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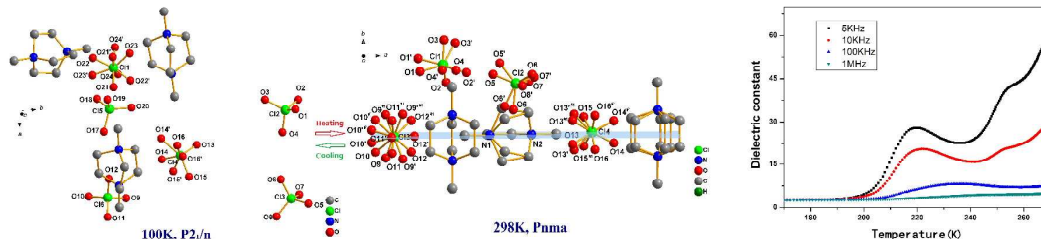
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A novel molecular-based phase change material, 1,4-dimethyl-1,4-diazabicyclo [2.2.2] octane bis(perchlorate), $C_8H_{18}N_2^{2+} \cdot 2ClO_4^-$, was synthesized. Differential scanning calorimetry (DSC) measurement detected that this compound underwent a reversible phase transition at ca. 201.7 K, which was also confirmed by dielectric measurements. The single crystal X-ray diffraction data suggests that the phase transition undergoes from a room temperature paraelectric phase with a space group of Pnma to a low temperature paraelectric one with a space group of P2₁/n. The order-disorder transition of ClO_4^- anions and the ordering of twisting motions of dabco ring may drive the phase transition.



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ARTICLE TYPE

Temperature-induced reversible structural phase transition of 1,4-dimethyl-1,4-diazabicyclo[2.2.2]octane bis(perchlorate)

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1,4-Dimethyl-1,4-diazabicyclo[2.2.2]octane bis(perchlorate), $C_8H_{18}N_2^{2+} \cdot 2ClO_4^-$, was synthesized and separated as colorless rodlike crystals. Differential scanning calorimetry (DSC) measurement detected that this compound underwent a reversible phase transition at ca. 201.7 K with a hysteresis of 5.1 K width, which was also confirmed by dielectric measurements. Single crystal X-ray diffraction data suggested that there was a transition from a room temperature phase with the space group of Pnma ($a=15.5417(14)$ Å, $b=13.3677(12)$ Å, $c=20.7728(19)$ Å, $V=4315.7(7)$ Å³ and $Z=12$) to a low temperature one with a space group of P2₁/n ($a=13.331(3)$ Å, $b=15.185(4)$ Å, $c=20.477(5)$ Å, $\beta=90.895(3)^\circ$, $V=4144.8(17)$ Å³ and $Z=12$), and symmetry breaking occurred with an Aizu notation of mmmF2/m. The order-disorder transition of ClO_4^- anions and the ordering of twisting motions of dabco ring may drive the phase transition.

Introduction

Because of discovering the phase transition materials including the ferroelectrics, substantial attention has recently been focused on the simple molecular-ionic salts, which contain an organic cation and acid radicals, owing to they having potential applications in signal processing, data storage, sensing, and switchable dielectric devices, etc. [1]. It is crucial to prepare new temperature-triggered molecular-based phase transition materials, not only for the theoretical study the relationship of structure-property, but also for exploring the novel physical properties [2-4]. Constructing new types of compounds is the key problem in developing phase transition materials, which needs understanding the origin of phase transition deeply. Up to now, the order-disorder type is always the most commonly employed mechanism in the theory of phase change materials [5]. We have chosen 1,4-diazabicyclo-[2.2.2]octane (dabco) as an organic cation, not only due to its high order symmetry, but it allows the design of molecular-based phase transition materials, which has been verified recently, due to 'frozen' ordering or molecular rotation in the crystal lattice, which provides lots of room for us to explore phase transition materials from the viewpoint of structural engineering [6-8]. Due to the moderate size and highly symmetric shape, the well-known ball like anions such as ClO_4^- , are stable and prone to position changes with varying temperature and weak interactions in crystals. The interaction of the cations with the monovalent tetrahedral counter anions (e.g. ClO_4^- , BF_4^-) is expected to generate the phase transition materials. 1,4-diazabicyclo-[2.2.2]octane (dabco) forms monosalts with mineral acids, which have exceptional dielectric properties. These monosalts can be described by a general formula dabcoHX where

