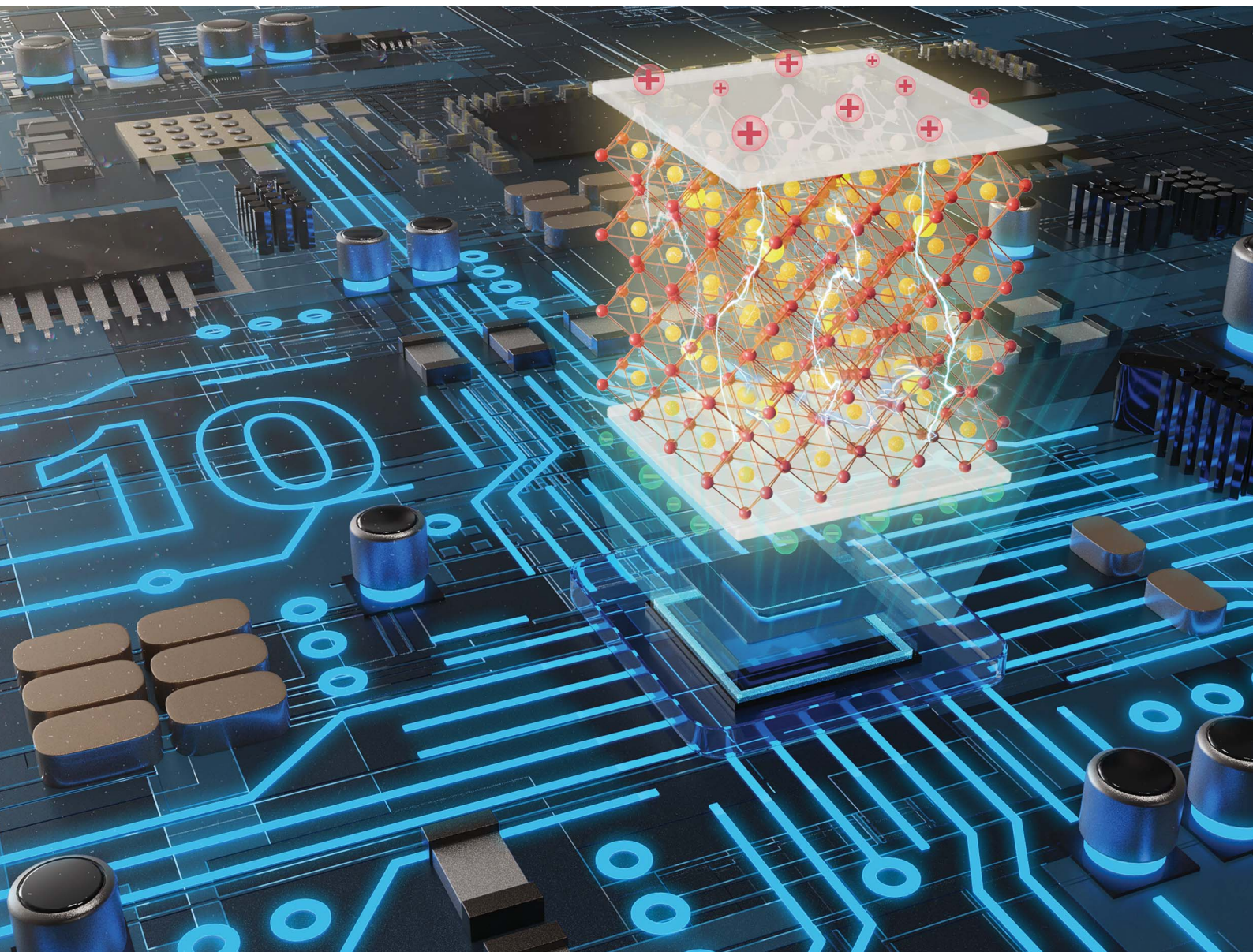


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**PAPER**

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# Enhancing energy storage performance in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -based lead-free relaxor ferroelectric ceramics along a stepwise optimization route†

Wen Wang,<sup>a</sup> Leiyang Zhang,<sup>a</sup> Yule Yang,<sup>a</sup> Wenjing Shi,<sup>a</sup> Yunyao Huang,<sup>a</sup> D. O. Alikin,<sup>b</sup> V. Ya. Shur,<sup>b</sup> Zhihao Lou,<sup>c</sup> Amei Zhang,<sup>d</sup> Xiaoyong Wei,<sup>a</sup> Dong Wang,<sup>e</sup> Feng Gao,<sup>b</sup> Hongliang Du<sup>\*c,d</sup> and Li Jin<sup>†a</sup>

Despite the fact that relaxor ferroelectrics (RFEs) have been extensively researched because of their various advantages, there are still barriers to simultaneously increasing their energy storage density ( $W_{\text{rec}}$ ) and efficiency ( $\eta$ ). By substituting  $\text{Bi}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$  (BMS) and optimizing the formation process, this study follows a stepwise optimization route to achieve comprehensive exceptional energy storage performance (ESP) in  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - $\text{Sr}_{0.85}\text{Bi}_{0.1}\text{TiO}_3$  (NBT-SBT)-based ceramics. On the premise of constructing a  $\text{Sr}^{2+}$ - $\text{Sr}^{2+}$  ion pair at the A-site to ensure a large polarization, the introduction of  $\text{Mg}^{2+}$  and  $\text{Sn}^{4+}$  ions at the B-site further induces a local disordered field and promotes polar nanoregions. Following that, the viscous polymer process (VPP) used to synthesize NBT-SBT-BMS ceramics can thin the thickness, reduce defects, and boost compactness, hence improving the polarization difference ( $\Delta P$ ) and breakdown strength ( $E_b$ ). Using the stepwise optimization route, we were able to attain a high  $\Delta P$  of  $64.6 \mu\text{C cm}^{-2}$  and an  $E_b$  of  $440 \text{ kV cm}^{-1}$  in  $0.92(0.65\text{NBT}-0.35\text{SBT})-0.08\text{BMS-VPP}$  ceramics. More crucially, an ultrahigh  $W_{\text{rec}}$  of  $7.5 \text{ J cm}^{-3}$  and a high  $\eta$  of 85% are simultaneously achieved, together with excellent temperature adaptability between 20 and 120 °C. Our superb ESP exceeds the majority of previously reported NBT-based ceramics, confirming the applicability of this stepwise optimization route to other similar high-performance dielectric ceramic designs.

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## 1. Introduction

Ceramic dielectric capacitors are capably competitive in electronic systems because of their high-power density, strong voltage resistance, and prominent reliability.<sup>1–3</sup> Their poor energy storage density, however, remains an impediment to meeting the demands for advanced electronic system integration and downsizing.<sup>4,5</sup> To compensate for this shortcoming, reduce energy loss, and adapt to diverse temperature

conditions, ceramic capacitors with high energy storage density ( $W_{\text{rec}}$ ), energy efficiency ( $\eta$ ), and great thermal adaptation are required.<sup>1</sup> The desirable  $W_{\text{rec}}$  and  $\eta$  are theoretically fulfilled by high breakdown strength ( $E_b$ ) and large polarization difference ( $\Delta P$ ) between maximum polarization ( $P_m$ ) and residual polarization ( $P_r$ ), based on polarization against electric field ( $P$ - $E$ ) hysteresis loops of ceramics.<sup>6</sup> In this regard, relaxor ferroelectrics (RFEs) have a high  $\Delta P$  value and a moderate  $E_b$ , giving them advantages and superiorities over ferroelectrics (FEs), antiferroelectrics (AFE), and linear dielectrics (LDs), all of which have advantages and disadvantages in energy storage applications.<sup>3</sup>

