Electronic supplementary information

Ultrahigh energy storage capacities in high-entropy relaxor ferroelectrics

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1. Material and methods

High-entropy $(1–x)(Bi_{0.375}Na_{0.3}Sr_{0.25}K_{0.075})TiO_3$-$x$$Bi(Mg_{0.5}Sn_{0.5})O_3$ ceramics (abbreviated as BNT-H100x) with x = 0.05, 0.10, 0.15, and 0.20 were synthesized through solid-reaction method with original materials including Bi_2O_3 (>99%), Na_2CO_3 (>99.8%), K_2CO_3 (>99%), TiO_2 (>98%), $SrCO_3$ (>99%), SnO_2 (>99.5%), and MgO (>98.5%) powders. The raw materials were dried at 110 °C for 12 h and then they were mixed by ball-milling in ethanol for 4 h. The mixed materials were then calcined at 880 °C for 2 h before they were ball-milled again for another 4 h. Powders obtained after drying were pressed into discs with a diameter of 9 mm and a thickness of 1 mm by isostatic pressure. These discs were sintered at 1180 °C for 120 min with a heating rate of 3 °C/min. For the VPP treatment, all powders were ball-milled again with 5% PVA solution to create a viscous substance. Then it was rolled into 0.6 mm thick flakes and cut into discs with a diameter of 10 mm. These discs produced by VPP was sintered at 1130 °C for 90 mins.

X-ray diffractometer (XRD; Panalytical, Cambridge, UK) was used to investigate phase structures of the samples. Sintered bulk ceramics were grinded into powders and then annealed at 500 °C for 4 h to relieve the internal stress. The TEM testing sample was fabricated by focused ion beam milling (FIB, Helios G4 CX, FEI, USA). A scanning electron microscope (SEM; quanta, FEG 250, FEI, Hillsboro, USA) was used to observes fresh surface of the sintered ceramics. The dark field images, the selected area electron diffraction (SAED) pattern, and high-resolution transmission electron microscope images were obtained by the spherical aberration corrected transmission electron microscope (AC-TEM, Titan Cubed Themis G2300, FEI, USA). The dielectric properties of ceramics were tested using a multi-frequency LCR meter (E4980AL, Keysight, USA). The test temperature was 30−450 °C and heat up at a rate of 3 °C/min. The test frequencies were 0.3, 1, 10, 100, and 1000 kHz. A ferroelectric instrument (TF analyzer 2000E, aixACCT, Aachen, Germany) was used to measure the hysteresis loops and current curves. The test samples were grinded to 2 mm thick and then coated with gold electrode on both sides. The pulsed behavior was collected through a charge-discharge instrument (CFD-003, Gogo Instruments Technology, China).

