Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Giant Electrocaloric Effect in a Molecular Ceramic

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Experimental Section

Synthesis of $HQReO_4$

All reagents and solvents in the syntheses were of reagent grade and used without further purification. The crystalline salt of $HQReO_4$ was obtained by evaporating equimolar solutions of perrhenic acid and quinuclidine. The molecular ceramics are obtained by automatic heating tableting machine (Hench Technologies). The molecular ceramic of $HQReO_4$ was prepared at 373 K with a pressure of 454 MPa. The pressure holding time was set at 15 minutes to ensure shaping of the molecular ceramics.

Characterization of $HQReO_4$

The P–E measurements were performed on a probe station equipped with a Precision Premier II Ferroelectric Tester (Radiant Technologies), and typical ac voltage with a triangular wave was applied at different frequencies. And the temperature was controlled by a mk2000B temperature controller (Instec, Inc.).

Differential scanning calorimetry (DSC) measurements were performed on a DSC 214 Polyma (NETZSCH, Inc.) under nitrogenatmosphere in aluminum crucibles with a heating or cooling rate of 5 K min^{-1}.

Complex dielectric permittivities were measured with a TH2828A impedance analyzer over the frequency range from 500 Hz to 1 MHz with an applied electric field of 0.5 V.

The Vickers hardness of a series of compounds was measured on a nanoindentation instrument (Hysitron, Inc.). 3-5 samples were tested for each compound.

