

Supplementary Materials

High-entropy and grain boundary engineering for enhanced energy storage performance in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based ceramics

Chongwen Yu¹, Dong-Xu Li¹, Zhenxiang Wang¹, Wenli Liu¹, You Zhang^{1,2}, Qi Zhou¹, Zhipeng Xu¹, Rui Qiu¹, Zong-Yang Shen¹

¹Jiangxi Key Laboratory of Advanced Ceramic Materials, China National Light Industry Key Laboratory of Functional Ceramic Materials, School of Materials Science and Engineering, Jingdezhen Ceramic University, Jingdezhen 333403, Jiangxi, China.

²Decorative Materials R&D Center, Ceramic Research Institute of Light Industry of China, Jingdezhen 333403, Jiangxi, China.

Correspondence to: Dr. Zong-Yang Shen, Jiangxi Key Laboratory of Advanced Ceramic Materials, China National Light Industry Key Laboratory of Functional Ceramic Materials, School of Materials Science and Engineering, Jingdezhen Ceramic University, Jingdezhen 333403, Jiangxi, China. E-mail: shenzongyang@jcu.edu.cn

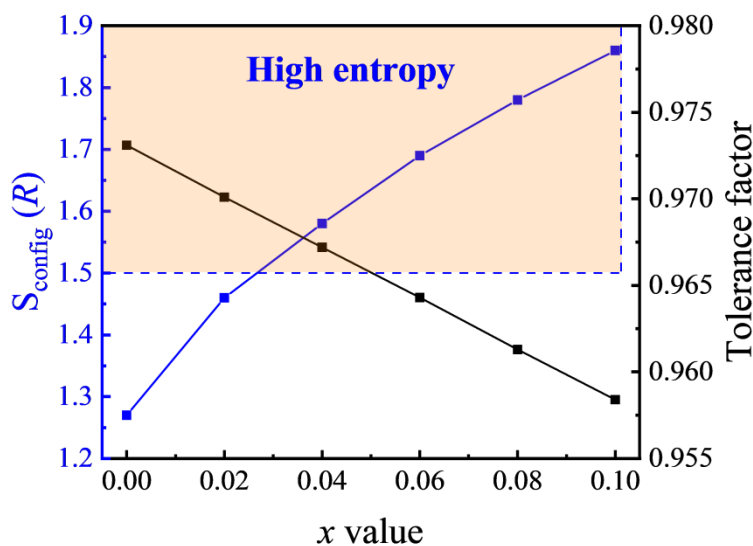


Figure S1. S_{config} and tolerance factors (t) of BNBST- x LMN ceramics as function of x value.

The tolerance factors (t) can be calculated by the following formula^[1]:

$$\bar{r}_A = \sum_{i=1}^m r_{Ai} x_{Ai}, \bar{r}_B = \sum_{j=1}^m r_{Bj} x_{Bj} \quad (S1)$$

$$t = \frac{\bar{r}_A + r_O}{\sqrt{2}(\bar{r}_B + r_O)} \quad (S2)$$

where, r_A , r_B , and r_O represent the radii of the A-site, B-site and O^{2-} ions, respectively.

As shown in **Figure S1**, t decreases as S_{config} increases, indicating that increase in conformational entropy maintains the octahedral tilt.

