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

Supporting Information

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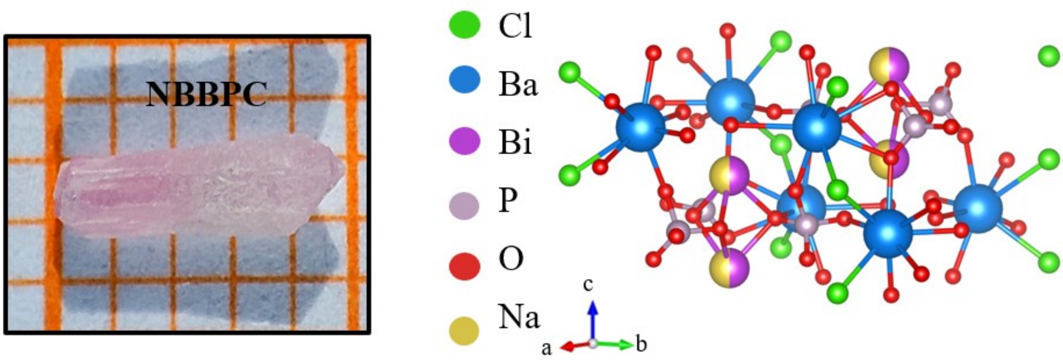
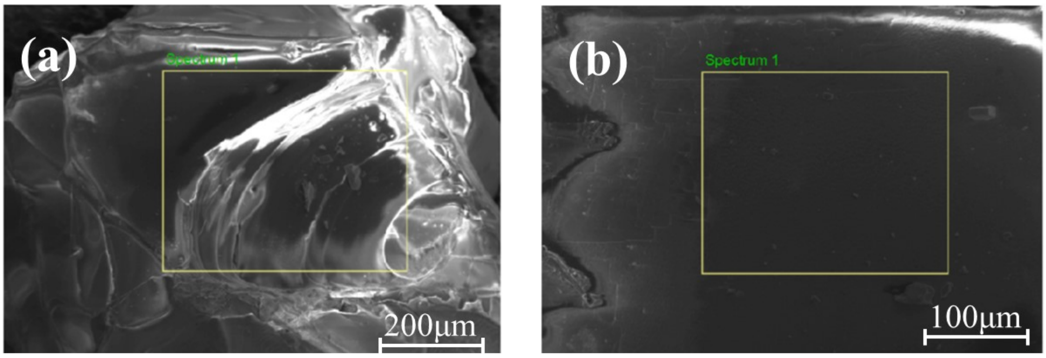
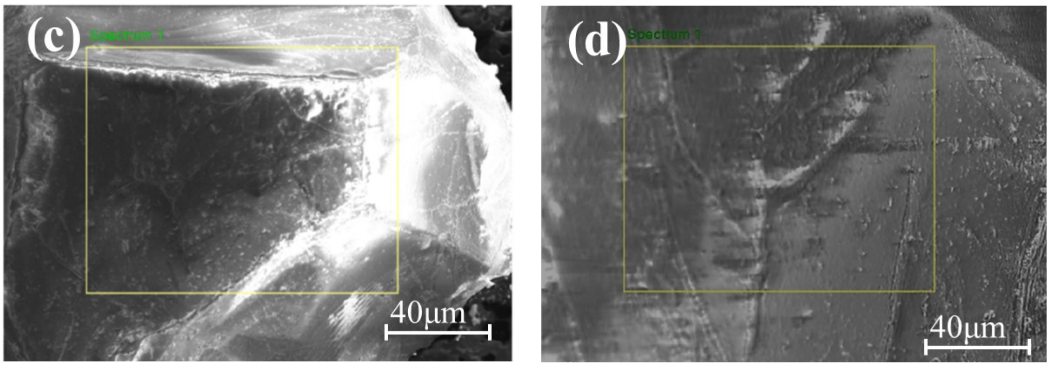


S1. BBNPC crystal samples and structure.



