Electronic Supplementary Information

Enhancing energy storage performance in $Na_{0.5}Bi_{0.5}TiO_3$-based lead-free relaxor ferroelectrics ceramics along stepwise optimization route

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1. Material and methods

1.1 Materials preparation

High purity (AR-grade) oxide powders of MgO, Na_2CO_3, $SrCO_3$, TiO_2, Bi_2O_3 and SnO_2 were regarded as raw materials and weighted in stoichiometric. These powders were milled for 6 h and calcined at 900 °C for 3 h. Meanwhile, some calcined powders of all components were uniaxially pressed into disc-shaped blocks (P=100 MPa, ϕ=12 mm), which were sintered at 1120-1150 °C for 3 h to form NBT-SBT-*x*BMS ceramics. Other calcined powders of *x*=0.08 (VPP) were mixed with PVA (5%), regrind for 1 h, dried to a sticky status, and then rolled repeatedly to form a green body (δ≈70 μm), which was then punched into a disc sample (ϕ=10 mm). They were heated to 750 °C for 2 h to eliminate PVA and sintered about 1100 °C for 2 h to obtain *x*=0.08 (VPP) ceramics.

1.2 Characterization of materials

X-ray diffraction (XRD, SmartLab, Rigaku, Japan) and transmission electron microscope (TEM, Talos F200X, FEI, USA) were used to analyze the crystal structure. The phase structure refinement was carried out by the FULLPROF software package (version

2000). The location of the atom and the calculation of the dipole vector were carried out by MATLAB (version R2020a) based on the brightness of the high-resolution atomic image. Scanning electron microscopy (SEM, Quanta FEG 250, FEI, USA) was used to reveal surfaces morphologies and elements distribution of thermally etched ceramic samples. Meanwhile, the grain size distributions were gained by Nano Measure software. Dielectric properties were measured by a multi-frequency LCR meter (E4980A, Agilent, USA). For the test of dielectric properties, the silver paste was coated on both sides of polished ceramics samples and sintered at 600 °C for 30 min. Polarization/current-electric field (*P*/*I*-*E*) curves were measured using an aixACCT TF analyzer 2000 (Aachen, Germany). The pulsed behavior was collected through a charge-discharge instrument (CFD-003, Gogo Instruments Technology, China). For the test of *P*-*E* hysteresis loops, FROC and charge-discharge curves, the gold electrode was coated on both sides of x=0.08 (VPP) ceramic samples, the thickness and electrode area were ~0.05-0.2 mm and 3.14 mm^2.

The first-order reversal curve (FORC) was measured using modulated triangle waves on a standard ferroelectric testing device (TF Analyzer 2000, aixACCT, Aachen, Germany). The Preisach density of FORC distribution was calculated from the descending branch of the main hysteresis loop of FORC through a differential method, described by the following Equation:

$$\rho_{\overline{FORC}}(E,E_r) = \frac{\partial^2 P_{\overline{FORC}}(E,E_r)}{\partial E_r \partial E}, \quad (1)$$

where the $P_{\overline{FORC}}$ is the polarization of FORC, the E_r is the reversal electric field, the E is the real testing electric field, the $\rho_{\overline{FORC}}$ is the Preisach density of FORC distribution, and the minus sign suggests that the FORC starts on the descending branch of the main hysteresis loop.

Tables

Table S1. The parameters and results of Rietveld crystal structure refinement for NBT-SBT-*x*BMS ceramics.

	x=0.02	x=0.04	x=0.08	x=0.12
Space group	*Pm*3*m*	*Pm*3*m*	*Pm*3*m*	*Pm*3*m*
a/b (Å)	3.90490	3.90793	3.91312	3.91817
V (Å^3)	59.543	59.682	59.920	60.152
R_{wp}	6.99%	6.73%	7.97%	7.24%
R_p	4.90%	4.71%	4.95%	4.73%
χ^2	1.76	1.76	1.81	1.83

Table S2. Comparison of W_{rec}, E_b and η between this work and other bulk ceramics.