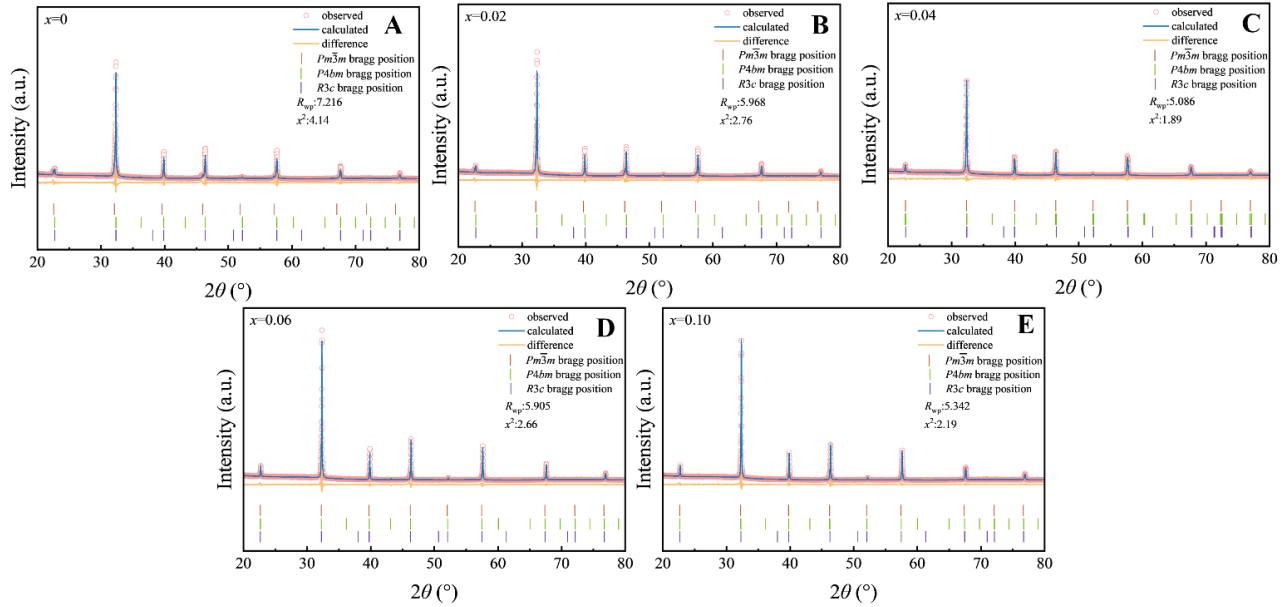


Figure S2. XRD refinement for representative (A) $x = 0$, (B) $x = 0.02$, (C) $x = 0.04$, (D) $x = 0.06$ and (E) $x = 0.10$ ceramics, respectively.

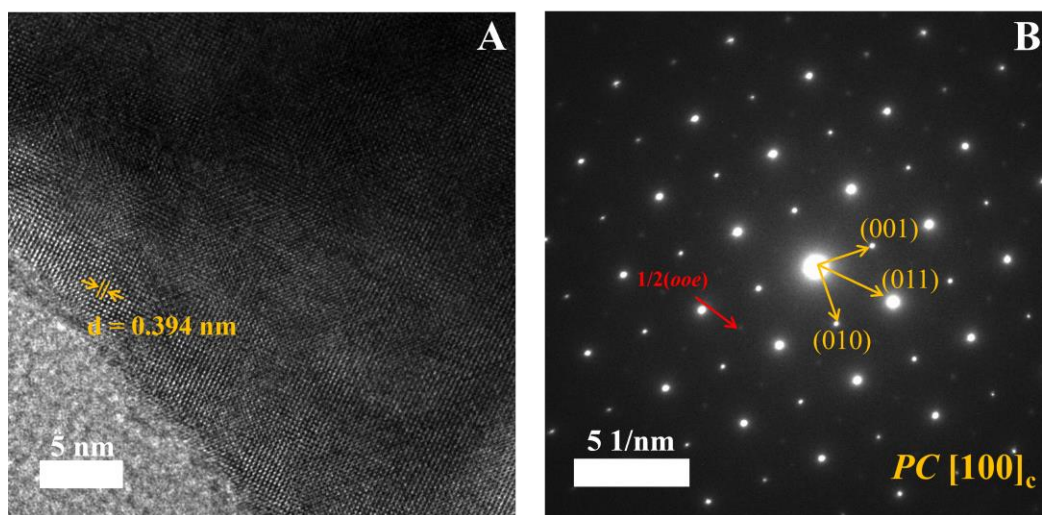


Figure S3. (A) HR-TEM images and (B) SAED patterns along the $[100]_c$ directions of $x = 0.08$ ceramic.

