Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

High Depolarization Temperature and Large Piezoelectricity in $BiScO_3$-$PbTiO_3$-$Bi(Zn_{1/2}Ti_{1/2})O_3$ Piezoelectric Energy Harvesting Ceramics

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Methods of Sample Preparation and Characterization: Bi_2O_3 (99%, Tianjin Fuchen chemical reagent factory), Pb_3O_4 (99%, Tianjin Fuchen chemical reagent factory), Sc_2O_3 (99.99%, Huizhou high purity rare earth metal materials Co, Ltd), TiO_2 (99%, Tianjin Fuchen chemical reagent factory), and ZnO (99%, Tianjin Fuchen chemical reagent factory) were used as raw materials. The main process flow includes ball milling, calcination (800 °C, 2 hours), granulation, pressing and sintering (1150 °C, 2 hours). X-ray diffraction (XRD; bruker D8 advance, Karlsruhe, Germany) and scanning electron microscopy (SEM; quanta 650, FEI, USA) were used to characterize the phase structure and cross section of sintered *z*BS-*x*PT-*y*BZT ceramics, respectively. Rietveld refinement was performed using TOtal PAttern Solution (TOPAS) software. The grain size of ceramic was measured and calculated by Nano Measurer software. The polarization process is to apply a DC electric field of 5 kV/mm to the *z*BS-*x*PT-*y*BZT ceramic immersed in silicone oil at 120 °C for 30 minutes. The dielectric, piezoelectric and ferroelectric properties of *z*BS-*x*PT-*y*BZT ceramics were characterized by commercial digital bridge (E4980A, Agilent Technologies, USA), quasi-static d_{33} tester

(ZJ-6A, China Academy of Acoustics) and ferroelectric test system (Precision Premier II, Radiant Technologies, Inc, USA). Finally, the *in-situ* high-temperature quasi-static d_{33} and high-temperature energy harvesting properties of these ceramics were measured by using the *in-situ* variable temperature d_{33} test system (TZFD-600, Harbin Julang Technology Co, Ltd) and the self-made high-temperature piezoelectric energy harvesting system.

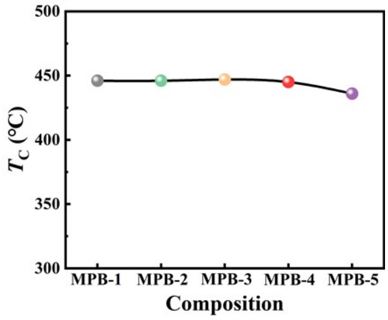

Fig. S1 The Curie temperature (T_C) of MPB-1~5 piezoceramics.

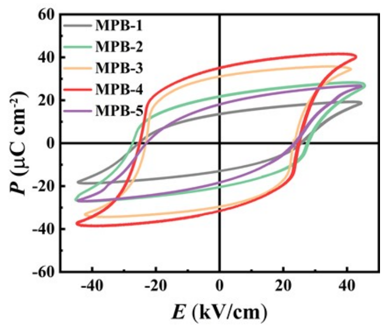

Fig. S2 The *P-E* loops of MPB-1~5 piezoceramics.

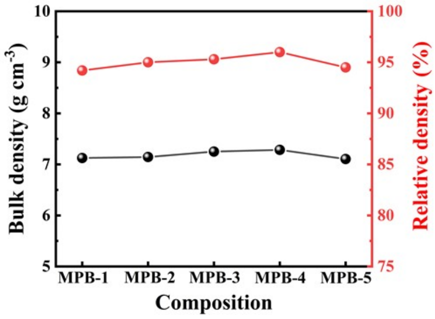

Fig. S3 The bulk density and relative density of the *z*BS-*x*PT-*y*BZT (MPB-1~5) ceramic samples.

