Supplementary Information

Giant electrocaloric response in thiourea under low electric field in the cryogenic region.

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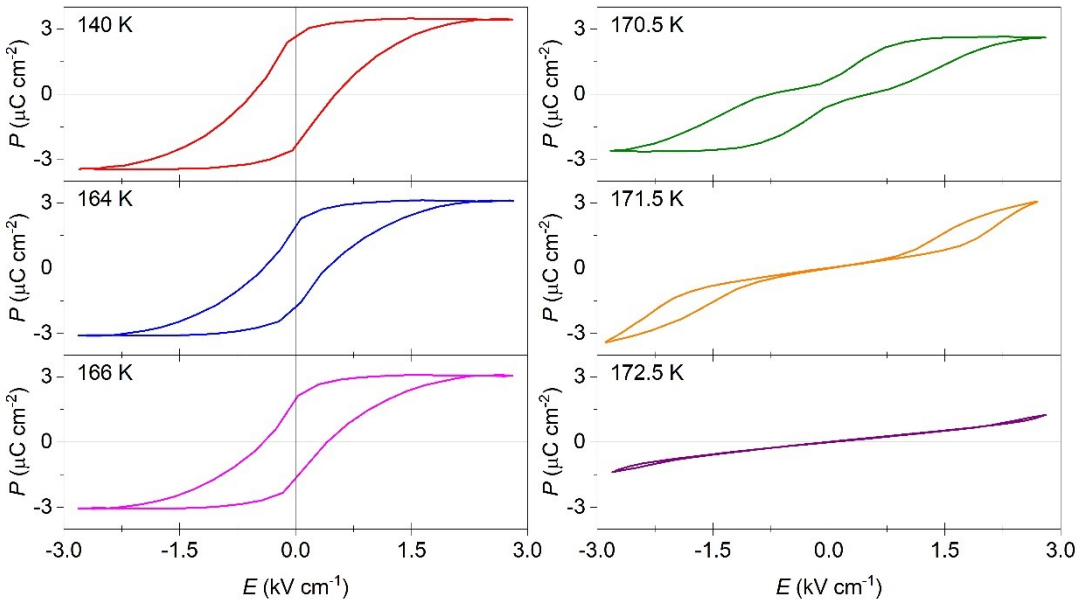

Figure S1. Selected polarization loops obtained at different temperatures below and above the transition temperature T_1.

