

Supporting Information

Collaboratively improved energy density and efficiency in NaNbO₃-based lead-free relaxor ferroelectrics via enhancing antiferrodistortion

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Table S1. Comparison of the charge-discharge performances between the $x = 0.04$ ceramic and some recently reported lead-free dielectric ceramics.

Compositions	P_D (MW/cm ³)	W_D (J/cm ³)	$t_{0.9}$ (ns)	E (kV/mm)	Ref.
Na _{0.7} Bi _{0.1} NbO ₃	62.5	0.56	155	10	1
0.92NaNbO ₃ -0.08Bi(Mg _{0.5} Ti _{0.5})O ₃ +MnO ₂	63.7	1.17	85	20	2
0.78NaNbO ₃ -0.22Ba(Mg _{1/3} Nb _{2/3})O ₃	47.6	0.47	45	14	3
0.68NaNbO ₃ -0.32(Bi _{0.5} Li _{0.5})TiO ₃	133.7	3.83	70	30	4
0.9NaNbO ₃ -0.1Bi(Ni _{1/2} Sn _{1/2})O ₃	100.5	1.11	43.6	20	5
0.85K _{0.5} Na _{0.5} NbO ₃ -0.15(K _{0.7} Bi _{0.3})NbO ₃	47.7	-	-	12	6
0.9(K _{0.5} Na _{0.5})NbO ₃ -0.1Bi(Zn _{2/3} Nb _{1/3})O ₃	154	2.5	-	25	7
0.91K _{0.5} Na _{0.5} NbO ₃ -0.09SrZrO ₃	-	1.41	126	25	8
Mn-doped Ag _{0.97} La _{0.01} NbO ₃	390	-	-	15	9
Ag _{0.97} Nd _{0.01} NbO ₃	54	0.56	59.2	18	10
0.85Bi _{0.5} K _{0.5} TiO ₃ -0.15Ba(Mg _{1/3} Nb _{2/3})O ₃	-	0.49	120	14	11
0.7(Na _{0.5} Bi _{0.5}) _{0.7} Sr _{0.3} TiO ₃ -0.3Sr(Ti _{0.85} Zr _{0.15})O ₃	41.2	1.17	125.6	12	12
0.8Bi _{0.5} Na _{0.5} TiO ₃ -0.2SrNb _{0.5} Al _{0.5} O ₃	131.75	-	-	30	13
0.93Na _{0.5} Bi _{0.5} TiO ₃ -0.07LiTaO ₃	22	0.52	100	10	14
0.75Bi _{0.58} Na _{0.42} TiO ₃ -0.25SrTiO ₃	147.04	1.9	118	30	15
0.5Na _{0.5} Bi _{0.5} TiO ₃ -0.5Sr _{0.85} Sm _{0.1} TiO ₃	188.6	1.5	69	18	16
0.6(Bi _{0.5} K _{0.5})TiO ₃ -0.3BaTiO ₃ -0.1NaNbO ₃	103.2	2.40	130	22	17
0.57BiFeO ₃ -0.33BaTiO ₃ -0.10NaNbO ₃	-	2.4	97	20	18
0.70(0.67BiFeO ₃ -0.33BaTiO ₃)-0.30(Sr _{0.7} Bi _{0.2})TiO ₃	14.46	0.18	250	10	19
0.7Ba _{0.85} Ca _{0.15} Zr _{0.1} Ti _{0.9} O ₃ -0.3Sr _{0.7} Bi _{0.2} TiO ₃	237.83	1.97	103	30	20
0.62Sr _{0.7} Bi _{0.2} TiO ₃ -0.38K _{0.5} Bi _{0.5} TiO ₃	49.5	1.81	360	22	21
Sr _{0.35} Bi _{0.35} K _{0.25} TiO ₃ +Er ₂ O ₃	39.6	1.51	325	20	22
Ca _{0.5} Sr _{0.5} Ti _{0.85} Zr _{0.15} O ₃	17.6	0.19	22	12	23
0.35BiFeO ₃ -0.65SrTiO ₃	280	3.3	166	35	24
$x = 0.04$	340	4.5	27	37.5	This work

Table S2. Refined structural parameters of (0.9- x)NN-0.1BT- x BF ceramic powders.