X= ClO_4^- and BF_4^- [9]. Taking all these into consideration, we report a new compound herein with reversible structural phase transition properties, 1,4-dimethyl-1,4-diazabicyclo[2.2.2]octane bis(perchlorate), as a continuation of our systematic studies of phase transitions [10]. Which was based on the potential bridging ligand, 1,4-dimethyl-1,4-diazabicyclo[2.2.2]octane-1,4-diiumbromide. The complex can be described by a general formula $(CH_3\text{-Dabco-}CH_3)_2^+ \cdot 2Br^-$, which was further characterized by variable-temperature single crystal X-ray diffraction, differential scanning calorimetry (DSC) and dielectric constant measurements.

Experimental

Materials and measurements

All reagent-grade chemicals and solvents were obtained from commercial sources and used without further purification. Infrared spectra were recorded on a SHIMADZU IR prestige-21 FTIR-8400S spectrometer in the range of 4000–500 cm⁻¹ with samples in the form of potassium bromide pellets. X-ray powder diffraction (XRPD) data were collected by a Siemens D5005 diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å). Elemental analyses were taken on a Perkin-Elmer 240C elemental analyzer. Thermo gravimetric analyses (TGA) were conducted on a NETZSCH TG 209 F3 thermo gravimeter with the heating rate of 10 K/min in a N₂ atmosphere.

Table 1 Crystallographic data for **1** at 298K, 150K and 100K

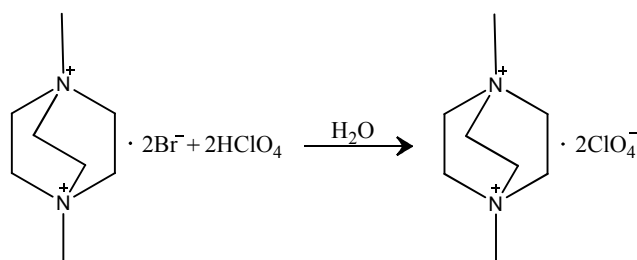
<i>T</i> (K)	298	150	100
Empirical formula	C ₈ H ₁₈ Cl ₂ N ₂ O ₈	C ₈ H ₁₈ Cl ₂ N ₂ O ₈	C ₈ H ₁₈ Cl ₂ N ₂ O ₈
Formula weight	341.14	341.14	341.14
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pnma	P2 ₁ /n	P2 ₁ /n
<i>a</i> (Å)	15.5417(14)	13.365(3)	13.331(3)
<i>b</i> (Å)	13.3677(12)	15.240(3)	15.185(4)
<i>c</i> (Å)	20.7728(19)	20.431(4)	20.477(5)
<i>α</i> (°)	90	90	90
<i>β</i> (°)	90	90.719(2)	90.895(3)
<i>γ</i> (°)	90	90	90
<i>V</i> (Å ³)	4315.7(7)	4161.2(14)	4144.8(17)
<i>Z</i>	12	4	12
<i>D_c</i> (g/m ³)	1.575	1.634	1.640
<i>μ</i> (mm ⁻¹)	0.489	0.507	0.509
<i>F</i> (000)	2136	2136	2136
<i>θ</i> range [°]	1.64 to 25.68	1.00 to 25.60	0.99 to 25.68
Collected reflections	32689	31453	31339
Unique reflections	4284	7776	7783
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0787, 0.1863	0.0643, 0.1542	0.0737, 0.1834
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.1060, 0.2117	0.0747, 0.1639	0.0890, 0.2039
GOF	1.048	1.104	1.059
Largest peak and hole (e · Å ⁻³)	0.564 and -0.632	1.478 and -0.768	1.428 and -0.775

Synthesis of compound **1**

5 1,4-dimethyl-1,4-diazabicyclo [2.2.2]octane-1,4-dium dibromide (3.02 g, 10 mmol) and Perchloric acid (2 g, 20 mmol) were mixed in aqueous solution (30 ml) (Scheme 1). After being stirred for 30 min in air, the reaction mixture solution was evaporated slowly at room temperature for 3 days, and colorless rodlike crystals were
 10 obtained in 53% yield (based on Perchloric acid). IR spectra of compound **1**: 3438(s), 3041(vs), 2999(vs), 2898(w), 2018(s), 1629(w), 1468(vs), 1375(s), 1335(s), 1105(vs), 919(w), 885(s), 843(s), 622(w). Anal. (%) calcd for C₈H₁₈Cl₂N₂O₅: C, 32.78; H, 6.19; N, 9.56; Found: C, 32.71; H, 6.13; N, 9.49. (Caution!
 15 Although no problems have been encountered herein, perchlorates are potentially explosive and should be handled with care and only in small quantities).