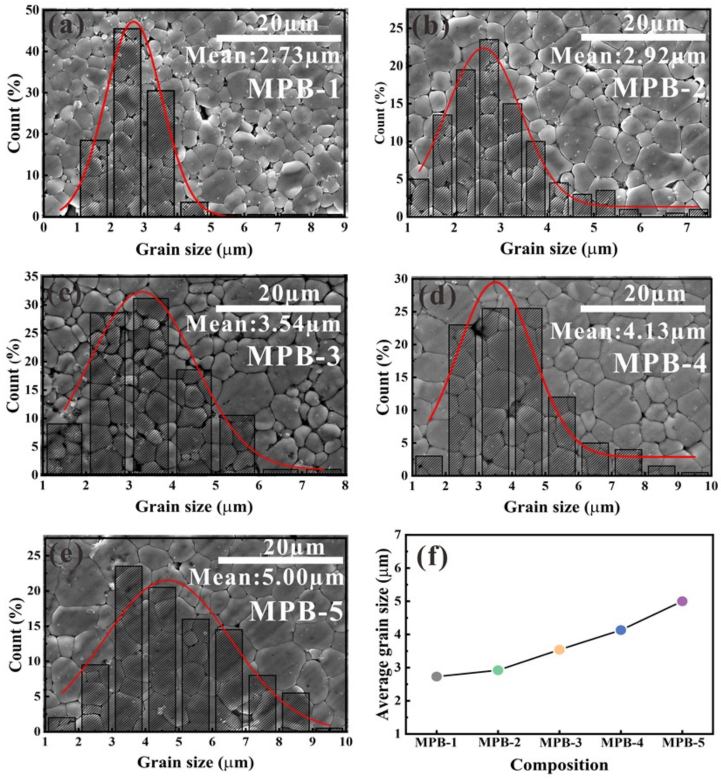

Fig. S4 SEM images of fresh cross-section and the average grain size distributions for the *z*BS-*x*PT-*y*BZT ceramics: (a) MPB-1, (b) MPB-2, (c) MPB-3, (d) MPB-4, (e) MPB-5. (f) The average grain size values of the *z*BS-*x*PT-*y*BZT (MPB-1~5) ceramics.

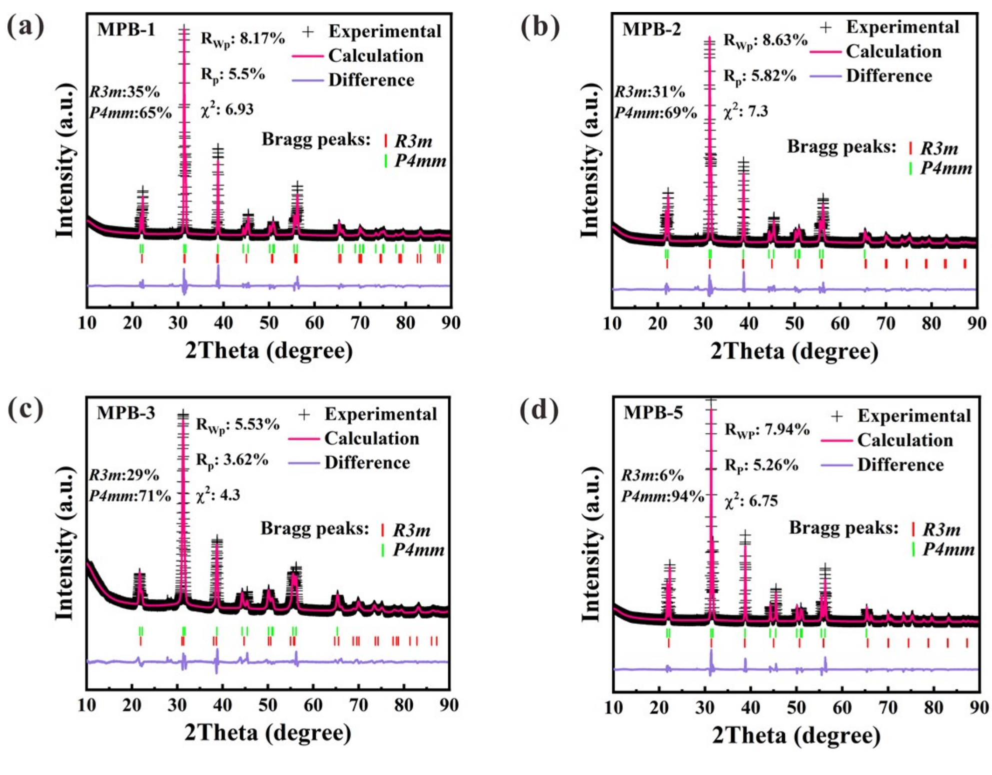

Fig. S5 Rietveld refinement of XRD patterns for the *z*BS-*x*PT-*y*BZT ceramics: (a) MPB-1, (b) MPB-2, (c) MPB-3, (d) MPB-5

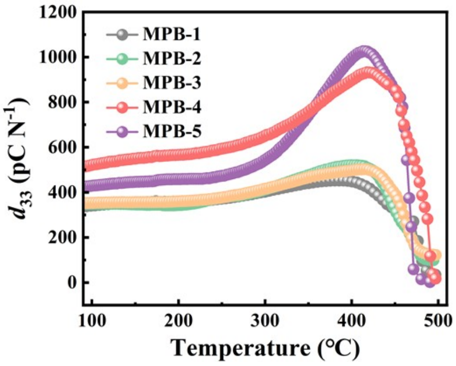

Fig. S6 The temperature-dependent *in-situ* quasi-static piezoelectric constant d_{33} of the poled *z*BS-*x*PT-*y*BZT (MPB-1~5) ceramic samples.

