Supplementary Information

$(Bi_{1/6}Na_{1/6}Ba_{1/6}Sr_{1/6}Ca_{1/6}Pb_{1/6})TiO_3$-based high-entropy dielectric ceramics with ultrahigh recoverable energy density and high energy storage efficiency

Hao Wang[1], Ji Zhang[1,*], Shunshun Jiang[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

Materials and methods

BNBSCP-*x*Zr (*x* = 0-0.14) ceramics were synthesized by solid-state reaction with related oxides and carbonates of Bi_2O_3 (99.9%), Na_2CO_3 (99.99%), $BaCO_3$ (99.95%), $SrCO_3$ (99.95%), $CaCO_3$ (99.99%), PbO (99.9%), TiO_2 (99%), ZrO_2 (99%) (Aladdin). First, the above materials were weighted according to composition design, and mixed by planetary ball mill in absolute alcohol for 10 hours. Then the dried mixtures were calcined at 900°C for 2 hours in the covered alumina crucible, which was ball-milled for another 10 hours. Afterwards, the dried powders were suppressed into pellets with the help of binder under 8 MPa, and further compacted by cold isostatic pressing under 150 MPa. After the pyrolysis of binder at 600°C, the green pellets buried by powder with the same composition were sintered at 1180-1230°C for 3 hours in the covered alumina crucible to obtain ceramic samples.

The samples' crystal structure was characterized by X-ray diffraction (XRD, Bruker D8) and the surface microstructure was observed by scanning electron microscope (SEM, TESCAN mira4). To characterize the dielectric behaviors, the ceramics were polished, coated by silver paste as electrodes and measured by an LCR meter (Agilent E4980A). A ferroelectric tester (Radiant Technologies) with temperature controlling system and commercial charge-discharge device (PolyK Technologies) were employed to determine the energy storage performances.

Figures and Tables

Table S1 The ionic radii of BNBSCP-xZr ceramics.

	ionic radius (Å)	coordination number
Bi^{3+}	1.36	12
Na^{+}	1.39	12
Ba^{2+}	1.61	12
Sr^{2+}	1.44	12
Ca^{2+}	1.34	12
Pb^{2+}	1.49	12
Ti^{4+}	0.605	6
Zr^{4+}	0.72	6
O^{2-}	1.4	6

Table S2 The t and S_{config} values of BNBSCP-xZr ceramics.

	t	S_{config}
$x = 0$	1.0010	1.79
$x = 0.05$	0.9981	1.99
$x = 0.08$	0.9964	2.07
$x = 0.10$	0.9953	2.12
$x = 0.12$	0.9942	2.16
$x = 0.14$	0.9930	2.2

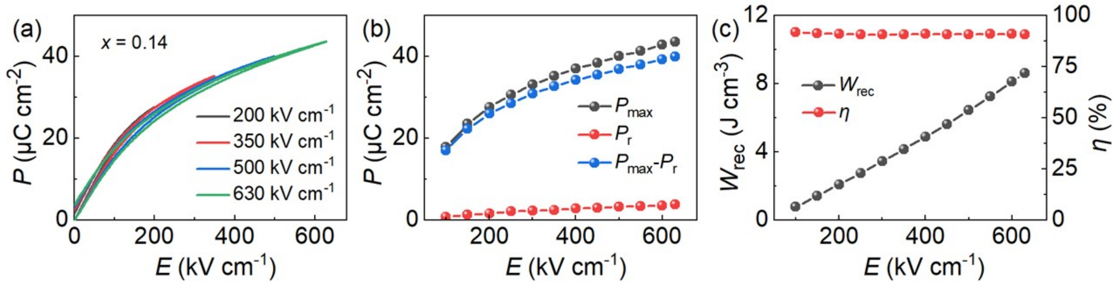

Fig S1 P-E loops of x = 0.14 and corresponding variation of P_{max}, P_r, P_{max}-P_r and W_{rec}, η under various electric fields.

Table S3 Comparison of energy storage properties between this work and recently reported ceramic capacitors.

Compositions	E (kV/cm)	W_{rec} (J/cm^3)	η (%)	Reference
x = 0.10	500	6.3	89.2	This work
x = 0.12	610	8.8	92.5	This work
x = 0.14	630	8.6	90.6	This work
$0.8(0.95Bi_{0.5}Na_{0.5}TiO_3$-$0.05SrZrO_3)$-$0.2NaNbO_3$	350	5.55	85	4
$0.90(Bi_{0.5}Na_{0.5})_{0.65}Sr_{0.35}TiO_3$-$0.10Bi(Mg_{0.5}Zr_{0.5})O_3$	522	8.46	85.9	10
$0.62Na_{0.5}Bi_{0.5}TiO_3$-$0.3Sr_{0.7}Bi_{0.2}TiO_3$-$0.08BiMg_{2/3}Nb_{1/3}O_3$	470	7.5	92	11
$0.80Bi_{0.5}Na_{0.5}TiO_3$-$0.20SrNb_{0.5}Al_{0.5}O_3$	520	6.64	96.5	34
$0.75Bi_{0.58}Na_{0.42}TiO_3$-$0.25SrTiO_3$	535	5.63	94	35
$0.90(0.55Bi_{0.5}Na_{0.5}TiO_3$-$0.45Sr_{0.7}Bi_{0.2}TiO_3)$-$0.10ZnO$	400	5.84	93	36
$0.78(Bi_{0.5}Na_{0.5})TiO_3$-$0.22NaNbO_3$	390	7.02	85	37
$0.7(0.85Bi_{0.5}Na_{0.5}TiO_3$-$0.15NaNbO_3)$-$0.3(Sr_{1.05}Bi_{0.3})ScO_3$	540	7.3	80	38
$0.48BiFeO_3$-$0.4SrTiO_3$-$0.12La(Mg_{2/3}Nb_{1/3})O_3$+0.1wt.% MnO_2	450	6.3	74.3	39
$0.7(0.6BiFeO_3$-$0.4SrTiO_3)$-$0.3Sr_{0.7}Bi_{0.2}TiO_3$	440	5.61	86.76	40
$0.85(0.65BiFeO_3$-$0.35BaTiO_3)$-$0.15Sr_{0.7}Bi_{0.2}TiO_3$	330	4.95	73	41