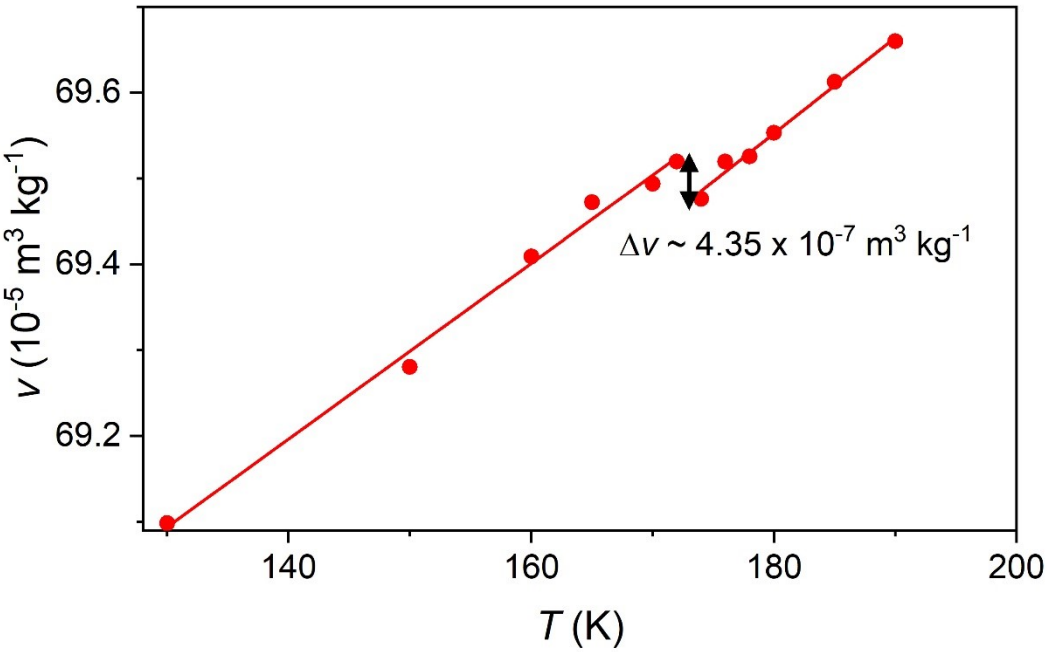

Figure S2. Specific volume as a function of temperature obtained by single crystal x-ray diffraction at different temperatures, highlighting a specific volume change of 4.35 x 10-7 m^3 kg^{-1} across the phase transition from phase I to phase II.

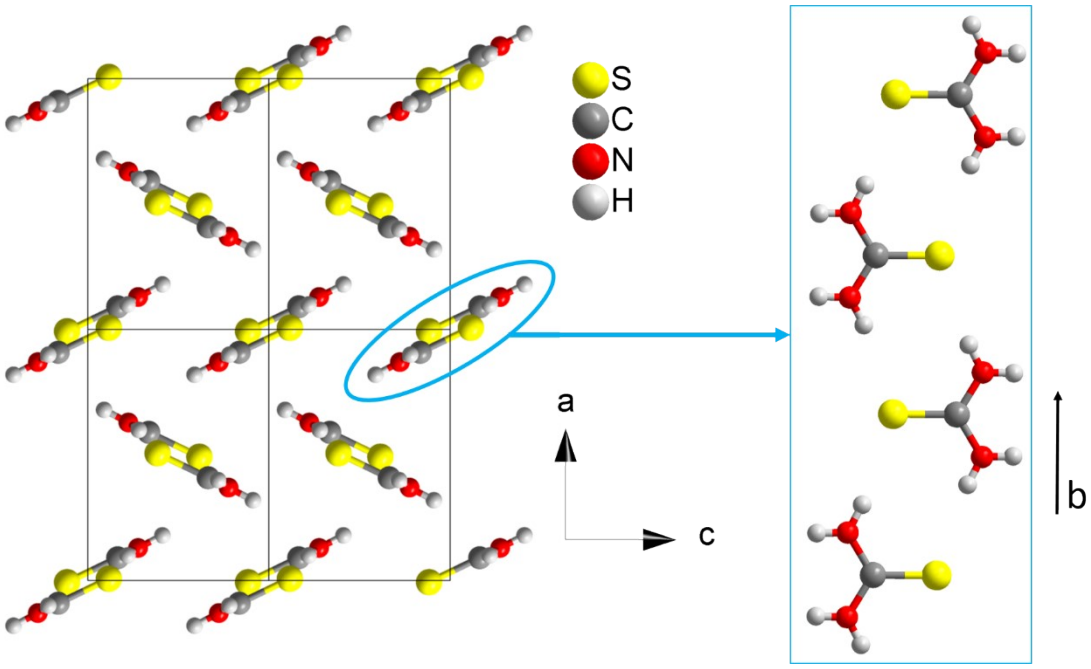

Figure S3. Crystal structures obtained by single-crystal x-ray diffraction at *T* = 250 K view along *b*-axis (left) and detail showing alternate orientation of the thiourea molecules induced by H-bonds as observed along the *b*-axis.

