Supporting Information

The strong electrocaloric effect in molecular ferroelectric $ImClO_4$ with ultrahigh electrocaloric strength

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Experimental section

Synthesis of $ImClO_4$ crystal

In this work, all reagents and solvents were commercial and implemented without further purification. The imidazolium perchlorate $[C_3N_2H_5]ClO_4$ crystal was directly synthesized by evaporating the homogeneous aqueous solution containing equal molar amounts of imidazolium (98%, Aladdin) and perchloric acid ($HClO_4$) (Analytically pure, Sinopharm Chemical Reagent) at room temperature for few weeks. The as-prepared $ImClO_4$ crystals were polished to smooth pieces with a thickness of ~300 μm. The gold electrodes were deposited onto the surfaces of the crystal pieces with masks by an ion-sputtering instrument. The diameter of the electrodes is 0.5 mm.

Material characterization

Polarization versus electric field (*P*-*E*) hysteresis loops of the crystal were characterized by a Polarization Loop Test System (PolyK Technologies, USA). The relative dielectric constants and losses of $ImClO_4$ were tested by impedance analyzer (E4980A; Agilent technologies company, Palo Alto, CA) from 280 K to 390 K with frequencies of 1 kHz, 10 kHz, 100 kHz, and 1 MHz, respectively. The information of phase and crystalline structure under different temperatures (323 K, 353 K, 373 K, 383 K, and 393 K) were analyzed by an XRD with a Cu Kα radiation (Empyrean, PANalytical B.V., Netherlands). The scan range is 10°-50° with a scan rate of 5° min^{-1}. The crystal information was analyzed from the results of XRD curves using the Celcef3 and MDI Jade software. Differential scanning calorimetry (DSC, TA Instrument Q100) was conducted from 290 K to 390 K at heating and cooling rates of 5 K min^{-1}. Raman spectra were recorded at different temperature (300 K, 350 K, and 390 K) with a

HORIBA LabRAM HR Evolution spectrometer system with the 532 nm line of an air-cooled Ar-ion laser.

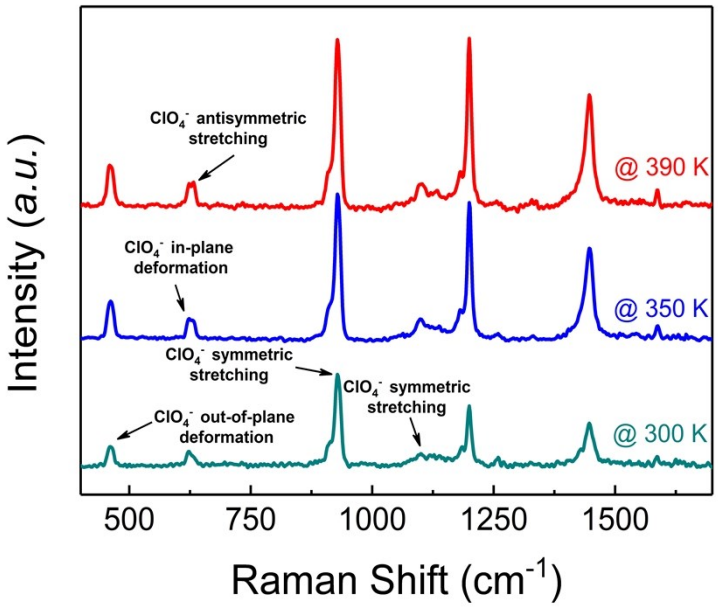

Fig. S1. Raman spectra of $ImClO_4$ crystal at different temperatures.

