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## Achieving outstanding energy storage behaviors *via* combinatorial optimization design in BNT-based relaxor ferroelectric ceramics under medium–low electric fields

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As the development of electronic components has become highly integrated and diversified, dielectric ceramic energy storage capacitors have attracted wide attention due to their high-power density, low cost and ability to operate at high temperatures. In this work, we have designed  $(0.8 - x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - 0.2\text{BaZr}_{0.3}\text{Ti}_{0.7}\text{O}_3 - x\text{NaNbO}_3$  (abbreviated as  $(0.8 - x)\text{BNT} - 0.2\text{BZT} - x\text{NN}$ ) lead-free relaxor ferroelectric ceramics and successfully optimized the energy storage performance by synergistically modifying critical factors affecting energy storage properties. The  $0.7\text{BNT} - 0.2\text{BZT} - 0.1\text{NN}$  ceramic achieved high maximum polarization ( $P_{\text{max}} = 42.1 \mu\text{C cm}^{-2}$ ), extremely low remnant polarization, recoverable energy storage density ( $W_{\text{rec}} = 3.53 \text{ J cm}^{-3}$ ), efficiency ( $\eta = 93.5\%$ ) and  $W_{\text{rec}}/E = 160.45 \text{ J (kV m}^{-2})$  under a medium–low electric field ( $E = 220 \text{ kV cm}^{-1}$ ). The simultaneous achievement of high energy storage density and efficiency under lower electric fields is due to the expansion of the octahedral framework facilitated by  $\text{Ba}^{2+}$  and  $\text{Zr}^{4+}$ , which promotes ion displacement.  $\text{NaNbO}_3$  can further improve relaxor behaviors, compensating for polarization losses caused by relaxation and enhancing breakdown field strength. Furthermore, it also exhibits excellent electric field stability ( $30 - 220 \text{ kV cm}^{-1}$ ,  $\Delta\eta < 0.7\%$ ), thermal stability ( $20 - 140^\circ\text{C}$ ,  $\Delta W_{\text{rec}} < 7.2\%$ ), and frequency stability ( $1 - 100 \text{ Hz}$ ,  $\Delta W_{\text{rec}} < 5.3\%$ ). This work provides an option for the selection of dielectric capacitors under limited electric field conditions.

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### 1. Introduction

Energy storage technologies have been an indispensable topic for social development and progress. With the trend of electronic devices moving towards portability, miniaturization, and stabilization, the development of energy storage devices with small volume, low cost, wide operating temperature, and excellent performance is crucial. Ceramic-based dielectric capacitors, characterized by high power density, a wide operating temperature range, controllable and coordinated performance, and long cycle life, have become ideal for future pulse power systems.<sup>1–4</sup>

The energy storage density of dielectric capacitors remains relatively low, still exhibiting a certain gap compared to batteries and electrochemical capacitors. Therefore, enhancing the energy storage density of dielectric capacitors has become an important challenge. The energy storage properties of dielectric

capacitors can be evaluated using the following formulas:<sup>5–7</sup>

$$W_{\text{tot}} = \int_0^{P_{\text{max}}} E dP$$

$$W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} E dP$$

$$\eta = \frac{W_{\text{rec}}}{W_{\text{tot}}} \times 100\%$$

where  $W_{\text{tot}}$ ,  $W_{\text{rec}}$ , and  $\eta$  represent the total energy density, recoverable energy density, and efficiency, respectively.  $P_{\text{max}}$ ,  $P_r$ , and  $E$  represent the maximum polarization, remnant polarization, and electric field, respectively. From the above formulas, it can be inferred that achieving high energy storage density in dielectric ceramic materials requires high  $P_{\text{max}}$ , low  $P_r$ , and high breakdown field strength ( $E_b$ ). For instance, Chen *et al.*<sup>8</sup> introduced  $\text{CaTi}_{0.5}\text{Zr}_{0.5}\text{O}_3$  into the  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - \text{NaNbO}_3$  matrix, which significantly altered the grain size and conductivity, leading to an increase in the  $E_b$ . Ultimately, BNT–NN/ $x$ CZT composites with  $x = 7 \text{ wt\%}$  achieved optimal energy storage properties ( $W_{\text{rec}} = 4.93 \text{ J cm}^{-3}$ ,  $\eta = 93.3\%$ ) at  $410 \text{ kV cm}^{-1}$ . Zhang

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*et al.*<sup>9</sup> induced defect dipoles and reduced oxygen vacancy concentrations in  $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$  through the doping of CuO. A high  $W_{\text{rec}}$  of  $4.17 \text{ J cm}^{-3}$  and an  $\eta$  of 89.5% are achieved under a medium electric field ( $\sim 350 \text{ kV cm}^{-1}$ ). Li *et al.*<sup>10</sup> introduced  $\text{La}^{3+}$  and  $\text{Ta}^{5+}$  ions into the A/B sites of antiferroelectric  $\text{AgNbO}_3$ , which shifted the electric field-induced antiferroelectric-ferroelectric phase transition to higher fields. The  $\text{Ag}_{0.94}\text{La}_{0.02}\text{Nb}_{0.8}\text{Ta}_{0.2}\text{O}_3$  ceramic achieved a  $W_{\text{rec}}$  of  $6.73 \text{ J cm}^{-3}$  and an  $\eta$  of 74.1% under an electric field of  $540 \text{ kV cm}^{-1}$ . Although higher  $W_{\text{rec}}$  can be achieved at higher electric field strengths, the contribution of the electric field to polarization is low. It typically requires  $P_{\text{max}}$  at  $400 \text{ kV cm}^{-1}$  to achieve  $40 \mu\text{C cm}^{-2}$ . This limitation not only increases the energy loss during the charging process of dielectric capacitors, but also raises the risk and breakdown probability when operating under high electric fields. Additional insulation protection devices and driving instruments need to be applied to the capacitors, anticipating higher working electric field strengths. Therefore, it is necessary to develop dielectric energy storage materials capable of simultaneously achieving high energy density and energy storage efficiency under moderate to low electric fields ( $< 250 \text{ kV cm}^{-1}$ ).

