of A-O bonds caused by the increase in the lattice constant and the off-center displacement of the A-site cations along

the crystallographic axis [19, 20]. As x increases, the Raman peaks at around 228 cm^{-1} , 243 cm^{-1} and 276 cm^{-1} become more obvious, which is attributed to the formation and increase of Ta-O bonds after doping. In addition, the Raman mode at around 322 cm^{-1} shows a gradually increasing FWHM trend, indicating a gradual broadening (Fig. S1(b)). Meanwhile, the Raman modes near $200\text{-}400\text{ cm}^{-1}$ show a gradual redshift trend (Fig. 2(c)). These mean the formation of a weakly polar pseudo-cubic relaxation structure [21, 22]. This phenomenon can be attributed to the increase in the degree of structural disorder that accompanies increasing x , which elevates the configurational entropy. The mode at around 506 cm^{-1} becomes obvious. The mode at around 609 cm^{-1} shows a gradually increasing FWHM trend with the increasing x , indicating a gradual broadening (Fig. S1(c)). Meanwhile, the modes in the range of $400\text{-}700\text{ cm}^{-1}$ exhibit a trend of blueshift (Fig.2(d)). This could be explained by the increased structural disorder and oxygen octahedral distortion caused by ionic doping and introduction of charge defects, which means a reduction in the size of PNRs and an enhancement in relaxor properties [23-25].

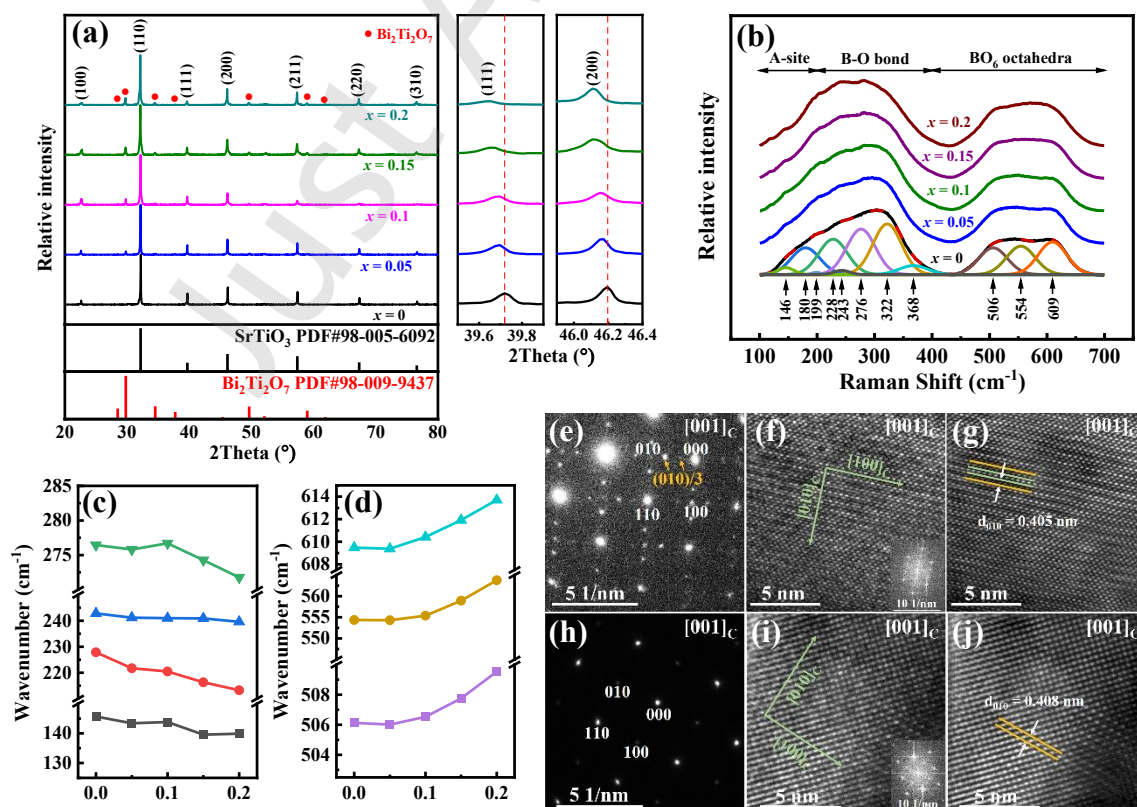


Fig. 2 (a) XRD patterns of SBKT-100xNT and the magnified (111) and (200) diffraction peaks; (b-d) Raman spectra of SBKT-100xNT and the variation of wavenumbers for some related Raman modes. SAED patterns (e), HR-TEM images and the corresponding FFT patterns (inset) (f), and inverse FFT (g) after applying filter of SBKT along $[001]_c$ directions. SAED patterns (h), HR-TEM images and the corresponding FFT patterns (inset) (i), and inverse FFT (j) after applying filter of SBKT-10NT along $[001]_c$ directions.

In high-resolution TEM (HR-TEM), (011)/3, (010)/3 and (101)/3 superlattice structure appears in some local regions of SBKT (Figs. 2(e-g) and Figs. S1(d-e)). The corresponding diffraction patterns were detected in selected area electron diffraction (SAED) and FFT, and a three-fold modulation superlattice for the basic cell superlattice was observed along every direction. This indicates the presence of short-range ordered structures in the SBKT, which is related to the introduction of numerous polar structures. According to the previous work, Bi^{3+} and K^+ tend to occupy adjacent sites based on Pauling's rule of electroneutrality, and the ion off-centered displacement caused by coulomb gravitation affects adjacent lattices, increasing the degree of ionic order [3, 4]. However, no periodic modulation structures were found in SBKT-10NT sample (Figs. 2(h-j) and Figs. S1(f-g)). This means that with the introduction of NT and the formation of various charge defects, the ordered structure is further broken, leading to the enhanced ionic and charge disorder, serious lattice distortion and increased entropy [13]. This makes the ordered structure of SBKT-10NT smaller in scale and harder to observe in TEM. The XPS spectra figures of the Bi 4f, K 2p, Na 1s, Ta 4f and Bi 5d for the sample with $x = 0.1$ are shown in the Figs. 3(a-d). The Bi $4f_{7/2}$ and Bi $4f_{5/2}$ peaks of SBKT-10NT are located at 158.79 eV and 164.09 eV (Fig. 3(a)), indicating that Bi exists as Bi^{3+} in this composition [26]. The XPS spectrum of K 2p exhibits spin-orbit splitting doublets (K $2p_{3/2}$ and K $2p_{1/2}$) [27]. In addition, a set of weak secondary doublets, denoted as K $2p_{3/2}'$ and K $2p_{1/2}'$, appears at higher binding-energy positions (Fig. 3(b)). This indicates that two types of K^+ ions with different coordination environments are detected in the XPS spectra. For SBKT-10NT, K $2p_{3/2}$ and K $2p_{1/2}$ are centered at 291.15 eV and 293.95 eV, indicating that K mainly exists as K^+ within the perovskite lattice; the higher binding energy