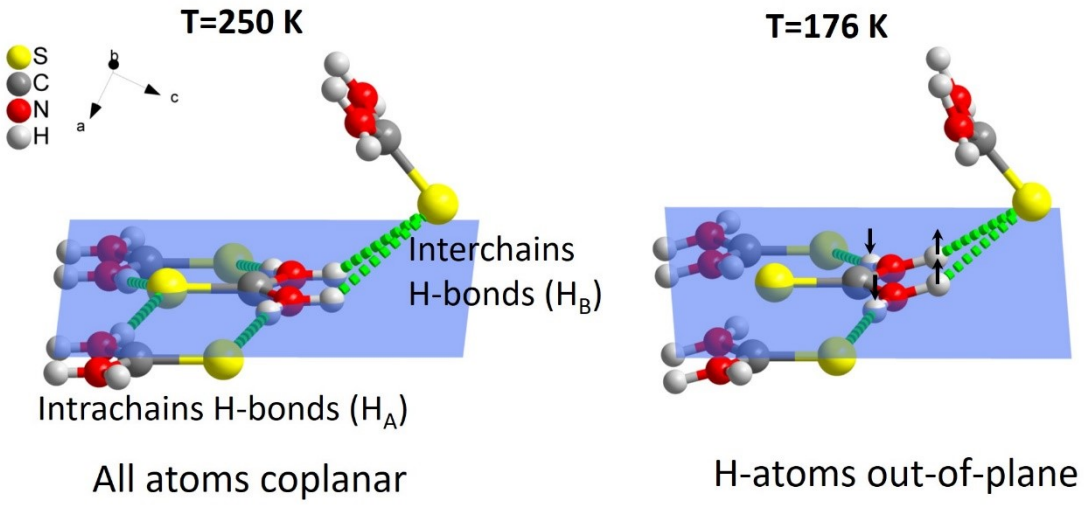

Figure S4. Details of the obtained crystal structure at *T* = 250 K and *T* = 176 K. Left image shows the two types of H-bonds: (i) intrachains H-bonds along the *b*-axis chains (labelled with A) and (ii) interchains H-bonds between neighbouring chains in the *a*-*c* plane. Note: at 250 K (left image) all the atoms in the same *b*-axis chain are co-planar, while at 170 K (right image) there is a out-of-plane shift of the H-atoms responsible for the modulated phases.

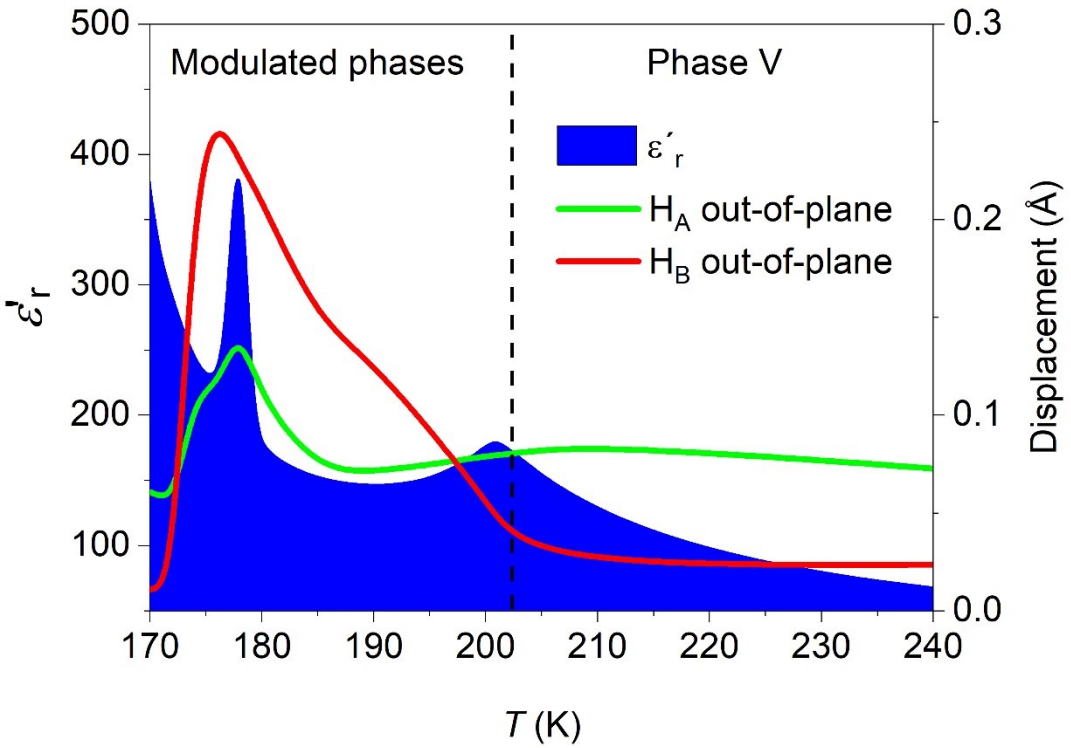

Figure S5. Blue curve shows the relative dielectric permittivity vs T curve of thiourea. Red and green lines show the displacement of H atoms out-of-plane versus temperature. H_A atoms are involved in intrachain hydrogen bonds and H_B in interchain hydrogen bonds.