In this work, we introduced  $\text{NaNbO}_3$  (NN) into the  $0.8\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.2\text{BaZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$  (BNT–BZT) matrix to construct the  $(0.8 - x)\text{BNT}\text{--}0.2\text{BZT}\text{--}x\text{NN}$  relaxor ferroelectric ceramics for achieving excellent energy storage behaviors. The design ideas of this work are shown in Fig. 1. The roles of the ferroelectrically active ions  $\text{Bi}^{3+}$ ,  $\text{Na}^+$ , and  $\text{Ti}^{4+}$  are to generate locally correlated electric dipoles. The presence of  $\text{Ba}^{2+}$  and  $\text{Zr}^{4+}$  with larger ionic radii can expand the  $[\text{AO}_{12}]$  cube-octahedral and  $[\text{BO}_6]$  octahedral main frameworks, providing space for ion displacement while partially disrupting the long-range ordered ferroelectric domains.<sup>11,12</sup> The BNT–BZT ceramic exhibits high  $P_{\text{max}}$ , but the energy storage efficiency is still low due to the large  $P_r$ . Upon the introduction of NN, the macroscopic ferroelectric

domains will be further disrupted, leading to significant reductions in  $P_r$  and the coercive field ( $E_c$ ). The lone electrons in the outer 5s orbitals of  $\text{Nb}^{5+}$  and  $\text{Na}^+$  can compensate for the polarization loss caused by relaxation.<sup>13</sup> In addition, the large bandgap of NN ( $\sim 3.58 \text{ eV}$ ) can enhance the insulation performance of the system, thus improving the  $E_b$ .<sup>14</sup> Based on the above composition design, the  $0.7\text{BNT}\text{--}0.2\text{BZT}\text{--}0.1\text{NN}$  ceramic exhibits weak local correlation but highly extendable unit polarization vectors, demonstrating high  $P_{\text{max}}$ , extremely low  $P_r$  and excellent energy storage performance. It achieves  $W_{\text{rec}} = 3.53 \text{ J cm}^{-3}$ ,  $\eta = 93.5\%$ , and  $W/E = 160.45 \text{ J (kV m}^{-2})$  under medium-low electric fields ( $220 \text{ kV cm}^{-1}$ ).

## 2. Experimental

**Materials preparation:**  $(0.8 - x)\text{BNT}\text{--}0.2\text{BZT}\text{--}x\text{NN}$  ( $x = 0, 0.1, 0.2$ , and  $0.3$ ) ceramics were prepared *via* the conventional solid-state reaction method using  $\text{Bi}_2\text{O}_3$  (99%),  $\text{Na}_2\text{CO}_3$  (99.8%),  $\text{BaCO}_3$  (99%),  $\text{TiO}_2$  (99%),  $\text{ZrO}_2$  (99%), and  $\text{Nb}_2\text{O}_5$  (99.5%) as raw materials. The raw materials were first weighed according to the stoichiometric ratio. They were then milled in an attrition mill using anhydrous ethanol as the milling medium for 12 h in a planetary ball mill and dried. Subsequently, the mixed powders were sintered at  $850^\circ\text{C}$  for 4 h, subjected to secondary milling for 12 hours, and dried again. After drying, the powders were thoroughly mixed and ground with a 5 wt% polyvinyl alcohol (PVA) solution. The resulting powder was pressed into discs with a diameter of 8 mm and a thickness of 0.5 mm, followed by sintering. The sintering process involved two steps: 1. Holding at  $650^\circ\text{C}$  for 2 h to remove PVA with a heating rate of  $4^\circ\text{C min}^{-1}$ . 2. Upon completion of removing PVA, ramping up to  $1090^\circ\text{C}$  and holding for 2 h for the final sintering, with a heating rate of  $5^\circ\text{C min}^{-1}$ .

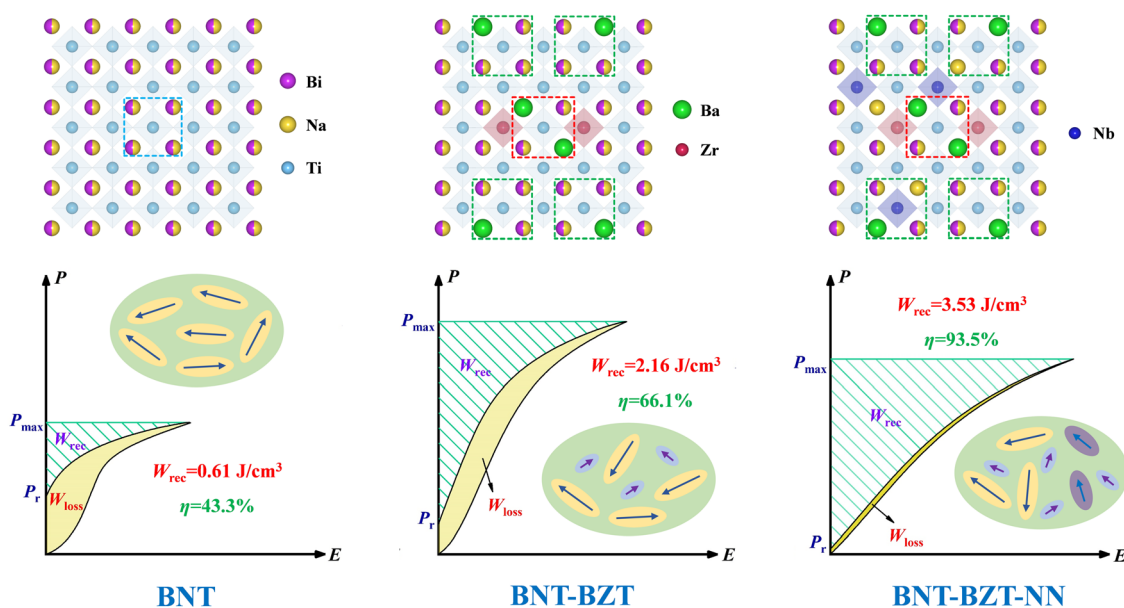


Fig. 1 The design strategy for improving energy storage behaviors of  $(0.8 - x)\text{BNT}\text{--}0.2\text{BZT}\text{--}x\text{NN}$  ceramics.

**Characterization:** The crystal structure and phase composition information of  $(0.8 - x)\text{BNT}-0.2\text{BZT}-x\text{NN}$  ceramics were obtained through X-ray diffraction (XRD, D8 Advanced, Bruker, Germany). The surface morphology images of the samples were photographed using a field emission scanning electron microscope (FESEM, SU8220, Japan). The dielectric properties of the ceramics were measured at different temperatures and frequencies using a Wayne Kerr 6500B system. The room temperature ferroelectric properties (1 Hz, 20 °C), thermal stability (1 Hz, 20–140 °C) and frequency stability (1 Hz–100 Hz, 20 °C) were recorded with a ferroelectric analyzer (TF Analyzer 3000E, Germany).