K 2p_{3/2}' and K 2p_{1/2}' peaks are situated at 292.64 eV and 295.44 eV, which are primarily associated with low-coordination K⁺ in the second phase [28]. The Na 1s XPS spectrum presents a symmetric single peak at 1071 eV, confirming that Na exists as Na⁺ in the ceramic lattice (Fig. 3(c)) [29]. Within the binding energy range of 24-30 eV, the XPS signals of Bi 5d and Ta 4f overlap with each other (Fig. 3(d)) [30]. In the Ta 4f spectrum, Ta 4f_{7/2} and Ta 4f_{5/2} are located at 25.36 eV and 27.26 eV, giving a spin-orbit splitting separation of 1.9 eV. This confirms that Ta mainly exists as Ta⁵⁺ in the SBKT lattice [31]. Based on the identification of the ionic valence state and ionic radius of these ions, the formation of the charged defects K_{Sr}['], Bi_{Sr}[•], Na_{Sr}['] and Ta_{Ti}[•] can be determined. Meanwhile, semi-quantitative elemental analysis using XPS on SBKT-NT ceramics was performed. No significant Na and Ta elements were detected in the SBKT sample. As x increased from 0.1 to 0.2, the atomic percentage of Na increased from 2.34% to 4.35%, and the atomic percentage of Ta increased from 2.83% to 5.29%. This indicates that Na_{Sr}['] and Ta_{Ti}[•] charged defects increase with increasing doping content.

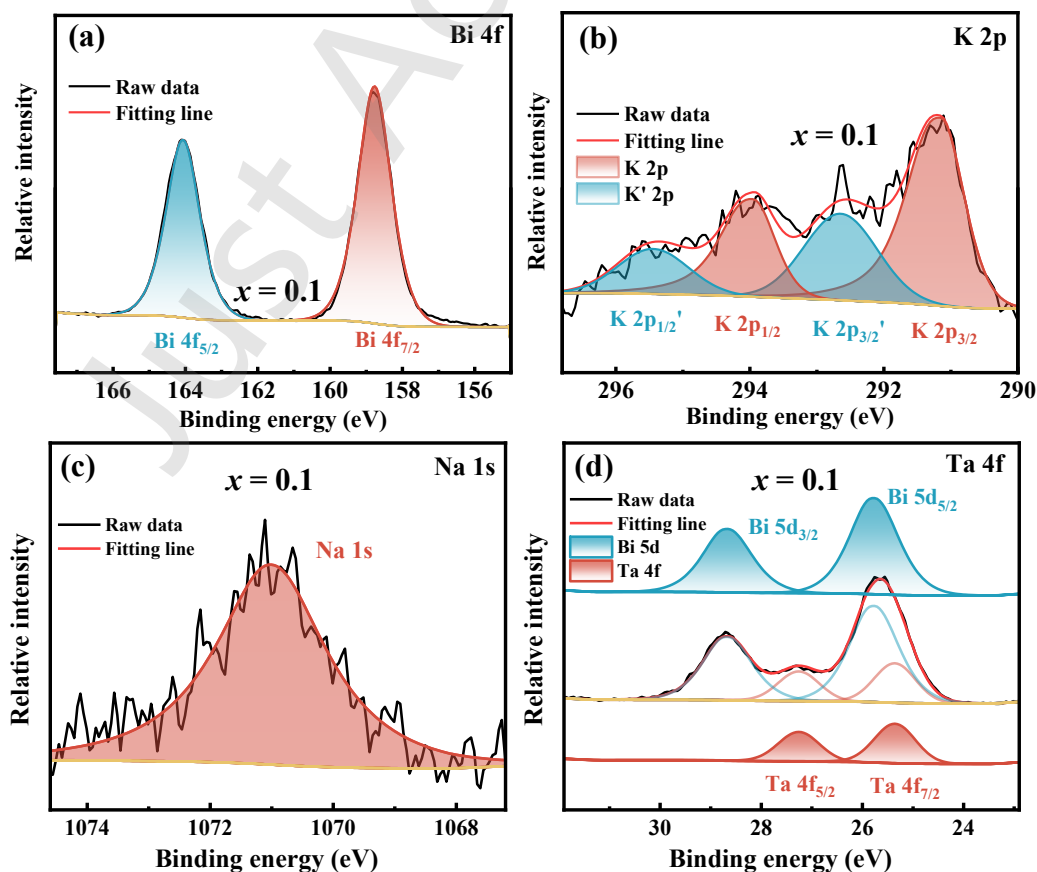


Fig. 3 (a) XPS spectra of the Bi 4f for SBKT-10NT; (b) K 2p peak profile for SBKT-10NT; (c) Na 1s peak profile for SBKT-10NT; (d) Ta 4f and Bi 5d peak profile for SBKT-10NT.

As x increases, the average grain size of the sample first decreases from 1.02 μm ($x = 0$) to 0.56 μm ($x = 0.1$), and then increases to 0.76 μm ($x = 0.2$) (Figs. S2(a-e)). The decrease in average grain size can be explained from the following four aspects: (1) the comparatively lower ion mobility of Ta^{5+} , which possess greater atomic mass and larger ionic radii than Ti^{4+} , contributes to inhibit the growth of crystalline grains; (2) ion doping induces cation deficiencies, which enhance the grain boundary pinning effect and inhibit the migration of grain boundaries; (3) local donor doping of Ta^{5+} can hinder oxygen vacancies formation, thereby hindering mass transfer during sintering; (4) according to the sluggish diffusion effect caused by entropy increase, increased lattice distortion acts as a barrier to atomic mobility and concurrently elevates the energy required for crystallization [8, 13]. When $x \geq 0.15$, the increased content of the second phase due to excessive doping causes some grains to grow abnormally or excessively, resulting in an increase in the average grain size. Energy dispersive spectroscopy (EDS) tests were performed on both the dark and light phase in scanning electron microscopy (SEM) images based on backscattered electron mode of SBKT-10NT (Figs. S2(f-g)). Based on the atomic ratio calculated from the EDS test results, the dark phase is the main phase SBKT-10NT with a high-entropy components ($\Delta S_{\text{config}} \approx 1.72 \text{ R}$) (Fig. S3(a)), and the light phase with larger grains is the secondary phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ -based materials (Fig. S3(b)). Meanwhile, the entropy value of the ceramic component when $x \geq 0.05$ exceeds 1.5R, belonging to the high-entropy component (Fig. S3(c)). SBKT-20NT ceramics showed a more abundant and aggregated second-phase distribution than SBKT-10NT, which is consistent with the XRD analysis results.

3.2 Dielectric properties analyses of SBKT-NT

The temperature dependence of dielectric properties for all samples exhibited a clear diffuse phase transition and frequency dispersion, which are typical characteristics of relaxor ferroelectrics (Fig. S4).