Single-crystal X-ray Crystallography

Single-crystal X-ray data were performed on a Bruker SMART-
 20 APEX II CCD with Mo-*K*_α radiation (λ = 0.71073 Å). A colorless rodlike crystal of approximate dimensions 0.30 × 0.30 × 0.20 mm was used in data collection at 298K, 150K and 100 K. Data processing including empirical absorption correction was performed using SADABS. The structures of **1** were solved by
 25 direct methods and refined by the full-matrix method based on *F*² by means of the SHELXLTL software package respectively [11]. Non-H atoms were refined anisotropically using all reflections with *I* > 2σ(*I*). All H atoms were found in the difference maps. However, carbon-bond H atoms were added geometrically and
 30 refined using riding model with Uiso = 1.2Ueq. Asymmetric units and packing views were drawn with DIAMOND (Brandenburg and Putz, 2005). Distances and angles between some atoms were calculated using DIAMOND and other calculations were carried out using SHELXLTL. Crystallographic data and structure refinement of the 298 K, 150K and 100 K phases are listed in
 35 Table 1.



Scheme 1 Synthesis of compound **1**

40 Dielectric Measurements

The complex dielectric permittivity ϵ ($\epsilon = \epsilon' - i\epsilon''$) was measured on Tonghui TH2828A in the frequency range from 5 KHz to 1 MHz with the temperature from 100 to 300 K respectively, at the AC voltage of 1 V. Pellet sample was prepared at 10 MPa and
 45 pressed powder pellet deposited with silver-conducting glue was used for dielectric studies.

DSC Measurement

The differential scanning calorimetry (DSC) analysis of crystal **1** (19.74 mg) were performed using a Perkin-Elmer Diamond DSC
 50 instrument in the temperature ranges of 160 to 260 K in aluminum crucibles, accompanied by a rate of 10 K/min on cooling/heating at atmospheric pressure. DSC curves of **1** obtained in a heating-cooling mode at 5 K/min, 10 K/min, 15 K/min and 20 K/min respectively, as shown in Figure S4.

XRPD

The phase purity of **1** was determined by XRPD. The XRPD of **1** at 100K, 120K, 150K, 183K, 223K, 248K and 298K, were shown in Fig. 1. The peak positions of the experimental and simulated
 60 XRPD patterns are in good agreement, as shown in Figure S5, S6, S7. The intensity differences may be attributed to the preferred orientation of the powder sample.

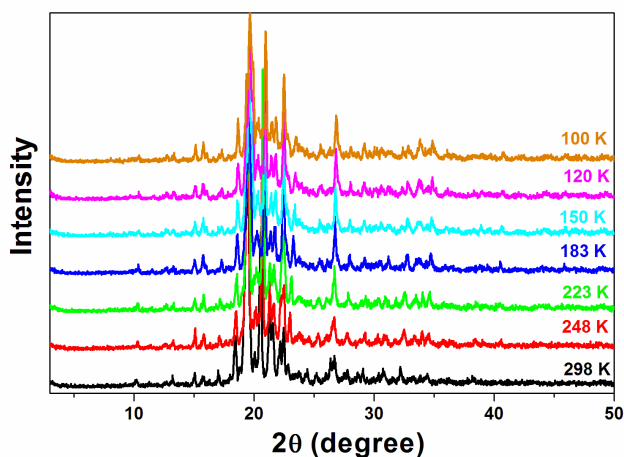


Fig.1 The XRPD of **1** at 100K, 120K, 150K, 183K, 223K, 248K and 298K respectively.

DSC

Differential Scanning Calorimetry (DSC) measurement is well-known as one of the thermodynamic methods which was used to confirm the phase transitions triggered by temperature. Heat anomalies can be observed when the compound undergoes structural phase transition during heating and cooling, accompanied by thermal entropy change. Reversible heat anomalies can be detected, these may be caused by the disorder-order of ClO_4^- , by DSC measurement upon heating and cooling. Upon cooling and then heating the crystalline sample, DSC shows a main exothermic peak at 201.7 K and a main endothermic peak at 206.8 K respectively, as showing in Fig. 2. This couple of exothermic and endothermic peaks represent a reversible phase transition, this phase transition is accompanied by release of heat and thermodynamic quantities (internal energy, enthalpy, volume etc.) are discontinuous, which is known as first order phase transition.