Ref.	Compositions	W_{rec} (J/cm^3)	E_b (kV/cm)	η (100%)
1	$0.85BaTiO_3$-$0.15Bi(Zn_{1/2}Sn_{1/2})O_3$	2.41	230	91.6
2	$0.88BaTiO_3$-$0.12Bi(Li_{0.5}Nb_{0.5})O_3$	2.032	270	88
3	$0.88BaTiO_3$-$0.12Bi(Ni_{2/3}Nb_{1/3})O_3$	2.09	200	95.9
4	$0.85BaTiO_3$-$0.15Bi(Mg_{1/2}Zr_{1/2})O_3$	1.25	185	95
5	$0.9BaTiO_3$-$0.1Bi(Ni_{1/2}Sn_{1/2})O_3$	2.526	240	93.89
6	$0.6BaTiO_3$-$0.4Bi(Mg_{1/2}Ti_{1/2})O_3$	4.49	340	93
7	$0.88(Ba_{0.8}Sr_{0.2})TiO_3$-$0.12Bi(Zn_{2/3}Nb_{1/3})O_3$	1.62	225	99.8
8	$0.9Ba_{0.65}Sr_{0.35}TiO_3$-$0.1Bi(Mg_{2/3}Nb_{1/3})O_3$	3.34	400	85.71
9	0.94 $BaTiO_3$-$0.06Bi_{2/3}(Mg_{1/3}Nb_{2/3})O_3$	4.55	520	90
10	$0.93Ba_{0.55}Sr_{0.45}TiO_3$-$0.07BiMg_{2/3}Nb_{1/3}O_3$	4.55	450	81.8
11	$0.56BiFeO_3$-$0.3BaTiO_3$-$0.14AgNbO_3$+5 *mol*‰CuO	2.1	195	84
12	$(Bi_{0.98}La_{0.02}FeO_3$-$0.48BaTiO_3$+0.3%MnO_2	1.22	140	58
13	$0.61BiFeO_3$-$0.33(Ba_{0.8}Sr_{0.2})TiO_3$-$0.06La(Mg_{2/3}Nb_{1/3})O_3$+0.1 *wt*% MnO_2+2 *wt*% $BaCu(B_2O_5)$	3.38	230	59
14	$0.62BiFeO_3$-$0.3BaTiO_3$-$0.08Nd(Zr_{0.5}Zn_{0.5})O_3$	2.45	240	72
15	$0.54BiFeO_3$-$0.34BaTiO_3$-$0.12(Sr_{0.7}Bi_{0.2})TiO_3$	1.74	150	74
16	$Bi_{0.83}Sm_{0.17}Fe_{0.95}Sc_{0.05}O_3$	2.21	230	76
17	$0.75(Bi_{0.85}Nd_{0.15})FeO_3$-$0.25BaTiO_3$+0.1 *wt*% MnO_2	1.82	170	41.3
18	$0.6BiFeO_3$-$0.34BaTiO_3$-$0.06Sr(Al_{0.5}Nb_{0.5})O_3$	1.75	155	65
19	$Sr_{0.3}(Bi_{0.7}Na_{0.67}Li_{0.03})_{0.5}TiO_3$	1.7	130	87.2
20	$(Na_{0.5}Bi_{0.5})_{0.7}Sr_{0.3}TiO_3$-$Sr(Ti_{0.85}Zr_{0.15})O_3$	3.13	262	91.14
21	$0.65(0.84Bi_{0.5}Na_{0.5}TiO_3$-$0.16Bi_{0.5}K_{0.5}TiO_3)$-$0.35(Sr_{0.7}Bi_{0.2})TiO_3$	4.06	350	87.3