As x increases, the samples show a trend of gradually decreasing maximum ϵ_r (ϵ_m) and the temperature of ϵ_m (T_m), and the dielectric peak gradually broadens (Fig. 4(a)). After doping, the increase in cell volume makes the B-O bond longer, which weakens the coupling effect and stability of the oxygen octahedron and enhances the relaxation state, resulting in a decrease in T_m [3]. Importantly, the various charge defects and polar units induced by NT doping results in high ionic and charge disorder, and the enhanced lattice distortion increase the inhomogeneity of local composition and structure, which is conducive to breaking the long-range ferroelectric domain structure, forming nanodomains or PNRs and enhancing relaxor ferroelectricity [13]. This leads to a decrease in the ϵ_r and a broadening of the dielectric peak. In addition, the gradual increase in the content of the second phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ with low ϵ_r (50-360 at 100 Hz), is also the reason why ϵ_r decreases with the increasing doping amount [3]. The degree of relaxation (γ) of all samples is fitted using modified Curie-Weiss law as follow, and the results are shown in Fig. S5 and Fig. 4(b).

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

where C is the Curie-Weiss constant. As x increases, the γ value of the sample gradually increases from 1.42 at $x = 0$ to 1.85 at $x = 0.15$, and remains above 1.8 as x continues to increase. The improvement in relaxation is closely related to the enhanced ionic and structural disorder after doping [32]. As γ gradually increases and the dielectric peak broadens, the temperature stability of ϵ_r gradually improves. When $x = 0.2$, the sample exhibits a small rate of change in ϵ_r , meeting the X7R specification (Fig. 4(c)). As x increases, T_m , which is located near room temperature, gradually decreases (Fig. 4(a)), indicating the decreased size of polar structure [33, 34]. After NT doping, the polar structure size is significantly reduced compared to SBKT, and the sample exhibits a morphology and distribution in which large and small-sized PNRs coexist (Figs. 4(d-g)). The evolution of the polar structures verifies the analysis of dielectric property change, and provides a structural basis for subsequent optimization of polarization behavior based on the multi-state polarization effect.

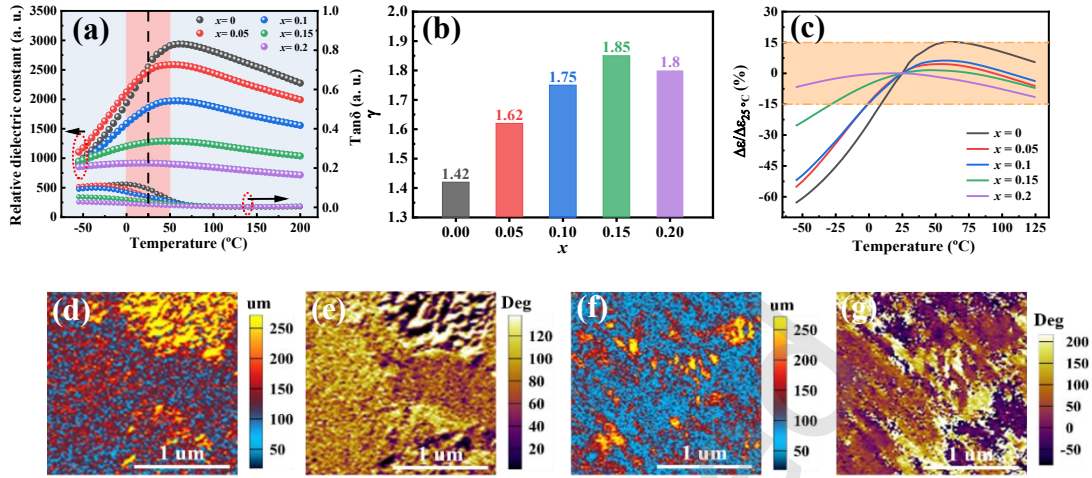


Fig. 4 (a) Temperature dependence of ϵ_r and loss for SBKT-100xNT in the temperature range of $-55^\circ\text{C} \sim 200^\circ\text{C}$ at 1 kHz; (b) γ of SBKT-100xNT recorded at 1 kHz; (c) The variation of ϵ_r deviation $\Delta\epsilon/\Delta\epsilon_{25^\circ\text{C}}$ under different temperatures of SBKT-100xNT; (d-e) In-plane PFM amplitude and phase images of SBKT; (f-g) In-plane PFM amplitude and phase images of SBKT-10NT.

3.3 Breakdown strength analysis of SBKT-NT

The BDS of SBKT-100xNT ceramics is fitted based on the Weibull distribution functions:

$$X_i = \ln(E_i) \quad (2)$$

$$Y_i = \ln\left(-\ln\left(1 - \frac{i}{n+1}\right)\right) \quad (3)$$

where i denotes the number of a specific sample, while E_i represents the corresponding BDS value for that sample, and n is the total count of samples in the test. As shown in Fig. S6, the shape parameters (β) of the fitting results for all samples are higher than 9, indicating that the results have excellent reliability. As x increases, the BDS value initially rises and reaches the highest value at $x = 0.1$ (Fig. 5(a)). When $x > 0.1$, the BDS gradually decreases with increasing x . A variety of factors affect BDS, including micromorphological characteristics, electrical properties, and heat-conducting performance.

For micromorphology, grain boundary resistance is usually greater than grain resistance, and grain boundaries can form Schottky barriers, hindering the transport of charge carriers [35]. Grain size (G) and BDS are inversely proportional: $BDS \propto G^{-1/2}$ [36]. The average grain size of SBKT-100 x NT ceramics gradually decreases with the increasing x from 0 to 0.1. This causes BDS to gradually strengthen [37]. The numerical simulation of breakdown paths for the sample with $x = 0$ and 0.1 was used to investigate the mechanism of BDS improvement due to grain size reduction. Simulation results show that the breakdown channels preferentially grow in large grain regions and low grain boundary density interfaces (Figs. 5(b-c)). This is because the breakdown critical energy of the grain boundary region is significantly higher than that of the grain region, making the grain boundary network a dielectric breakdown barrier and inhibiting the breakdown path growth along the grain boundary [38]. When $x = 0.1$, the average grain size of the prepared sample is significantly reduced, the grain boundary density is significantly increased, and the nominal breakdown electric field strength is higher than that of the sample with $x = 0$. This simulation conclusion is consistent with the experimental observation results.