x	Space group	Lattice parameters	V	R_{wp}	R_p	χ^2
			(Å ³)	(%)	(%)	
0	$P2_1ma$	a=5.4901(2), b=7.7609(2) Å, c=5.4890(1) Å, $\alpha=\beta=\gamma=90^\circ$	233.876(9)	5.90	3.92	3.81
0.04	$P2_1ma$	a=5.4995(2), b=7.7704(2) Å, c=5.4957(1) Å, $\alpha=\beta=\gamma=90^\circ$	234.852(12)	5.54	3.87	3.19

References

- [1] M.X. Zhou, R.H. Liang, Z.Y. Zhou, X.L. Dong, Superior energy storage properties and excellent stability of novel NaNbO₃-based lead-free ceramics with A-site vacancy obtained via a Bi₂O₃ substitution strategy, *J. Mater. Chem. A* 2018, **6**, 17896-17904.
- [2] A. Tian, R.Z. Zuo, H. Qi, M. Shi, Large energy-storage density in transition-metal oxide modified NaNbO₃-Bi(Mg_{1/2}Ti_{2/3})O₃ lead-free ceramics through regulating antiferroelectric phase structure, *J. Mater. Chem. A* 2020, **8**, 8352-8359.
- [3] C.C. Sun, X.L. Chen, J.P. Shi, F.H. Pang, X.Y. Dong, H.Y. Chen, K.G. Wang, X.J. Zhou, H.F. Zhou, Simultaneously with large energy density and high efficiency achieved in NaNbO₃-based relaxor ferroelectric ceramics, *J. Eur. Ceram. Soc.* 2021, **41**, 1891-1903.
- [4] A.W. Xie, R.Z. Zuo, Z.L. Qiao, Z.Q. Fu, T.F. Hu, L.F. Fei, NaNbO₃-(Bi_{0.5}Li_{0.5})TiO₃ lead-free relaxor ferroelectric capacitors with superior energy-storage performances via multiple synergistic design, *Adv. Energy Mater.* 2021, 2101378.
- [5] X.Y. Dong, X. Li, X. L. Chen, H.Y. Chen, C.C. Sun, J.P. Shi, F.H. Pang, H.F. Zhou, High energy storage density and power density achieved simultaneously in NaNbO₃-based lead-free ceramics via antiferroelectricity enhancement, *J. Materiomics* 2021, **7**, 629-639.
- [6] M. Zhang, H.B. Yang, D. Li, Y. Lin, Excellent energy density and power density achieved in K_{0.5}Na_{0.5}NbO₃-based ceramics with high optical transparency, *J. Alloy. Compd.* 2020, **829**, 154565.
- [7] Y. Huan, T. Wei, X.Z. Wang, X.M. Liu, P.Y. Zhao, X.H. Wang, Achieving ultrahigh energy storage efficiency in local-composition gradient-structured ferroelectric ceramics, *Chem. Eng. J.* 2021, **425**, 129506.

- [8] X.D. Ren, L. Jin, Z.H. Peng, B. Chen, X.S. Qiao, D. Wu, G.R. Li, H.L. Du, Z.P. Yang, X.L. Chao, Regulation of energy density and efficiency in transparent ceramics by grain refinement, *Chem. Eng. J.* 2020, **390**, 124566.
- [9] C.H. Xu, Z.Q. Fu, Z. Liu, L. Wang, S.G. Yan, X.F. Chen, F. Cao, X.L. Dong, G.S. Wang, La/Mn codoped AgNbO₃ lead-free antiferroelectric ceramics with large energy density and power density, *ACS Sustainable Chem. Eng.* 2018, **6**, 16151-16159.
- [10] P. Shi, X.J. Wang, X.J. Lou, C. Zhou, Q.D. Liu, L.Q. He, S. Yang, X.X. Zhang, Significantly enhanced energy storage properties of Nd³⁺ doped AgNbO₃ lead-free antiferroelectric ceramics, *J. Alloy. Compd.* 2021, **877**, 160162.
- [11] F. Li, X. Hou, T.Y. Li, R.J. Si, C.C. Wang, J.W. Zhai, Fine-grain induced outstanding energy storage performance in novel Bi_{0.5}K_{0.5}TiO₃-Ba(Mg_{1/3}Nb_{2/3})O₃ ceramics via a hot-pressing strategy, *J. Mater. Chem. C* 2019, **7**, 12127-12138.
- [12] D. Li, Y. Lin, M. Zhang, H.B. Yang, Achieved ultrahigh energy storage properties and outstanding charge-discharge performances in (Na_{0.5}Bi_{0.5})_{0.7}Sr_{0.3}TiO₃-based ceramics by introducing a linear additive, *Chem. Eng. J.* 2020, **392**, 123729.
- [13] F. Yan, X.F. Zhou, X. He, H.R. Bai, S.H. Wu, B. Shen, J.W. Zhai, Superior energy storage properties and excellent stability achieved in environment-friendly ferroelectrics via composition design strategy, *Nano Energy* 2020, **75**, 105012.
- [14] L. Zhang, Y.P. Pu, M. Chen, T.C. Wei, X. Peng, Novel Na_{0.5}Bi_{0.5}TiO₃ based, lead-free energy storage ceramics with high power and energy density and excellent high-temperature stability, *Chem. Eng. J.* 2020, **383**, 123154.

