

Supporting information

Above-Room-Temperature Ferroelastic Phase Transition in a Perovskite-Like Compound $[\text{N}(\text{CH}_3)_4][\text{Cd}(\text{N}_3)_3]$

Zi-Yi Du, Ying-Ping Zhao, Wei-Xiong Zhang,* Hao-Long Zhou, Chun-Ting He, Wei Xue, Bao-Ying Wang, Xiao-Ming Chen

Experimental details

Materials and instrumentations. All chemicals were obtained from commercial sources and used without further purification. FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellets from 4000 to 400 cm^{-1} . Powder X-Ray diffraction (PXRD) patterns (Cu-K α) were collected on a Bruker Advance D8 θ -2 θ diffractometer. Thermogravimetric analyses were carried out on a TA Q50 system at a heating rate of 5 $^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Differential Scanning calorimeter (DSC) measurement was performed by heating and cooling the powder sample (7.78 mg) in the temperature range of 228 – 383 K on a NETZSCH DSC 204F1 instrument. The measurement was carried out under a nitrogen atmosphere in aluminium crucibles with a heating/cooling rate of 5 K min^{-1} . The complex permittivity was measured using a Tonghui TH2828A LCR meter in a Mercury iTC cryogenic environment controller of Oxford Instrument.

Synthesis. Cadmium nitrate tetrahydrate (0.5 mmol) was added into an aqueous solution (15 mL) of sodium azide (6.0 mmol) and tetramethylammonium bromide (3.0 mmol), the resultant white suspension was filtered and then the clear solution was allowed to stand at room temperature. After two days later, colorless block-shaped crystals of **1** were deposited from the filtrates, in a *ca.* 55% yield based on Cd. The purity of the as-grown crystals was confirmed by X-ray powder diffraction (Fig. 2). IR data (KBr, cm^{-1}): 3378(m), 3030(m), 2955(m), 2069(s), 1483(s), 1417(m), 1340(m), 1327(m), 1290(m), 952(s), 640(m), 629(m), 612(m).

Caution! Although our sample never exploded during handling, azide metal complexes are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

Single-crystal X-ray crystallography. Diffraction intensities for a same crystal at 220 K, 300 K and 350 K were collected on an Oxford Gemini S Ultra CCD diffractometer with

graphite-monochromated Mo-K α radiation ($\lambda = 0.71073\text{\AA}$). The measurement temperatures were controlled by a dry nitrogen open flow using a Cryojet controller of Oxford Instrument, and corrected by a thermal couple at the crystal position. Absorption corrections were applied by using multi-scan program SADABS.^{S1} The structures were solved with direct method and refined with a full-matrix least-squares technique with the SHELXTL program package.^{S2} Anisotropic thermal parameters were applied to all non-hydrogen atoms. All the hydrogen atoms were generated geometrically. Crystallographic data and structural refinements for **1** under the three different temperatures are summarized in Table S1. Important bond lengths are listed in Table S2. More details about the crystallographic data have been deposited as Supplementary material.

Table S1 Summary of crystal data and structural refinements for **1** at three different temperatures.

Empirical formula	C ₄ H ₁₂ N ₁₀ Cd ₁		
Formula weight	312.64		
Temperature (K)	220(2)	300(2)	350(2)
Phase type	α	γ	δ
Crystal system	Monoclinic	Monoclinic	Cubic
Space group	<i>C2/c</i>	<i>P2₁/m</i>	<i>Pm-3m</i>
<i>a</i> (Å)	15.692(4)	6.3264(3)	6.5228(1)
<i>b</i> (Å)	8.8335(6)	13.3644(6)	6.5228(1)
<i>c</i> (Å)	9.529(6)	6.4349(3)	6.5228(1)
α /deg	90	90	90
β /deg	125.56(6)	90.023(4)	90
γ /deg	90	90	90
<i>V</i> /Å ³	1074.5(7)	544.06(4)	277.525(7)
<i>Z</i>	4	2	1
<i>D_{calcd}</i> /g cm ⁻³	1.933	1.908	1.871
μ /mm ⁻¹	2.021	1.996	1.956
GOF on F ²	1.088	1.097	1.057
R1, wR2 [<i>I</i> >2 σ (<i>I</i>)]	0.0184, 0.0365	0.0303, 0.0704	0.0199, 0.0474
R1, wR2 (all data)	0.0239, 0.0382	0.0414, 0.0763	0.0208, 0.0477

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2 \}^{1/2}$$

Table S2 Selected bond lengths (Å) for **1** at three different temperatures.

220 K			
Cd(1)–N(4)	2.333(3)	Cd(1)–N(1)	2.3415(18)
Cd(1)–N(3)#1	2.3477(19)		
300 K			
Cd(1)–N(1)	2.321(4)	Cd(1)–N(3')	2.33(3)
Cd(1)–N(5)	2.334(4)	Cd(1)–N(3)	2.35(3)
350 K			
Cd(1)–N(1)	2.319(9)		

Symmetry code: #1 – $x + 1/2, y + 1/2, -z + 1/2$.