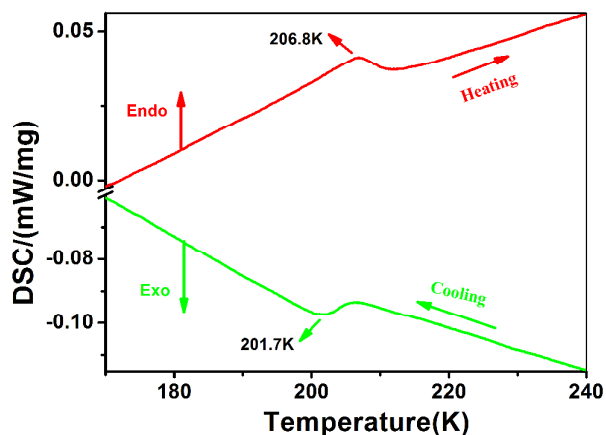
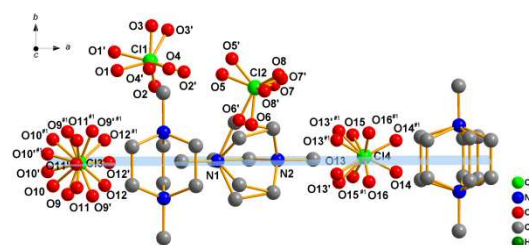


Fig.2 Caption DSC curves of **1** obtained in a heating-cooling mode.

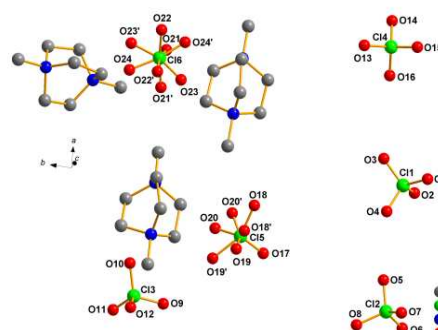
Crystal structure of **1**

In order to confirm the phase transition of **1**, the crystal structures were further resolved at 298K, 150K and 100K respectively, for forthcoming comparative investigation. (Fig. 3a-c). Variable-

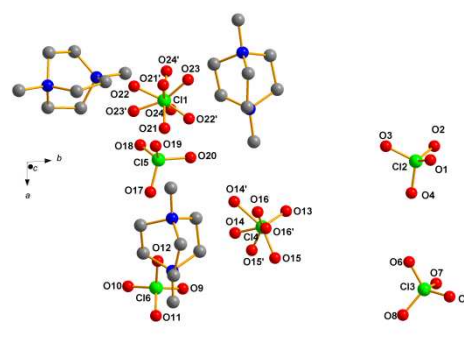
temperature X-ray single-crystal diffraction reveals that **1** belongs to the orthorhombic crystal system with a centrosymmetric space group of Pnma (No.62) and the point group D_{2h} , at room temperature (298 K). When the temperature decreases to 100 K, the crystal structure of **1** changes to a monoclinic crystal system with the centrosymmetric space group $\text{P2}_1/\text{n}$ (No.14) and the point group C_{2h} . During the cooling process, the symmetry breaking occurs with an Aizu notation of mmmF2/m [12].



(a)



(b)



(c)

Fig.3 View of coordination environment of **1** with atomic numbering scheme at (a) 298 K, (b) 150K, (c) 100K. Symmetry codes: #1 $x, -y+1/2, z$.

At room temperature (298 K), the crystals are in the orthorhombic space group Pnma (No. 62), with cell parameters of $a = 15.5417(14) \text{ \AA}$, $b = 13.3677(12) \text{ \AA}$, $c = 20.7728(19) \text{ \AA}$, $V = 4315.7(7) \text{ \AA}^3$ and $Z = 12$. At 150 K, the crystals transform to a monoclinic crystal system space group $\text{P2}_1/\text{n}$ (No.14). As to temperature 100K structure, the crystals adopt the same structure as that at 150K and slight difference can be seen by comparing the crystal data, which suggest that there is no occurrence of phase transition between 150K and 100K, the cell parameters of **1** measured at 100 K with cell parameters of $a = 13.331(3) \text{ \AA}$, $b =$

15.185(4) Å, $c = 20.477(5)$ Å, $\beta = 90.895(3)^\circ$, $V = 4144.8(17)$ Å³ and $Z = 12$. Visual inspection show no obvious changes at the three temperatures. Molecular (ion pair) volume decreases from 4315.7(7) Å³ in the orthorhombic cell to 4144.7(18) Å³ in the monoclinic cell, except the change of the lengths of a-axis and b-axis.