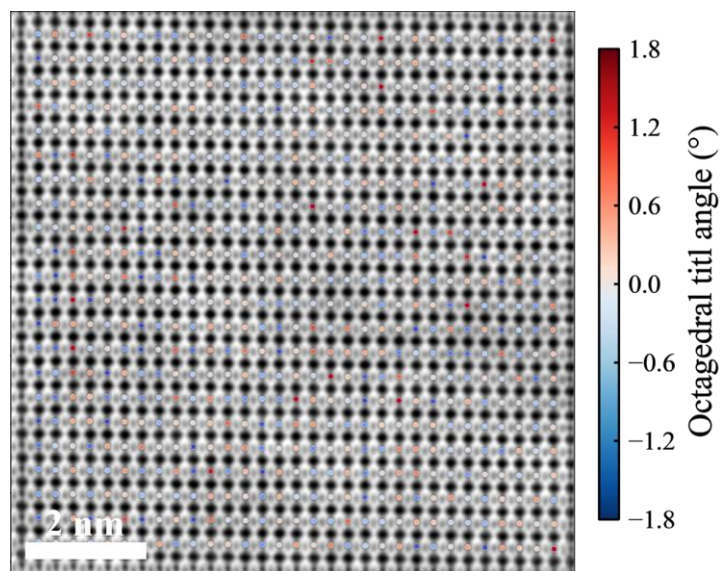


Figure S4. Oxygen octahedron tilt angles calculated using ABF imaging.

As shown in **Figure S4**, the alternating red and blue color contrasts indicate the random tilting of the oxygen octahedra.

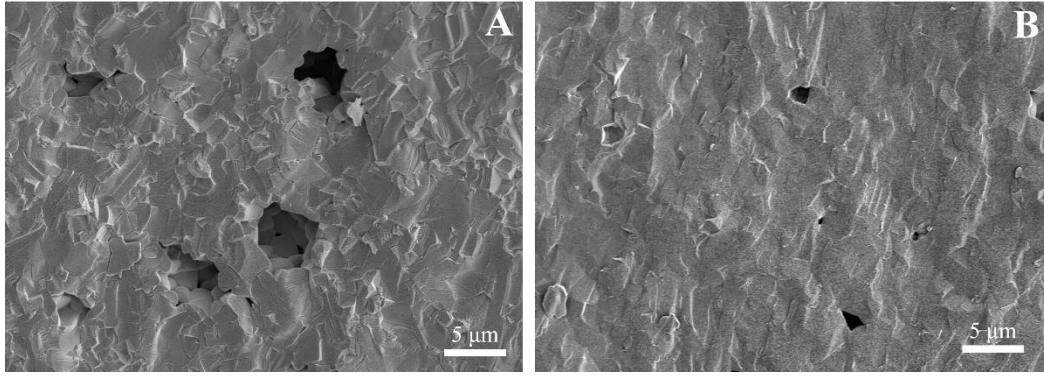


Figure S5. The cross-sectional SEM images of (A) pure BNBST and (B) BNBST-0.08LMN ceramics.