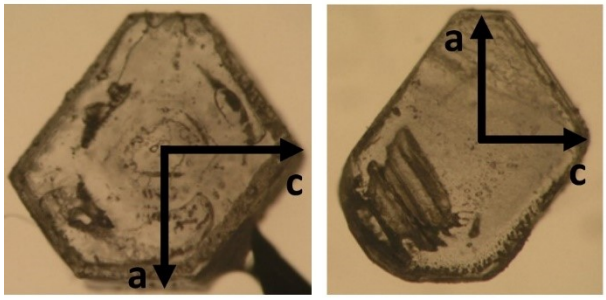

Figure S6. Example of hexagonal-plate shaped single crystals obtained for thiourea.

Table S1. Crystal data and structure refinement for Thiourea.

Empirical formula	CH_4N_2S						
Wavelength (Å)	0.71073						
Crystal size (mm^3)	0.107 x 0.052 x 0.031						
Formula weight	76.12						
F(000)	160						
Temperature (K)	100	130	150	160	165	170	172
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1ma$	$P2_1ma$	$P2_1ma$	$P2_1ma$	$P2_1ma$	$P2_1ma$	$P2_1ma$
Unit cell dimensions (Å)	a = 7.4719(6)	a = 7.4962(6)	a = 7.5124(7)	a = 7.5226(7)	a = 7.5278(7)	a = 7.5313(6)	a = 7.5339(5)
	b = 8.5164(7)	b = 8.5211(7)	b = 8.5241(8)	b = 8.5272(8)	b = 8.5286(8)	b = 8.5295(7)	b = 8.5311(6)
	c = 5.4671(3)	c = 5.4695(4)	c = 5.4702(4)	c = 5.4709(4)	c = 5.4712(4)	c = 5.4698(3)	c = 5.4689(3)
Volume ($Å^3$)	347.89(4)	349.37(5)	350.29(5)	350.94(5)	351.26(5)	351.37(4)	351.50(4)
Unit Cell refinement: # ref. [θ range (°)]	2481 [4.4 - 29.7]	2192 [4.4 - 28.3]	1998 [4.4 - 28.8]	1910 [4.4 - 28.2]	1846 [4.4 - 28.2]	2332 [4.4 - 28.8]	3169 [4.4 - 30.0]
Z	4						
Density calculated (Mg/m^3)	1.453	1.447	1.443	1.441	1.439	1.439	1.438
Absorption coefficient (mm^{-1})	0.673	0.670	0.668	0.667	0.666	0.666	0.666
Tmin, Tmax	0.89, 0.98	0.89, 0.98	0.89, 0.98	0.89, 0.98	0.89, 0.98	0.90, 0.98	0.93, 0.98
θ range for data collection (°)	2.39 - 30.51	2.39 - 30.49	2.39 - 30.48	2.39 - 30.54	2.39 - 30.53	2.39 - 30.54	2.39 - 30.53
Index ranges	-10<=h<=10 -12<=k<=12 -7<=l<=7						
Measured reflections	8571	8567	8612	8614	8614	8606	11666
Independent reflections	1127 [R(int)=0.0665]	1134 [R(int)=0.0676]	1133 [R(int)=0.0694]	1136 [R(int)=0.0736]	1138 [R(int)=0.0735]	1137 [R(int)=0.0582]	1137 [R(int)=0.0612]
Indep. Reflections [I>2σ(I)]	1027	1003	981	955	938	994	1001
Completeness (%)	100	100	100	99.8	99.8	99.5	99.7
Refinement method	Full-matrix least-squares on F^2						
Data / restraints / parameters	1127 / 1 / 60	1134 / 1 / 60	1133 / 1 / 60	1136 / 1 / 60	1138 / 1 / 60	1137 / 1 / 60	1137 / 1 / 60
Goodness-of-fit on F^2	1.085	1.045	1.078	1.080	1.071	1.082	1.097
Final R indices [I>2σ(I)]	R1 = 0.0319 wR2 = 0.0617	R1 = 0.0332 wR2 = 0.0674	R1 = 0.0353 wR2 = 0.0711	R1 = 0.0363 wR2 = 0.0766	R1 = 0.0370 wR2 = 0.0684	R1 = 0.0329 wR2 = 0.0650	R1 = 0.0294 wR2 = 0.0637
R indices (all data)	R1 = 0.0399 wR2 = 0.0653	R1 = 0.0429 wR2 = 0.0731	R1 = 0.0472 wR2 = 0.0770	R1 = 0.0512 wR2 = 0.0854	R1 = 0.0543 wR2 = 0.0786	R1 = 0.0433 wR2 = 0.0706	R1 = 0.0385 wR2 = 0.0683
Largest diff. peak and hole ($e \cdot Å^{-3}$)	0.500 and -0.264	0.323 and -0.311	0.238 and -0.248	0.377 and -0.257	0.311 and -0.291	0.289 and -0.258	0.233 and -0.255