Spectrum	O	Na	P	Cl	Ba	Bi
Spectrum 1	70.87	4.41	10.21	3.47	7.90	3.15

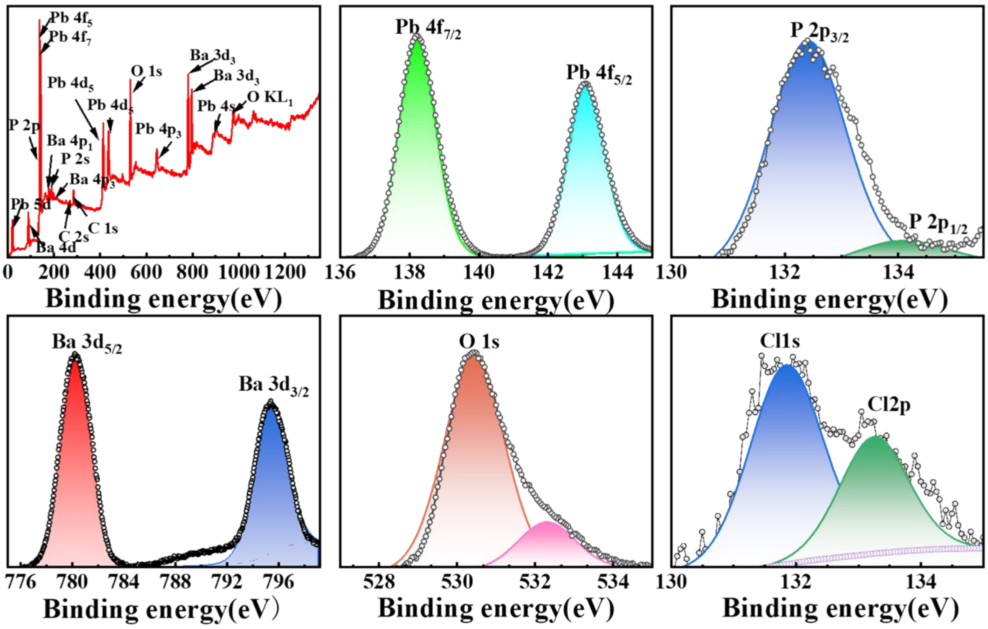
Spectrum	O	Na	Si	P	Cl	Ba	Bi
Spectrum 1	75.38	4.06	0.13	8.85	2.90	5.97	2.71



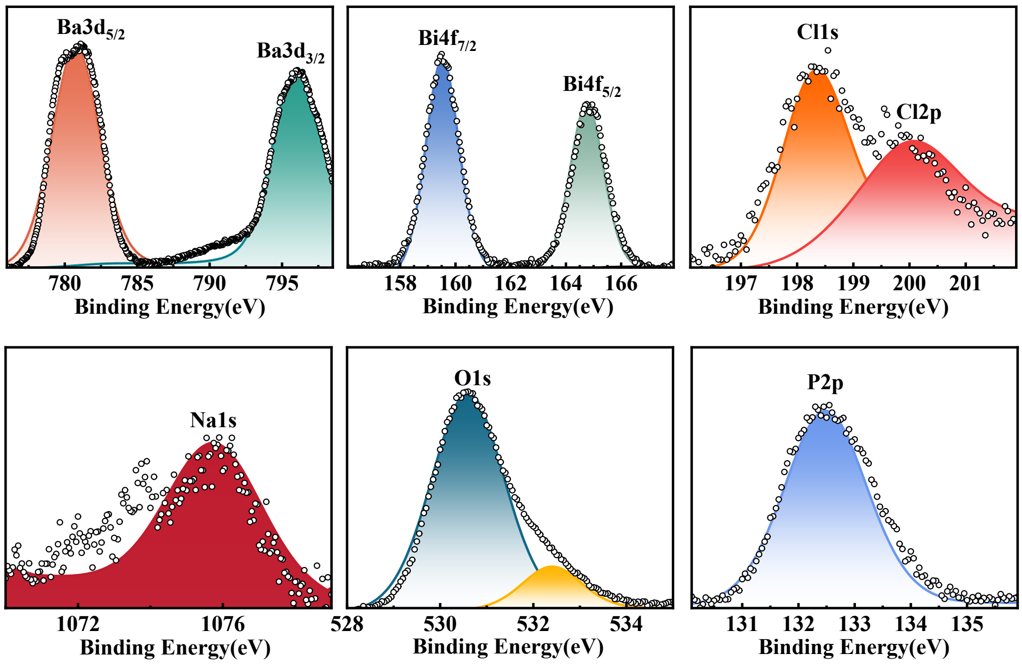
Spectrum	O	Na	Si	P	Cl	Ba	Pb
Spectrum 1	66.58	3.07	0.42	10.24	3.49	10.58	5.62