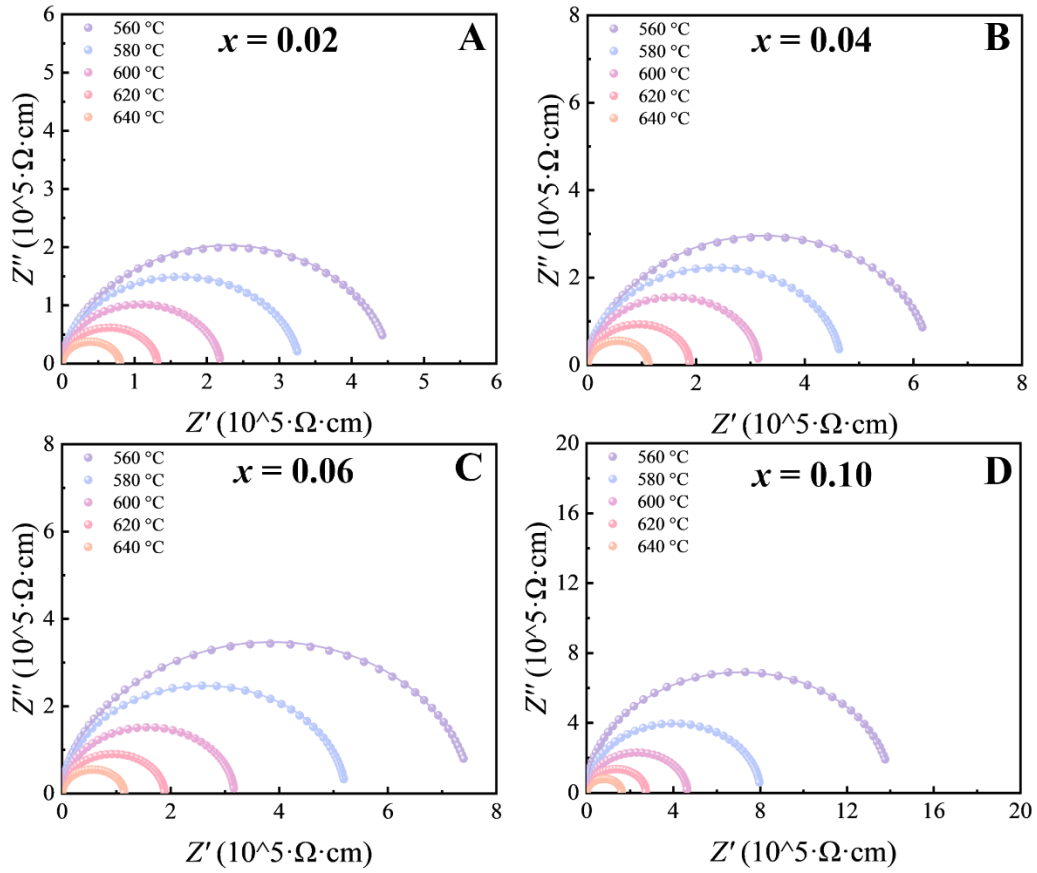


Figure S6. Complex impedance spectra of (A) $x = 0.02$, (B) $x = 0.04$, (C) $x = 0.06$, and (D) $x = 0.10$ ceramics at different temperatures.

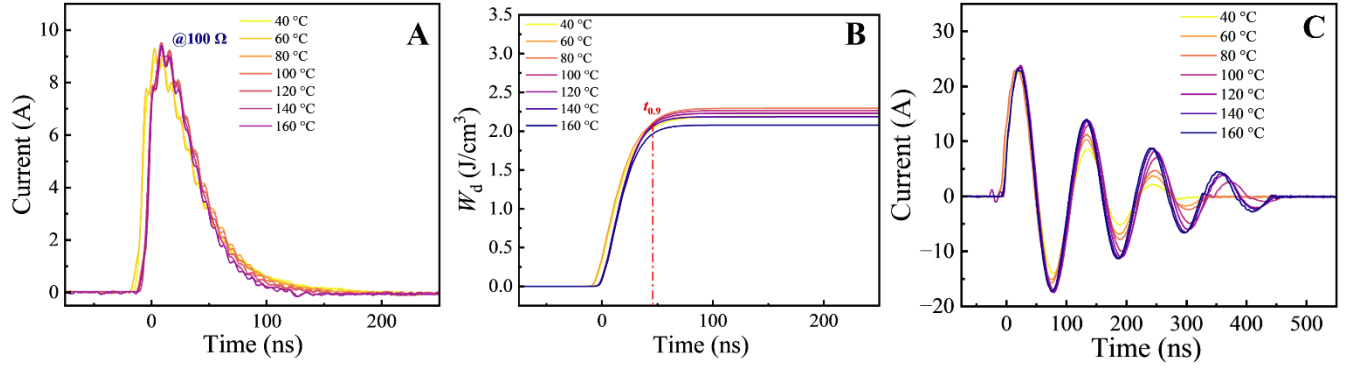


Figure S7. (A) Overdamped discharge curves and corresponding (B) W_d of BNBST-0.08LMN ceramic under 200 kV/cm at different temperatures. (C) Underdamped discharge curves of BNBST-0.08LMN ceramic under 200 kV/cm at different temperatures.