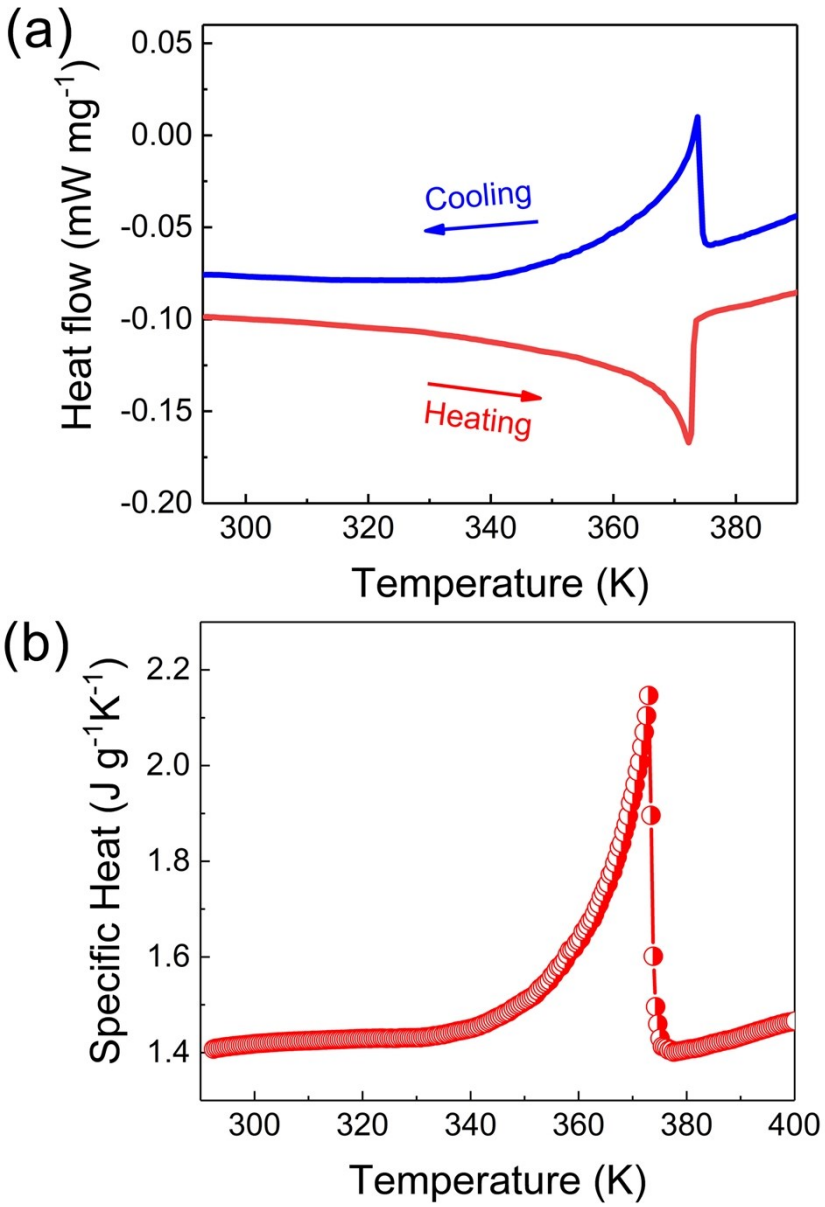

Fig. S2. (a) DSC curves of $ImClO_4$ testing from 280 K to 390 K acquired from heating and cooling processes. (b) The specific heat of $ImClO_4$.

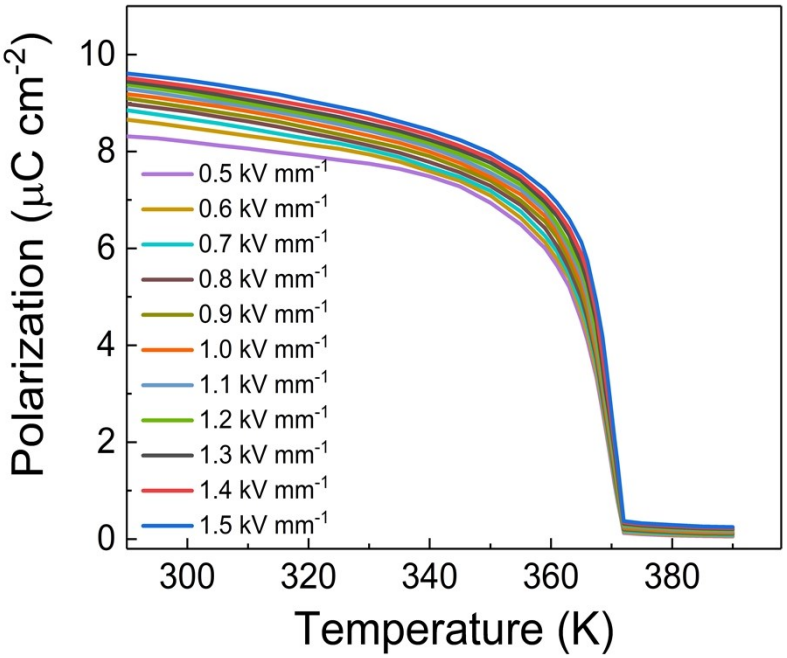

Fig. S3. Polarization as a function of temperature under different electric fields for $ImClO_4$ crystal.