Perovskite ( $\text{Na}_{0.5}\text{Bi}_{0.5}$ ) $\text{TiO}_3$  (NBT)-based RFE ceramics have been extensively studied in the past decade.<sup>4,5,7–15</sup> Because the valence electron configuration of  $\text{Bi}^{3+}$  ( $6s^2 6p^0$ ) is comparable to that of  $\text{Pb}^{2+}$  and orbital hybridization between Bi 6p and O 2p normally generates a higher  $P_m$ , prototypical NBT has a high  $P_m$  greater than  $40 \mu\text{C cm}^{-2}$ .<sup>1</sup> Nonetheless, its high  $P_r$  ( $38 \mu\text{C cm}^{-2}$ ) and relative square  $P$ - $E$  loop are detrimental to  $W_{\text{rec}}$  improvement. Based on this, one of the effective modification strategies for improving the energy storage performance (ESP) of NBT-based ceramics is chemical modification by substituting ( $\text{Sr}_{0.85}\text{Bi}_{0.1}$ ) $\text{TiO}_3$  (SBT) into NBT.<sup>7,16</sup> The total strength of the electrostatic bond of all adjacent cations to an anion is equal to

<sup>a</sup>Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, School of Electronic Science and Engineering, Xi'an Jiaotong University, Xi'an, 710049, China. E-mail: ljin@mail.xjtu.edu.cn

<sup>b</sup>School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, 620000, Russia

<sup>c</sup>State Key Laboratory of Solidification Processing, MIIT Key Laboratory of Radiation Detection Materials and Devices, USI Institute of Intelligence Materials and Structure, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China. E-mail: gaofeng@nwpu.edu.cn

<sup>d</sup>Multifunctional Electronic Ceramics Laboratory, College of Engineering, Xi'an International University, Xi'an 710077, China. E-mail: duhongliang@126.com

<sup>e</sup>Frontier Institute of Science and Technology and State Key Laboratory for Mechanical Behaviour of Materials, Xi'an Jiaotong University, Xi'an 710049, China

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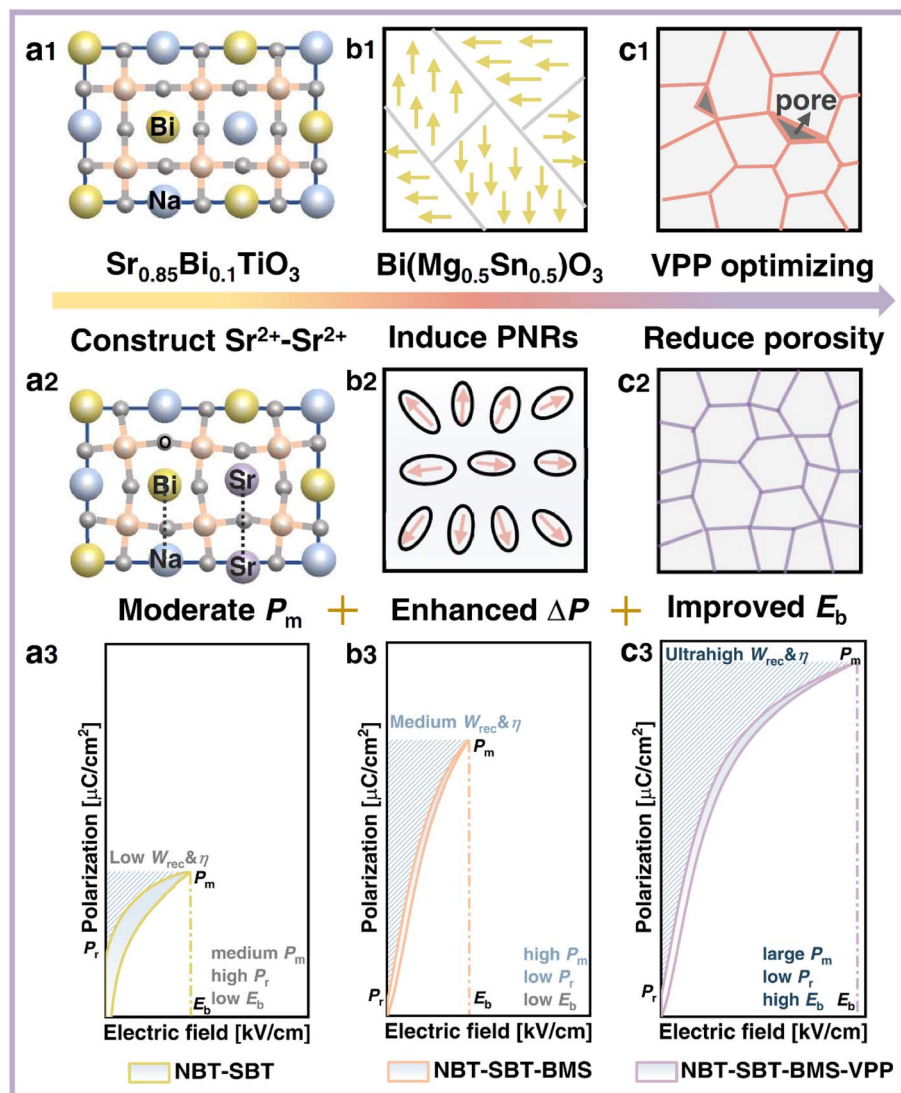


Fig. 1 Schematic diagram of a stepwise optimization route to enhance energy storage characteristics via (a1–a2) ion pairs construction, (b1–b2) domain engineering and (c1–c2) process optimization for NBT-based ceramics. (a3–c3) Schematic diagram of  $P$ – $E$  loops for realizing improved energy storage properties.

the anion's charge, according to the electrostatic valency principle. As a result, adjacently formed  $\text{Sr}^{2+}$ – $\text{Sr}^{2+}$  can replace  $\text{Bi}^{3+}$ – $\text{Na}^{3+}$  in the NBT-SBT system, as shown in Fig. 1(a1 and a2). Combined with Coulomb's law  $F = kq_1q_2/r^2$ , the distance of the former with  $q = +2_{\text{Sr}}$  is greater than that of the latter with  $q = +1_{\text{Na}}$  and  $q = +3_{\text{Bi}}$ . Following that, such a replacement is built by introducing SBT into NBT to cause A-position asymmetry, larger atomic space, and lattice distortion, resulting in a moderate  $P_m$ . Furthermore, due to its dielectric relaxation behavior over a wide temperature range, SBT can help to improve the thermal stability of ceramics.<sup>7</sup> In this case, NBT-SBT is chosen as the matrix for this work due to its high  $P_m$  and potential temperature characteristics, while its nonnegligible  $P_r$  and low  $E_b$  limit the ultimate excellent ESP, as depicted in Fig. 1(a3).

As a result, many studies have been conducted to improve the above two points of the NBT-SBT system by introducing niobate compounds such as  $\text{NaNbO}_3$  (NN),<sup>16</sup>  $\text{KNbO}_3$ ,<sup>17</sup>  $\text{AgNbO}_3$

(AN),<sup>18,19</sup> and  $(\text{Na}, \text{K})\text{NbO}_3$  (KNN) in this matrix.<sup>8</sup> For example, Wu *et al.* acquired an enhanced  $W_{\text{rec}}$  of  $3.08 \text{ J cm}^{-3}$  by incorporating NN into NBT-SBT systems with an increased  $E_b$  of  $220 \text{ kV cm}^{-1}$ .<sup>16</sup> Furthermore,  $\text{BiMeO}_3$  compounds (Me representing various cations) are frequently substituted into NBT-based systems to improve relaxation behavior and  $E_b$ , which are attributed to the strong polarizability of  $\text{Bi}^{3+}$  and the reduced grain size by large radius  $\text{Me}^{3+}$  ions.<sup>20,21</sup> As a result,  $\text{Bi}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$  (BMS), which has the potential to decrease  $P_r$  while increasing  $E_b$ , is chosen as the first optimization route, as shown in Fig. 1(b1 and b2). The difference in charge and ionic radius in the B-site induces a local disordered field, which contributes to the realization of the transition from microdomains to polar nanoregions (PNRs) that respond quickly to an applied electric field, thus maintaining a large  $\Delta P$  and improving  $E_b$ , as shown in Fig. 1(b3).