### 3. Results and discussion

Fig. 2(a) shows the XRD patterns of  $(0.8 - x)\text{BNT}-0.2\text{BZT}-x\text{NN}$  ceramics. All ceramic compositions exhibit a single perovskite structure without observable secondary phases, indicating that NN enters the BNT–BZT matrix to form a stable solid solution. As shown in Fig. 2(b), the peak position of the (200) diffraction peak gradually shifts to lower angles with increasing NN content. It is due to the lattice expansion caused by the substitution of  $\text{Ti}^{4+}$  (0.605 Å, CN = 6) with  $\text{Nb}^{5+}$  (0.64 Å, CN = 6) with a larger ionic radius.<sup>15,16</sup> The tolerance factor, which measures the stability of the perovskite system, can be calculated using the following equation:  $t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$ , where  $R_A$ ,  $R_B$  and  $R_O$  represent ionic radii of the A-site, B-site, and oxygen ions, respectively.<sup>17</sup> The tolerance factors of  $(0.8 - x)\text{BNT}-0.2\text{BZT}-x\text{NN}$  ceramics are 0.9848, 0.9845, 0.9842, and 0.9839, respectively. A decrease in the tolerance factor will cause a change in the direction of close-packed crystal planes for  $t < 1$ . The larger interstitial sites in the lattice facilitate the occurrence of ion displacement, relaxation behaviors and antiferroelectric distortion.

The surface microstructure images of  $(0.8 - x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics are shown in Fig. 3(a)–(d). The grain boundaries

of all samples are clear, and the grains are regular and compact with almost no visible pores. Approximately 100 grains are selected for the statistical analysis of the mean grain size, determined using the intercept method, as shown in Fig. 3(e). Initially, with the increase in  $x$ , the grain size decreased from 1.09  $\mu\text{m}$  at  $x = 0$  to 0.79  $\mu\text{m}$  at  $x = 0.1$ . It is explained that the substitution of larger ionic radius and atomic weight  $\text{Nb}^{5+}$  for  $\text{Ti}^{4+}$  increases the lattice strain energy, and the diffusion coefficient of  $\text{Nb}^{5+}$  is low, which inhibits crystal growth.<sup>18,19</sup> However, as the NN content further increases, the average grain size increases from 0.79  $\mu\text{m}$  at  $x = 0.1$  to 1.23  $\mu\text{m}$  at  $x = 0.3$ . This phenomenon is closely associated with the defect structure within the ceramic material. The volatilization of  $\text{Na}^+$  and  $\text{Bi}^{3+}$  introduces oxygen vacancies. During the high temperature sintering process, these vacancies facilitate mass transport within the ceramic, resulting in an enlargement of the grain size.<sup>20</sup> High density and low porosity are beneficial for improving the breakdown field strength of the ceramics.

Fig. 4(a)–(d) show the temperature-dependent behaviors of the dielectric constants ( $\epsilon_r$ ) and dielectric losses ( $\tan \delta$ ) of  $(0.8 - x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics in the frequency range of 1 kHz to 1 MHz. All samples exhibit characteristics of relaxor behaviors, including diffuse phase transitions and frequency dispersion. In undoped NN samples, two distinct dielectric peaks ( $T_s$  and  $T_m$ ) are observed.  $T_s$  corresponds to the thermal evolution of discrete polar nanoregions, while  $T_m$  corresponds to the phase transition from rhombohedral to tetragonal phases.<sup>21</sup> With the addition of NN, the  $T_s$  peaks significantly shift towards lower temperatures, corresponding to approximately 87.6 °C, 51.5 °C, and 20 °C, while the  $T_m$  peaks disappear. This phenomenon can be attributed to the stabilization of the  $P4bm$  polar nanoregions (PNRs) at high temperatures, leading to the observation of only low-temperature  $T_s$  anomaly transition peaks in the  $\epsilon_r$ - $T$  curves.<sup>22</sup> Similar features were also observed in other BNT-based ceramics modified with  $\text{NaNbO}_3$ ,  $\text{CaZrO}_3$ , and  $\text{NbTaO}_3$ .<sup>23–25</sup> It is noteworthy that the weak peaks ( $T_c$ ) appear in the high-temperature region [Fig. 4(b)–(d)], which is attributed to the contribution of the NN antiferroelectric phase.<sup>26</sup> The  $\epsilon_r$  gradually decreases with the increase in NN content. It can be explained by the increased compositional disorder, diffusion of polar nanoregions, and reorientation of ferroelectric domains, resulting in a dilution effect.<sup>27</sup> Furthermore, all samples exhibit relatively low dielectric losses ( $< 0.15$ ) from 20 °C to 450 °C, indicating their strong insulation capability over a wide temperature range.

In order to evaluate the ferroelectric properties of  $(0.8 - x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics, Fig. 5(a) and (b) illustrate the biaxial  $P$ - $E$  loops and variations of important parameters at 100 kV  $\text{cm}^{-1}$ . The sample with  $x = 0$  exhibits the highest  $P_{\text{max}}$  and  $\Delta P$ . However, this composition exhibits strong hysteresis and saturation polarization tendencies, which are not suitable for energy storage. After the introduction of NN, the  $P$ - $E$  loops exhibit a more elongated and linear shape. These elongated  $P$ - $E$  loops can reduce polarization losses during charging and discharging processes, thereby increasing energy storage density. Both  $P_{\text{max}}$  and  $\Delta P$  ( $P_{\text{max}} - P_r$ ) gradually decrease with

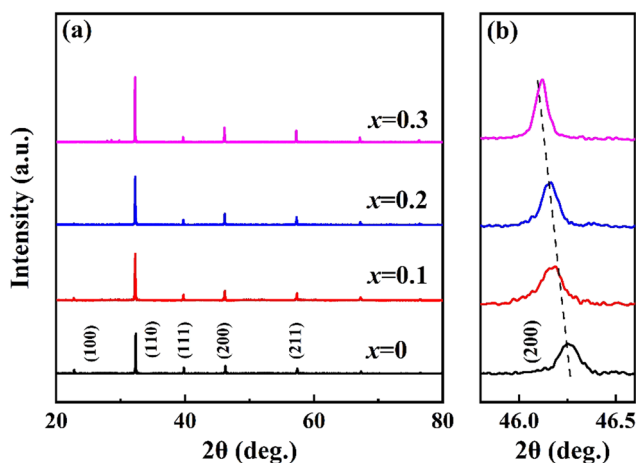


Fig. 2 (a) XRD pattern of  $(0.8 - x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics. (b) Partial enlargement of 45.8–46.6°.

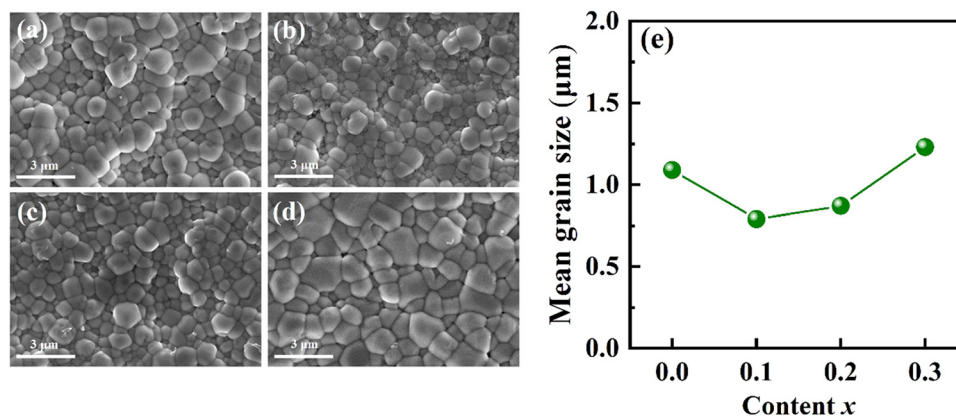


Fig. 3 (a)–(d) SEM images and (e) mean grain size with the increase of content  $x$  of  $(0.8 - x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics.