For electrical insulation properties, the conductive properties of SBKT-100 x NT can be holistically assessed by three distinct excitation mechanisms: electrical, optical, and thermal. Under the same electric field, the leakage current density of the sample gradually decreases as x increases to 0.1 (Fig. 5(d)). For optical band gap (E_g), as x increases from 0 to 0.1, the E_g of SBKT-100 x NT ceramics increases significantly (Fig. 5(e) and Figs. S7(a-e)), indicating that it becomes more difficult for electrons to transition from the valence band to the conduction band. This is related to the reduction in the number of charge carriers and the suppression of charge transport processes. Under the same temperature, the direct current (DC) conductivity (σ_{DC}) and the frequency of Z''/Z''_{max} peak value (f_{max}) decreases as x increases to 0.1, and the semicircle of the complex impedance diagram increases (Figs. 5(f-g) and Fig. S7(f)). Meanwhile, when x increases to 0.1, the difference of frequency ($f_{M''_{max}} - f_{Z''_{max}}$) gradually decreases (Figs. 5(h-i) and Figs. S8(a-d)), indicating a reduction in charge transport

patterns and an improvement in electrical homogeneity. The observed variations in conductive behavior under the applied multiphysics conditions reveal that optimal doping ($x = 0.1$) markedly enhances electrical insulation properties, resulting in an increase in BDS. This can be attributed to NT doping, entropy increase and the increase in the $\text{Bi}_2\text{Ti}_2\text{O}_7$ -based high-resistivity second phase, which causes suppression of carrier transport kinetics.

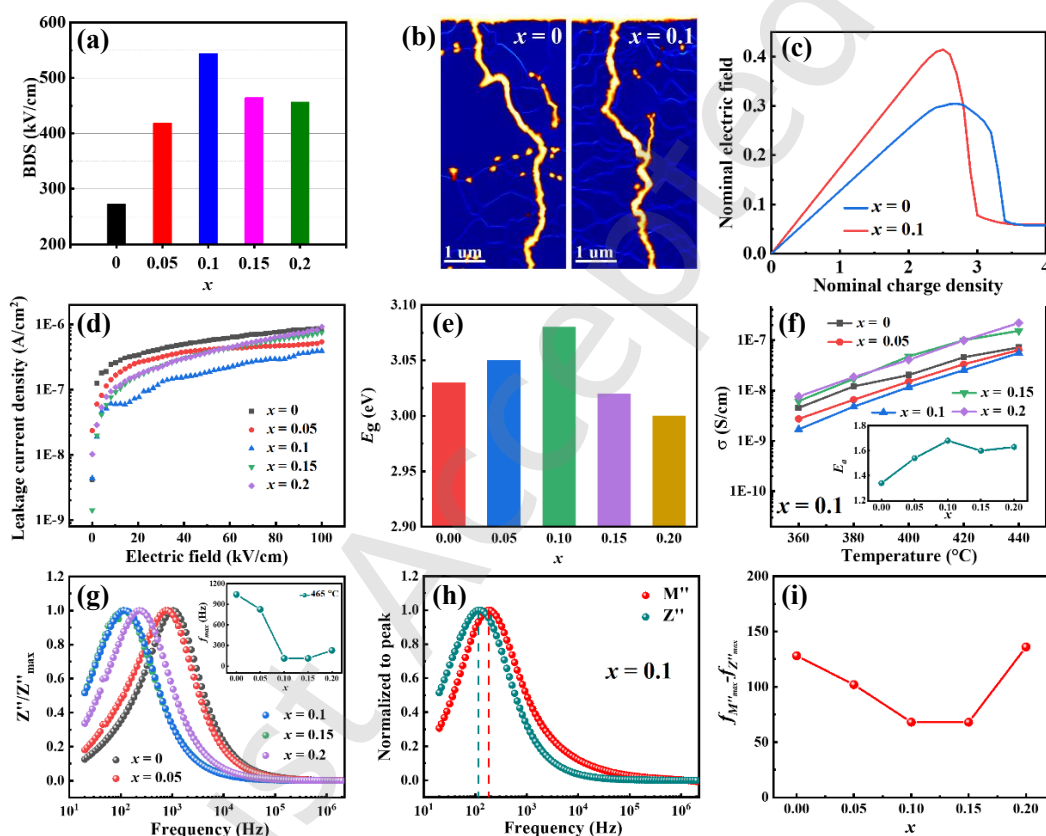


Fig. 5 (a) The BDS values of SBKT-100xNT ceramics. (b) The electric field distribution as well as the growth of breakdown paths for SBKT-100xNT with $x = 0$ and $x = 0.1$. (c) Nominal electric field of $x = 0$ and $x = 0.1$ sample. (d) Leakage current density of SBKT-100xNT under different electric fields. (e) E_g values of SBKT-100xNT. (f) Temperature dependence of σ_{DC} and conductance activation energy (E_a) values for SBKT-100xNT. (g) Frequency-dependent Z''/Z''_{max} of SBKT-100xNT at 465 °C, and the change of f_{max} corresponding to the Z''/Z''_{max} peak (inset). (h-i) Frequency dependence of normalized peaks of Z''/Z''_{max} and M''/M''_{max} for SBKT-100xNT.

To investigate the dominant mechanism of conductive behavior in depth, the E_a is calculated by Arrhenius equation based on σ_{DC} under different temperatures:

$$\sigma_{DC} = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad (4)$$

where σ_0 is pre-exponential factor, k_B is Boltzman constant. The detailed fitting method is shown in Figs. S8(e-i). Based on the E_a in the range of 0.5 eV to 2 eV, the conductivity mechanism of SBKT-100xNT is mainly oxygen vacancy transport (inset of Fig. 5(c)) [39]. E_a gradually increases as x increases from 0 to 0.1, indicating that the behavior of oxygen vacancy transport participating in conductivity becomes more difficult, which is related to the change of oxygen vacancy concentration and migration after doping. The oxygen vacancy formation energies (E_{fv}) before and after doping were calculated using first-principles calculations (Fig. 6(a)). After NT doping, E_{fv} increased significantly, indicating that oxygen vacancy formation became more difficult. The electron paramagnetic resonance (EPR) spectrum of SBKT-100xNT is shown in Fig. 6(b). For all samples shows the strong EPR peaks at the g value of ~ 2.003 , these peaks represent the paramagnetic centers caused by oxygen vacancies [40]. The EPR peak intensity gradually decreases with increasing x , indicating that the oxygen vacancy concentration gradually decreases with increasing doping concentration [40]. This is due to Ta^{5+} doping inhibiting the formation of oxygen vacancies and the reduction of structural vacancies. Ta^{5+} substitution for Ti^{4+} creates A-site cation vacancies in the local structure, which can capture oxygen vacancies [8]. Meanwhile, the substitution of Ti^{4+} by the donor Nb^{5+} provides excess electrons, contributing to the suppression of oxygen vacancy formation [41]. Furthermore, the oxygen vacancy migration energy barrier calculated by first-principles significantly increases after NT doping, indicating a more difficult oxygen vacancy migration process in SBKT-NT (Fig. S9(a)). The increase in entropy after NT doping results in greater lattice distortion, increased structural and ionic disorder, and more grain boundaries forming, combined with the increased $Bi_2Ti_2O_7$ -based high-resistivity second phase, which inhibits oxygen vacancy migration and enhances electron collisions [13].