In addition, the  $E_b$  is affected by other factors such as thickness, grain size, porosity, and so on, so many measures to improve the  $E_b$  have been implemented around these factors.<sup>22</sup> Li *et al.*, for example, achieved an increased  $E_b$  of 600 kV cm<sup>-1</sup> in K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>-Bi(Zn<sub>2/3</sub>Ta<sub>1/3</sub>)O<sub>3</sub> ceramics by reducing thickness and porosity through repeated rolling.<sup>23</sup> Yan *et al.* also achieved a high  $E_b$  of 500 kV cm<sup>-1</sup> in Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-SrNb<sub>0.5</sub>Al<sub>0.5</sub>O<sub>3</sub> ceramics using the tape casting technique.<sup>24</sup> As a result, the viscous polymer process (VPP)<sup>25,26</sup> is used in the second optimization route to increase the  $E_b$  of NBT-SBT-BMS ceramics, as shown in Fig. 1(c1 and c2). The NBT-SBT-BMS ceramic powders are treated with PVA, hot water, acetic acid, and repeated rolling to obtain thinner, less defective, and denser VPP ceramics, which ultimately helps to obtain higher  $E_b$  and improve ESP, as indicated in Fig. 1(c3).

Along the stepwise optimization route depicted in Fig. 1. NBT-SBT-BMS-VPP ceramics are synthesized by introducing BMS and optimizing the VPP process in the NBT-SBT matrix with the formation of Sr<sup>2+</sup>-Sr<sup>2+</sup> ion pairs, which improve  $P_m$ , reduce  $P_r$  and finally improve  $E_b$ . In summary, the

0.92(0.65NBT-0.35SBT)-0.08BMS-VPP ceramics optimized by this progressive strategy achieve an ultrahigh  $W_{rec}$  of 7.5 J cm<sup>-3</sup> and a high  $\eta$  of 85% at a large  $\Delta P$  of 64.6  $\mu$ C cm<sup>-2</sup> ( $E_b = 440$  kV cm<sup>-1</sup>), as well as excellent temperature applicability within 20–120 °C.

## 2. Experimental

(1-x)(0.65Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>-0.35Sr<sub>0.85</sub>Bi<sub>0.1</sub>TiO<sub>3</sub>)-xBi(Mg<sub>0.5</sub>Sn<sub>0.5</sub>)O<sub>3</sub> ceramics (abbreviated as NBT-SBT-xBMS, x = 0.02, 0.04, 0.08, and 0.12) were first prepared using the solid-state reaction method, and then the x = 0.08 component was optimized using the VPP process. ESI† contains information on the experimental procedure and characterization.

## 3. Results and discussion

The crystalline structure detected by XRD for NBT-SBT-xBMS ceramics is shown in Fig. 2(a), all of which are solid soluble perovskite structures except for the second phase caused by Bi

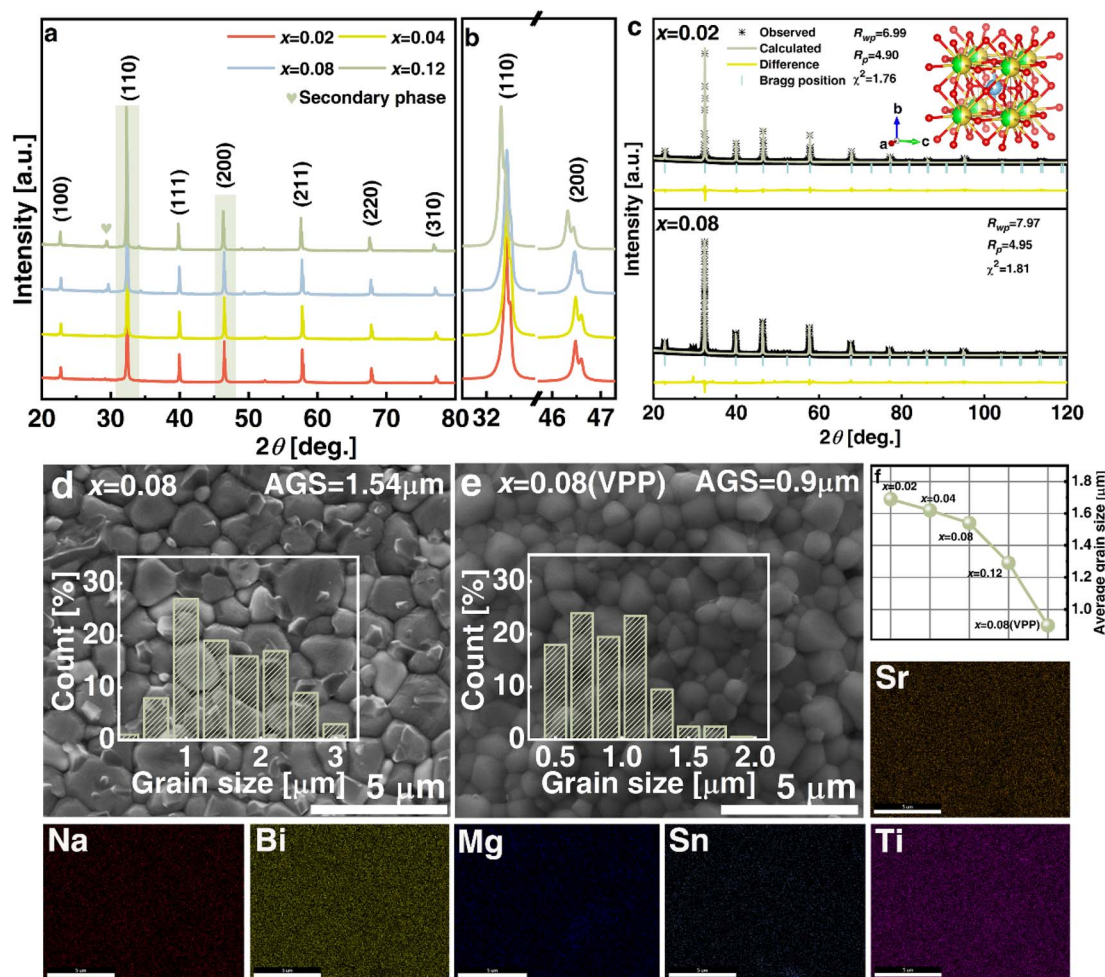


Fig. 2 XRD patterns of NBT-SBT-xBMS ceramics (a) in the range 20–80° and (b) the enlarged XRD profiles of the (110) and (200) peaks. (c) Rietveld refinements for x = 0.02 and x = 0.08 ceramics. The SEM micrographs of (d) x = 0.08 and (e) x = 0.08 (VPP) ceramics. The insets are average grain size distributions. (f) The average grain size (AGS) of NBT-SBT-xBMS ceramics. (Sr–Ti) The energy-dispersive X-ray spectroscopy (EDS) mapping images of x = 0.08 ceramics.