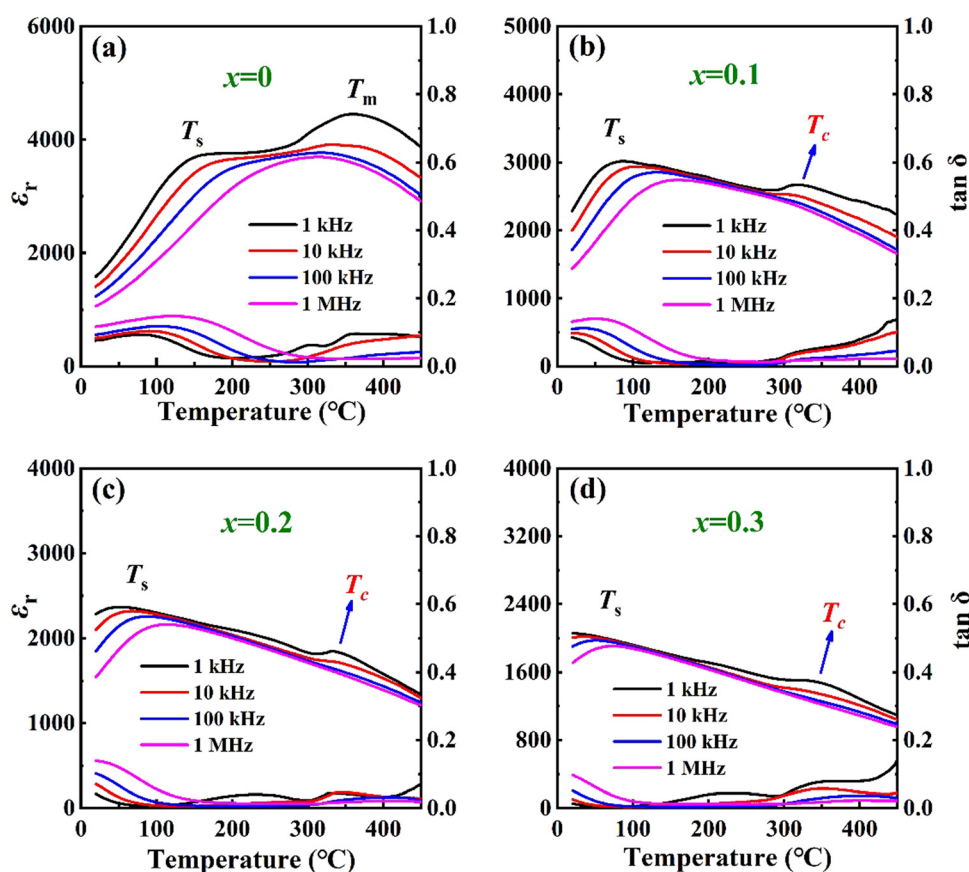


Fig. 4 (a)–(d) Temperature dependence of  $\epsilon_r$  and  $\tan \delta$  of  $(0.8 - x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics at different frequencies.

increasing  $x$  content, while  $P_r$  decreases initially and then stabilizes. These results are consistent with the observations from the  $\epsilon_r$ - $T$  curves, attributed to the disruption of partial long-range order in the system by A-site  $\text{Na}^+$  and B-site  $\text{Nb}^{5+}$ , thereby increasing the relaxor behaviors of ceramics. The formation of polar nanoregions is facilitated by the presence of local disorder, and the recovery of ferroelectric domains to their initial orientations upon the removal of external electric fields is made easier by the existence of local random electric

fields. Furthermore, the gradual increase in the content of the weakly polar  $P4bm$  phase, along with these factors, collectively contributes to the decrease in both  $P_{\text{max}}$  and  $P_r$ .

Fig. 6(a) displays the unipolar  $P$ - $E$  loops of  $(0.8 - x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramic samples under critical electric fields, in order to comprehensively evaluate their energy storage performance. It is obvious that the curvature of the  $P$ - $E$  loops decreases with an increase in the NN content due to the delayed saturation of polarization saturation. For samples with NN



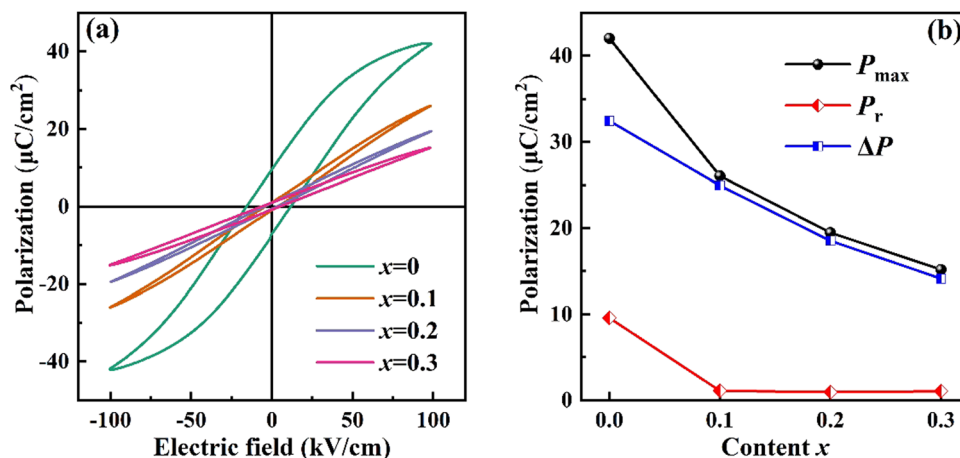


Fig. 5 (a) The bipolar  $P$ - $E$  loops at  $100 \text{ kV cm}^{-1}$  of  $(0.8-x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics and (b)  $P_{\text{max}}$ ,  $P_r$  and  $\Delta P$  ( $P_{\text{max}}-P_r$ ) as a function of  $x$  content.