Table S1. The ESP of some reported lead-free ceramics

Systems	W_{rec} (J/cm ³)	E_b (kV/cm)	Ref
(1-x)(Ba _{0.8} Sr _{0.2})TiO ₃ - xBi(Zn _{2/3} Nb _{1/3})O ₃	1.62	225	[2]
(1-x)BaTiO ₃ -xBi(Mg _{1/2} Hf _{1/2})O ₃	3.38	240	[3]
(1-x)BaTiO ₃ - x[0.9(Sr _{0.7} Bi _{0.2})TiO ₃ - 0.1Bi(Mg _{0.5} Zr _{0.5})O ₃]	3.99	370	[4]
(1-x)Ba _{0.85} Ca _{0.15} Zr _{0.1} Ti _{0.9} O ₃ - xBiMg _{2/3} Nb _{1/3} O ₃	3.80	405	[5]

0.4BiScO ₃ -(0.6-x)BaTiO ₃ - xNaNbO ₃	4.59	410	[6]
0.45(Na _{0.5} Bi _{0.5})TiO ₃ - 0.55(Sr _{0.7} Bi _{0.2})TiO ₃ -xAlN	5.50	360	[7]
0.9Bi _{0.5} Na _{0.5} TiO ₃ - 0.1Bi _{0.2} Sr _{0.7} TiO ₃ -xNaNbO ₃	3.28	190	[8]
(Bi _{0.47} Sm _{0.03} Na _{0.5-x}) _{0.94} Ba _{0.06} TiO ₃	4.61	290	[9]
(Na _{0.4-0.5x} Sr _x K _{0.1} Bi _{0.5-} 0.5x)(Ti _{0.8} Zr _{0.05} Sn _{0.1} Hf _{0.05})O ₃	7.30	580	[10]
Na _{0.325} Bi _{0.395} Sr _{0.245} TiO ₃ -xBN	5.28	640	[11]
Na _{0.4} K _{0.1} Bi _{0.5} TiO ₃ @SrZrO ₃ - xBiMg _{0.5} Sn _{0.5} O ₃ @SiO ₂	3.91	301	[12]
Ba _{0.12} Na _{0.3} Bi _{0.3} Sr _{0.28-} 1.5x□0.5xSm _x TiO ₃	2.10	120	[13]
Ba _{0.105} Na _{0.325} Sr _{0.245-} 1.5x□0.5xBi _{0.325+x} TiO ₃	1.79	110	[14]
(1-x)(0.75Na _{0.5} Bi _{0.5} TiO ₃ - 0.25SrTiO ₃)-xLa(Mg _{2/3} Ta _{1/3})O ₃	3.17	246	[15]

(1- x)(Na _{0.2} Bi _{0.2} Ba _{0.2} Sr _{0.2} Ca _{0.2})TiO ₃ - x NaNbO ₃	3.50	310	[16]
0.5(Bi _{0.5} Na _{0.5})TiO ₃ -0.5SrTiO ₃ - x CuO	2.19	230	[17]
(1- x)[0.76Bi _{0.5} Na _{0.5} TiO ₃ - 0.24NaNbO ₃]- x Sr _{0.7} Bi _{0.2} TiO ₃	3.12	200	[18]
(Na _{0.2} Bi _{0.2} Ca _{0.2} Sr _{0.2} Ba _{0.2})TiO ₃	1.32	110	[19]
SCS-derived Sr _{0.7} Bi _{0.2} TiO ₃	5.20	543	[20]
(1- x)(Bi _{0.47} La _{0.03} Na _{0.5}) _{0.94} Ba _{0.06} TiO ₃ - x SrTi _{0.875} Nb _{0.1} O ₃	4.18	380	[21]
(Sr _{1-x-y-2ϕ} Na _y Bi _x Ca _{ϕ})TiO ₃	5.98	440	[22]
Na _{0.70} Sr _{0.15} Nb _{0.75} Ta _{0.25} O ₃	10.37	850	[23]
0.94NaNbO ₃ -0.06CaHfO ₃ - $x\%$ MnO ₂	1.68	240	[24]
(1- x)K _{0.5} Na _{0.5} NbO ₃ - x Sr _{0.7} La _{0.2} ZrO ₃	5.29	490	[25]