volatilization during the high-temperature process and labeled at 28–29°. The enlarged (110) peaks in Fig. 2(b) shift to the left as BMS content increases, as does cell volume, because bigger radius  $\text{Mg}^{2+}$  (72 pm) and  $\text{Sn}^{4+}$  (69 pm) ions replace  $\text{Ti}^{4+}$  ions (60.5 pm). Similarly, the cleaved (200) peaks show that ceramics are not cubic in structure but have pseudocubic symmetry, as determined by the Rietveld refinements of all compositions in Table S1† and Fig. 2(c). The average structures are  $Pm\bar{3}m$ , according to the fitting  $R$ -factors in the refinement results, and the changes in lattice parameters and cell volume are consistent with the XRD analyses. Furthermore, Fig. 2(d) and (e) compare the SEM micro appearances and average grain size (AGS) distributions of  $x = 0.08$  and  $x = 0.08$  (VPP) ceramics, with the

latter being denser than the former due to the reduced porosity achieved through VPP processing. Fig. 2(f) shows the AGS distribution results of each ceramic component, with the AGS steadily decreasing from 1.69, 1.62, 1.54, 1.29 to 0.9  $\mu\text{m}$  with the addition of BMS and VPP. The element distributions (EDS) of the optimal VPP object ( $x = 0.08$ ) are then shown in Fig. 2(Sr–Ti), exhibiting the chemical uniformity of the elements Sr, Na, Bi, Mg, Sn, and Ti. As is generally known, grain size, porosity, and compactness are all parameters that can influence the  $E_b$  of ceramics by varying the quantity of high-insulating grain boundaries.<sup>2,22</sup> As a result, the  $E_b$  of NBT-SBT- $x$ BMS ceramics is evaluated in terms of the Weibull distribution, as illustrated in Fig. 3(a), where all data obey the distribution and fit out the

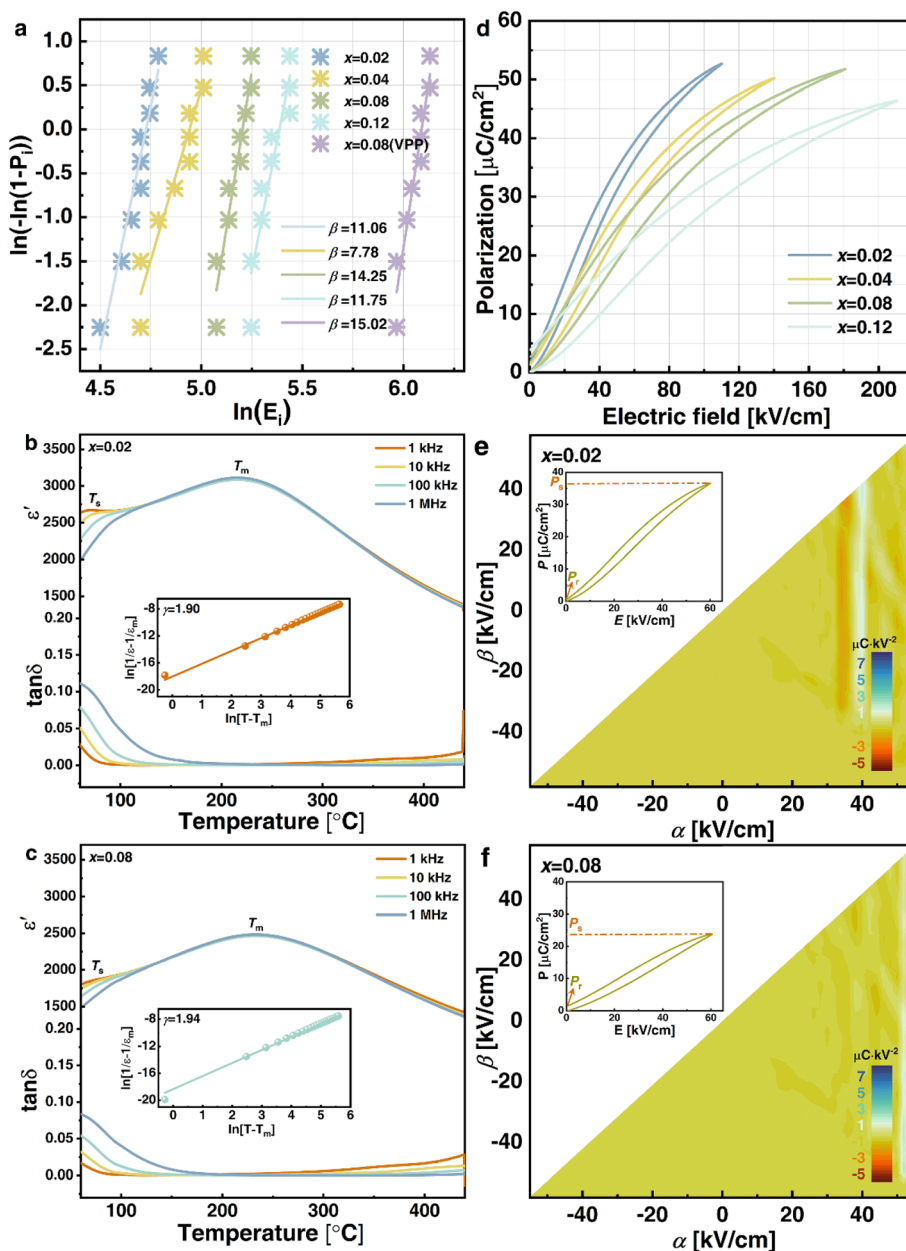


Fig. 3 (a) Weibull distributions of NBT-SBT- $x$ BMS ceramics. Temperature dependent permittivity ( $\epsilon'$ ) and loss tangent ( $\tan \delta$ ) at 1–1000 kHz of (b)  $x = 0.02$  and (c)  $x = 0.08$  ceramics. The insets are  $\ln(1/\epsilon' - 1/\epsilon'_{\max})$  versus  $\ln(T - T_{\max})$ . (d) Unipolar  $P$ - $E$  loops under the critical electric field of NBT-SBT- $x$ BMS ceramics. Evolution of the FORC distribution of (e)  $x = 0.02$  and (f)  $x = 0.08$  ceramics.



reliable value  $\beta$ . The increasing  $E_b$  is inversely proportional to the decreasing AGS, which conforms to the relationship between them, *i.e.*,  $E_b \propto 1/\sqrt{G}$ , where  $G$  represents the AGS.<sup>22</sup>

Fig. 3(b) and (c) show the temperature dependences of dielectric properties for  $x = 0.02$  and  $0.08$  ceramics. The noticeable frequency dispersion at a low temperature of about  $60\text{ }^\circ\text{C}$  in the loss tangent ( $\tan \delta$ ) –  $T$  curves of these two ceramics can be detected as the one dielectric anomaly ( $T_s$  peak) in the corresponding permittivity ( $\epsilon'$ ) –  $T$  spectrum, which is created by the thermal evolution of PNRs.<sup>27,28</sup> In contrast, another dielectric anomaly ( $T_m$  peak) corresponding to maximum permittivity  $\epsilon_m$  exists in the high-temperature area of  $250\text{ }^\circ\text{C}$  due to the weak frequency dispersion. After doping additional BMS, the  $\epsilon'$  of  $x = 0.08$  ceramics dramatically falls compared to  $x = 0.02$  and  $0.08$  ceramics due to increasing cation disorder at A- and B-sites as well as the broken long-range ferroelectric order. Furthermore, the dielectric peak of  $x = 0.08$  ceramics becomes wide and flat, which improves relaxor behavior, increases the thermal stable interval, and contributes to ESP temperature stability. In order to determine the diffuseness degree of  $x = 0.02$  and  $0.08$  ceramics further, the modified Curie–Weiss law is used as follows:<sup>29</sup>

$$\frac{1}{\epsilon'} - \frac{1}{\epsilon_m} = \frac{(T - T_m)^\gamma}{C}, \quad (1)$$