Table S1. Crystal data and structure refinement for Thiourea (Cont.)

Empirical formula	CH_4N_2S						
Wavelength (Å)	0.71073						
Crystal size (mm^3)	0.107 x 0.052 x 0.031						
Formula weight	76.12						
F(000)	160						
Temperature (K)	174	176	178	180	185	190	200
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnma**	*Pnma**	*Pnma**	*Pnma**	*Pnma**	*Pnma**	*Pnma**
Unit cell dimensions (Å)	a = 7.5366(6)	a = 7.5395(6)	a = 7.5411(6)	a = 7.5433(6)	a = 7.5486(6)	a = 7.5532(6)	a = 7.5624(6)
	b = 8.5309(7)	b = 8.5321(7)	b = 8.5319(7)	b = 8.5325(7)	b = 8.5341(7)	b = 8.5353(7)	b = 8.5355(7)
	c = 5.4636(3)	c = 5.4642(3)	c = 5.4637(3)	c = 5.4638(3)	c = 5.4636(3)	c = 5.4633(3)	c = 5.4619(3)
Volume ($Å^3$)	351.28(4)	351.50(4)	351.53(4)	351.67(4)	351.97(4)	352.21(4)	352.56(4)
Unit Cell refinement: # ref. [θ range (°)]	2770 [4.4 - 30.1]	2745 [4.4 - 30.0]	2736 [4.4 - 30.0]	2700 [4.4 - 30.0]	2626 [4.4 - 30.0]	2563 [4.4 - 30.0]	2545 [4.4 - 30.1]
Z	4						
Density calculated (Mg/m^3)	1.439	1.438	1.438	1.438	1.437	1.436	1.434
Absorption coefficient (mm^{-1})	0.666	0.666	0.666	0.666	0.665	0.665	0.664
Tmin, Tmax	0.90, 0.98	0.91, 0.98	0.88, 0.98	0.89, 0.98	0.91, 0.98	0.90, 0.98	0.93, 0.98
θ range for data collection (°)	4.43 - 30.53	4.43 - 30.52	4.43 - 30.52	4.43 - 30.52	4.43 - 30.51	4.43 - 30.54	4.43 - 30.54
Index ranges	-10<=h<=10 -12<=k<=12 -7<=l<=7						
Measured reflections	10993	11033	11025	11100	11165	11177	11305
Independent reflections	570 [R(int)=0.0785]	570 [R(int)=0.0786]	570 [R(int)=0.0778]	570 [R(int)=0.0779]	570 [R(int)=0.0758]	571 [R(int)=0.0726]	573 [R(int)=0.0667]
Indep. Reflections [I>2σ(I)]	489	480	478	480	464	459	444
Completeness (%)	99.8	99.8	99.8	99.8	99.8	99.8	99.8
Refinement method	Full-matrix least-squares on F^2						
Data / restraints / parameters	570 / 0 / 30	570 / 0 / 30	570 / 0 / 30	570 / 0 / 30	570 / 0 / 30	571 / 0 / 30	573 / 0 / 30
Goodness-of-fit on F^2	1.246	1.261	1.229	1.218	1.168	1.134	1.150
Final R indices [I>2σ(I)]	R1 = 0.0693 wR2 = 0.1312	R1 = 0.0647 wR2 = 0.1310	R1 = 0.0618 wR2 = 0.1194	R1 = 0.0591 wR2 = 0.1125	R1 = 0.0484 wR2 = 0.0924	R1 = 0.0400 wR2 = 0.0810	R1 = 0.0304 wR2 = 0.0676
R indices (all data)	R1 = 0.0811 wR2 = 0.1358	R1 = 0.0781 wR2 = 0.1360	R1 = 0.0741 wR2 = 0.1243	R1 = 0.0709 wR2 = 0.1167	R1 = 0.0609 wR2 = 0.0978	R1 = 0.0538 wR2 = 0.0861	R1 = 0.0461 wR2 = 0.0743
Largest diff. peak and hole ($e \cdot Å^{-3}$)	0.371 and -0.629	0.409 and -0.619	0.362 and -0.549	0.349 and -0.504	0.284 and -0.304	0.273 and -0.313	0.225 and -0.247