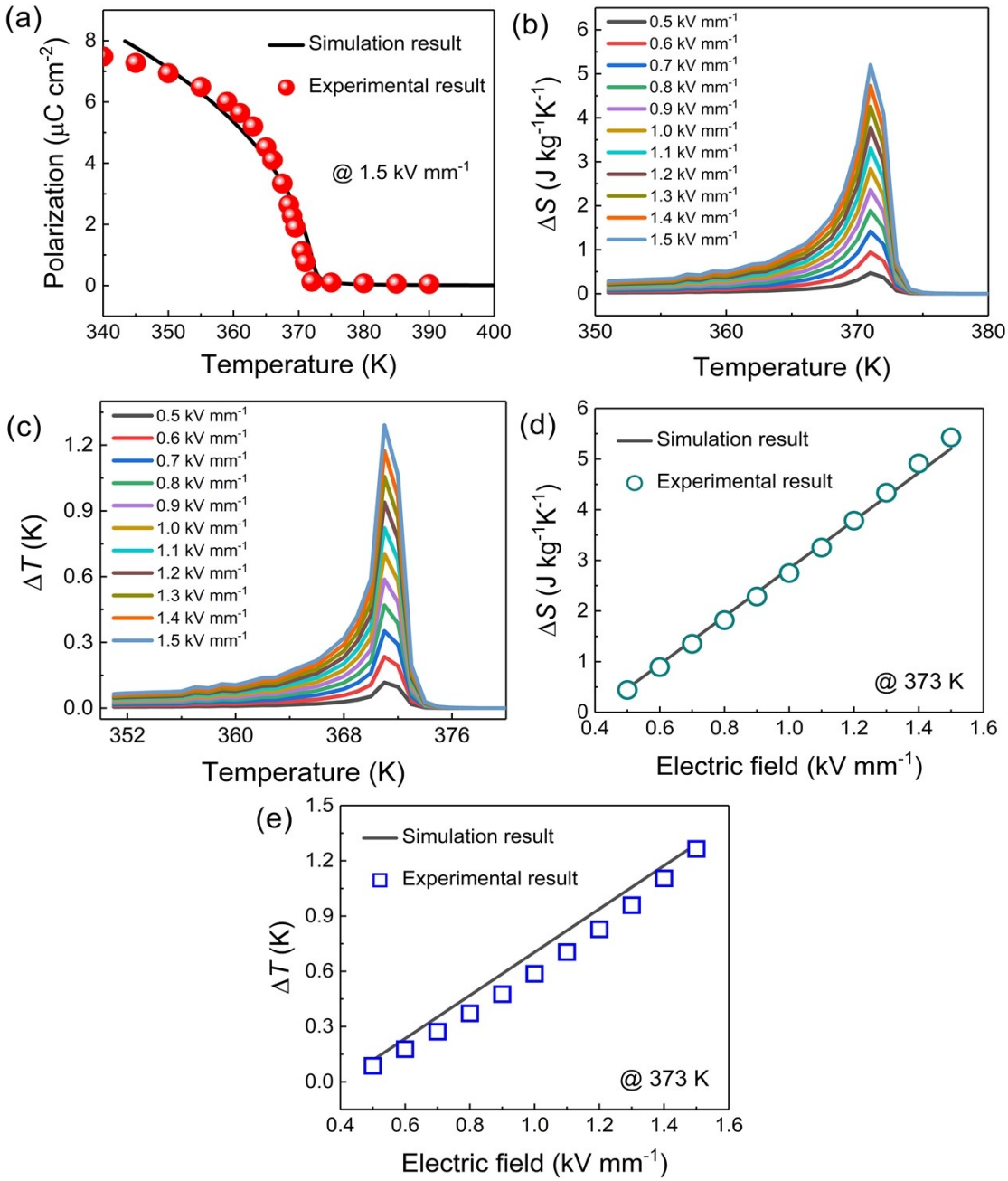

Fig. S4 (a) Comparison of the experimental and simulated temperature-dependent polarization of $ImClO_4$. The simulation of (b) entropy change and (c) temperature change under increasing electric fields calculated by thermodynamics. (d) and (e) Comparison of the experimental and simulated ΔS and ΔT of $ImClO_4$ as a function of electric fields.