where  $C$  and  $\gamma$  are the Curie constant and diffusion coefficient, respectively. The  $\ln(1/\epsilon' - 1/\epsilon_m) - \ln(T - T_m)$  curves of  $x = 0.02$  and  $0.08$  ceramics are respectively plotted and fitted in the insets of Fig. 3(b) and (c). When  $x$  changes from  $0.02$  to  $0.08$ , the  $\gamma$  values increase from  $1.90$  to  $1.94$ . As a result, the  $x = 0.08$

ceramic has a greater diffuse state, which can be attributed to cation confusion, FE long-range breaking, and the effects of PNRs.<sup>30,31</sup> Fig. 3(d) depicts the unipolar  $P$ – $E$  loops of NBT-SBT- $x$ BMS ceramics under critical electric fields. When the amount of BMS dopants varies from  $0.02$  to  $0.12$ , the  $P$ – $E$  loops become flat and fat, accompanied by an increase in  $P_r$ . Despite the fact that the  $P_m$  of all compositions falls when subjected to the same electric field, the  $P_m$  can also be maintained at high electric fields produced by increasing BMS concentrations. Meanwhile, for  $x = 0.02, 0.04, 0.08,$  and  $0.12$ , the  $E_b$  is  $110, 140, 180,$  and  $210\text{ kV cm}^{-1}$ , respectively. The first-order reversal curves (FORCs) of  $x = 0.02$  and  $x = 0.08$  ceramics under  $60\text{ kV cm}^{-1}$  are executed in Fig. 3(e) and (f), separately. The high concentration region of  $x = 0.02$  ceramic exhibits a significant nonlinear polarization behavior, based on the different polarization intensity and behavior reflected by the background shade.<sup>32</sup> As a result, the increased  $P_m$  in the inset curves is generated by domain flipping and domain wall motion driven by ferroelectric behavior. In the case of  $x = 0.08$  ceramic, the high-strength region near the origin becomes more dispersed, and the area of long-range polarization order gradually declines, implying that the ferroelectricity is weakened, the long-range FE order is broken, and relaxor behaviour is enhanced.

Bright-field transmission electron microscopy (TEM) examination is performed to observe the domain morphology in order to better investigate the physical mechanism of the remarkable ESP in the optimal  $x = 0.08$  ceramic, as shown in Fig. 4(a). Because of the introduction of BMS, micron-sized PNRs have clearly replaced huge ferroelectric domains in ceramics. The lattice spacing confirms the average structure of pseudocubic

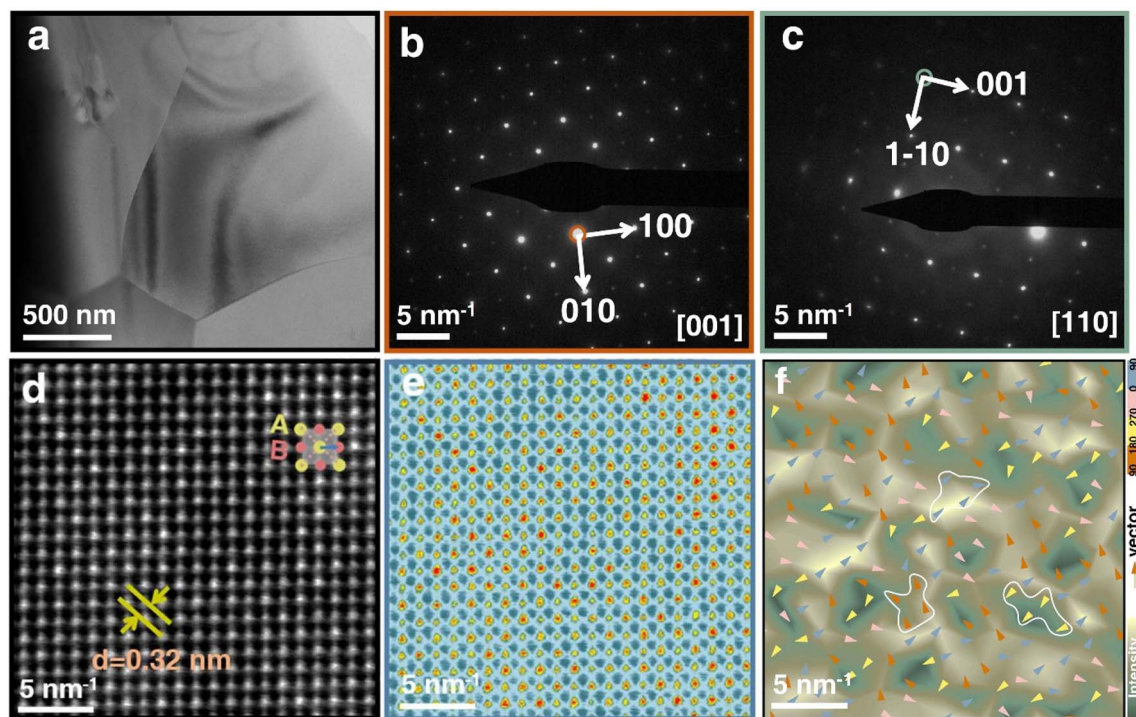


Fig. 4 TEM images of  $x = 0.08$  ceramics: (a) bright-field, SAED patterns along (b)  $[001]_C$  and (c)  $[110]_C$ , (d) HR-TEM images, (e) atomic brightness contrast extracted from (d), and (f) the spontaneous polarization vectors calculated from the displacement of the B-site cations.

symmetry, according to the selected-area electron diffraction (SAED) patterns along the [001] and [110] zone axes of the  $x = 0.08$  ceramic grains shown in Fig. 4(b) and (c), which is consistent with the XRD refinement results. The high-resolution TEM (HR-TEM) images in Fig. 4(d) and concomitant brightness distribution in Fig. 4(e) of the  $x = 0.08$  ceramic jointly point out the A- and B-sites atom positions. As a result, the spontaneous polarization vector is identified as the distance from the cationic B-site to the nearest four A-site centers. Based on this assumption, Fig. 4(f) depicts the intensity and orientation of spontaneous polarization, as shown by the back color distribution and arrow direction, respectively. Meanwhile, four-angle interval arrow vectors (0-90-180-270-360°) divided into four colors correspond to different back color regions showing polarization intensity. PNRs are regions (indicated by a white line) composed of polarization vectors of the same color and orientation, where the (2–4) nm PNRs and domain structure in the  $x = 0.08$  ceramic are helpful for improving  $\Delta P$  and ESP.

Fig. 5(a–c) show the unipolar  $P$ - $E$  loops and relative  $I$ - $E$  curves of  $x = 0.02$ , 0.08, and 0.08 (VPP) ceramics under various electric fields. Because of the comparatively obvious hysteresis embedded in the  $P$ - $E$  loops, the  $x = 0.02$  ceramics in Fig. 5(a) exhibit weak RFE features, with low  $E_b$  as well as significant  $P_m$