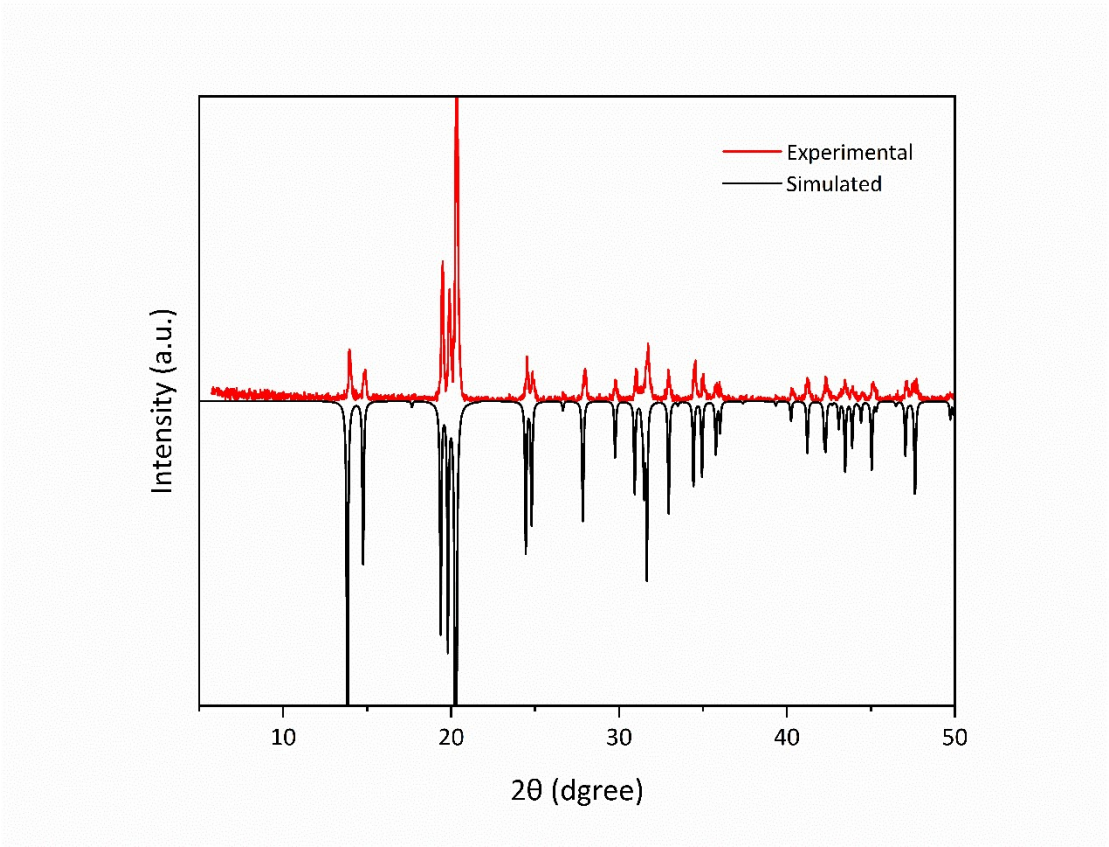

Figure S1. XRD patterns of $HQReO_4$ measured at 300K

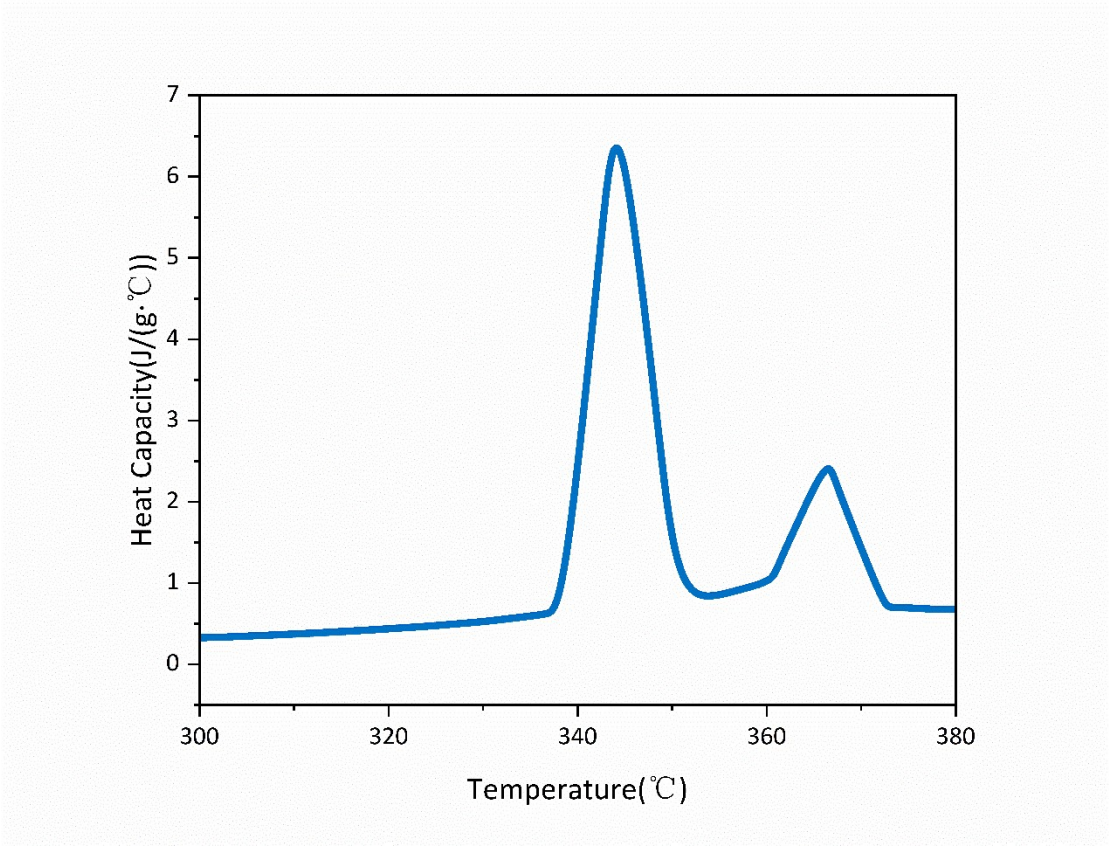

Figure S2. Temperature-dependent Heat capacity-temperature curve of $HQReO_4$

The Landau theory of phase transition was developed to describe the phase transition behaviour of ferroelectrics near the transition point.