22	$0.8Bi_{0.5}Na_{0.5}TiO_3$-$0.2NaTaO_3$	4.21	380	77.8
23	$(Na_{0.25}Bi_{0.25}Sr_{0.5})(Ti_{0.8}Sn_{0.2})O_3$	3.4	310	90
24	$0.8Bi_{0.5}Na_{0.5}TiO_3$-$0.2SrNb_{0.5}Al_{0.5}O_3$	6.64	520	96.5
25	$0.96(0.65Bi_{0.5}Na_{0.5}TiO_3$-$0.35Sr_{0.85}Bi_{0.1}TiO_3)$-$0.04NaNbO_3$	3.08	220	81.4
26	$0.95(0.6Bi_{0.5}Na_{0.5}TiO_3$-$0.4Sr_{0.7}Bi_{0.2}TiO_3)$-$0.05AgNbO_3$	3.62	246	89
27	$0.75Bi_{0.58}Na_{0.42}TiO_3$-$0.25SrTiO_3$	5.63	535	94
28	$0.9(K_{0.5}Na_{0.5})NbO_3$-$0.1BiFeO_3$	2	206	60.5
29	$0.8(K_{0.5}Na_{0.5})NbO_3$-$0.2Sr(Sc_{0.5}Nb_{0.5})O_3$	2.48	295	81.4
30	$0.85K_{0.5}Na_{0.5}NbO_3$-$0.15Bi(Zn_{0.5}Zr_{0.5})O_3$	3.5	326	86.8
31	$0.91K_{0.5}Na_{0.5}NbO_3$-$0.09SrZrO_3$	2.81	370	80
32	$0.9(K_{0.5}Na_{0.5})NbO_3$-$0.1Bi(Mg_{2/3}Nb_{1/3})O_3$	4.08	300	62.7
33	$0.8(K_{0.5}Na_{0.5})NbO_3$-$0.2SrTiO_3$	4.03	400	52
34	$0.85K_{0.5}Na_{0.5}NbO_3$-$0.15(K_{0.7}Bi_{0.3})NbO_3$	3.39	330	51.7
35	$0.825(K_{0.5}Na_{0.5})NbO_3$-$0.175Sr(Sc_{0.5}Nb_{0.5})O_3$	2.67	395	60
36	$Gd_{0.04}Ag_{0.88}NbO_3$	4.5	290	64
37	$Ag_{0.91}Bi_{0.03}NbO_3$	2.6	200	86
38	$Ag_{0.94}La_{0.02}NbO_3$	3.12	230	63
39	$AgTa_{0.15}Nb_{0.85}O_3$	4.2	230	69
40	Mn-$La_{0.01}Ag_{0.97}NbO_3$	3.2	150	62
41	$AgNbO_3$-0.1*wt*% WO_3	3.3	200	50
42	$Sm_{0.03}Ag_{0.91}NbO_3$	5.2	290	69
43	$0.45AgNbO_3$-$0.55AgTaO_3$	6.3	470	90
44	$Ag_{0.97}Nd_{0.01}Ta_{0.20}Nb_{0.80}O_3$	6.5	370	71
45	$Ca_{0.5}Sr_{0.5}Ti_{0.85}Zr_{0.15}O_3$-$O_2$	3.37	440	96
46	$(Ca_{0.5}Sr_{0.5})_{0.8875}La_{0.075}TiO_3$	2.07	370	93

47	$0.9CaTiO_3$-$0.1BiScO_3$	1.55	270	90.4
48	$Ca_{0.5}Sr_{0.5}Ti_{0.9}Zr_{0.1}O_3$	2.05	390	95
49	$Ca_{0.5}Sr_{0.5}Ti_{0.97}Sn_{0.03}O_3$	2.06	330	95
50	$Ca_{0.5}Sr_{0.5}(Ta_{0.024}Ti_{0.97})O_3$-2 *wt*% SiO_2	2	360	96
This work	0.92(0.65 $Bi_{0.5}Na_{0.5}TiO_3$-$0.35Sr_{0.85}Bi_{0.1}TiO_3$)-0.08$Bi(Mg_{0.5}Sn_{0.5})O_3$-VPP	7.5	440	85.4

Table S3. Comparison of temperature stability between this work and other bulk ceramic capacitors.

