Supplementary Information for

Ultrahigh energy storage density, high efficiency and superior thermal stability in $Bi_{0.5}Na_{0.5}TiO_3$-based relaxor ferroelectric ceramics *via* constructing multiphase structures

Yi-Ning Huang[1], Ji Zhang[1,*], Jiajia Wang[1], Jing Wang[2,*], Yaojin Wang[1,*]

[1] School of Materials Science and Engineering, Nanjing University of Science & Technology, Nanjing 210094, China

[2] State Key Laboratory of Mechanics and Control of Mechanical Structures, College of Aerospace Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

[*]Corresponding authors: jizhang@njust.edu.cn; wang-jing@nuaa.edu.cn; yjwang@njust.edu.cn

Experimental Procedure

(1-x)$Bi_{0.5}Na_{0.5}TiO_3$-$x$$Ba_{0.7}Sr_{0.3}Zr_{0.8}Sn_{0.2}O_3$ ceramics with x = 0, 0.10, 0.15, 0.00, 0.25 were fabricated by solid-state reaction. High purity oxides and carbonate of Bi_2O_3 (99.9%), Na_2CO_3 (99.99%), TiO_2 (99%), $BaCO_3$ (99.95%), $SrCO_3$ (99.95%), ZrO_2 (99%), SnO_2 (99.5%, all from Aladdin) were selected as starting materials and weighted according to designed composition. Then, all the weighted powders were mixed with ethanol and with ZrO_2 balls in nylon tank by a planetary ball mill. Afterwards, the slurry was dried, and calcined at 800°C. Subsequently, the calcined powders were ball-milled again, dried and mixed with polyvinyl butyral as binder, then pressed into disks with thickness of ~1 mm and diameter of ~10 mm under 10 MPa. The binder was removed at 600°C with increasing rate of 2°C/min. Eventually, the green disks were pressed again under 120 MPa by cold isostatic pressing and sintered at 1150°C. The increasing and decreasing rate for temperature variety were both 5°C/min. During sintering, the samples were embedded in powders with the same composition to suppress the volatilization of Bi and Na.

Crystalline structure of ceramics was detected by X-ray diffraction (XRD, PANalytical), and the FULLPROF software was adopted to perform the structural refinement. The microstructure was confirmed by field-emission scanning electron microscopy (SEM, Zeiss Ultra-55). For dielectric property measurements, the surfaces of the polished disks were covered with silver paste and fired at 550 °C for 30 min. The temperature-dependent permittivity (ε_r) and loss (tanδ) were measured using an LCR meter (Agilent E4980A, Santa Clara, CA) at various frequencies. The specific electric breakdown strength of each sample was collected by a voltage-withstand test device (Trek 610D, PolyK Technologies), and the polarization-electric field (*P*-*E*) curves were tested by a ferroelectric analyzer (Radiant Technologies). The charge-discharge property was characterized by a specially RLC load circuit (PK-CPR1701, PolyK Technologies). For *P*-*E* loops and direct charge/discharge, the sample thickness and electrode area are 0.1 mm and 0.785 mm^2 (1 mm in diameter).

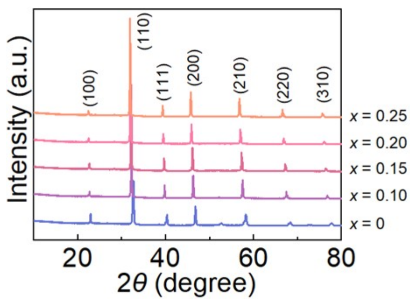

Fig. S1 XRD patterns of (1-*x*)BNT-*x*BSZS ceramics.