$0.88(0.67BiFeO_3$-$0.33BaTiO_3)$-$0.12Na_{0.73}Bi_{0.09}NbO_3$	410	5.57	83.8	42
$0.5Bi_{1.02}FeO_3$-$0.37BaTiO_3$-$0.13Bi(Zn_{2/3}(Nb_{0.85}Ta_{0.15})_{1/3})O_3$	410	4.85	80	43
$0.85(0.67BiFeO_3$-$0.33BaTiO_3)$-$0.15Sr(Nb_{0.5}Al_{0.5})O_3$	300	3.95	85.9	44
$0.85(0.8BaTiO_3$-$0.2Bi_{0.5}Na_{0.5}TiO_3)$-$0.15CaZrO_3$	540	9.04	87.2	15
$0.90BaTiO_3$-$0.10Bi(Mg_{0.5}Zr_{0.5})O_3$@$SiO_2$	345	3.41	85.1	45
$0.9Ba_{0.65}Sr_{0.35}TiO_3$-$0.1Bi(Mg_{2/3}Nb_{1/3})O_3$	400	3.34	85.71	46
$0.9[0.9Ba_{0.8}Ca_{0.2}TiO_3$-$0.1Bi(Li_{1/3}Zr_{2/3})O_3]$-$0.1Bi_{0.5}Na_{0.5}TiO_3$	368	4.23	93.4	47
$0.6BaTiO_3$-$0.4Bi(Mg_{1/2}Ti_{1/2})O_3$	340	4.49	93	48
$0.93Ba_{0.55}Sr_{0.45}TiO_3$-$0.07BiMg_{2/3}Nb_{1/3}O_3$	450	4.55	81.8	49
$0.85K_{0.5}Na_{0.5}NbO_3$-$0.15Bi(Zn_{2/3}Ta_{1/3})O_3$	600	6.7	92	16
$0.85K_{0.5}Na_{0.5}NbO_3$-$0.15Bi(Ni_{0.5}Zr_{0.5})O_3$	870	8.09	88.46	17
$0.975K_{0.5}Na_{0.5}NbO_3$-$0.025LaBiO_3$	340	3.60	74.2	50
$0.925(K_{0.5}N_{a0.5})NbO_3$-$0.075Bi(Zn_{2/3}(Ta_{0.5}Nb_{0.5})_{1/3})O_3$	307	4.02	87.4	51
$0.9K_{0.5}Na_{0.5}NbO_3$-$0.1BiFeO_3$	206	2	61	52
$AgNb_{0.85}Ta_{0.15}O_3$	233	4.2	69	8
$Ag_{0.97}Nd_{0.01}Ta_{0.20}Nb_{0.80}O_3$	370	6.5	71	9
$0.94AgNbO_3$-$0.06Ca(Hf_{0.2}Ti_{0.8})O_3$	300	5.4	66	53
$AgNb_{0.45}Ta_{0.55}O_3$	470	6.3	90	54
$Ag_{0.76}La_{0.08}NbO_3$	476	7.01	77	55
$0.76NaNbO_3$-$0.24(Bi_{0.5}Na_{0.5})TiO_3$	680	12.2	69	33
$0.88NaNbO_3$-$0.12(Bi_{0.9}Na_{0.1})(Fe_{0.8}Ti_{0.2})O_3$	820	12.7	82.5	56
$(Na_{0.91}Bi_{0.09})(Nb_{0.94}Mg_{0.06})O_3$	760	10.9	83	57
$0.75[0.90NaNbO_3$-$0.10Bi(Mg_{0.5}Ta_{0.5})O_3]$-$0.25(Bi_{0.5}Na_{0.5})_{0.7}Sr_{0.3}TiO_3$	800	8	90.4	58
$0.96(0.8NaNbO_3$-$0.2SrTiO_3)$-$0.04Bi(Zn_{0.5}Sn_{0.5})O_3$	570	5.82	92.3	59
$0.68NaNbO_3$-$0.32(Bi_{0.5}Li_{0.5})TiO_3$	485	8.73	80.1	60
$[(K_{0.2}Na_{0.8})_{0.8}Li_{0.08}Ba_{0.02}Bi_{0.1}](Nb_{0.68}Sc_{0.02}Hf_{0.08}Zr_{0.1}Ta_{0.08}Sb_{0.04})O_3$	740	10.06	90.8	20
$0.8(Na_{0.2}Bi_{0.2}Ba_{0.2}Sr_{0.2}Ca_{0.2})TiO_3$-$0.2NaNbO_3$	310	3.51	77.7	21
$(Na_{0.2}Bi_{0.2}Ba_{0.2}Sr_{0.2}Ca_{0.2})TiO_3$-2mol% PbO	584	8.2	92.2	23