Num.	Compositions	Temperature (°C)	W_{rec} (J/cm^3)	Ref.
1	$0.65(0.84Bi_{0.5}Na_{0.5}TiO_3$-$0.16K_{0.5}Bi_{0.5}TiO_3)$-$0.35Bi_{0.2}Sr_{0.7}TiO_3$	30-160	1.71-1.98	[21]
2	$0.61BiFeO_3$-$0.33(Ba_{0.8}Sr_{0.2})TiO_3$-$0.06La(Mg_{2/3}Nb_{1/3})O_3$+0.1 *wt*% MnO_2+2 *wt*% $BaCu(B_2O_5)$	30-170	1.16-1.29	[13]
3	$Ag_{0.76}La_{0.08}NbO_3$	20-120	2.46-2.7	[51]
4	$(0.85BaTiO_3$-$0.15Bi(Zn_{1/2}Sn_{1/2})O_3$	20-160	0.99-1.13	[1]
5	$0.9Sr_{0.7}Bi_{0.2}TiO_3$-$0.1Bi(Ni_{2/3}Nb_{1/3})O_3$	30-120	2.06-2.22	[52]
6	$Na_{0.7}Bi_{0.1}NbO_3$	20-120	2.38-2.48	[53]
7	$0.825(K_{0.5}Na_{0.5})NbO_3$-$0.175Sr(Sc_{0.5}Nb_{0.5})O_3$	30-150	0.77-0.86	[35]
This work	$0.92(0.65\ Bi_{0.5}Na_{0.5}TiO_3$-$0.35Sr_{0.85}Bi_{0.1}TiO_3)$-$0.08Bi(Mg_{0.5}Sn_{0.5})O_3$-VPP	30-120	3.6-3.9	

References

1. M. Zhou, R. Liang, Z. Zhou, et al. *J. Mater. Chem. C* 2018, **6**, 8528-8537.
2. W. Li, D. Zhou, L. Pang, et al., *J. Mater. Chem. A* 2017, **7**, 19607-19612.
3. M. Zhou, R. Liang, Z. Zhou, et al., *Ceram. Int.* 2019, **45**, 3582-3590.
4. X. Jiang, H. Hao, S. Zhang, et al., *J. Eur. Ceram. Soc.* 2019, **39**, 1103-1109.
5. F. Si, B. Tang, Z. Fang, et al., *Ceram. Int.* 2019, **45**, 17580-17590.
6. Q. Hu, Y. Tian, Q. Zhu, et al., *Nano Energy* 2020, **67**, 104264.
7. L. Zhang, L. Pang, W. Li, et al., *J. Eur. Ceram. Soc.* 2020, **40**, 3343-3347.
8. Z. Dai, J. Xie, W. Liu, et al. *ACS Appl. Mater. Interfaces* 2020, **12**, 30289-30296.
9. H. Yang, Z. Lu, L. Li, et al., *ACS Appl. Mater. Interfaces* 2020, **12**, 43942-43949.
10. W. Huang, Y. Chen, X. Li, *Appl. Phys. Lett.* 2018, **113**, 203902.
11. H. Sun, X. Wang, Q. Sun, et al., *J. Eur. Ceram. Soc.* 2020, **40**, 2929-2935.
12. L. Zhu, X. Lei, L. Zhao, et al., *Ceram. Int.* 2019, **45**, 20266-20275.
13. H. Yang, H. Qi and R. Zuo, *J. Eur. Ceram. Soc.* 2019, **39**, 2673-2679.
14. G. Wang, J. Li, X. Zhang, et al., *Energy Environ. Sci.* 2019, **12**, 582-588.
15. F. Li, J. Zhai, B. Shen, et al., *J. Alloys Compd.* 2019, **803**, 185-192.
16. X. Gao, Y. Li, J. Chen, et al., *J. Eur. Ceram. Soc.* 2019, **39**, 2331-2338.
17. D. Wang, Z. Fan, D. Zhou, et al., *J. Mater. Chem. A* 2018, **6**, 4133-4144.
18. N. Liu, R. Liang, X. Zhao, et al., *J. Am. Ceram. Soc.* 2018, **101**, 3259-3265.
19. J. Wu, Riekehr L, et al., *Nano energy* 2018, **50**, 723-732.
20. D. Li, D. Zhou, W. Liu, et al., *Chem. Eng. J.* 2021, **20**, 129601.
21. D. Hu, Z. Pan, X. Zhang, et al., *J. Mater. Chem. C* 2020, **8**, 591-601.
22. X. Zhou, H. Qi, Z. Yan, et al., *ACS Appl. Mater. Interfaces* 2019, **11**, 43107-43115.
23. L. Yang, X. Kong, Z. Cheng, et al., *J. Mater. Chem. A* 2019, **7**, 8573-8580.
24. F. Yan, X. Zhou, X. He, et al. *Nano Energy* 2020, **75**, 105012.
25. Y. Wu, Y. Fan, N. Liu, et al., *J. Mater. Chem. C* 2019, **7**, 6222-6230.
26. X. Qiao, D. Wu, F. Zhang, et al., *J. Mater. Chem. C* 2019, **7**, 10514-10520.
27. F. Yan, K. Huang, T. Jiang, et al., *Energy Storage Mater.* 2020, **30**, 392-400.
28. Z. Yang, F. Gao, H. Du, et al., *Nano Energy* 2019, **58**, 768-777.