and  $P_r$  values. Under the same electric field,  $P_m$  falls and  $P_r$  increases after the addition of 0.08 mole BMS in Fig. 5(b) compared to  $x = 0.02$ . Despite this, BMS has greatly improved the  $E_b$  of  $x = 0.08$  to give a  $P_m$  value that is still high under this breakdown field. As a result,  $x = 0.08$  is determined for further VPP to synthesize  $x = 0.08$  (VPP) ceramics in Fig. 5(c), which intuitively have slimmer  $P$ - $E$  loops. The VPP reduces thickness, flaws, and porosity, resulting in greatly higher  $E_b$ , equally high  $P_m$ , and significantly reduced  $P_r$ . The foregoing trends of  $x = 0.02$ , 0.08, and 0.08 (VPP) ceramics are independently reflected in the specific performance parameters ( $E_b$ ,  $P_m$ ,  $P_r$ ,  $W_{\text{rec}}$ , and  $\eta$ ) observed under different electric fields in Fig. 5(d–f). With a low  $E_b$  of 110 kV cm<sup>-1</sup> for  $x = 0.02$  ceramics in Fig. 5(d), the large  $P_m$  of 52.68  $\mu\text{C cm}^{-2}$  and  $P_r$  of 1.66  $\mu\text{C cm}^{-2}$  result in an undesired ESP ( $W_{\text{rec}} = 2.1 \text{ J cm}^{-3}$ ,  $\eta = 87\%$ ). Then under the function of BMS for  $x = 0.08$  ceramics in Fig. 5(e), the enhanced  $E_b$  (180 kV cm<sup>-1</sup>) boosts the modified  $W_{\text{rec}}$  (3.2 J cm<sup>-3</sup>) but the increased  $P_r$  (2.65  $\mu\text{C cm}^{-2}$ ) cause a reduced  $\eta$  of 85%. The ESP has yet to meet the actual application requirements. As a result, the ESP of  $x = 0.08$  ceramics is naturally enhanced by VPP, achieving ultrahigh  $W_{\text{rec}}$  of 7.5 J cm<sup>-3</sup> and  $\eta$  of 85% under  $E_b$  of 440 kV cm<sup>-1</sup> as shown in Fig. 5(f). Fig. 5(g) depicts the effects of key parameters such as  $E_b$  and  $P_m - P_r$  on  $W_{\text{rec}}$  for the three

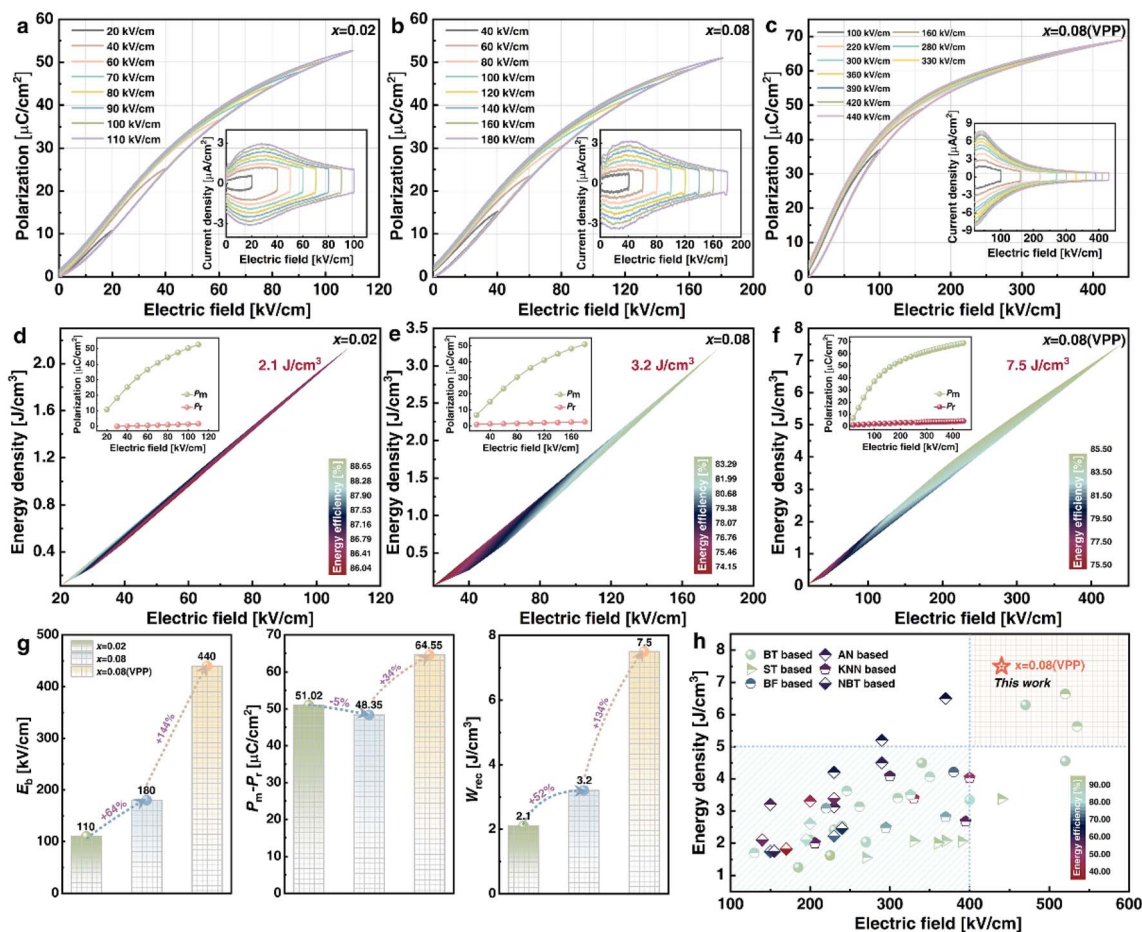


Fig. 5 (a–c) Unipolar  $P$ - $E$  loops, (d–f) the calculated  $W_{\text{rec}}$  and  $\eta$  of at different electric fields for  $x = 0.02$ ,  $x = 0.08$  and  $x = 0.08$  (VPP) ceramics. (g) Comparison of  $E_b$ ,  $P_m - P_r$  and  $W_{\text{rec}}$  values among  $x = 0.02$ ,  $x = 0.08$  and  $x = 0.08$  (VPP) ceramics. (h) Comparison of  $W_{\text{rec}}$ ,  $\eta$  and  $E_b$  between this work and other reported lead-free ceramics.



ceramics. As 0.08 mol. BMS and VPP act sequentially to improve  $E_b$  from  $110 \text{ kV cm}^{-1}$  by 64% to  $180 \text{ kV cm}^{-1}$  and subsequently by 144% to  $440 \text{ kV cm}^{-1}$ , the  $\Delta P$  decreases by 5% from  $51.02 \mu\text{C cm}^{-2}$  to  $64.55 \mu\text{C cm}^{-2}$ . As a result, the massive increase in  $W_{\text{rec}}$  from 2.1 to  $7.5 \text{ J cm}^{-3}$  is ultimately realized in  $x = 0.08$  (VPP) ceramics, which is primarily attributed to the overall improved  $E_b$  and  $\Delta P$ . In addition, a succession of  $E_b$ ,  $W_{\text{rec}}$ , and  $\eta$  between our work and BaTiO<sub>3</sub> (BT), AN, SrTiO<sub>3</sub> (ST), KNN, BiFeO<sub>3</sub> (BF), and NBT-based ceramics are shown in Fig. 5(h).<sup>10,15,16,18,22,33-77</sup>

Most ceramic performance parameters are spread in the lower left and upper right corners of each system, with  $E_b$  below  $400 \text{ kV cm}^{-1}$  linearly corresponding to  $W_{\text{rec}}$  below  $5 \text{ J cm}^{-3}$  and *vice versa*. However, the  $x = 0.08$  (VPP) ceramic with  $W_{\text{rec}}$  of  $7.5 \text{ J cm}^{-3}$  and  $\eta$  of 85% improves on the prior ESP of roughly  $400 \text{ kV cm}^{-1}$ , broadening the application prospect.