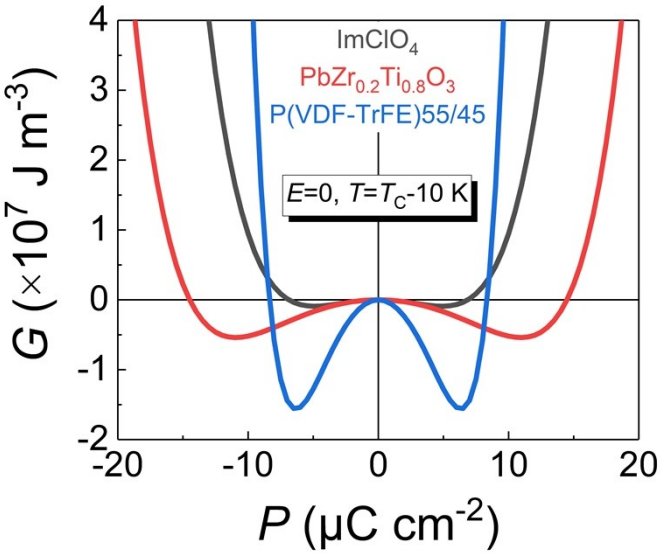

Fig. S5. Free energy of $ImClO_4$, $PbZr_{0.2}Ti_{0.8}O_3$, and P(VDF-TrFE) 55/45 at $T=T_c$-10 K.

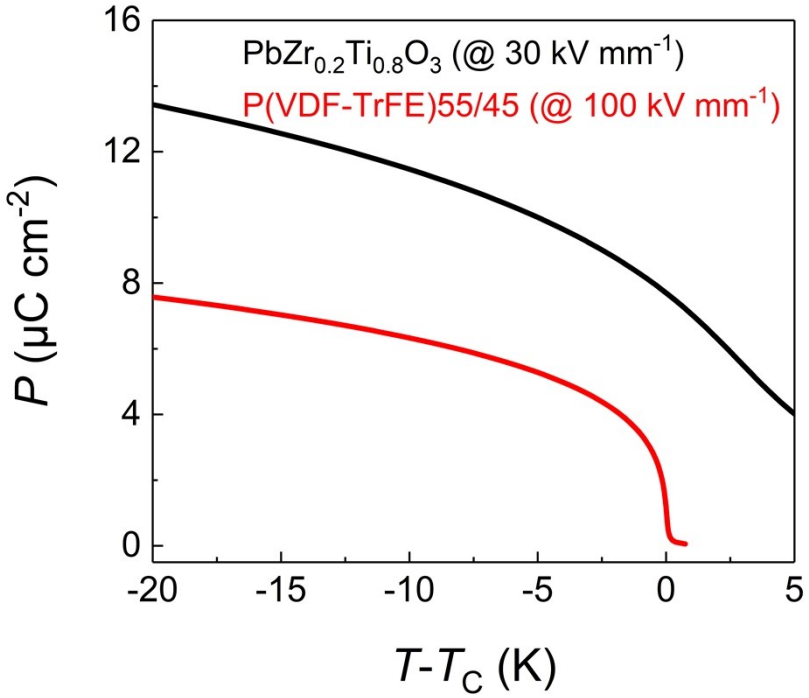

Fig. S6 The calculated polarization of $PbZr_{0.2}Ti_{0.8}O_3$ and P(VDF-TrFE)55/45 as a function of temperature.

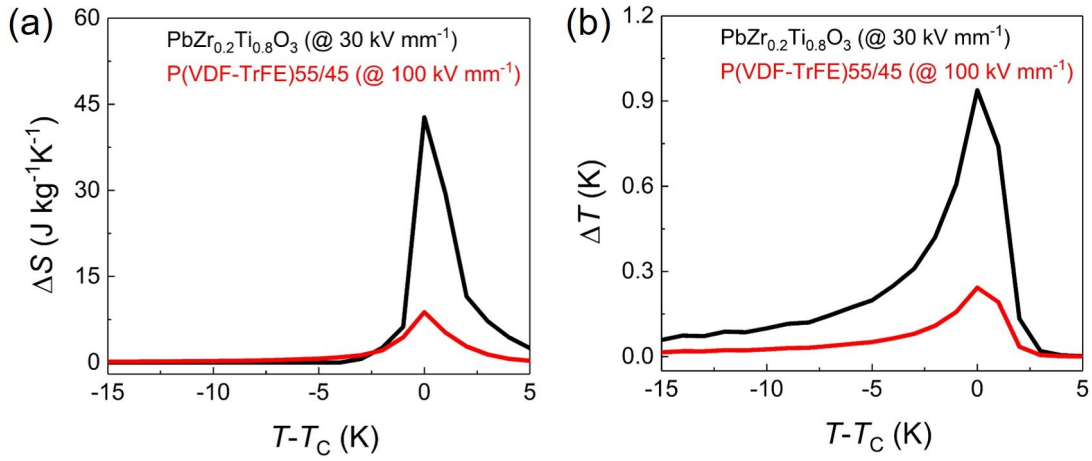

Fig. S7 The calculated (a) Δ*S* and (b) Δ*T* of $PbZr_{0.2}Ti_{0.8}O_3$ and P(VDF-TrFE)55/45.