* Main averaged structure (not considering the modulation).

Table S1. Crystal data and structure refinement for Thiourea (Cont. 2)

Empirical formula	CH_4N_2S		
Wavelength (Å)	0.71073		
Crystal size (mm^3)	0.107 x 0.052 x 0.031		
Formula weight	76.12		
F(000)	160		
Temperature (K)	202	210	250
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*
Unit cell dimensions (Å)	a = 7.5656(6)	a = 7.5709(6)	a = 7.6093(6)
	b = 8.5369(7)	b = 8.5349(7)	b = 8.5410(8)
	c = 5.4620(3)	c = 5.4627(3)	c = 5.4750(3)
Volume ($Å^3$)	352.77(4)	352.98(4)	355.83(5)
Unit Cell refinement: # ref. [θ range (°)]	2556 [4.4 - 29.4]	2510 [4.4 - 30.1]	2156 [4.4 - 28.7]
Z	4		
Density calculated (Mg/m^3)	1.433	1.432	1.421
Absorption coefficient (mm^{-1})	0.664	0.663	0.658
Tmin, Tmax	0.93, 0.98	0.93, 0.98	0.92, 0.98
θ range for data collection (°)	4.43 - 30.53	4.43 - 30.56	4.42 - 30.53
Index ranges	-10<=h<=10 -12<=k<=12 -7<=l<=7		
Measured reflections	11343	11441	11531
Independent reflections	573 [R(int)=0.0646]	575 [R(int)=0.0651]	579 [R(int)=0.0679]
Indep. Reflections [I>2σ(I)]	447	453	422
Completeness (%)	99.8	99.7	99.8
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	573 / 0 / 30	575 / 0 / 30	579 / 0 / 30
Goodness-of-fit on F^2	1.110	1.079	1.122
Final R indices [I>2σ(I)]	R1 = 0.0290 wR2 = 0.0671	R1 = 0.0286 wR2 = 0.0684	R1 = 0.0325 wR2 = 0.0728
R indices (all data)	R1 = 0.0416 wR2 = 0.0723	R1 = 0.0427 wR2 = 0.0746	R1 = 0.0538 wR2 = 0.0816
Largest diff. peak and hole ($e·Å^{-3}$)	0.216 and -0.212	0.181 and -0.234	0.197 and -0.216

Table S2. Out-of-plane hydrogen bonds intrachain and interchain distances.

T (K)	H_A intrachain distance (Å)	H_B interchain distance (Å)
100	0.048	0.006
130	0.053	0.015
150	0.081	0.040
160	0.054	0.019
165	0.062	0.024
170	0.064	0.009
172	0.052	0.011
174	0.111	0.216
176	0.114	0.254
178	0.146	0.230
180	0.107	0.210
185	0.072	0.148
190	0.070	0.128
200	0.079	0.058
202	0.080	0.038
210	0.086	0.022
250	0.068	0.024