Spectrum	O	Na	Si	P	Cl	Ba	Pb
Spectrum 1	55.97	6.06	0.72	12.71	4.14	13.68	6.72

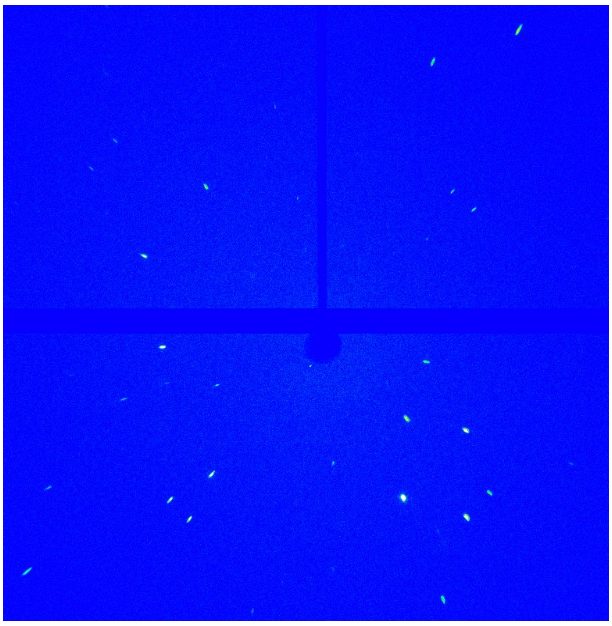
S2. (a) & (b) SEM morphology and EDS elemental content of BBPNC. (c) & (d) SEM morphology and EDS elemental content of BPPC.



S3.BPPCXPS data.



S4.BBNPCXPS data.



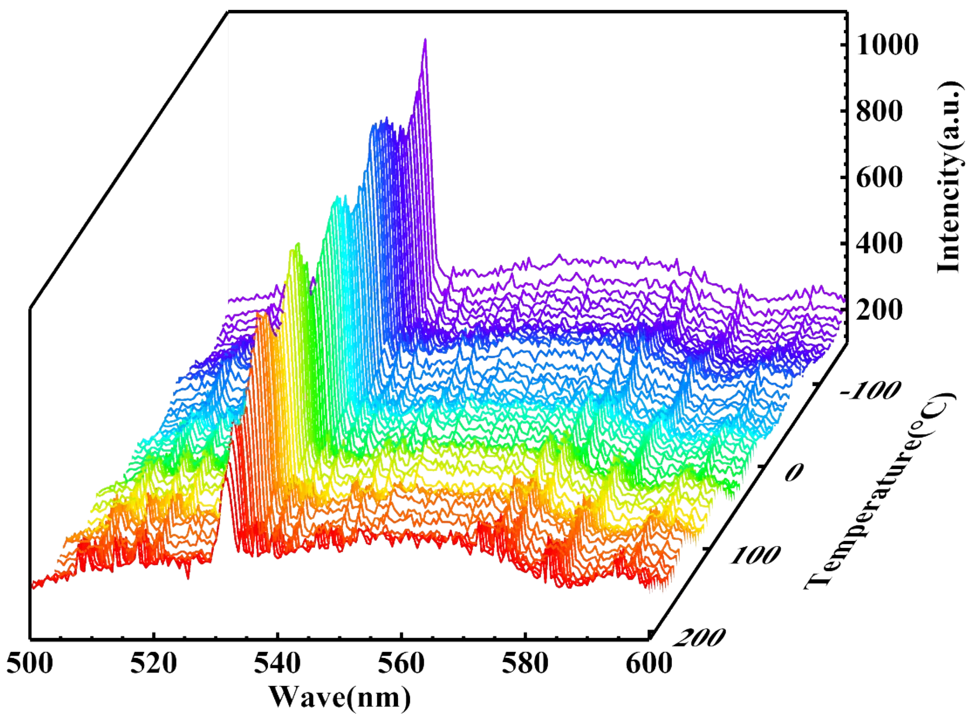
S5.[001] Directional single-crystal diffraction spots.