Supporting note S1: Thermodynamic Calculations:

We used a hybridized approach of combining experimentally calculated results with equations derived from the Ginzburg-Landau-Dovenshire theory. To be exact, equations S3 an S4 were fitted by the method of least squares with experimental results represented in Fig. S3 to get the values of coefficients.

The total free energy of improper ferroelectric materials generally can be expressed by,

$$G = \alpha_1(T - T_0)P^2 + \alpha_{11}P^4 + \alpha_{111}P^6 - PE \quad \text{(S1)}$$

The spontaneous polarization can be calculated from,

$$0 = (\frac{\partial G}{\partial P})_{P=P_s} = 2\alpha_1(T - T_o)P_s + 4\alpha_{11}{P_s}^3 + 6\alpha_{111}{P_s}^5 - E \quad \text{(S2)}$$

Where,

$$\chi = \frac{1}{\varepsilon} = \frac{1}{\varepsilon_r \varepsilon_0} = 2\alpha_1 \quad \text{(S3)}$$

Values of the coefficients α_{11} and α_{111} were extracted from the experimental *P-T* plots for a range of applied fields using the fitting equation given as:

$$T - T_o = \frac{4\alpha_{11}{P_s}^3 + 6\alpha_{111}{P_s}^5 - E}{2\alpha_1 P_s} \quad \text{(S4)}$$

The values of the constants thus calculated are given in table S1. Temperature and entropy change were calculated using equations below for a range of electric fields.

$$\Delta S = -\int_{E_1}^{E_2} \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_E dE \quad \text{(S5)}$$

$$\Delta T = -\int_{E_1}^{E_2} \frac{T}{\rho C_p}\left(\frac{\partial P}{\partial T}\right)_E dE \quad \text{(S6)}$$

The same model and technique were employed on $PbZr_{0.2}Ti_{0.8}O_3$ and P(VDF-TrFE)55/45. For the calculation of Gibbs free energy vs polarization (shown as Fig. 4(a) in manuscript), Eq. S1 (with *E=0*) was used. Whereas for thermodynamically simulated polarization vs electric field

loops (shown as Fig. 4(b) in manuscript), Eq. S2 was used for all three materials.

Table S1. The crystal cell parameters of $ImClO_4$ at the ferroelectric phase (293 K) and the paraelectric phase (323 K).

		Ferroelectric phase		Paraelectric phase	
		Reported [S1]	Experiment	Reported [S1]	Experiment
Crystal system		Trigonal		Trigonal	
Space group		*R3m*		*R-3m*	
Unit-cell parameters	a (Å)	5.484	5.484	5.554	5.549
	α (º)	95.18	95.16	95.30	95.35
	V (Å^3)	162.78	162.8	168.98	168.4

Table S2. Values of Constants extracted by fitting experimental data over Ginzburg-Landau-Dovenshire theory

Coefficient	α_1	α_{11}	α_{111}
Extracted value	7.533×10^7 J m C^{-2} K^{-1}	1.5×10^{11} J m^5 C^{-4}	2×10^{12} J m^9 C^{-6}

Table S3. Densities of $ImClO_4$, $PbZr_{0.2}Ti_{0.8}O_3$ and P(VDF-TrFE)55/45 used in this work

Material	$ImClO_4$	$PbZr_{0.2}Ti_{0.8}O_3$	P(VDF-TrFE)55/45
Density	1.719 g cm^{-3}	7.920 g cm^{-3}	1.890 g cm^{-3}

Table S4. Thermodynamic calculated EC strength of $ImClO_4$, $PbZr_{0.2}Ti_{0.8}O_3$, and P(VDF-TrFE)55/45.

Electrocaloric strength	$ImClO_4$	$PbZr_{0.2}Ti_{0.8}O_3$	P(VDF-TrFE)55/45
$\|\Delta S/\Delta E\|$ (Jmm $K^{-1}kg^{-1}kV^{-1}$)	3.16	1.42	0.0878
$\|\Delta T/\Delta E\|$ (Kmm kV^{-1})	0.858	0.031	0.0024

Reference

[S1] Z. Pająk, P. Czarnecki, B. Szafrańska, H. Małuszyńska and Z. Fojud, *J. Chem. Phys.* 2006, **124**, 144502.