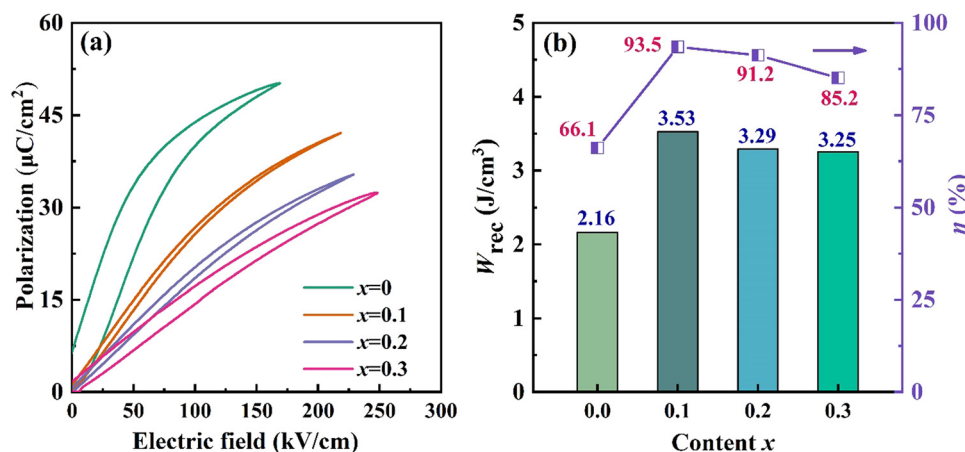


Fig. 6 (a) Unipolar  $P$ - $E$  loops at critical electric fields of  $(0.8-x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics and (b)  $W_{\text{rec}}$  and  $\eta$  are calculated from (a).

content ranging from 0 to 0.3, the  $E_b$  is measured to be 170, 220, 230 and  $250 \text{ kV cm}^{-1}$ , respectively. As expected, NN widened the bandgap of the system and improved its insulating properties, resulting in an enhanced  $E_b$ . The values for  $W_{\text{rec}}$  and  $\eta$  of  $(0.8-x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics were calculated from the unipolar  $P$ - $E$  loops and are presented in Fig. 6(b). The  $W_{\text{rec}}$  and  $\eta$  increased from  $2.16 \text{ J cm}^{-3}$  and 66.1% for  $x=0$  to  $3.53 \text{ J cm}^{-3}$  and 93.5% for  $x=0.1$ , respectively, resulting in a percentage change of 63.4% and 41.5%, respectively. However,  $W_{\text{rec}}$  and  $\eta$  slightly decreased with the further increase in  $x$ . This decrease is primarily attributed to the enhancement of relaxor behaviors and the merging of domain switching caused by the reinforcement of antiferroelectric phases. The delay of polarization saturation, the improvement of relaxation and the increase in  $E_b$  significantly enhance the energy storage capability of  $(0.8-x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics.

Fig. 7(a)-(f) show the unipolar  $P$ - $E$  loops,  $W_{\text{rec}}$ , and  $\eta$  of  $(1-x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics ( $x=0-0.2$ ) under different electric fields. The overall shape of the  $P$ - $E$  loops for all samples remained unchanged as the electric field increased, while  $W_{\text{rec}}$

almost linearly increased with the electric field. In the sample with  $x=0$ ,  $P_{\text{max}}$  increased from  $11.6 \mu\text{C cm}^{-2}$  at  $30 \text{ kV cm}^{-1}$  to  $50.2 \mu\text{C cm}^{-2}$  at  $170 \text{ kV cm}^{-1}$ . Owing to the presence of  $\text{Ba}^{2+}$  and  $\text{Zr}^{4+}$  with large ionic radii, the octahedral framework is expanded and sufficient space is provided for ion displacement, thus enabling a significant  $P_{\text{max}}$  to be achieved even at lower electric field. Although moderate  $W_{\text{rec}}$  ( $\sim 2.16 \text{ J cm}^{-3}$ ) was achieved in the  $0.8\text{BNT}-0.2\text{BZT}$  ceramic, due to the low  $\eta$  ( $\sim 66.1\%$ ), it is still not suitable for energy storage in dielectric capacitors. Consistent with the intended design of this work, the incorporation of NN has enhanced relaxation and compensated for polarization losses, while exhibiting high local polarity. Thus, the sample with  $x=0.1$  exhibits a large  $P_{\text{max}}$  ( $\sim 42.1 \mu\text{C cm}^{-2}$ ) at  $220 \text{ kV cm}^{-1}$ , a small  $P_r$  ( $\sim 1.1 \mu\text{C cm}^{-2}$ ), high  $W_{\text{rec}}$  ( $\sim 3.53 \text{ J cm}^{-3}$ ),  $\eta$  ( $\sim 93.5\%$ ), and  $W_{\text{rec}}/E$  ( $\sim 160.45 \text{ J (kV m}^{-2})$ ). Interestingly,  $\eta$  shows almost no dependence on the electric field, with a variation rate of less than 0.7%. It indicates that the  $\eta$  of  $0.7\text{BNT}-0.2\text{BZT}-0.1\text{NN}$  ceramic has outstanding electric field stability. In the sample with  $x=0.2$ , due to the enhancement of relaxation and antiferroelectricity, polar domains grow

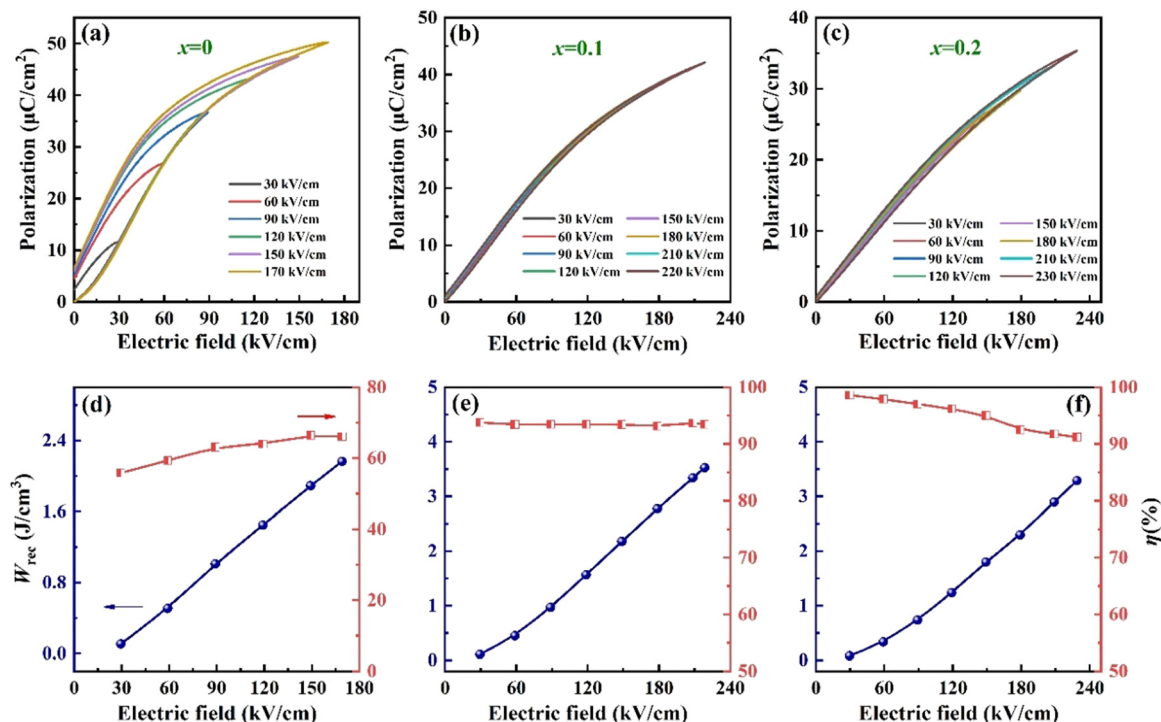


Fig. 7 (a)–(c) Unipolar  $P$ - $E$  loops under different electric fields, and (d)–(f) electric-field dependence of  $W_{\text{rec}}$  and  $\eta$ .