$(1-x)(0.92\text{NaNbO}_3-$	7.04	646	[26]
$0.08\text{BiNi}_{0.67}\text{Ta}_{0.33}\text{O}_3)-x\text{CaTiO}_3$			
$(\text{Na}_{0.7-3y}\text{Bi}_{0.1}\text{Yb}_y\text{Tm}_y)(\text{Nb}_{1-}$	5.37	395	[27]
$_{13x/5}\text{Zr}_x\text{Ta}_x\text{Hf}_x)\text{O}_3$			
$(1-$	6.50	450	This work
$x)(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.7}(\text{Ba}_{0.3}\text{Sr}_{0.7})_{0.3}\text{TiO}_3-$			
$x\text{La}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$			

Reference

1. Reaney, I.M.; Enrico L. Colla, E.L.C.; Nava Setter, N.S. Dielectric and Structural Characteristics of Ba- and Sr-based Complex Perovskites as a Function of Tolerance Factor. *Jpn. J. Appl. Phys.* **1994**, *33*, 3984, doi:10.1143/jjap.33.3984.
2. Zhang, L.; Pang, L.X.; Li, W.B.; Zhou, D. Extreme high energy storage efficiency in perovskite structured $(1-x)(\text{Ba}_{0.8}\text{Sr}_{0.2})\text{TiO}_3-x\text{Bi}(\text{Zn}_{2/3}\text{Nb}_{1/3})\text{O}_3$ ($0.04 \leq x \leq 0.16$) ceramics. *J. Eur. Ceram. Soc.* **2020**, *40*, 3343-3347, doi:10.1016/j.jeurceramsoc.2020.03.015.
3. Liu, Z.G.; Li, M.D.; Tang, Z.H.; Tang, X.G. Enhanced energy storage density and efficiency in lead-free $\text{Bi}(\text{Mg}_{1/2}\text{Hf}_{1/2})\text{O}_3$ -modified BaTiO_3 ceramics. *Chem. Eng. J.* **2021**, *418*, 129379, doi:10.1016/j.cej.2021.129379.

4. Hu, D.; Pan, Z.; Tan, X.; Yang, F.; Ding, J.; Zhang, X.; Li, P.; Liu, J.; Zhai, J.; Pan, H. Optimization the energy density and efficiency of BaTiO₃-based ceramics for capacitor applications. *Chem. Eng. J.* **2021**, *409*, 127375, doi:10.1016/j.cej.2020.127375.
5. Dai, Z.; Xie, J.; Chen, Z.; Zhou, S.; Liu, J.; Liu, W.; Xi, Z.; Ren, X. Improved energy storage density and efficiency of (1-x)Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O₃-xBiMg_{2/3}Nb_{1/3}O₃ lead-free ceramics. *Chem. Eng. J.* **2021**, *410*, 128341, doi:10.1016/j.cej.2020.128341.
6. Joseph, J.; Cheng, Z.; Zhang, S. NaNbO₃ modified BiScO₃-BaTiO₃ dielectrics for high-temperature energy storage applications. *J. Materiomics* **2022**, *8*, 731-738, doi:10.1016/j.jmat.2022.04.005.
7. You, D.; Tan, H.; Yan, Z.; Gao, H.; Chen, S.; Ma, W.; Fan, P.; Tran, N.-M.-A.; Liu, Y.; Salamon, D.; et al. Enhanced Dielectric Energy Storage Performance of 0.45Na_{0.5}Bi_{0.5}TiO₃-0.55Sr_{0.7}Bi_{0.2}TiO₃/AlN 0–3 Type Lead-Free Composite Ceramics. *ACS Appl. Mater. Interfaces* **2022**, *14*, 17652-17661, doi:10.1021/acsami.2c01406.
8. Yang, Y.; Liu, Z.; Guo, K.; Mao, P.; Xie, B.; Liang, B.; Mao, Y.; Sun, H. Deciphering the relationships among phase boundary, domain structure, and excellent electrical properties of ternary Bi_{0.5}Na_{0.5}TiO₃-Bi_{0.2}Sr_{0.7}TiO₃-NaNbO₃ ferroelectrics. *Ceram. Int.* **2024**, *50*, 48174-48182, doi:10.1016/j.ceramint.2024.09.167.
9. Shen, Y.; Wu, L.; Zhao, J.; Liu, J.; Tang, L.; Chen, X.; Li, H.; Su, Z.; Zhang, Y.; Zhai, J.; et al. Constructing novel binary Bi_{0.5}Na_{0.5}TiO₃-based composite ceramics for excellent energy storage performances via defect engineering. *Chem. Eng. J.* **2022**, *439*, 135762, doi:10.1016/j.cej.2022.135762.