Therefore, for the reasons mentioned above, E_a and electrical insulation are enhanced, resulting in an increase in BDS. However, when x exceeds 0.1, the abnormal grain growth and element volatilization caused by the increase in the content of the second phase lead to an increase in charge defects, resulting in a decrease in electrical insulation performance. This includes an increase in leakage current density, σ_{DC} , f_{max} and $f_{M''max}$ - $f_{Z''max}$, and a decrease in complex impedance plot semicircle, E_g and E_a .

The thermal conductivity gradually increases as x increases and reaches maximum at $x = 0.1$. This is because the concentration of oxygen vacancies which are effective phonon scattering centers gradually decreases, resulting in rapid heat release and high BDS of $x = 0.1$ sample (Fig. 6(e)) [42]. With an increase in x beyond 0.1, the thermal conductivity is observed to decline. This reduction can be attributed to the rise in average atomic mass and ionic radius resulting from excessive NT doping [42, 43].

For the decay of BDS after x is greater than 0.1, one of the main reasons is the increase and aggregation of the second phase with low ϵ_r . To investigate the mechanism by which phase distribution affects BDS, phase-field simulations were conducted for the samples with $x = 0.1$ and 0.2. The simulation model is based on backscattered SEM images, and the methods for confirming the ϵ_r of each phase are listed in and under Table S1. The second phase possesses a much lower ϵ_r than the main phase, and the second phase in $x = 0.2$ sample is more abundant and aggregated than that in $x = 0.1$ sample (Figs. S10(a) and S10(c)). This results in the $x = 0.2$ sample exhibiting severely disordered equipotential lines (Figs. S10(b) and S10(d)) and numerous regions of high LEF (Figs. 6(f) and 6(g)). Compared to the $x = 0.1$ sample, the $x = 0.2$ sample exhibited a higher content of the second phase. This increased second phase content resulted in a wider distribution and localized aggregation of the second phase within the sample. On one hand, because the ϵ_r of the second phase is much lower than that of the main phase, a sudden change in the ϵ_r occurs at the interface between the two phases. This significantly amplifies the electric field on the side with the lower ϵ_r , causing the second phase to withstand more voltage fall [44, 45]. On the other hand, the aggregation of the second phase creates

more regions with small radii of curvature, sharp points, acute-angled geometric distributions, and fine gaps. This leads to dense charge accumulation in these localized areas, causing severe compression of the equipotential lines and inducing abrupt, nonlinear changes in the local potential gradient [44, 46]. Therefore, the overall equipotential lines disorder in the $x = 0.2$ sample is more severe than that in the $x = 0.1$ sample, and this phenomenon and mechanism are particularly evident in the marked region. These result in the $x = 0.2$ sample exhibiting a higher LEF. The maximum LEF of $x = 0.2$ sample is ~ 1088 kV/cm, which is higher than that of $x = 0.1$ sample (~ 774 kV/cm). Based on this, when $x > 0.1$, the increase in LEF, along with the decrease in electrical insulation performance and thermal conductivity, increases the possibility of breakdown, thereby deteriorating the BDS of the sample.

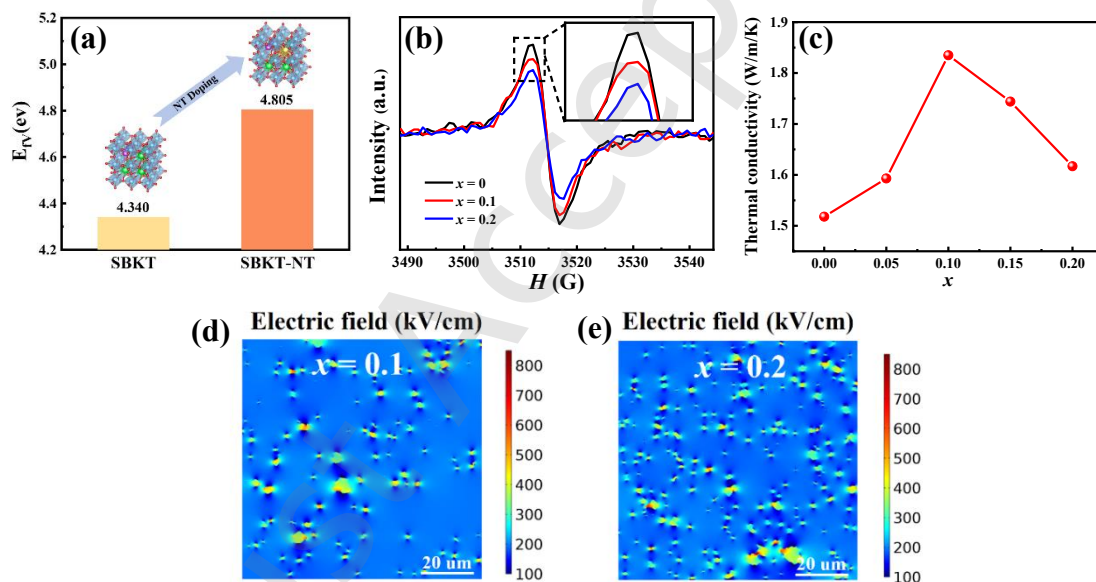


Fig. 6 (a) The oxygen vacancy formation energy before and after NT doping. (b) EPR spectra of $(1-x)$ SBKT-100xNT ceramics recorded at room temperature. (c) Thermal conductivity of SBKT-100xNT under room temperature. (d-e) The LEF of SBKT-100xNT with $x = 0.1$ and 0.2 .

3.4 Energy storage and pulsed charge-discharge performance of SBKT-NT

SBKT ceramics with large polar structures possess superior $P_{\max}$ and P_r , resulting in a broad P - E loops with large hysteresis and high current density peaks in the J - E curves (Fig. S10(e-g)). With the increasing x , a reduction in P_r is observed, resulting in gradual thinning of P - E loops. Meanwhile, the

current density peaks near zero electric field, which is caused by PNRs switching, gradually broaden and weaken. The FORC were used to observe the evolution of polarization characteristics (Fig. 7(a-f)). SBKT exhibits several non-uniform zones with high intensity clustering around the central area. This phenomenon is attributed to the high macroscopic polarization of the material, caused by domain wall movement and the reversal of large domains under a relatively weak electric field [47]. When the electric field increases, SBKT shows reduced FORC intensity because the domain switching reaches saturation, indicating obvious ferroelectric characteristics and significant nonlinearity in polarization response [47]. As x increases, the FORC intensity gradually decreases and becomes more uniformly distributed, indicating a weakening of the polarization nonlinearity characteristics.