and merge under higher electric fields, leading to slightly lower  $W_{\text{rec}}$  and  $\eta$  compared to the sample with  $x = 0.1$ . Furthermore, a comparison with recent reported work on lead-free ceramic energy storage properties is presented in Table 1.<sup>8,23,27–37</sup> Our work is very significant as it not only maintains higher  $W_{\text{rec}}$  and  $\eta$ , but also has a leading  $W_{\text{rec}}/E$  under a low electric field.  $(1 - x)\text{BNT}-\text{BZT}-x\text{NN}$  ceramics will shine in future energy storage components of power systems.

Components used for pulse energy storage inevitably generate heat during operation and need to work in some harsh environments. Therefore, the temperature and frequency stability of dielectric energy storage ceramics are crucial in practical applications. Fig. 8(a) shows the  $P$ - $E$  loops of the  $0.7\text{BNT}-0.2\text{BZT}-0.1\text{NN}$  ceramic at different temperatures at  $150 \text{ kV cm}^{-1}$ . Fig. 8(b) summarizes the changes in energy storage parameters. As the

temperature increases,  $W_{\text{rec}}$  and  $\eta$  initially increase slightly and then decrease. It can be attributed to the increase in weakly polar phases, which leads to a slight increase in  $W_{\text{rec}}$  and  $\eta$  due to the decrease in  $P_{\text{max}}$  and  $P_r$ . As the temperature continues to rise,  $P_{\text{max}}$  further decreases along with an increase in  $P_r$  and leakage current, causing  $W_{\text{rec}}$  and  $\eta$  to decrease (see the inset of Fig. 8(a)). Within the range of  $20$ – $140^\circ\text{C}$ ,  $W_{\text{rec}}$  only decreases by  $7.2\%$ , and  $\eta$  remains above  $90\%$ . The energy storage performance of  $0.7\text{BNT}-0.2\text{BZT}-0.1\text{NN}$  ceramics at different frequencies under  $120 \text{ kV cm}^{-1}$  is shown in Fig. 8(c) and (d). The shape of the  $P$ - $E$  loops remains unchanged at different frequencies. With increasing test frequency, the ferroelectric domains cannot respond in time, so  $W_{\text{rec}}$  and  $\eta$  gradually decrease. The sample only experiences a  $5.3\%$  decrease in  $W_{\text{rec}}$  and maintains  $\eta$  of over  $85\%$  at frequencies ranging from  $1$  to  $100 \text{ Hz}$ . In conclusion,

Table 1 A comparison of the energy storage behaviors between this work and other reported lead-free ceramics in recent years

Composition	$W_{\text{rec}}$ ( $\text{J cm}^{-3}$ )	$\eta$ (%)	$E$ ( $\text{kV cm}^{-1}$ )	$W_{\text{rec}}/E$ ( $\text{J kV m}^{-2}$ )	Ref.
$0.7\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.3\text{NaNbO}_3: 7\%\text{CaZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$	4.93	93.3	410	120.24	8
$0.8(0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.06\text{BaTiO}_3)-0.2\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$	1.88	82.15	150	125.33	27
$\text{Bi}_{0.395}\text{Na}_{0.325}\text{Sr}_{0.245}\text{TiO}_3-\text{Ca}_{0.7}\text{La}_{0.2}\text{TiO}_3$	8.30	80	660	125.76	28
$0.94(\text{Na}_{0.88}\text{Sm}_{0.04}\text{NbO}_3)-0.06(\text{BiFeO}_3)$	4.00	80	460	86.96	29
$0.875\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-0.125\text{Bi}(\text{Sr}_{0.5}\text{Zr}_{0.5})\text{O}_3$	2.95	84	245	120.41	23
$0.925(\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3)-0.075\text{Bi}(\text{Zn}_{2/3}(\text{Ta}_{0.5}\text{Nb}_{0.5})_{1/3}\text{O}_3)$	4.05	87.4	307	131.92	30
$\text{Mn}-0.97\text{AgNbO}_3-0.03\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$	3.40	62	220	154.55	31
$0.85\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-0.15\text{Bi}(\text{Zn}_{2/3}\text{Ta}_{1/3})\text{O}_3$	6.70	92	600	111.67	32
$0.925\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3-0.025\text{BiMg}_{2/3}\text{Nb}_{1/3}\text{O}_3$	3.81	90.5	405	94.07	33
$0.7(\text{Bi}_{0.47}\text{La}_{0.03}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3-0.3\text{SrTi}_{0.875}\text{Nb}_{0.1}\text{O}_3$	4.2	89.3	380	110.53	34
$0.82\text{NaNbO}_3-0.18\text{Ba}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$	3.55	84.1	450	78.89	35
$0.8\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.2\text{Sm}_{1/3}\text{Sr}_{1/2}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	7.3	78.2	480	152.08	36
$0.9(0.6\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.4\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3)-0.1\text{SmFeO}_3$	7.2	86	430	167.44	37
$0.7\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.2\text{BaZr}_{0.3}\text{Ti}_{0.7}\text{O}_3-0.1\text{NaNbO}_3$	3.53	93.5	220	160.45	This work