- [15] F. Yan, K.W. Huang, T. Jiang, X.F. Zhou, Y.J. Shi, G.L. Ge, B. Shen, J.W. Zhai, Significantly enhanced energy storage density and efficiency of BNT-based perovskite ceramics via A-site defect engineering, *Energy Storage Mater.* 2020, **30**, 392-400.
- [16] D. Li, D. Zhou, W.Y. Liu, P.J. Wang, Y. Guo, X.G. Yao, H.X. Lin, Enhanced energy storage properties achieved in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -based ceramics via composition design and domain engineering, *Chem. Eng. J.* 2021, **419**, 129601.
- [17] L. Chen, F.X. Long, H. Qi, H. Liu, S.Q. Deng, J. Chen, Outstanding energy storage performance in high-hardness $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ -based lead-free relaxors via multi-scale synergistic design, *Adv. Funct. Mater.* 2021, 2110478.
- [18] H. Qi, A.W. Xie, A. Tian, R.Z. Zuo, Superior energy-storage capacitors with simultaneously giant energy density and efficiency using nanodomain engineered $\text{BiFeO}_3\text{-BaTiO}_3\text{-NaNbO}_3$ lead-free bulk ferroelectrics, *Adv. Energy Mater.* 2019, 1903338.
- [19] Z.T. Chen, X.Y. Bu, B.X. Ruan, J. Du, P. Zheng, L.L. Li, F. Wen, W.F. Bai, W. Wu, L. Zheng, Y. Zhang, Simultaneously achieving high energy storage density and efficiency under low electric field in BiFeO_3 -based lead-free relaxor ferroelectric ceramics, *J. Eur. Ceram. Soc.* 2020, **40**, 5450-5457.
- [20] C. Shi, F. Yan, G.L. Ge, Y.Q. Wei, J.W. Zhai, W. Yao, Significantly enhanced energy storage performances and power density in $(1-x)\text{BCZT}-x\text{SBT}$ lead-free ceramics via synergistic optimization strategy, *Chem. Eng. J.* 2021, **426**, 130800.
- [21] P. Zhao, B. Tang, Z.X. Fang, F. Si, C.T. Yang, G. Liu, S.R. Zhang, Structure, dielectric and relaxor properties of $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3\text{-K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ lead-free ceramics for energy storage applications, *J. Materiomics* 2021, **7**, 195-207.

- [22] P. Zhao, B. Tang, Z.X. Fang, F. Si, C.T. Yang, S.R. Zhang, Improved dielectric breakdown strength and energy storage properties in Er_2O_3 modified $\text{Sr}_{0.35}\text{Bi}_{0.35}\text{K}_{0.25}\text{TiO}_3$, *Chem. Eng. J.* 2021, **403**, 126290.
- [23] Y.P Pu, W. Wang, X. Guo, R.K. Shi, M.D. Yang, J.W. Li, Enhancing the energy storage properties of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ -based lead-free linear dielectric ceramics with excellent stability through regulating grain boundary defects, *J. Mater. Chem. C* 2019, **7**, 14384-14393.
- [24] F. Yan, H.R. Bai, G.L. Ge, J.F. Lin, C. Shi, K. Zhu, B. Shen, J.W. Zhai, S.J. Zhang, Composition and structure optimized BiFeO_3 - SrTiO_3 lead-free ceramics with ultrahigh energy storage performance, *Small* 2022, 2106515.