The above observed phenomena collectively indicate an enhancement in the relaxor ferroelectric properties of the material as x increases. This behavior is primarily attributed to the lattice distortion and various charge defects introducing induced by the NT doping and the entropy increase. The large random field generated by the strong chemical disorder and multi-charge defects polar units forming disrupts the long-range ferroelectric ordered state, and promote the formation of multi-state polar structures with local polymorphic distortions [48]. This induces weaker coupled small sized PNRs and makes the polarization to reorientate with small stress and energy barrier [13]. Meanwhile, Ta^{5+} doping weakens the B-O bond, increasing ferroelectric instability and relaxor states. As a result of these factors, the sample with $x \geq 0.05$ shows nearly negligible P_r , linear-like P - E loops, gradually widening J - E current density peaks, and delayed polarization saturation under strong electric field. These characteristics contribute to high-efficiency energy storage. Furthermore, the A-sites occupied by Bi^{3+} form positive charge centers, and the A-sites occupied by Na^+ and K^+ form negative charge centers. The introduction of these negative and positive charge centers can cause the multi-state off-centered displacement based on Coulomb force and form electric dipole moments (D), which in turn contribute to the increase in polar states and the enhancement of polarization intensity (Figs. S10(h-i)). This effect induces multiple local polarization sites and enhances structural disorder, together with the increase in

polarization entropy and low polarization rearrangement stress, contributing to the improvement of polarization degree under electric field [48]. The local structural order, the internal atomic-scale polar orientations and their spatial distribution of the SBKT-10NT ceramics were further probed by processing the high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image along $[001]_c$ in order to observe the polar state. The quantitative c/a ratio of the sample is shown in Fig. S10(j). The c/a ratio mapping shows a nearly uniform value of around 1, indicating that the main phase is mainly a pseudo-cubic structure, which is consistent with the analysis results of XRD and TEM. Quantitative polar vector map was built based on the off-centering atomic displacements, which effectively reflects the local structural order and the types and distribution of polar states (Fig. 7(g)). The direction of the arrows indicates the direction of the polarization vectors, while their magnitudes correspond to the polarization intensity. The polarization vectors vary in magnitude within the range of 0-40 pm (Fig. 7(h)). The polar units with coexisting strong and weak polarization can be observed, and a high average polarization magnitude (~ 11.48 pm) is estimated (Fig. 7(i)). Meanwhile, the magnitude and distribution of the polarization angle exhibit multiple orientation states (Figs. 7(j-k)). This demonstrates that polarization states are diverse, proving the existence of polymorphic polarization [49]. Islands-like polar units with consistent orientation and sizes of 1-3 nm can be observed, which correspond to ultrafine PNRs with a high-density random distribution. These small sized and polymorphic PNRs exhibit prominent dynamic characteristics, which diminish the anisotropy of polarization directions and reduce the energy barriers associated with domain-wall motion, indicating a rapid and reversible reorientation process under external electric fields [50]. These nanodomains have strong polarization strength and weak interdomain interactions, and tend to revert spontaneously to their original states upon removal of the applied field [50]. Such intrinsic relaxor behavior gives rise to the reduced P_r , decreased hysteresis loss, while maintaining a large $P_{\max}$. These unique characteristics originate from the lattice fluctuations and structural disorder caused by the

[49].

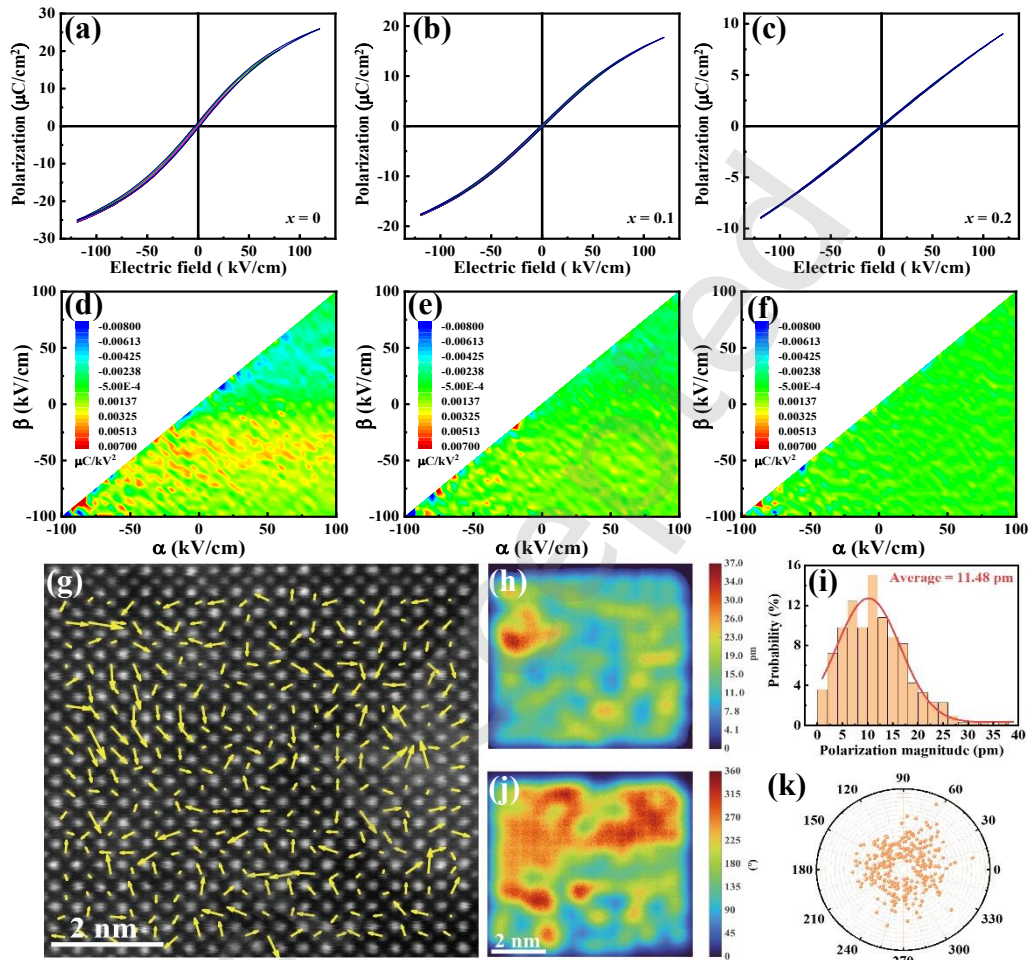


Fig. 7 (a-c) The FORC loops of SBKT-100xNT (only 6 out of the total 60 loops); (d-f) Evolution of the FORC distribution of SBKT-100xNT; (g) Quantitative polar vector map along [001]_c of SBKT-10NT; Corresponding polarity amplitude distribution chart (h) and statistical chart (i); Corresponding polarity angle distribution diagram (j) and statistical diagram (k).