29. B. Qu, H. Du and Z. Yang, *J. Mater. Chem. C* 2016, **4**, 1795-1803.
30. M. Zhang, H. Yang, D. Li, et al., *J. Mater. Chem. C* 2020, **8**, 8777-8785.
31. X. Ren, L. Jin, Z. Peng, et al., *Chem. Eng. J.* 2020, **390**, 124566.
32. T. Shao, H. Du, H. Ma, et al., *J. Mater. Chem. A* 2017, **5**, 554-563.
33. Z. Yang, H. Du, S. Qu, et al., *J. Mater. Chem. A* 2016, **4**, 13778-13785.
34. M. Zhang, H. Yang, D. Li, et al., *J. Alloys Compd.* 2020, **829**, 154565.
35. Z. Dai, D. Li, Z. Zhou, et al., *Chem. Eng. J.* 2022, **427,** 131959.
36. S. Li, H. Nie, G. Wang, et al., *J. Mater. Chem. C* 2019, **7**, 1551-1560.
37. Y. Tian, L. Jin, H. Zhang, et al., *J. Mater. Chem. A* 2017, **5**, 17525-17531.
38. N. Luo, K. Han, L. Liu, et al., *J. Am. Ceram. Soc.* 2019, **102**, 4640-4647.
39. L. Zhao, Q. Liu, J. Gao, et al., *Adv. Mater.* 2017, **29**, 1701824.
40. C. Xu, Z. Fu, Z. Liu, et al., *ACS Sustain. Chem. Eng.* 2018, **6**, 16151-16159.
41. L. Zhao, J. Gao, Q. Liu, et al., *ACS Appl. Mater. Interfaces* 2018, **10**, 819-826.
42. N. Luo, K. Han, F. Zhuo, et al., *J. Mater. Chem. A* 2019, **7**, 14118-14128.
43. N. Luo, K. Han, Cabral M J, et al., *Nat. Commun.* 2020, **11**, 4824.
44. B. W. Lu Z, Wang G, et al., *Nano Energy* 2021, **79**, 105423.
45. Y. Pu, W. Wang, X. Guo, et al., *J. Mater. Chem. C* 2019, **7**, 14384-14393.
46. W. Wang, Y. Pu, X. Guo, et al., *Ceram. Int.* 2019, **45**, 14684-14690.
47. B. Luo, X. Wang, E. Tian, et al., *ACS Appl. Mater. Interfaces* 2017, **9**, 19963-19972.
48. W. Wang, Y. Pu, X. Guo, et al., *J. Eur. Ceram. Soc.* 2019, **39**, 5236-5242.
49. W. Wang, Y. Pu, X. Guo, et al., *Ceram. Int.* 2020, **46**, 11484-11491.
50. W. Wang, Y. Pu, X. Guo, et al., *J. Alloys Compd.* 2020, **817**, 152695.
51. S. Li, T. Hu, H. Nie, et al., *Energy Storage Mater.* 2021, **34**, 417-426.
52. Y. Ding, P. Li, J. He, et al., *Compos. B. Eng.* 2022, **230**, 109493.
53. M. Zhou, R. Liang, Z. Zhou, et al., *J. Mater. Chem. A* 2018, **6**, 17896-17904.