According to LGD theory, the free energy of HQReO4 is expressed as:

$$G=G_0+\frac{\alpha}{2}(T-T_0)P^2+\frac{\beta}{4}P^4+\frac{\gamma}{6}P^6-PE \qquad (S1)$$

Where,

$$\alpha=(\varepsilon_0 C)^{-1} \qquad (S2)$$

It is known that,

$$dA=-SdT+X_I dx_i+E_m dD_m,$$
$$dH=TdS-x_I dX_i-D_m dE_m,$$
$$dH_1=TdS-x_I dX_i+E_m dD_m,$$
$$dH_2=TdS+X_I dx_i-D_m dE_m, \qquad (S3)$$
$$dG=-SdT-x_I dX_i-D_m dE_m,$$
$$dG_1=-SdT-x_I dX_i+E_m dD_m,$$
$$dG_2=-SdT+X_I dx_i-D_m dE_m,$$

$$G=G_0+\frac{1}{2}\alpha(T-T_0)D^2+\frac{1}{4}\beta D^4+\frac{1}{6}\gamma D^6 \qquad (S4)$$

Where T is temperature, S is entropy, X is stress, x is strain, E is electric field and D is electric displacement which could also be expressed as polarization (P).

From equation S3 and S4, it can be figured out that,

$$\frac{\partial G_1}{\partial D}=E=\alpha(T-T_0)D+\beta D^3+\gamma D^5 \qquad (S5)$$

When E = 0,

$$P_s^2=-\frac{\beta}{2\gamma}\left\{1+\left[1-4\alpha\gamma\beta^{-2}(T-T_0)\right]^{1/2}\right\} \qquad (S6)$$

When the temperature is at the Curie temperature, The ferroelectric phase has the same G as the paraelectric phase. From equation (S4), it can be expressed as:

$$\frac{1}{2}\alpha(T_c-T_0)P_{sc}^2+\frac{1}{4}\beta P_{sc}^4+\frac{1}{6}\gamma P_{sc}^6=0 \qquad (S7)$$

$$\alpha(T_c-T_0)P_{sc}+\beta P_{sc}^3+\gamma P_{sc}^6=0 \qquad (S8)$$

From equation (S7) and (S8),

$$T_c=T_0+\frac{3\beta^2}{16\alpha\gamma} \qquad (S9)$$

From equation (S7) and (S8), it can be easily figured out that,

$$\beta=16\alpha(T_0-T_C)/(3P_{s0}^2) \qquad (S10)$$

$$\gamma=16\alpha(T_C-T_0)/(3P_{s0}^4) \qquad (S11)$$

The values of the constants calculated are given in table. S1.