10. Shi, W.; Meng, M.; Zhang, L.; Chen, F.; Yang, Y.; Shur, V.; Jing, R.; Liu, G.; Jin, L. High-entropy engineering of BNKT-based ceramics enables ultrastable dielectric energy storage. *Chem. Eng. J.* **2025**, 522, 167352, doi:10.1016/j.cej.2025.167352.
11. Tang, L.; Pan, Z.; Zhao, J.; Shen, Y.; Chen, X.; Li, H.; Li, P.; Liu, J.; Zhai, J. Nanoscale grain sizes in BNT-based ceramics with superb energy storage performances via coating boron nitride nanosheets. *Chem. Eng. J.* **2023**, 455, 140524, doi:10.1016/j.cej.2022.140524.
12. Zhang, X.; Zhao, L.; Qiu, Y.; Wang, Y.; Fan, Y.; Liu, X.; Cui, B. Achieving comprehensive temperature-stable energy storage properties in core-shell $\text{Na}_{0.4}\text{K}_{0.1}\text{Bi}_{0.5}\text{TiO}_3@(\text{SrZrO}_3\text{-BiMg}_{0.5}\text{Sn}_{0.5}\text{O}_3)@ \text{SiO}_2$ ceramics via a multi-scale synergistic optimization. *Chem. Eng. J.* **2023**, 462, 142251, doi:10.1016/j.cej.2023.142251.
13. Li, D.-X.; Deng, W.; Shen, Z.-Y.; Li, Z.; Zeng, X.; Shi, X.; Zhang, Y.; Luo, W.; Song, F.; Wu, C.F. Aliovalent Sm-doping enables BNT-based relaxor ferroelectric ceramics with > 90% energy efficiency. *J. Adv. Ceram.* **2024**, 13, 2043-2050, doi:10.26599/jac.2024.9220999.
14. Li, Z.; Li, D.-X.; Shen, Z.-Y.; Zeng, X.; Song, F.; Luo, W.; Wang, X.; Wang, Z.; Li, Y. Remarkably enhanced dielectric stability and energy storage properties in BNT-BST relaxor ceramics by A-site defect engineering for pulsed power applications. *J. Adv. Ceram.* **2022**, 11, 283-294, doi:10.1007/s40145-021-0532-8.
15. Wu, C.; Qiu, X.; Chen, L.; Liu, C.; Zhao, H.; Ge, W.; Liu, Z.; Yao, M. A strategy to achieve high energy storage performance under a relatively low electric field in NBT-based ceramics. *J. Alloys Compd.* **2022**, 910, 164851, doi:10.1016/j.jallcom.2022.164851.