Table S1 The Refined structural parameters of (1-*x*)BNT-*x*BSZS ceramics.

	x = 0	*x* = 0.10		*x* = 0.15		*x* = 0.20		*x* = 0.25	
Space group	*R3c*	*R3c* (84%)	*P4bm* (16%)	*R3c* (67%)	*P4bm* (33%)	*R3c* (56%)	*P4bm* (44%)	*R3c* (32%)	*P4bm* (68%)
a (Å)	5.4816	5.5465	5.5503	5.5706	5.5685	5.5940	5.5935	5.6171	5.6155
b (Å)	5.4816	5.5465	5.5503	5.5706	5.5685	5.5940	5.5934	5.6171	5.6155
c (Å)	13.5342	13.5834	3.9230	13.6411	3.9393	13.7022	3.9594	13.7536	3.9745
α	90°	90°	90°	90°	90°	90°	90°	90°	90°
β	90°	90°	90°	90°	90°	90°	90°	90°	90°
γ	120°	120°	90°	120°	90°	120°	90°	120°	90°
Cell volume	352.195	361.885	120.853	366.593	122.148	371.335	123.875	375.809	125.332
R_{wp}	6.56	8.42		7.92		7.90		8.30	
R_p	4.83	4.75		4.65		4.68		4.64	
χ^2	5.25	9.25		7.91		7.15		8.94	

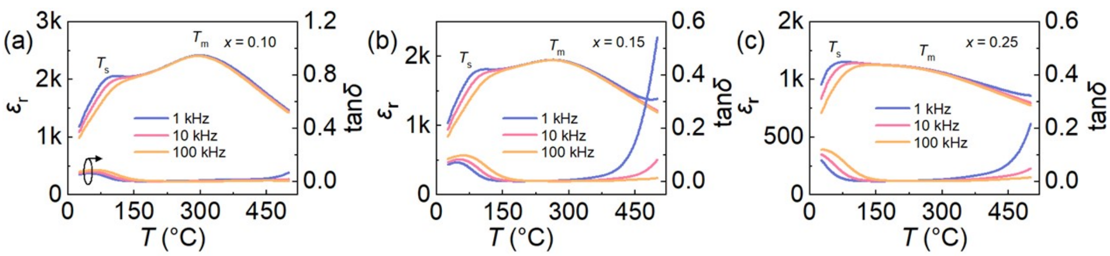

Fig. S2 Temperature-dependent permittivity (ε_r) and loss (tanδ) of (a) x = 0.10, (b) x = 0.15, (c) x = 0.25.

Table S2 β values of BNT-BSZS ceramics.

Composition	$x = 0$	$x = 0.10$	$x = 0.15$	$x = 0.20$	$x = 0.25$
β	18.1	13.7	8.5	12.7	10.1

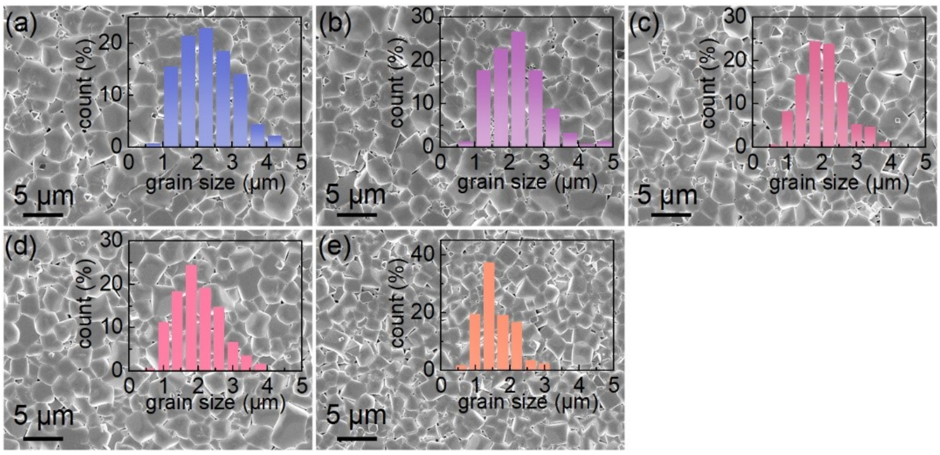

Fig. S3 SEM morphologies of BNT-BSZS ceramics and corresponding grain size distribution: (a) $x = 0$, (b) $x = 0.10$, (c) $x = 0.15$, (d) $x = 0.20$, (e) $x = 0.25$.