Table. S1. Values of Constants calculated by Ginzburg-Landau-Dovenshire theory

Coefficient	α	β	γ
Extracted value	4.71×10^{7}	-2.36×10^{12}	5.526×10^{15}

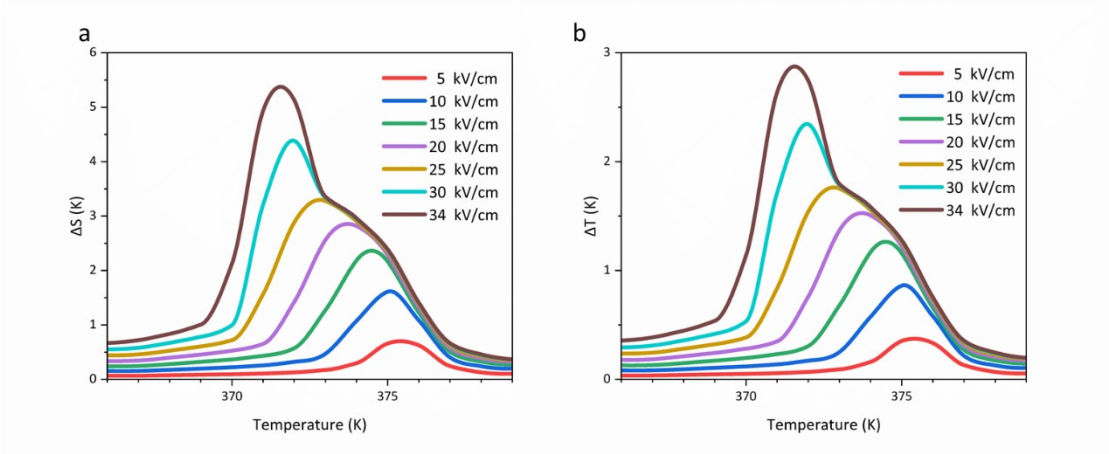

Figure S3. The simulation of (a) entropy change and (b) temperature change calculated by thermodynamics.

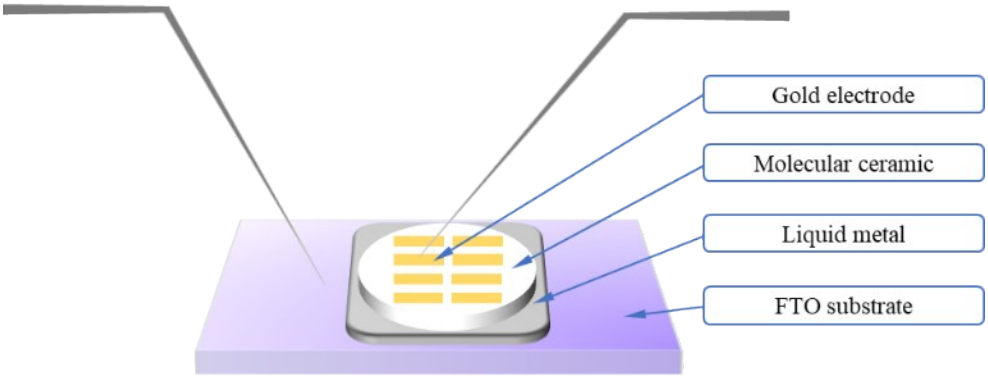

Figure S4. *P-E* measurement schematic diagram.

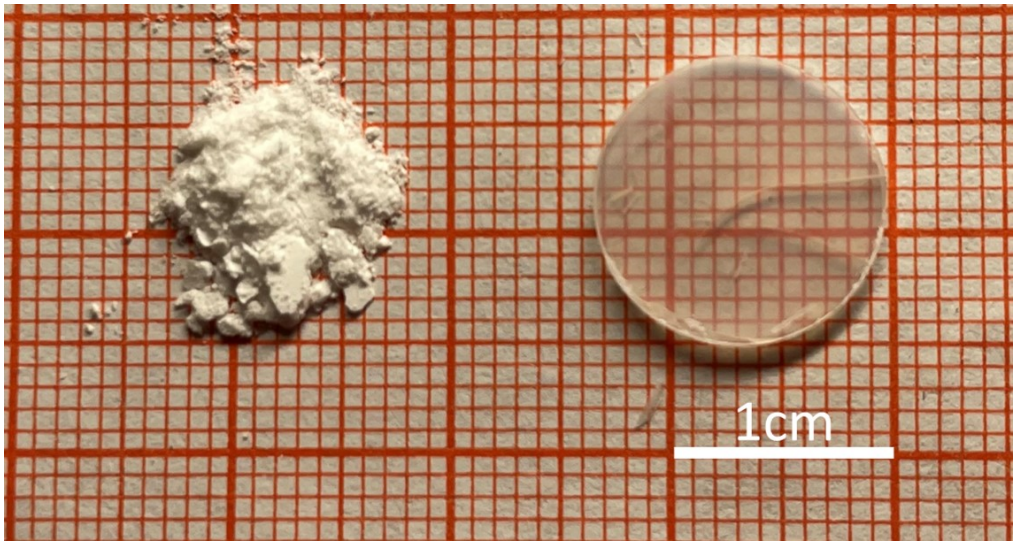

Figure. S5. Optical image of $HQReO_4$ in powder form (left) and molecular ceramic form(right).