Based on these, SBKT-10NT is considered the optimal sample due to its high $P_{\max}$, the highest BDS and low P_r , and has great potential to demonstrate excellent energy storage performance. The energy storage performance can be evaluated by the following equations:

$$W = \int_0^{P_{\max}} E dP \quad (5)$$

$$W_{\text{rec}} = \int_{P_r}^{P_{\max}} E dP \quad (6)$$

$$\eta = W_{\text{rec}} / W \times 100\% \quad (7)$$

where E is the applied electric field. The SBKT-10NT ceramics exhibit excellent energy storage performance with a high W of 5.68 J/cm³, W_{rec} of 5 J/cm³ and a high η of 88.1% under 490 kV/cm (Fig. 8(a-b) and Fig. S11(a)). Among many Bi- and Sr-based energy storage ceramics recently reported, the energy storage performance of SBKT-10NT is in the upper-middle range (Fig. 8(c) and Table S2). Although there is a certain gap between the absolute performance values and the reported highest boundary level, the prepared SBKT-10NT ceramic exhibits excellent comprehensive energy storage performance under the moderate electric field. This makes it a promising candidate for pulsed energy storage scenarios requiring moderate operating electric fields. The stability of energy storage performance in wide temperature and frequency, and the fatigue resistance performance of SBKT-10NT ceramic are shown in Fig. S11. The sample shows slim P - E loops under various conditions, meaning a stable relaxor ferroelectric properties. For temperature stability (Fig. S11(b-d)), the $P_{\max}$ and P_r slightly decreases with the increasing temperatures from -50 °C to 150 °C due to the increased dynamics, decreased size, and enhanced thermal fluctuations of PNRs. This causes a slight fluctuation of W_{rec} and an increase in η , but the W_{rec} and η still show small rate of change ($\Delta W_{\text{rec}} \approx 3.3\%$, $\Delta \eta \approx 7.2\%$). For frequency stability (Fig. S11(e-g)), the P_r slightly increases with the stable $P_{\max}$ as the increasing frequency from 10 Hz to 500 Hz due to the lag in polar structure switching. This causes a slight decrease of W_{rec} and η , but the W_{rec} and η still show small rate of change ($\Delta W_{\text{rec}} \approx 1.9\%$, $\Delta \eta \approx 3.5\%$). For fatigue resistance (Fig. S11(h-j)), the $P_{\max}$, P_r and energy storage performance exhibit excellent stability within 10⁵ cycles, and the W_{rec} and η still show small rate of change ($\Delta W_{\text{rec}} \approx 0.5\%$, $\Delta \eta \approx 0.3\%$). The excellent energy storage performance stability is attributed to the high relaxation characteristics and strong diffused phase transition process. Meanwhile, the polymorphic oxygen

octahedral tilt system induced by high entropy effect and charge defects introducing endows the sample with excellent temperature stability, and the rapid response with small stress under the electric field changing of weakly correlated PNRs endows the sample with excellent frequency stability and fatigue resistance [48].

Overdamped and underdamped charge-discharge tests were performed on the sample to evaluate the pulsed charging-discharging performance of SBKT-10NT. The electric field dependence of overdamped current-time curves is shown in Fig. S12(a). The discharge energy density (W_d) can be calculated by the following equation:

$$W_d = R \int i^2(t) dt / V \quad (8)$$

where V is the sample volume, and R is the load resistance (100 Ω). The time required to release 90% of W_d is $t_{0.9}$. The W_d -time curves and the change of W_d and $t_{0.9}$ under different electric field are shown in Fig. S12(b) and Fig. S12(c). The SBKT-10NT ceramics exhibits a high W_d of 1.61 J/cm³ with a short $t_{0.9}$ of 0.31 μ s at 220 kV/cm. Due to the increased viscous force clamping the domain walls and the discharged energy dissipation caused by the equivalent series resistance, W_d under the same electric field is usually less than W_{rec} [51, 52]. The electric field dependence of underdamped current-time curves of SBKT-10NT ceramics is shown in Fig. S12(d). The period time (T_p) can be calculated by the following equation:

$$T_p = 2\pi / \omega = 2\pi / \sqrt{\frac{1}{LC} - \left(\frac{R}{2L}\right)^2} \quad (9)$$

where C is capacitance, L is inductance, and R is resistance. L and R are constants in the same circuit, so T_p is only affected by C . Under various applied electric fields, T_p is approximately 0.36 μ s and remains stable (Fig. S12(e)), indicating a weak dielectric nonlinearity and low energy loss [53]. The discharge current density (C_D) and power density (P_D) can be evaluated by the following equations:

$$C_D = \frac{I_{\max}}{S} \quad (10)$$

$$P_D = \frac{EI_{\max}}{2S} \quad (11)$$

where $I_{\max}$, E and S represent the maximum discharge current, the applied electric field and the electrode area, respectively. The $I_{\max}$, C_D and P_D of SBKT-10NT ceramics are shown in Fig. S12(f). With the electric field increases, the $I_{\max}$, C_D and P_D gradually increase, and the sample exhibits high C_D of 366.3 A/cm² and P_D of 38.5 MW/cm³ at 210 kV/cm. This is superior to many recently reported Bi- and Sr-based energy storage ceramics (Fig. S12(g) and Table S3).

The temperature dependence of underdamped current-time curves, $I_{\max}$, C_D and P_D of SBKT-10NT ceramics are shown in Fig. 8(d). The underdamped charging and discharging behavior of the sample is similar at different temperatures. As the temperature increases, T_p at $\sim 0.37 \mu\text{s}$ shows a slight trend of first increasing and then decreasing (Fig. S13(a)). This phenomenon is related to the C -temperature characteristics, and the trend is consistent with the ε_r -temperature variation of the sample. As temperature increases, the size of PNRs decreases, causing $I_{\max}$, C_D and P_D to show an increasing trend, but the P_D still shows a small variation of $\sim 6\%$. The temperature dependence of overdamped current-time curves and W_d of SBKT-10NT ceramics are shown in Fig. 8(e). The overdamped charging and discharging behavior of the sample is similar at different temperatures, and the discharge current remains almost unchanged (Fig. S13(b)). Due to the reduction in the size of the PNRs, the polarization response speed increases, causing $t_{0.9}$ to gradually decrease with increasing temperature from 25 °C to 150 °C (Fig. S13(c)). The W_d shows a small variation of $\sim 5\%$. The fatigue resistance characteristics of pulse charge-discharge performance under different temperatures (25 °C and 150 °C) for SBKT-10NT ceramics are evaluated. The overdamped charging and discharging behavior of the sample is similar within 10^5 cycles under 25 °C and 150 °C (Fig. S13(d-e)), and both W_d show a small variation less than 2.7% with stable $t_{0.9}$ and discharge current (Fig. S13(f-i)). Furthermore, the underdamped current-time curves of SBKT-10NT ceramics before and after 10^5 cycles under 25 °C and 150 °C are shown in Fig. S13(j). The P_D shows a small variation of $\sim 3\%$ before and after 10^5 cycles under 25 °C and 150 °C (Fig. S13(k)). Therefore, due to the high relaxation and BDS caused by high-entropy effect and

charge defects regulation, SBKT-10NT ceramics exhibit good temperature stability and long cycle life, making it a promising candidate for pulse energy storage.