Tabel.S1 Cell parameters of $Ba_6Pb_{3.2}P_6O_{24}Cl_2$.

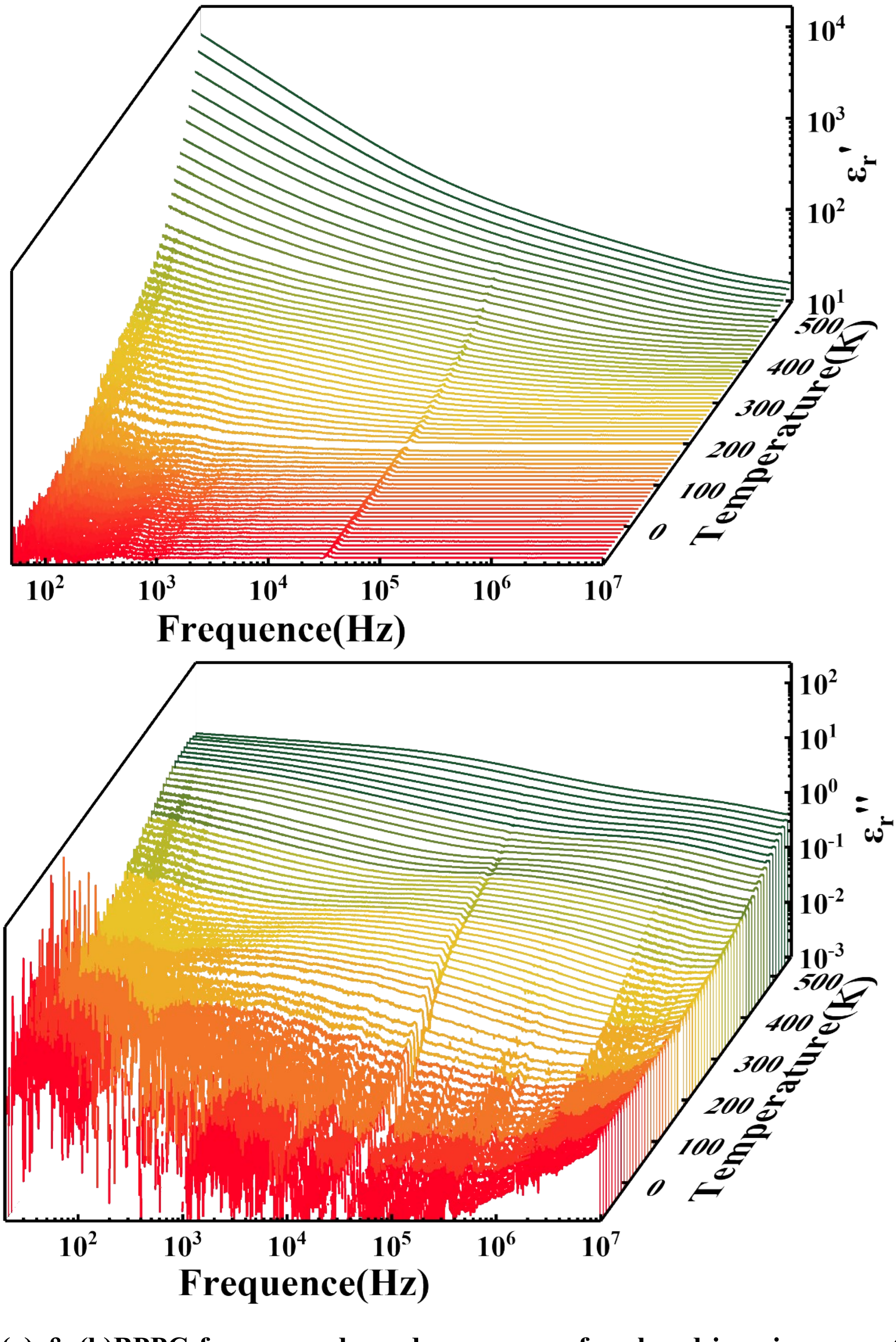
Formula	**$Ba_6Pb_{3.2}P_6O_{24}Cl_2$**
fw	2080.11
Space group	$P6_3$
a,Å	10.2299
b,Å	10.2299
c,Å	7.5680
α,β,deg	90
γ,deg	120
V, Å^3	685.89
Z	1
D_{calcd},g cm^{-3}	5.036
GOF on F^2	1.068
R1, wR2 [I > 2s (I)]	0.0528, 0.0984
R1, wR2 (all data)	0.0343, 0.1008