SEM appearances of  $x = 0.02$  and 0.08 ceramics in Fig. 6(a) and (b) are utilized as the matrix structure for a series of COMSOL simulations to validate the definite relationship

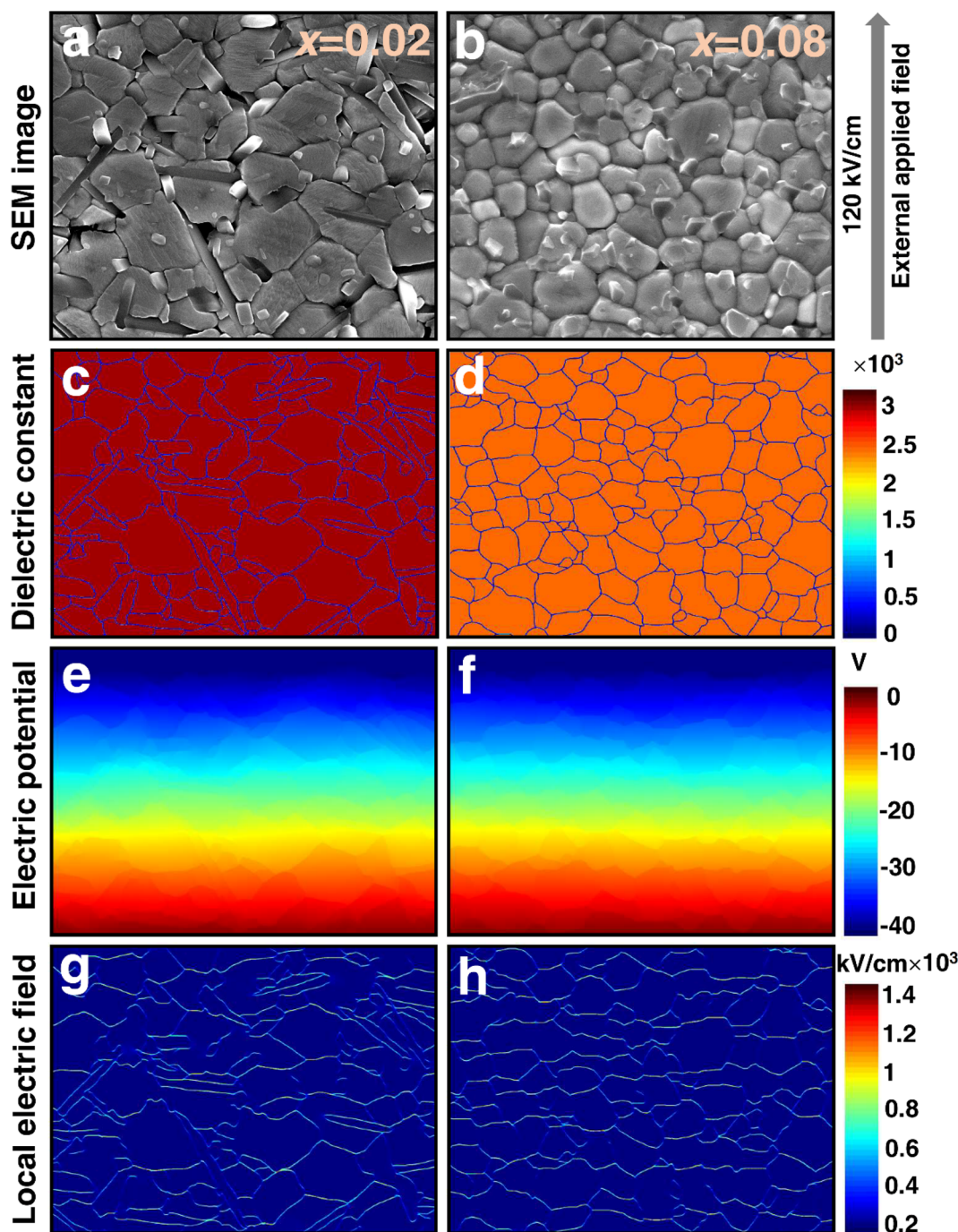


Fig. 6 The SEM of (a)  $x = 0.02$  and (b)  $x = 0.08$  ceramics as basic structures of the simulation. The  $\epsilon_r$  distribution of (c)  $x = 0.02$  and (d)  $x = 0.08$  ceramics. The electric potential distribution of (e)  $x = 0.02$  and (f)  $x = 0.08$  ceramics. The local electric field distribution of (g)  $x = 0.02$  and (h)  $x = 0.08$  ceramics.