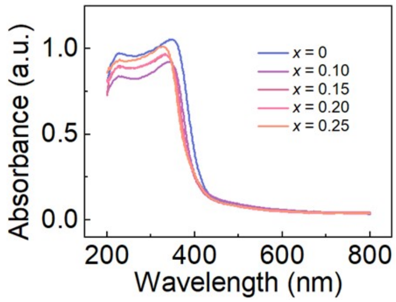

Fig. S4 UV-vis absorption spectrum of BNT-BSZS ceramics.

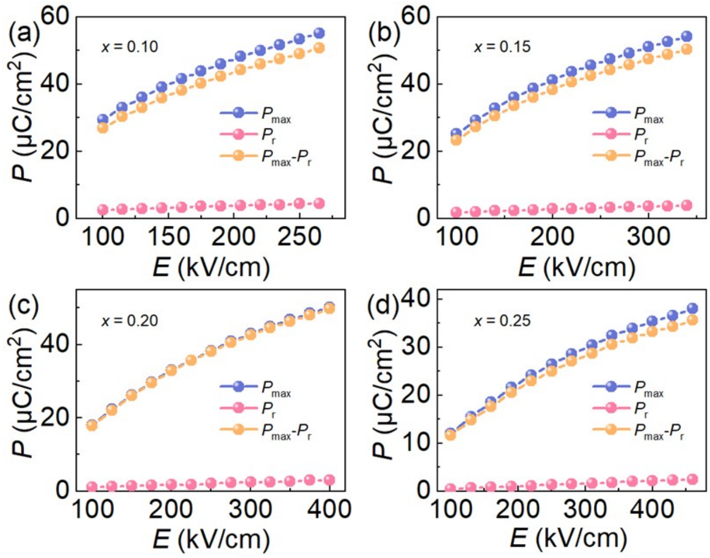

Fig. S5 Electric field dependent P_{max}, P_{r} and P_{max}-P_{r} of (a) x = 0.10, (b) x = 0.15, (c) x = 0.20, (d) x = 0.25,

Table S3 Comparison of energy storage properties between this work and recently reported BNT-based ceramics.