Tabel.S2 Cell parameters of $Ba_6Bi_2Na_2P_6O_{24}Cl_2$.

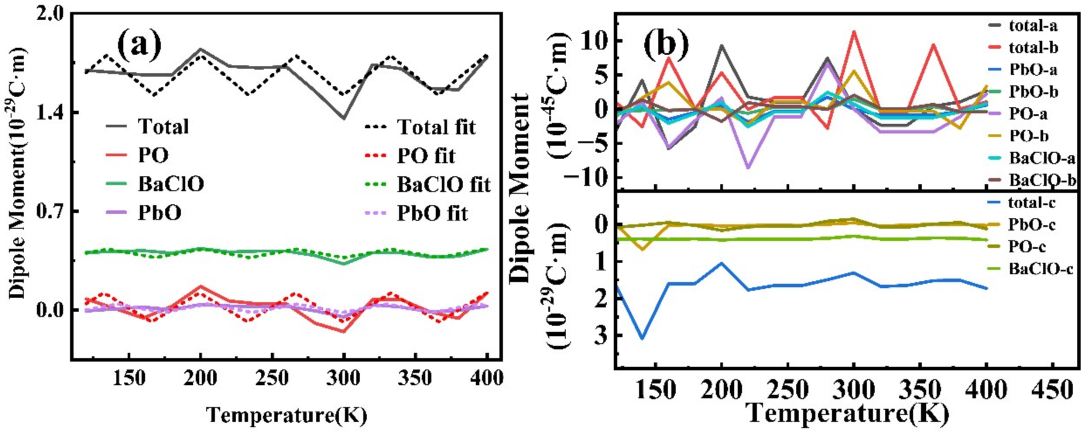
Formula	$Ba_6Bi_2Na_2P_6O_{24}Cl_2$
fw	1928.70
Space group	$P6_3$
a,Å	10.0732
b,Å	10.0732
c,Å	7.4666
α,β,deg	90
γ,deg	120
V, $Å^3$	656.13
Z	1
D_{calcd},g cm^{-3}	4.881
GOF on F^2	1.086
R1, wR2 [I > 2s (I)]	0.0419, 0.0911
R1, wR2 (all data)	0.0373, 0.0938



S6.SHG signal strength of BPPC in the 500-600 nm interval under 200-400 K.



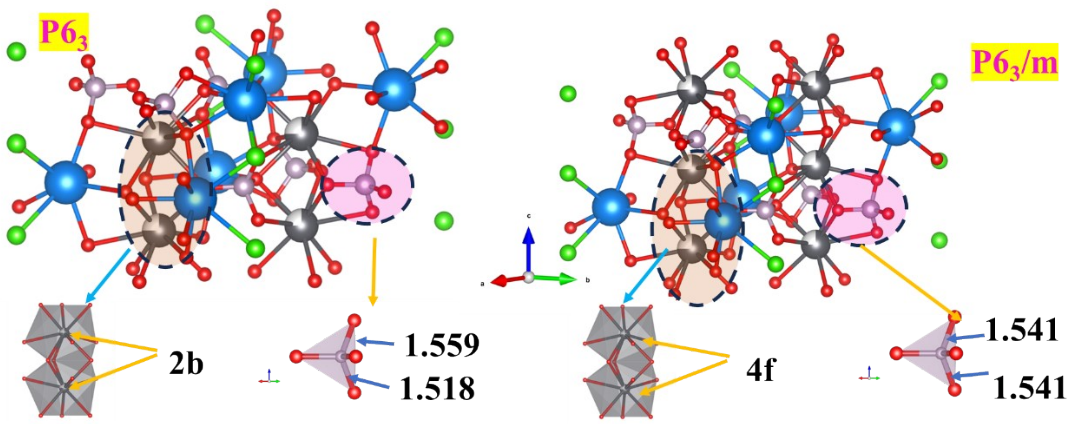
S7. (a) & (b)BPPC frequency dependence curve of real and imaginary parts of dielectric constant at 170-800 K.