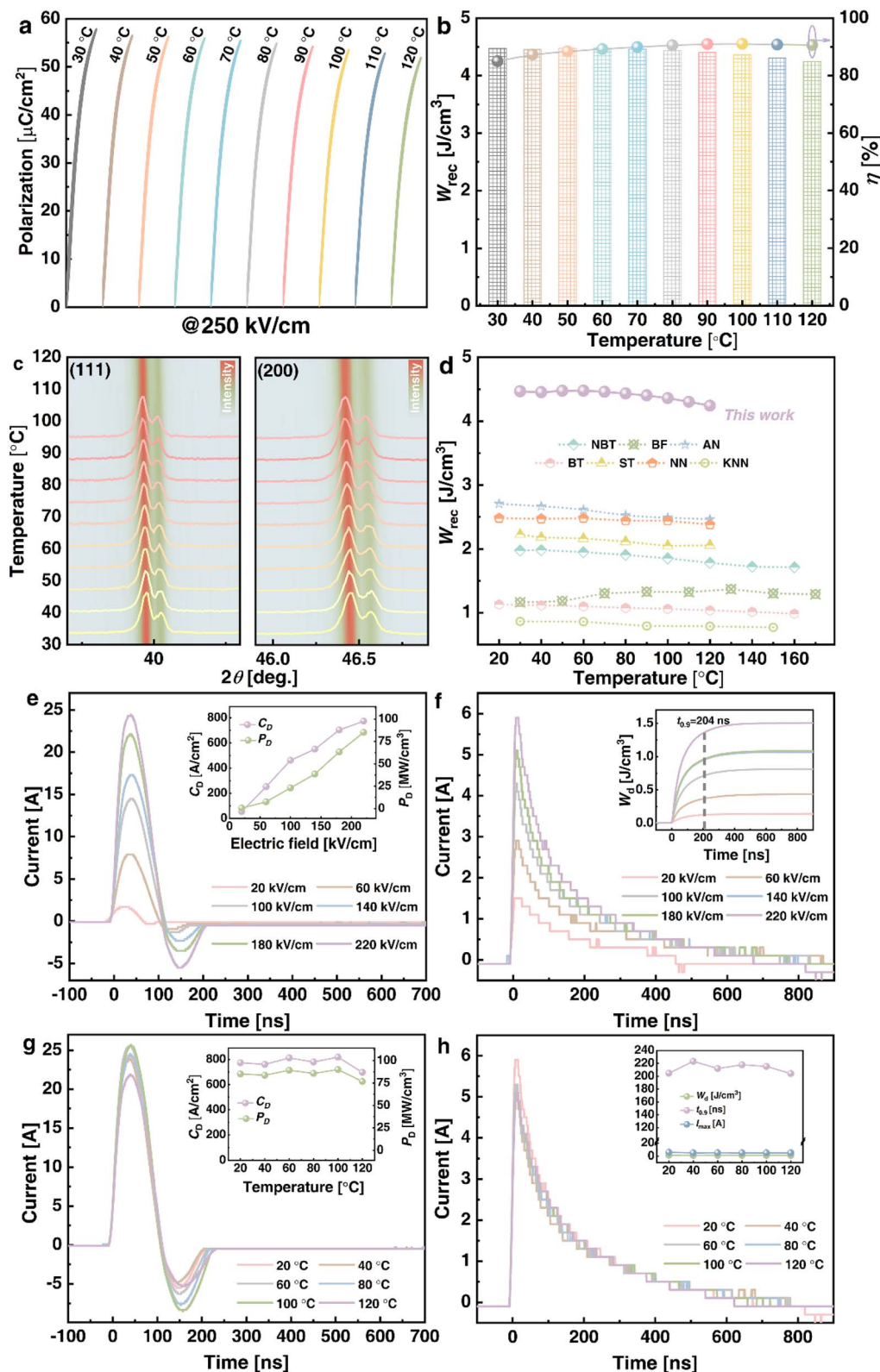


Fig. 7 (a) Unipolar  $P$ - $E$  loops (measured at 250 kV cm<sup>-1</sup>) and (b)  $W_{rec}$  and  $\eta$  as functions of temperature for  $x = 0.08$  (VPP) ceramics. (c) Temperature evolution of XRD patterns for  $x = 0.08$  (VPP) ceramics from 30 °C to 120 °C at selected angles of 39.5–40.5° and 46–47°. (d) Comparison of  $W_{rec}$  at temperatures between this work and some recently reported lead-free ceramics. (e) Underdamped discharge and (f) overdamped discharge waveforms of the  $x = 0.08$  (VPP) ceramic under various electric fields and ambient temperature. (g) Underdamped discharge and (h) overdamped discharge waveforms of the  $x = 0.08$  (VPP) ceramic measured in the temperature range from 20 to 120 °C under 220 kV cm<sup>-1</sup>.

between microstructure and electrical properties. Because of the clear separation of grain boundaries and grains in these two ceramics, their own  $\epsilon'$  of 3090 and 2469 at 1 kHz obtained from Fig. 3(b) and (d) are assigned as belonging to the grains, and the  $\epsilon'$  of the grain boundaries is one-tenth of it. Following this setting, the model presented by Randall *et al.*<sup>78</sup> is used to simulate  $x = 0.02$  and  $0.08$  ceramics, and the corresponding results are displayed in Fig. 6(c) and (d), respectively. Under a simulated external electric field of  $120 \text{ kV cm}^{-1}$  applied to  $x = 0.02$  and  $0.08$  ceramics, the grain distributions of  $x = 0.08$  are more uniform and denser than those of  $x = 0.02$ , resulting in a greater average electric potential, as shown in Fig. 6(e) and (f). Furthermore, when combined with the finer grains in  $x = 0.08$  ceramics, Fig. 6(g) and (h) shows that  $x = 0.08$  ceramics have more grain boundaries (shown in yellow) correlating to a strong local electric field, resulting in a higher  $E_b$ .

Aside from obtaining superior ESP at RT, its temperature adaptability throughout a broad temperature range is critical for energy storage applications. Fig. 7(a) and (b) exhibit the unipolar  $P$ - $E$  loops and corresponding  $W_{\text{rec}}$  and  $\eta$  of  $x = 0.08$  (VPP) ceramics from 30 to  $120 \text{ }^\circ\text{C}$  at  $250 \text{ kV cm}^{-1}$ . Although  $P_m$  will certainly reduce slightly as temperature rises, the  $P$ - $E$  loops will always remain slim, and  $P_r$  will likewise decrease. With the same changes in  $P_m$  and  $P_r$ ,  $W_{\text{rec}}$  remains stable at  $4.47$  to  $4.25 \text{ J cm}^{-3}$  and the  $\eta$  rises from  $85$  to  $91\%$ . As a result, the combined  $W_{\text{rec}}$  of  $4.4 \text{ J cm}^{-3}$  and  $\eta$  of  $89\%$  with fluctuations of less than  $\pm 5\%$  and  $\pm 6\%$  indicate that stable thermal reactivity is attained in  $x = 0.08$  (VPP) ceramics. Similarly, at  $30$ – $120 \text{ }^\circ\text{C}$ , the XRD patterns of the (111) and (200) peaks at  $39.5$ – $40.5^\circ$  and  $46$ – $47^\circ$  are shown in Fig. 7(c). The shape and intensity of the diffraction peak reflected by the background color essentially remain unchanged as the temperature changes. This structural evolution law can also be used to demonstrate the temperature independence of  $x = 0.08$  (VPP) ceramics, which have superior ESP performance than other ceramic systems at various temperatures [see Fig. 7(d)].<sup>15,36,66,74,79–81</sup> In comparison to chosen NBT, BF, AN, BT, ST, NN, and KNN-based ceramics,  $x = 0.08$  (VPP) ceramics stand out due to  $W_{\text{rec}}$  of  $4.25 \text{ J cm}^{-3}$  and  $\eta$  of  $89\%$ . Furthermore, the charge–discharge behaviors are critical for  $x = 0.08$  (VPP) ceramics and are depicted in Fig. 7(e–h). The underdamped  $I$ - $t$  curves from  $20$  to  $220 \text{ kV cm}^{-1}$  are displayed in Fig. 7(e). All curves perpendicularly increase as the electric field varies. Under  $220 \text{ kV cm}^{-1}$ , the maximum current ( $I_{\text{max}}$ ), current density ( $C_D = I_{\text{max}}/S$ ), and power density ( $P_D = EI_{\text{max}}/2S$ ) are  $24.5 \text{ A}$ ,  $780.25 \text{ A cm}^{-2}$  and  $85.83 \text{ MW cm}^{-3}$ , respectively. Fig. 7(f) shows the overdamped  $I$ - $t$  curves in the same electric field range, while the corresponding discharged energy density ( $W_d = R \int i^2 dt / V$ ,  $R = 100 \text{ } \Omega$ )<sup>82</sup> is  $1.51 \text{ J cm}^{-3}$  and discharge time ( $t_{0.9}$ ) is maintained within  $204 \text{ ns}$ . These two types of waveforms from  $20$  to  $120 \text{ }^\circ\text{C}$  are also gathered in Fig. 7(g) and (h) for analyzing the temperature applicability of  $x = 0.08$  (VPP) ceramics. Even if the waveforms and derived values change with temperature, its  $I_{\text{max}}$ ,  $C_D$ , and  $P_D$  remain stable at  $120 \text{ }^\circ\text{C}$ , which are  $21.9 \text{ A}$ ,  $697.45 \text{ A cm}^{-2}$ , and  $76.72 \text{ MW cm}^{-3}$ , respectively, with a  $W_d$  of  $1.26 \text{ J cm}^{-3}$  and  $t_{0.9}$  of  $204 \text{ ns}$ . As a result,  $x = 0.08$  (VPP) ceramics exhibit superior thermal independence and competitiveness in energy storage and pulse performance.

## 4. Conclusions

To summarize, the stepwise optimization route is used to achieve comprehensive outstanding ESP in 0.65NBT-0.35BST-based ceramics by gradually introducing the BMS and implementing the VPP technique. Specifically, after generating a  $\text{Sr}^{2+}$ - $\text{Sr}^{2+}$  ion pair at the A-site to assure a high  $P_m$ , the introduction of  $\text{Mg}^{2+}$  and  $\text{Sn}^{4+}$  ions at the B-site promotes PNRs and repeated rolling for ceramics increases compactness, which improve the  $\Delta P$  and  $E_b$  in order. As a result, 0.92(0.65NBT-0.35BST)-0.08BMS-VPP ceramics obtain an ultrahigh  $W_{\text{rec}}$  of  $7.5 \text{ J cm}^{-3}$  and a high  $\eta$  of  $85\%$  under the action of a huge  $\Delta P$  of  $64.6 \text{ } \mu\text{C cm}^{-2}$  at  $440 \text{ kV cm}^{-1}$ , as well as stable thermal reactivity within  $20$ – $120 \text{ }^\circ\text{C}$ . Such superior ESP benefits from the high polarization intensity, breaks the previous values at almost the breakdown electric field, and outperforms the majority of reported NBT-based ceramics, demonstrating the applicability of the stepwise optimization route for designing other similar high-performance dielectric ceramics.

## Conflicts of interest

There are no conflicts to declare.

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