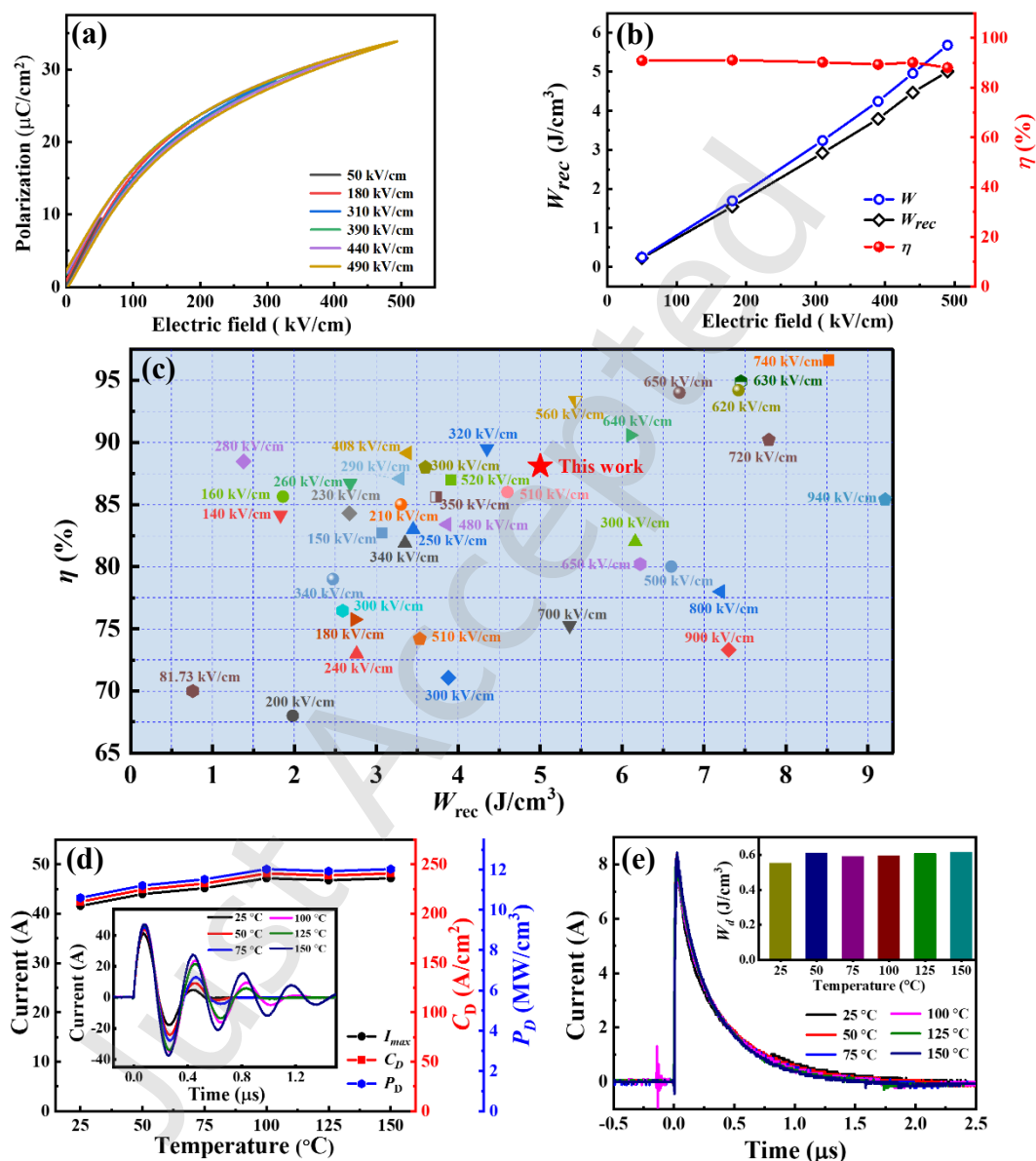


Fig. 8 (a) The P - E loops of SBKT-10NT at 10 Hz under different electric fields; (b) The energy storage properties of SBKT-10NT at 10 Hz under different electric fields; (c) Contrast of energy storage properties of various energy storage ceramics; (d) The change of I_{max} , C_D , P_D and underdamped current-time curves of SBKT-10NT as functions of temperatures at 100 kV/cm ; (e) The overdamped current-time curves and the change of W_d for SBKT-10NT at various temperatures at 100 kV/cm .

4 Conclusion

In summary, NT was introduced in the SBKT, and SBKT-100xNT ceramics was prepared. Based on the multi-sites charged defects synergistic regulation strategy, the microstructure was optimized in multi-dimensions, thereby achieving optimization of polarization behavior and breakdown behavior. The introduction of Na^+ at A-site contributes to the multi-state polarization effect; the introduction of Ta^{5+} at B-site enhances ferroelectric instability; and the introduction of multiple charged defect states increases ionic and charge disorder. Based on these, the long-range ordered structure is broken, small-sized polar structures increase, relaxor ferroelectricity is enhanced, and polarization saturation is weakened, allowing $P_{\max}$ to remain at a high level while P_r is reduced. Meanwhile, the substitution of Ta^{5+} at B-site with high valence and large radius, combined with the entropy increase effect and the high-resistivity second phase formation, enhances the electrical insulation, and the formation and transport of oxygen vacancies at O-site are suppressed, resulting in a significant improvement in BDS. As a result, SBKT-10NT ceramics exhibit low P_r , high BDS and $P_{\max}$, thereby demonstrating high energy storage density of 5.68 J/cm^3 with high efficiency of 88.1% at moderate operating electric fields 490 kV/cm . The performance synergic improvement mechanism was revealed by investigating the evolution of microstructure, breakdown and polarization behavior through fine structure observation, first-principles calculations, numerical simulation and electrical performance characterization. Furthermore, the energy storage performance shows small variations in wide temperature ($-50\sim 150^\circ\text{C}$), frequency ($10\sim 500 \text{ Hz}$) and cycle numbers (10^5). The sample also possesses good pulsed charging-discharging performance with thermal stability and a long cycle life (10^5 cycles at 25°C and 150°C). Therefore, SBKT-10NT ceramic is a promising candidate for advanced pulse energy storage capacitor. Our future optimization direction for SBKT-based systems will focus on further improving energy storage performance, such as fine defect modulation, process optimization, or composite structures.

Electronic Supplementary Material (ESM)

Electronic Supplementary Material: Supplementary material (add a brief description) is available in the online version of this article.

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Author contributions

Jun Yang: Participated in the planning of research, designed and carried out the research, analyzed the experimental data, and wrote a draft of the manuscript. Peng Zhao: Designed and carried out the research, participated in some experiments, analyzed the experimental data, wrote a draft of the manuscript, contributed to the article language and writing. Xiaofang Luo, Hairong Wang, Chunhua Liu and Yujun Yang: Designed and carried out the research, analyzed the experimental data, participated in some experiments, and took part in discussions. Shuo Zhou and Kui Chen: Carried out the research, participated in some experiments, analyzed the experimental data. Bin Tang: Supervised and directed the project, directed some experiments, participated in some data analysis, and contributed to the article language and writing.

Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

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