Compositions	E (kV/cm)	W_{rec} (J/cm^3)	η (%)	Reference
$x = 0.10$	265	4.9	82	This work
$x = 0.15$	340	6.3	87.5	This work
$x = 0.20$	400	7.4	88.7	This work
$x = 0.25$	460	6.6	90.2	This work
$0.62Na_{0.5}Bi_{0.5}TiO_3$-$0.3Sr_{0.7}Bi_{0.2}TiO_3$-$0.08BiMg_{2/3}Nb_{1/3}O_3$	470	7.5	92	7
$0.90(Bi_{0.5}Na_{0.5})_{0.65}Sr_{0.35}TiO_3$-$0.10Bi(Mg_{0.5}Zr_{0.5})O_3$	522	8.46	85.9	9
$0.55Bi_{0.5}Na_{0.5}TiO_3$-$0.45Sr_{0.7}La_{0.2}TiO_3$	338	4.14	92.2	13
$0.8(0.95Bi_{0.5}Na_{0.5}TiO_3$-$0.05SrZrO_3)$-$0.2NaNbO_3$	350	5.55	85	23
$0.85(Bi_{0.5}Na_{0.5})_{0.7}Sr_{0.3}TiO_3$-$0.15Bi(Mg_{0.5}Sn_{0.5})O_3$	280	3.76	78.8	26
$0.80Bi_{0.5}Na_{0.5}TiO_3$-$0.20SrNb_{0.5}Al_{0.5}O_3$	520	6.64	96.5	29
$0.84Bi_{0.5}Na_{0.5}TiO_3$-$0.16KNbO_3$	320	5.2	88	30
$0.78(Bi_{0.5}Na_{0.5})TiO_3$-$0.22NaNbO_3$	390	7.02	85	31
$0.7(0.85Bi_{0.5}Na_{0.5}TiO_3$-$0.15NaNbO_3)$-$0.3(Sr_{1.05}Bi_{0.3})ScO_3$	540	7.3	80	32
$0.90(Na_{0.5}Bi_{0.5})_{0.7}Sr_{0.3}TiO_3$-$0.10Bi(Ni_{0.5}Sn_{0.5})O_3$	270	4.18	83.64	33
$0.86(Na_{0.5}Bi_{0.5})_{0.6}Sr_{0.4}TiO_3$-$0.14Sr_{0.7}La_{0.2}ZrO_3$	322	3.45	90.1	34
$0.85Na_{0.5}Bi_{0.5}TiO_3$-$0.15CaZr_{0.5}Ti_{0.5}O_3$	297.7	4.37	81.4	35
$0.5Na_{0.5}Bi_{0.5}TiO_3$-$0.5Sr_{0.85}Sm_{0.1}TiO_3$	422	5.02	90	36
$0.6Bi_{0.5}Na_{0.5}TiO_3$-$0.4Sr_{0.7}Sm_{0.2}TiO_3$	260	3.52	84.2	37
$0.86(0.93Na_{1/2}Bi_{1/2}TiO_3$-$0.07BaTiO_3)$-$0.14K_{1/2}Bi_{1/2}(Zn_{1/3}Nb_{2/3})O_3$	290	5.1	80	38
$0.45Na_{0.5}Bi_{0.5}TiO_3$-$0.55Sr_{0.7}Bi_{0.2}TiO_3$/6wt%AlN	360	5.53	90	39
$0.6[0.955(Bi_{0.5}Na_{0.5})TiO_3$-$0.045Ba(Al_{0.5}Ta_{0.5})O_3]$-$0.4CaTiO_3$	440	5.81	97.8	40
$0.7Na_{0.5}Bi_{0.5}TiO_3$-$0.3NaNbO_3$/7wt%$CaZr_{0.5}Ti_{0.5}O_3$	410	4.93	93.3	41
$0.65Bi_{0.5}Na_{0.4}K_{0.1}TiO_3$-$0.35[2/3SrTiO_3$-$1/3Bi(Mg_{2/3}Nb_{1/3})O_3]$	290	4.43	86	42
$0.75Bi_{0.58}Na_{0.42}TiO_3$-$0.25SrTiO_3$	535	5.63	94	43

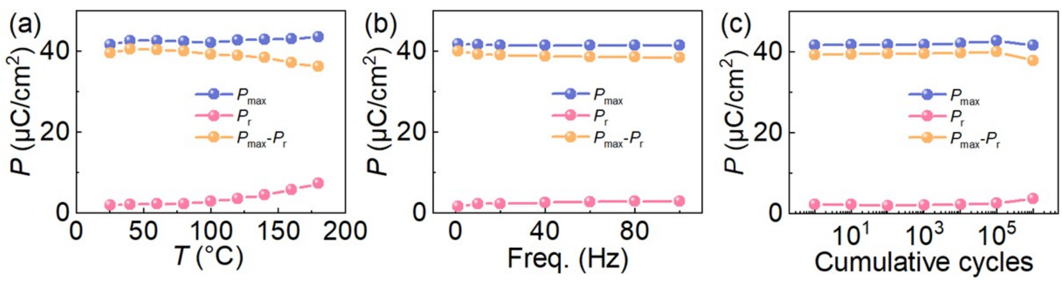

Fig. S6 Evolution of P_{max}, P_{r} and P_{max}-P_{r} of x = 0.2 under different temperatures, frequencies and cycling numbers.