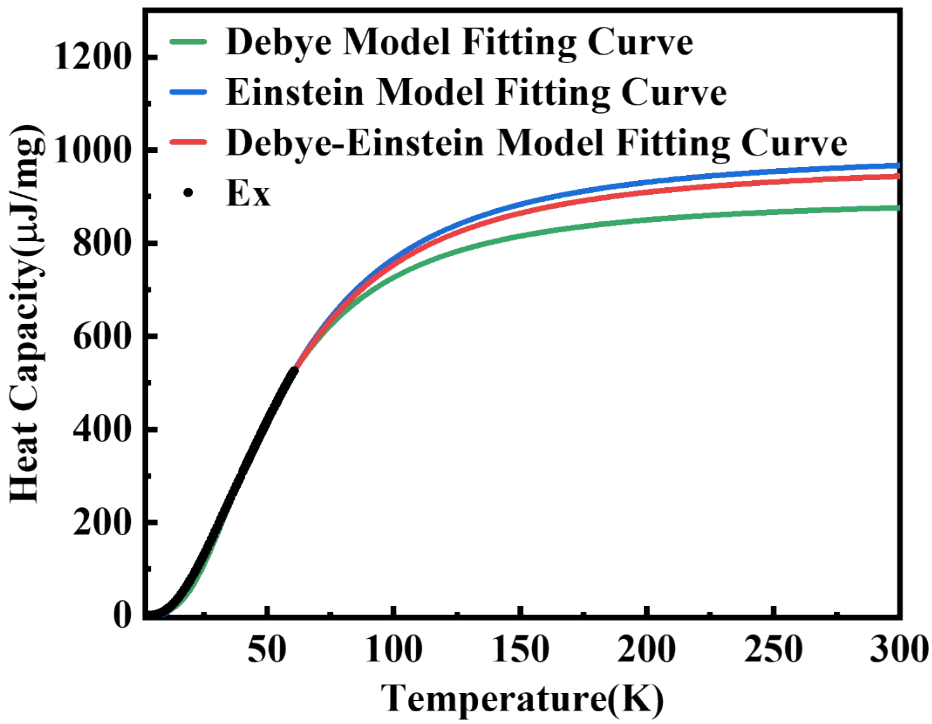
S8. (a) Calculation of electric dipole moments and Fourier triangular wave fitting of dipole moment vibrations for single crystal tests at 20 K intervals from 120-400 K. (b) The electric dipole moment components in directions a, b, and c are calculated for single crystal experiments at intervals of 20 K in the range of 120-400 K.

Table S3. $P6_3/m$ simulation of structural atomic positions

Atom($P6_3/m$)	x (Å)	Y(Å)	z (Å)	Occ	Site
Pb	0.33333	0.66667	0.00002	0.80	4f
Ba	0.26025	0.25160	0.25000	1.00	6h
P	0.03710	0.41040	0.25000	1.00	6h
Cl	0.00000	0.00000	0.00000	1.00	2b
O	0.48460	0.13540	0.25000	1.00	6h
O	0.12530	0.58590	0.25000	1.00	6h
O	0.08760	0.35850	0.08450	1.00	12i



S9. $P6_3$ vs. $P6_3/m$ space group comparison.