In the RT phase (298K) crystal structure of **1**, as shown in Fig. 3a, it is found interestingly that the ClO₄⁻ anions are all disordered, which may result in the formation of a higher symmetry (Pnma). Meanwhile, the atoms of N1, N2 which come from the C₈H₁₈N₂²⁺ cations combined with the atoms of Cl3 and Cl4 from the discrete ClO₄⁻ anions, lie on a common crystallographic mirror plane in the crystal of **1** (Fig. 3a). The ClO₄⁻ anions are seriously disordered with the distances of Cl–O from 1.28(3) Å to 1.505(15) Å, which were in good agreement with those observed in similar compounds [13].

In the LTP crystal structure at 150 K, the disordered ClO₄⁻ anions are frozen and become relatively ordered, as shown in Fig. 3b, part of the ClO₄⁻ anions adopt an ideal tetrahedral geometry with the distances of Cl–O from 1.401(5) Å to 1.454(5) Å and the angles of O–Cl–O from 107.2(3)° to 112.8(4)°, these lengths of bonds are similar to those observed in the higher-temperature phase. However, there are still having seriously disordered ClO₄⁻ anions with O atoms over two positions.

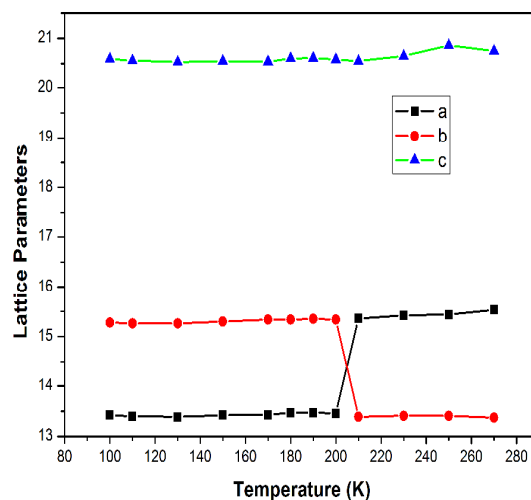
In the lower-temperature phase (LTP, 100 K), as shown in Fig. 3c, part of the ClO₄⁻ anions adopt an ideal tetrahedral geometry with the distances of Cl–O from 1.413(6) Å to 1.456(5) Å and the angles of O–Cl–O from 107.7(3)° to 114.0(4)°, which are comparable to those in the HTP at 298K. In addition, there were still part of disordered ClO₄⁻ anions as those in the LTP (150K). Meanwhile, the conformations of the rings of dabco were different significantly between HTP (298 K) and LTP (150 K, 100 K) phases. It is notable that at LTP (100K), the bonds of N–C–C–N in the three dabco rings exhibit large twisting conformations with the torsion angles from 14.156° to 23.260°.

X-ray crystal structures of **1** were measured at 298 K, 270 K, 250 K, 230 K, 210 K, 200 K, 190 K, 180 K, 170 K, 160 K, 150 K, 140 K, 130 K, 120 K, 110 K and 100 K respectively. The cell parameters of **1** measured from 270 K to 210 K are slightly different from those measured at room temperature (298K), i.e. in other words, the influence of thermal expansion and contraction can be excluded. Thus, we can get a conclusion that there is no phase transition at 210 K. Particularly compared with those at 210K, the crystal cell parameters of **1** change dramatically at 200K. In addition, there were no obvious change in crystal cell parameters of **1** measured from 200K to 100K, indicating the absence of phase transition (Fig. 4). The LTP structure keeps a modest change of a axis lengths compared to those in the RTP. However, a distinct change occurred in the length of a-axis, b-axis (Fig. 4a) and β angle (Fig. 4b). Phase transition between 200 and 210 K were confirmed by X-ray diffraction at various temperatures. At higher temperatures (210–298 K) no phase transitions occurs and the crystals are in the orthorhombic space group Pnma; At lower temperatures crystals transforms to a monoclinic crystal system. These measurements are in coincidence with DSC data.