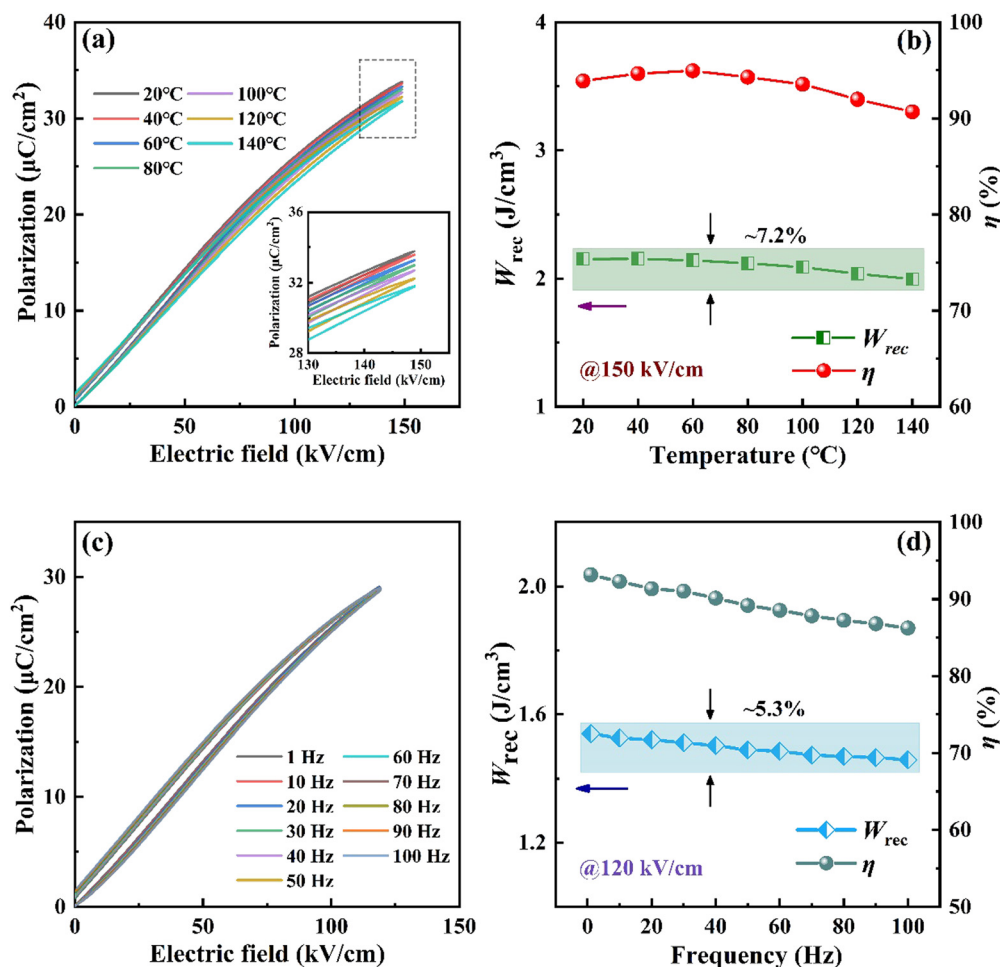


Fig. 8 Unipolar  $P$ - $E$  loops and energy storage properties of 0.7BNT-0.2BZT-0.1NN ceramic at (a) and (b) different temperatures and (c) and (d) different frequencies. The inset in (a) shows a localized magnified view of  $P_{\max}$ .

0.7BNT-0.2BZT-0.1NN ceramics exhibit excellent thermal/frequency stability, making them an ideal candidate material for high-performance ceramic capacitors.

## 4. Conclusions

In summary, we have successfully synthesized  $(0.8 - x)\text{BNT} - 0.2\text{BZT} - x\text{NN}$  relaxor ferroelectric ceramics with desirable energy storage behaviors using a solid-state reaction method. The regulation of key factors influencing energy storage properties, such as the dielectric relaxation behaviors and  $E_b$  of ceramics, has been significantly improved based on component design. The addition of NN to BNT-BZT results in an unordered polarization local structure with alternating weak and strong polar clusters, resulting in high  $P_{\max}$  and low  $P_r$  at the macroscopic level. The 0.7BNT-0.2BZT-NN ceramic exhibits excellent  $W_{\text{rec}}$  ( $\sim 3.53 \text{ J cm}^{-3}$ ), ultra-high  $\eta$  ( $\sim 93.5\%$ ) and leading  $W_{\text{rec}}/E$  ( $\sim 160.45 \text{ J (kV m}^{-2})$ ) at  $220 \text{ kV cm}^{-1}$ . In addition, this ceramic shows outstanding electric field stability ( $30\text{--}220 \text{ kV cm}^{-1}$ ,  $\Delta\eta < 0.7\%$ ), thermal stability ( $20\text{--}140^\circ\text{C}$ ,  $\Delta W_{\text{rec}} < 7.2\%$ ), and frequency stability ( $1\text{--}100 \text{ Hz}$ ,  $\Delta W_{\text{rec}} < 5.3\%$ ). These results

suggest that the 0.7BNT-0.2BZT-NN ceramic has great potential for application in advanced pulsed power systems.

## Author contributions

Jian Yang: writing – original draft preparation, data curation, methodology, conceptualization and supervision. Xiaolong Zhu: investigation, methodology, and writing – reviewing and editing. Haotian Wang: formal analysis and writing – reviewing and editing. Yixiao Zhang: writing – reviewing and editing. Pengfei Guan: methodology validation and writing – review and editing. Shiguang Yan: resources. Ming Zheng: formal analysis, methodology, funding acquisition, and writing – reviewing and editing.