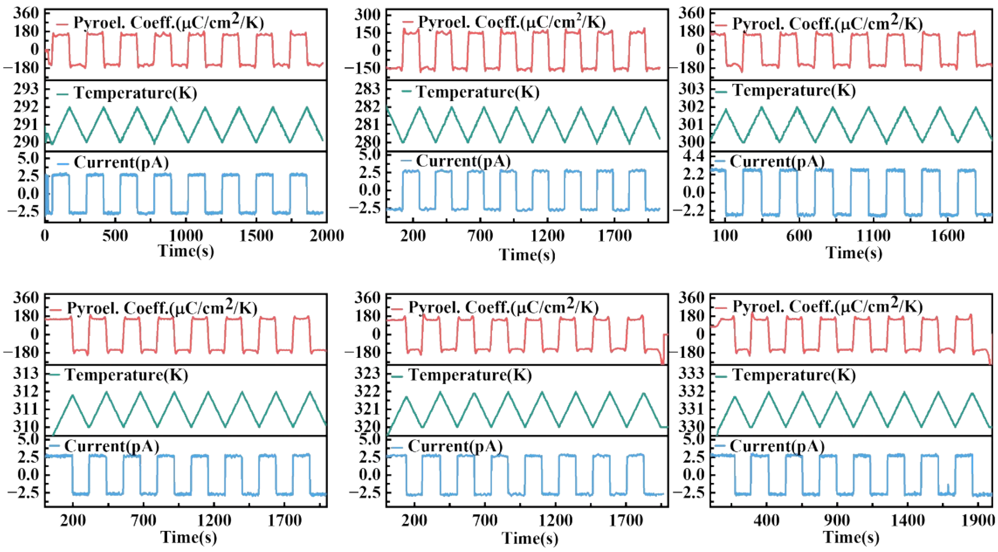
S10. Debye model, Einstein model, Debye-Einstein model specific heat fitting structure.

The Debye-Einstein Model various fitting parameters (1)：

$$C_p = 9aNR\left(\frac{T}{\theta_{Debye}}\right)^3 \int_0^{\frac{\theta_{Debye}}{T}} e^T \frac{T^4}{(e^T-1)^2} + (1-a)b3NR\left(\frac{\theta_{E1}}{T}\right)^2 e^{\frac{\frac{\theta_{E1}}{T}}{(e^{\frac{\theta_{E1}}{T}}-1)^2}} + (1-a)(1-b)3NR\left(\cdots\right. \; e^{\frac{\frac{\theta_{E2}}{T}}{(e^{\frac{\theta_{E2}}{T}}-1)^2}}$$

(1)

Where N, θ_{Debye} and $\theta_{E1(E2)}$ are Avogadro number, characteristic Debye temperature and characteristic Einstein temperature respectively. The parameter a is the proportion of Debye model. The parameter b is the proportion of Einstein model.



S11.Circulating current response and pyroelectric coefficient at different temperatures

Table S4. Comparison of room-temperature pyroelectric-related properties between BPPC and other famous inorganic pyroelectrics.
where $F_i=p_s/C_v$, $F_v=p_s/\varepsilon' C_v$, $F_D= p_s/C_v(\varepsilon' \tan\delta)^{1/2}$, $F_E= p_s^2/\varepsilon'(C_v)^2$

Materials	p_s μC/m2/K	C_v MJ/m³/K	ε' (10 kHz)	tanδ (10 kHz)	F_i 10^{-10} m/V	F_v m²/C	F_D 10^{-5} Pa$^{1/2}$	F_E 10^{-11} m³/J
BPPC	108	1.475	10.47	0.002	0.732	0.7	4.935	5.12
$LiTaO_3$[1]	190	3.2	47	0.005	0.59	0.14	1.22	0.75
PZT[2]	350	3.2	471	0.005	1.09	0.026	0.71	0.25
$LiNbO_3$[1]	96	2.7	31		0.35	0.14		0.41
$BaTiO_3$[3]	200	2.5	1200		0.8	0.008		0.53
ZnO[4]	9.4	3.1	11		0.03	0.03		0.08
$Li_2B_4O_7$[5]	30	3.3	2	0.03	0.09	0.53	0.37	0.93
SBN[5]	550	2.2	400	0.003	2.48	0.07	2.26	1.74
$NaNO_2$[5]	40	2.2	4		0.182	0.514		0.93
PMN-28PT：Mn[6]	980	2.44	650	0.0005	4.02	0.062	7.05	2.5
34PIN-34PMN-32PT[6]	705	2.5	525	0.002	2.82	0.054	2.75	1.5

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