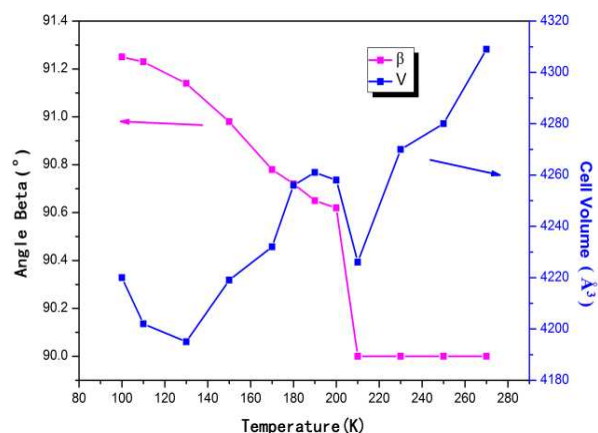
Dielectric Properties

It is well-known that the phase transition will accompany

anomaly of physical properties near the structure phase transition point, such as the dielectric constant[14]. Herein, we measured the temperature- and frequency-dependent dielectric properties to confirm the phase transition and molecular motions in complex **1**, and plots of the dielectric constant (ϵ') versus temperature at different frequencies are displayed in Fig. 5.



(a)



(b)

Fig.4 Caption(a) Temperature dependences of unit-cell length parameters of **1**. (b) Temperature dependences of angle beta and cell volume of **1**.

As expected, a clear dielectric anomaly occurred at about 200K in the dielectric constant upon heating as shown in Fig. 5, which corresponds to the result of DSC and mutations of cell parameters very well. Thus, phase transition triggered by temperature results in dielectric anomaly. Furthermore, these figures show the following features: (i) **1** has an invariant ϵ' (about 2.7) in the low-temperature regime below 190.0 K; (ii) the dielectric constant rapidly increase when the temperature rises above 200.0 K, and no maximum peak appears in the plots of ϵ' versus T below 220.3 K; (iii) the increases in the dielectric constant with temperature depend strongly on the frequency of the ac electric field, which is obvious when the frequency is 5 KHz. In addition, continuously increasing the frequency from $5 \times 10^3 \rightarrow 10^4 \rightarrow 10^5 \rightarrow 10^6$ Hz gradually decreases the dielectric constant, which are 27.9, 20.6,

8.4, 4.5 respectively. These features of the dielectric properties reveal compound **1** was a potential tunable dielectric material.

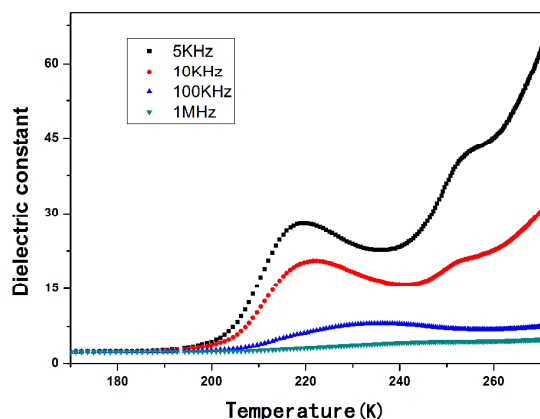


Fig.5 Caption Temperature-dependent dielectric constant of **1** at different frequencies.

Conclusions

In summary, DSC, dielectric measurement and variable-temperature structural analysis revealed that 1,4-dimethyl-1,4-diazabicyclo[2.2.2]octane bis(perchlorate) underwent a reversible phase transition at ca. 201.7 K. Crystal structures of **1** obtained at 298 K, 150 K and 100 K revealed that it reversibly transformed from the HTP space group of Pnma to the LTP space group of P2₁/n. Symmetry breaking occurred with an Aizu notion of mmmF2/m[12]. High symmetry of ClO₄⁻ anions, which were prone to the transition of order-disorder under different temperature, along with the ordering of twisting motions of dabco ring probably drove the phase transition.

Acknowledgements

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Notes and references

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Electronic supplementary information (ESI) available: Crystallographic information (in CIF format) of complex **1**, these data have been deposited at the Cambridge Crystallography Data Centre: CCDC 1044458 for 298 K, 1044459 for 150 K, and 1044460 for 100 K. In addition, IR, PXRD, and TGA of complex **1** in Electronic supplementary information.

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