## Data availability

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

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 L. T. Yang, X. Kong, F. Li, H. Hao, Z. X. Cheng, H. X. Liu, J. F. Li and S. J. Zhang, *Prog. Mater. Sci.*, 2019, **102**, 72–108.
- 2 G. Wang, Z. L. Lu, Y. Li, L. H. Li, H. F. Ji, A. Feteira, D. Zhou, D. W. Wang, S. J. Zhang and I. M. Reaney, *Chem. Rev.*, 2021, **121**, 6124–6172.
- 3 C. W. Sun, J. A. Alonso and J. J. Bian, *Adv. Energy Mater.*, 2021, **11**, 2000459.
- 4 X. H. Fan, J. Wang, H. Yuan, Z. H. Zheng, J. Zhang and K. J. Zhu, *J. Adv. Ceram.*, 2023, **12**, 649–680.
- 5 H. Pan, F. Li, Y. Liu, Q. H. Zhang, M. Wang, S. Lan, Y. P. Zheng, J. Ma, L. Gu, Y. Shen, P. Yu, S. J. Zhang, L. Q. Chen, Y. H. Lin and C. W. Nan, *Science*, 2019, **365**, 578–582.
- 6 X. P. Zhu, Y. F. Gao, P. Shi, R. R. Kang, F. Kang, W. J. Qiao, J. Y. Zhao, Z. Wang, Y. Yuan and X. J. Lou, *Nano Energy*, 2022, **98**, 107276.
- 7 Z. Y. Che, L. Ma, G. G. Luo, C. Xu, Z. Y. Cen, Q. Feng, X. Y. Chen, K. L. Ren and N. N. Luo, *Nano Energy*, 2022, **100**, 107484.
- 8 Y. Chen, Y. Huang, Y. D. Zuo, H. S. Wang, K. Liu, B. Y. Fan, Q. F. Zhang, G. Z. Zhang, S. L. Jiang and M. Shen, *J. Eur. Ceram. Soc.*, 2022, **42**, 6985–6996.
- 9 X. Z. Zhang, P. Zheng, L. L. Li, F. Wen, W. F. Bai, J. J. Zhang, L. Zheng and Y. Zhang, *Scr. Mater.*, 2022, **211**, 114514.
- 10 B. Y. Li, Z. N. Yan, X. F. Zhou, H. Qi, V. Koval, X. G. Luo, H. Luo, H. X. Yan and D. Zhang, *ACS Appl. Mater. Interfaces*, 2023, **15**, 4246–4256.
- 11 H. Liu, Z. Sun, J. Zhang, H. Luo, Y. Zhang, A. Sanson, M. Hinterstein, L. Liu, J. C. Neufeind and J. Chen, *J. Am. Chem. Soc.*, 2024, **146**, 3498–3507.
- 12 I. Levin, W. J. Laws, D. Wang and I. M. Reaney, *Appl. Phys. Lett.*, 2017, **111**, 212902.
- 13 W. J. Shi, Y. L. Yang, L. Y. Zhang, R. Y. Jing, Q. Y. Hu, D. O. Alikin, V. Y. Shur, J. H. Gao, X. Y. Wei and L. Jin, *Ceram. Int.*, 2022, **48**, 6512–6519.
- 14 Y. Ning, Y. Pu, C. Wu, S. Zhou, L. Zhang, J. Zhang, X. Zhang and Y. Shang, *J. Mater. Sci. Technol.*, 2023, **145**, 66–73.
- 15 Y. Zhang, A. W. Xie, J. Fu, X. W. Jiang, T. Y. Li, C. Zhou and R. Z. Zuo, *ACS Appl. Mater. Interfaces*, 2022, **14**, 40043–40051.
- 16 Z. C. Liu, P. R. Ren, C. B. Long, X. Wang, Y. H. Wan and G. Y. Zhao, *J. Alloys Compd.*, 2017, **721**, 538–544.
- 17 Y. Yin, J. R. Yu, Y. C. Tang, A. Z. Song, H. Liu, D. Yang, J. F. Li, L. Zhao and B. P. Zhang, *J. Mater. Sci.*, 2022, **8**, 611–617.
- 18 K. Y. Wang, W. H. Li, R. K. Zhao, X. G. Tang, S. Y. Zhang, Y. S. Zhang, J. Hu, Z. H. Shen, Y. P. Jiang and X. B. Guo, *Ceram. Int.*, 2024, **50**, 5276–5284.
- 19 X. Qiao, D. Wu, F. Zhang, M. Niu, B. Chen, X. Zhao, P. Liang, L. Wei, X. Chao and Z. Yang, *J. Eur. Ceram. Soc.*, 2019, **39**, 4778–4784.
- 20 X. B. Zhang, G. S. Chen, Z. X. Liu, X. L. Miao, Z. H. Zhang, D. Y. Chen, K. H. Lam, M. Zeng, X. S. Gao and J. M. Liu, *Chem. Eng. J.*, 2024, **480**, 147973.
- 21 C. B. Long, Z. Q. Su, H. M. Song, A. W. Xu, L. J. Liu, Y. Li, K. Zheng, W. Ren, H. J. Wu and X. D. Ding, *Energy Storage Mater.*, 2024, **65**, 103055.
- 22 W. X. Jia, Y. D. Hou, M. P. Zheng and M. K. Zhu, *J. Alloys Compd.*, 2017, **724**, 306–315.
- 23 W. X. Luo, M. X. Wu, Y. F. Han, X. Zhou, L. J. Liu, Q. W. He, P. R. Ren, H. M. Yang, H. Yang, Q. Wang, Z. H. Chen, X. H. Liang and Z. F. Chen, *J. Am. Ceram. Soc.*, 2023, **106**, 4723–4731.
- 24 M. Acosta, J. D. Zang, W. Jo and J. Rödel, *J. Eur. Ceram. Soc.*, 2012, **32**, 4327–4334.
- 25 Q. Xu, H. X. Liu, L. Zhang, J. Xie, H. Hao, M. H. Cao, Z. H. Yao and M. T. Lanagan, *RSC Adv.*, 2016, **6**, 59280–59291.
- 26 Z. Y. Liu, H. Q. Fan, J. S. Lu, Y. Q. Mao and Y. Zhao, *J. Eur. Ceram. Soc.*, 2018, **38**, 2871–2878.
- 27 Z. Li, J. Y. Zhang, C. B. Wang, Z. X. Wang, N. N. Lei, L. F. Zheng, D. J. Long, X. T. Wei, J. Zhang, Z. Wang, X. Yan, T. Ai, D. W. Wang and Y. H. Niu, *Ceram. Int.*, 2023, **49**, 38735–38742.
- 28 L. M. Tang, Z. Y. Yu, Z. B. Pan, J. H. Zhao, Z. Q. Fu, X. Q. Chen, H. H. Li, P. Li, J. J. Liu and J. W. Zhai, *Small*, 2023, **19**, 2302346.
- 29 X. J. Meng, Z. Y. Yang, Y. Yuan, B. Tang and S. R. Zhang, *Chem. Eng. J.*, 2023, **477**, 147097.
- 30 X. Z. Wang, Y. Huan, P. Y. Zhao, X. M. Liu, T. Wei, Q. W. Zhang and X. H. Wang, *J. Mater. Sci.*, 2021, **7**, 780–789.
- 31 Y. H. Xu, Y. Guo, Q. Liu, G. D. Wang, J. L. Bai, J. J. Tian, L. Lin and Y. Tian, *J. Eur. Ceram. Soc.*, 2020, **40**, 56–62.
- 32 D. Li, D. Zhou, D. Wang, W. C. Zhao, Y. Guo and Z. Q. Shi, *Adv. Funct. Mater.*, 2022, **32**, 2111776.
- 33 Z. H. Dai, J. L. Xie, Z. B. Chen, S. Zhou, J. J. Liu, W. G. Liu, Z. Z. Xi and X. B. Ren, *Chem. Eng. J.*, 2021, **410**, 128341.
- 34 L. K. Wu, L. M. Tang, Y. Z. Zhai, Y. L. Zhang, J. J. Sun, D. Hu, Z. B. Pan, Z. Su, Y. Zhang and J. J. Liu, *J. Mater. Sci.*, 2022, **8**, 537–544.
- 35 G. F. Liu, L. Chen, H. F. Yu, Z. F. Zhang, J. Wu, C. Zhou, H. Qi and J. Chen, *Chem. Eng. J.*, 2023, **474**, 145705.
- 36 Q. Zheng, B. Xie, Y. Tian, Q. Wang, H. Luo, Z. Liu and H. Zhang, *J. Mater. Sci.*, 2023, DOI: [10.1016/j.jmat.2023.10.005](https://doi.org/10.1016/j.jmat.2023.10.005).
- 37 Q. Zheng, B. Xie, Q. Wang, F. Xue, K. Guo, Z. Liu, P. Mao, W. Cao, H. Luo and H. Zhang, *Chem. Eng. J.*, 2024, **483**, 149154.