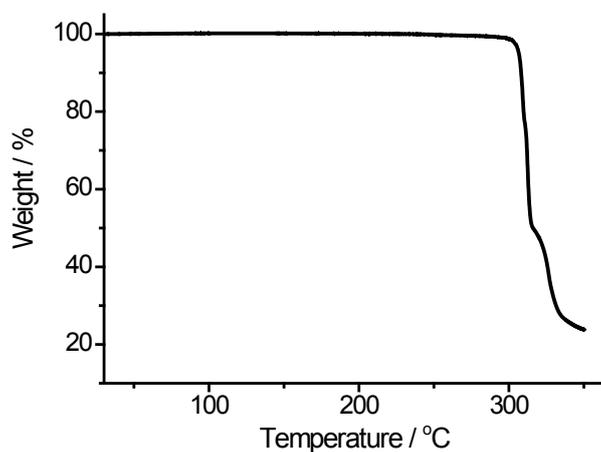


Fig. S1 TGA curve for **1**.

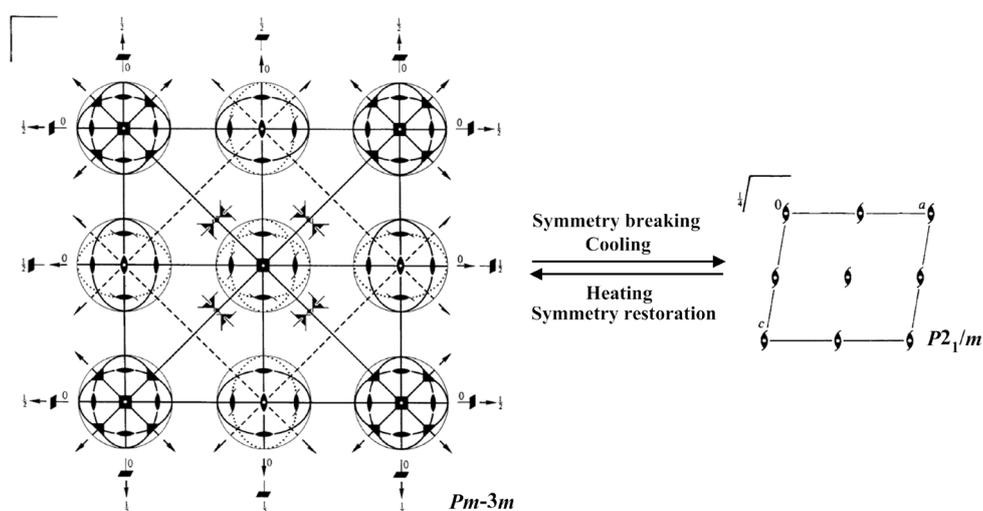


Fig. S2 Symmetry breaking process in **1** during temperature cooling down and heating up processes (The space-group diagrams are copied from reference 22).

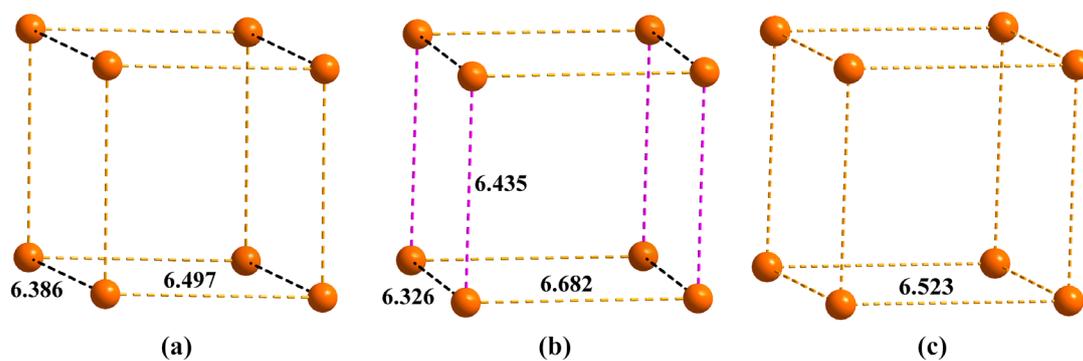


Fig. S3 The Cd···Cd distances (Å) among the cage unit of **1** at 220 K (a), 300 K (b), and 350 K (c).

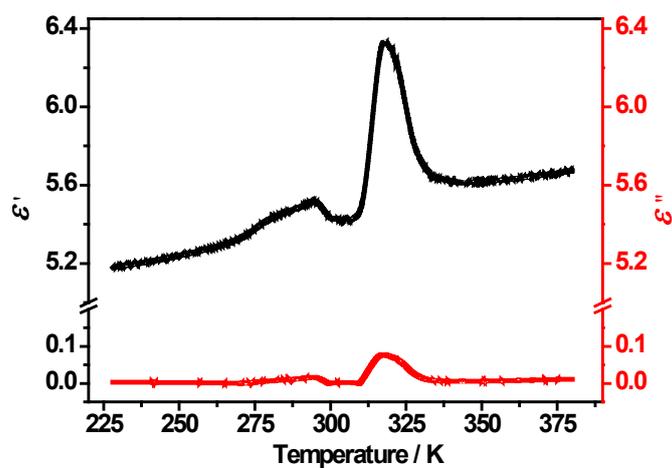


Fig. S4 Temperature dependence of real part (ϵ') and imaginary part (ϵ'') of the complex permittivity for powder-pressed pellet of **1** at 100 KHz.

References

- S1 *APEX2*, *SADABS* and *SAINT*. Bruker AXS Inc.: Madison, Wisconsin, USA. 2008.
S2 G. M. Sheldrick, *SHELX-96 Program for Crystal Structure Determination*, 1996.