Figures

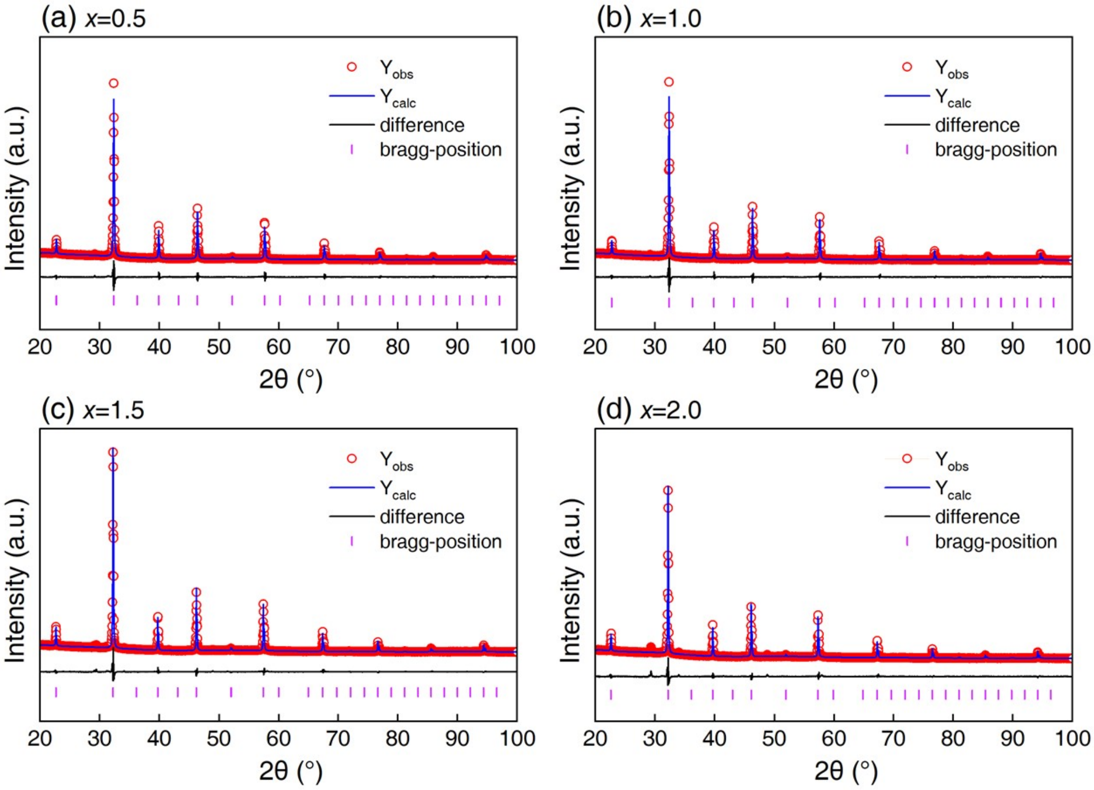

Fig. S1. Results of structure refinement forBNT-H100*x* ceramics. (a) $x = 0.05$, (b) $x = 0.10$, (c) $x = 0.15$, and (d) $x = 0.20$.

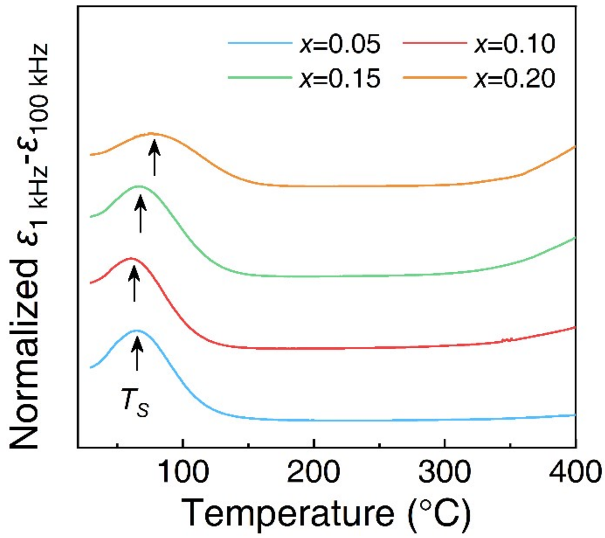

Fig. S2. Normalized $\varepsilon_{1\ kHz}$–$\varepsilon_{100\ kHz}$ as a function of temperature from RT to 400 °C. Here $\varepsilon_{1\ kHz}$ and $\varepsilon_{100\ kHz}$ were the ε_r measured at 1 kHz and 100 kHz, respectively. The characteristic temperature (T_s) is indicated by the vertical arrow.

Table S1

Atomic configurational entropy S_{config} of BNT-H100x ceramics.

x	0.05	0.10	0.15	0.20
S_{config}	1.49R	1.63R	1.73R	1.82R

Table S2

Rietveld crystal refinement parameters of BNT-H100*x* ceramics.

Chemical formula		$x = 0.5$	$x = 1.0$	$x = 1.5$	$x = 2.0$
Space group		*P*4*bm*	*P*4*bm*	*P*4*bm*	*P*4*bm*
Cell parameter (Å)	*a*	5.5456(9)	5.5494(3)	5.5595(6)	5.5672(9)
	c	3.9208(7)	3.9234(4)	3.9308(2)	3.9365(4)
Density (g/cm^3)		5.842(1)	6.002(3)	6.133(1)	6.273(9)
Volume (Å^3)		120.585	120.827	121.496	6.246
R-factors	R_{wp}	5.813	6.038	5.762	5.71
	χ^2	2.64	2.68	2.63	2.84
No. of profile points		6005	6005	6005	6005

Table S3

Comparison of ESP between various representative lead-free systems.