16. Ning, Y.; Pu, Y.; Wu, C.; Zhou, S.; Zhang, L.; Zhang, J.; Zhang, X.; Shang, Y. Enhanced capacitive energy storage and dielectric temperature stability of A-site disordered high-entropy perovskite oxides. *J. Mater. Sci. Technol.* **2023**, *145*, 66-73, doi:10.1016/j.jmst.2022.10.053.
17. Zhang, F.; Qiao, X.; Shi, Q.; Chao, X.; Yang, Z.; Wu, D. High energy storage density realized in Bi_{0.5}Na_{0.5}TiO₃-based relaxor ferroelectric ceramics at ultralow sintering temperature. *J. Eur. Ceram. Soc.* **2021**, *41*, 368-375, doi:10.1016/j.jeurceramsoc.2020.07.067.
18. Zhao, X.; Bai, W.; Ding, Y.; Wang, L.; Wu, S.; Zheng, P.; Li, P.; Zhai, J. Tailoring high energy density with superior stability under low electric field in novel (Bi_{0.5}Na_{0.5})TiO₃-based relaxor ferroelectric ceramics. *J. Eur. Ceram. Soc.* **2020**, *40*, 4475-4486, doi:10.1016/j.jeurceramsoc.2020.05.078.
19. Wang, T.; Li, Y.; Zhang, X.; Zhang, D.; Gong, W. Simultaneous excellent energy storage density and efficiency under applied low electric field for high entropy relaxor ferroelectric ceramics. *Mater. Res. Bull.* **2023**, *157*, 112024, doi:10.1016/j.materresbull.2022.112024.
20. Zuo, C.; Yang, S.; Cao, Z.; Yu, H.; Wei, X. Excellent energy storage and hardness performance of Sr_{0.7}Bi_{0.2}TiO₃ ceramics fabricated by solution combustion-synthesized nanopowders. *Chem. Eng. J.* **2022**, *442*, 136330, doi:10.1016/j.cej.2022.136330.
21. Wu, L.; Tang, L.; Zhai, Y.; Zhang, Y.; Sun, J.; Hu, D.; Pan, Z.; Su, Z.; Zhang, Y.; Liu, J. Enhanced energy-storage performance in BNT-based lead-free dielectric ceramics via introducing SrTi_{0.875}Nb_{0.1}O₃. *J. Materiomics* **2022**, *8*, 537-544, doi:10.1016/j.jmat.2022.01.003.

22. Liu, L.; Liu, Y.; Hao, J.; Chen, J.; Li, P.; Chen, S.; Fu, P.; Li, W.; Zhai, J. Multi-scale collaborative optimization of SrTiO₃-based energy storage ceramics with high performance and excellent stability. *Nano Energy* **2023**, *109*, 108275, doi:10.1016/j.nanoen.2023.108275.
23. Lv, Z.; Han, B.; Liu, Z.; Guo, S.; Dai, K.; Cao, F.; Hu, Z.; Wang, G. Achieving excellent energy storage properties in lead-free ceramics via competing FE/AFE phase coexistence. *Energy Storage Mater.* **2025**, *77*, 104205, doi:10.1016/j.ensm.2025.104205.
24. Yin, Y.; Yu, J.R.; Tang, Y.C.; Song, A.Z.; Liu, H.; Yang, D.; Li, J.F.; Zhao, L.; Zhang, B.-P. Enhanced energy storage properties and antiferroelectric stability of Mn-doped NaNbO₃-CaHfO₃ lead-free ceramics: Regulating phase structure and tolerance factor. *J. Materiomics* **2022**, *8*, 611-617, doi:10.1016/j.jmat.2021.11.013.
25. Chai, Q.; Zhang, F.; Zhou, Q.; Peng, Z.; Wu, D.; Liang, P.; Wei, L.; Chao, X.; Yang, Z. Superior Energy Storage Properties and Optical Transparency in K_{0.5}Na_{0.5}NbO₃-Based Dielectric Ceramics via Multiple Synergistic Strategies. *Small* **2023**, *19*, 2207464, doi:10.1002/smll.202207464.
26. Wu, S.; Fu, B.; Zhang, J.; Du, H.; Zong, Q.; Wang, J.; Pan, Z.; Bai, W.; Zheng, P. Superb Energy Storage Capability for NaNbO₃-Based Ceramics Featuring Labyrinthine Submicro-Domains with Clustered Lattice Distortions. *Small* **2023**, *19*, 2303915, doi:10.1002/smll.202303915.
27. Zeng, X.; Lin, J.; Chen, Y.; Wang, S.; Zhou, P.; Yu, F.; Wu, X.; Gao, M.; Zhao, C.; Lin, T.; et al. Superior Energy Storage Capability and Fluorescence Negative Thermal Expansion of NaNbO₃-Based Transparent Ceramics by Synergistic Optimization. *Small* **2024**, *20*, 2309992, doi:10.1002/smll.202309992.