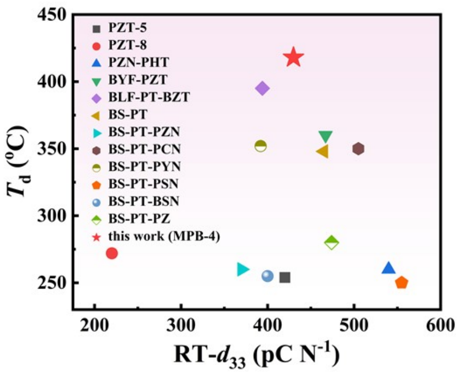

Fig. S7 Comparison of room-temperature d_{33} and T_d between the BS-PT-BZT (MPB-4 in this work) piezoceramic and other representative lead-based perovskite piezoceramics.[1-10]

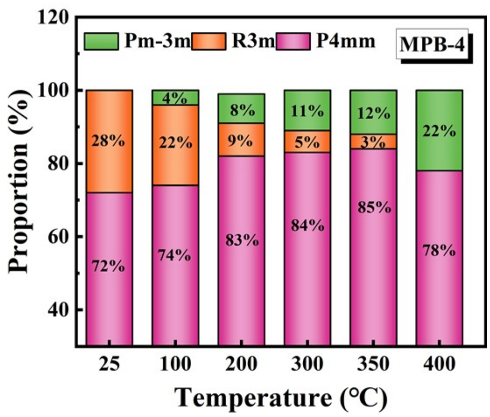

Fig. S8 The phase proportions of the MPB-4 piezoceramic at different temperatures.

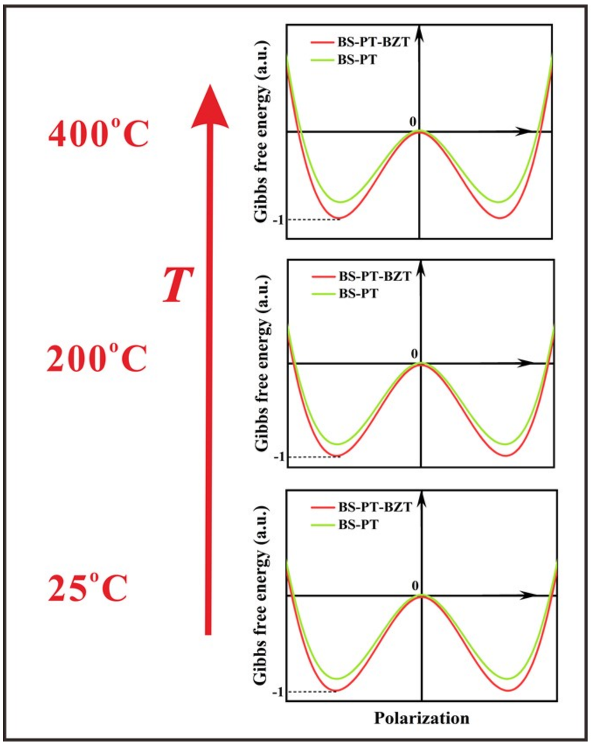

Fig. S9 The Gibbs free energy of BS-PT-BZT (MPB-4) and BS-PT located at MPB piezoceramics.[11]

Table S1. Comparison of room temperature d_{33}, high-temperature d_{33} (measured at T_d), T_d between the BS-PT-BZT (MPB-4, this work) piezoceramics and other typical lead-based piezoceramics[1-6].

Material	d_{33} (pC N^{-1}) at 25°C	d_{33} (pC N^{-1}) at T_d	T_d (°C)	Ref.
PZT-5	410	571	250	1
PZT-8	218	338	270	1
BS-PT	420	360	348	12
BS-PT-BY	438	665	348	13
BS-PT-PZ	474	430	343	7
BS-PT-BSN	450	460	275	14
BS-PT-BZH	420	762	373	11
BS-PT-BZT	430	932	418	This work

Table S2. The crystal structure parameters of the 0.36BS-0.62PT-0.02BZT (BS-PT-BZT, MPB-4 in this work) and the our previously reported 0.36BS-0.64PT (BS-PT64, MPB of (1-x)BS-xPT)[11] derived from the Rietveld refinement at different temperatures.

Materials	T_{test} (°C)	Space group	Phase content (%)	a (Å)	c (Å)	R_{wp} (%)	R_p (%)	χ^2
BS-PT64[11]	200	*P4mm*	72	4.0037	4.0745	6.32	4.58	3.26
		R3m	28	4.0380	4.0380			
	400	*P4mm*	60.5	4.0191	4.0631	7.15	5.04	3.1
		R3m	39.5	4.0312	4.0312			
BS-PT-BZT	200	*P4mm*	83	4.0010	4.0771	8.82	6.09	6.78
		R3m	9	4.1219	4.1219			
		Pm-3m	8	4.0149	4.0149			
	400	*P4mm*	78	4.0170	4.0651	9.53	7.2	6.76
		R3m	0	0	0			
		Pm-3m	22	4.0245	4.0245			

Table S3. Related parameters for Gibbs free energy calculations.[5, 15]

α_{ijk} coefficient	Formulas and values
α_1	$\alpha_1(T)=\frac{T-T_0}{2\varepsilon_0 C}$
α_{11}	$3.614\times10^7 m^5/C^2F$
α_{12}	$3.233\times10^8 m^5/C^2F$
α_{111}	$1.859\times10^8 m^9/C^4F$
α_{112}	$5\times10^8 m^9/C^4F$
α_{123}	$-3.5\times10^9 m^9/C^4F$

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