Composition	E (kV/cm)	W_{rec} (J/cm^3)	η (%)	Ref.
$0.7374Na_{0.5}Bi_{0.5}TiO_3$-$0.2625BaSnO_3$	200	1.99	8.6	1
$0.94(0.65Bi_{0.5}Na_{0.5}TiO_3$-$0.35Bi_{0.1}Sr_{0.85}TiO_3)$-$0.06(K_{0.5}Na_{0.5}NbO_3)$	180	2.65	84.6	2
0.55BNT-$0.45(Bi_{0.2}Sr_{0.7}TiO_3)$	200	2.5	95	3
0.96(0.65BNT-$0.35Sr_{0.85}Bi_{0.1}TiO_3)$-$0.04NaNbO_3$	220	3.08	81.4	4
0.5BNT-$0.5SrTiO_3$-1.5 mol% CuO	230	2.2	72.39	5
0.9(0.7BNT-$0.3SrTiO_3)$-$0.1Bi(Nb_{0.5}Mg_{0.5})O_3$	240	3.46	78	6
0.6BNT-$0.4Sr_{0.7}Sm_{0.2}TiO_3$	260	3.52	84.2	7
$0.90(Na_{0.5}Bi_{0.5})_{0.7}Sr_{0.3}TiO_3$-$0.10Bi(Ni_{0.5}Sn_{0.5})O_3$	270	4.18	83.64	8
$0.6(Bi_{0.51}Na_{0.47})TiO_3$-$0.4Ba(Zr_{0.3}Ti_{0.7})O_3$	280	3.1	91	9
$0.6(Ba_{0.7}Sr_{0.3})(Zr_{0.2}Ti_{0.8})O_3$-$0.4(Na_{0.5}Bi_{0.5})TiO_3$	289	3.72	94.3	10
$(Na_{0.25}Bi_{0.25}Sr_{0.5})(Ti_{0.8}Sn_{0.2})O_3$	310	3.4	90	11
0.9(0.65 BNT-$0.35Bi_{0.2}Sr_{0.7}TiO_3)$-$0.1CaZrO_3$	330	2.9	80	12
0.85(0.55BNT-$0.45Sr_{0.7}La_{0.2}TiO_3)$-$0.15Bi(Mg_{2/3}Nb_{1/3})O_3$	338	3.88	85	13
0.65(0.84BNT-$0.16K_{0.5}Bi_{0.5}TiO_3)$-$0.35(Bi_{0.2}Sr_{0.7}TiO_3)$	350	4.06	87.3	14
0.88BNT-$0.12CaZr_{0.5}Ti_{0.5}O_3$	378.3	4.77	69	15
0.8(0.65BNT-$0.35Bi_{0.2}Sr_{0.7}TiO_3)$-$0.2BaSnO_3$	380	3.75	84.8	16
0.85(0.94BNT-$0.06BaTiO_3)$-$0.15BiMg_{2/3}Nb_{1/3}O_3$	420	6.3	80	17
$(Na_{0.5}Bi_{0.5})_{0.7}Sr_{0.3}TiO_3$-$Ba(Mg_{1/3}Nb_{2/3})O_3$	460	5.5	90.1	18
$0.90(Bi_{0.5}Na_{0.5})_{0.65}Sr_{0.35}TiO_3$-$0.10Bi(Mg_{0.5}Zr_{0.5})O_3$	522	8.46	85.9	19
$0.75Bi_{0.58}Na_{0.42}TiO_3$-$0.25SrTiO_3$	535	5.63	94	20
0.7(0.85BNT-$0.15NaNbO_3)$-$0.3(Sr_{1.05}Bi_{0.3})ScO_3$	540	7.3	80	21
BSZT-BMN	552	5.92	81.7	22
$(Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5})_{0.96}Sr_{0.04}Ti_{0.99}Ta_{0.01}O_3$-0.70BNT-	572	6.78	89.7	23

$0.30SrNb_{0.5}Al_{0.5}O_3$				
$0.96(0.8NaNbO_3\text{-}0.2SrTiO_3)\text{-}0.04Bi(Zn_{0.5}Sn_{0.5})O_3$	570	5.82	92.3	24
$0.78NaNbO_3\text{-}0.22Bi(Mg_{2/3}Ta_{1/3})O_3$	620	5.01	86.8	25
$Bi_{1.5}Zn_{0.75}Mg_{0.25}Nb_{0.75}Ta_{0.75}O_7$	650	2.72	91	26
$(Ag_{0.80}Bi_{0.04}Sr_{0.04})NbO_3$	720	7.9	75.5	27
$0.85(Ba_{0.8}Sr_{0.2})TiO_3\text{-}0.15Bi(Mg_{0.5}Zr_{0.5})O_3$	720	10.3	88	28
$(Na_{0.91}Bi_{0.09})(Nb_{0.94}Mg_{0.06})O_3$	783	10.9	83	29
$0.75[0.9NN\text{-}0.1Bi(Mg_{0.5}Ta_{0.5})O_3]\text{-}0.25(Bi_{0.5}Na_{0.5})0.7Sr_{0.3}TiO_3$	800	8	90.4	30
$0.85K_{0.5}Na_{0.5}NbO_3\text{-}0.15SrTiO_3$	400	4.03	52	31
$0.8K_{0.5}Na_{0.5}NbO_3\text{-}0.2SrTiO_3$	400	3.67	72.1	
$0.92NaNbO_3\text{-}0.08Bi(Mg_{0.5}Ti_{0.5})O_3$	480	5.57	71	32
$BaTiO_3\text{-}0.06Bi_{2/3}(Mg_{1/3}Nb_{2/3})O_3$	520	4.55	91	33
This work	610	11.29	90	

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