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Disorder−Order Ferroelectric Transition in the Metal Formate Framework of $[NH_4][Zn(HCOO)_3]$

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Abstract: A three-dimensional chiral metal formate framework compound, $[NH_4][Zn(HCOO)_3]$, undergoes a paraelectric−ferroelectric phase transition at 191 K triggered by the disorder−order transition of NH_4^+ cations within the structure.

Ferroelectric materials are of importance and interest in both basic scientific concerns and versatile technological applications.[1−3] The majorities are perovskite oxides[1,2] such as $BaTiO_3$ and lead zirconate titanate (PZT); hydrogen-bonded inorganic salts such as Rochelle salt, potassium dihydrogen phosphate (KDP), and triglycine sulfate (TGS);[1] and recently reported organic ones.[3] In the later classes, H bonding plays the key role in the electric ordering. The recently developed metal−organic frameworks (MOFs) have shown various properties or functionalities due to their hybrid inorganic−organic nature,[4] but ferroelectric MOFs still remain scarce.[5,6] Except for the symmetry requirement[2] for ferroelectrics, H-bonding systems can easily be created within MOFs if suitable components with H-bond donors and acceptors are chosen and properly organized in the solid state. Therefore, MOFs are promising candidates for ferroelectrics.[4a,6a] On the other hand, the combination of the magnetism of MOFs with ferroelectricity should result in multiferroelectrics.[6−9] In this context, we have systematically explored magnetic metal formate frameworks templated by protonated organic amines.[7] Cheetham and other workers[8] have shown that in our first-reported magnetic perovskite $[(CH_3)_2NH_2][M^{II}(HCOO)_3]$ series[9] the antiferroelectricity occurs in the 160−185 K range and that the disorder−order transition of the $(CH_3)_2NH_2^+$ template is the origin of electric ordering. We observed that the porous magnetic host framework of $[Mn_3(HCOO)_6]$ with polar guests can lead to interesting dielectric properties, including ferroelectricity.[10] These are new multiferroics. Very recently, we have found that the $[NH_4][M^{II}(HCOO)_3]$ series[11] shows a structural phase transition in which the disordered NH_4^+ cation at room temperature (RT) becomes ordered at low temperature (LT). In this communication, we report that $[NH_4][Zn(HCOO)_3]$ (**1**) shows a paraelectric−ferroelectric transition at the critical temperature $T_C = 191$ K, as characterized by single-crystal X-ray diffraction (XRD), dielectric anomaly, dielectric hysteresis loop, and preliminary thermodynamic studies, and we show that this is related to the disorder−order transition of the NH_4^+ cations within the structure.

1 was prepared by reaction of ammonium formate, formic acid, and $Zn(ClO_4)\cdot 6H_2O$ in methanol (see the Supporting Information). The bulk phase purity was verified by powder XRD (Figure S1 in the Supporting Information), and the material was thermally stable up to 100 °C (Figure S2). The slow diffusion method afforded hexagonal plate or bipyramidal crystals (Figure S3) up to 2 mm in size.

The structures of **1** at both 290 and 110 K were determined (Figure 1; also see Figure S4 and Tables S1 and S2). Here we focus on H-bonding systems and structural changes related to the ferroelectricity of **1**. At 290 K, the crystal belongs to the hexagonal space group $P6_322$, which has the nonpolar point group D_6, with $a^{290K} = 7.3084(2)$ Å, $c^{290K} = 8.1705(3)$ Å, and $V^{290K} = 377.94(2)$ Å^3. The crystal structure is the same as that of $[NH_4][M(HCOO)_3]$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+});[11a] it features a three-dimensional chiral anionic $[Zn(HCOO)_3^-]$ framework having a $(4^9\cdot 6^6)$ network topology[12] (Figure 1a), with the arrays of NH_4^+ cations located in the framework's helical channels along the *c* direction (Figure S4a). Each octahedral Zn^{2+} node connects to six neighbors through anti−anti formate bridges. In the channel, the unique NH_4^+ cation shows disorder in a trigonal antiprism and forms $6 \times {}^2/_3 = 4$ N−H···O hydrogen bonds to the anionic framework, with a N···O distance of 2.972 Å and a N−H···O angle of 161° (Figure 1b). The disorder of the NH_4^+ indicates the competition among different H-bonding sites at room temperature. Disorder of protonated ammine cations has been observed for many metal formate compounds.[7−9,11,13]

1 was observed to undergo a structural phase transition at ∼190 K, accompanied by the tripling of the unit cell, the disorder−order transition of NH_4^+ with related structure changes (Figure 1 and Figures S4b and S5), and a change in space group from $P6_322$ to the polar $P6_3$. The length of c^{110K} axis, 8.2015(2) Å, is slightly longer than c^{290K}, while a^{110K} becomes the diagonal $(a-b)^{290K}$ of the $(ab)^{290K}$ rhombus, whose length of 12.5919(3) Å is very close to $3^{1/2}a^{290K}$; therefore, $V^{110K} = 1126.18(5)$ Å^3, which is almost equal to $3V^{290K}$. The tripling of the unit cell at 110 K was also evidenced by the observation of weak diffraction spots in the oscillation image at 110 K that were not observed at 290 K (Figure S5). Thus, the unique channel at (0, 0, *z*) in the 290 K structure was split into three unique channels at (0, 0, *z*), ($^2/_3$, $^1/_3$, *z*), and ($^1/_3$, $^2/_3$, *z*), locating three unique, ordered, tetrahedral NH_4^+ cations, each with one apical and three basal N−H groups. Each basal N−H group forms a stronger H bond to the metal formate framework, with N···O distances of 2.830−2.864 Å and N−H···O angles of 167−175°. The apical N−H group, with the N−H directing *c* axis, still forms a trifurcated acceptor-type H bond,[14] with N···O distances of 3.075−3.120 Å and N−H···O angles of 103−105°. It is noted that within the unit cell, the NH_4^+ cations in the channels at ($^2/_3$, $^1/_3$, *z*) and ($^1/_3$, $^2/_3$, *z*) have their apical N−H groups pointing in the +*c* direction, but the NH_4^+ cations in the channel at (0, 0, *z*) have the apical N−H groups pointing in the opposite direction. More importantly, the N atoms of the NH_4^+ cations in the three channels are shifted by −0.36, −0.38, and +0.40 Å along the *c* direction with respect to the anionic framework compared to the zero shift in the 290 K structure, which has a zero shift (Figure S4); this indicates the double potential wells for the NH_4^+ cations in the channel. These are related to the polar LT structure and the observed

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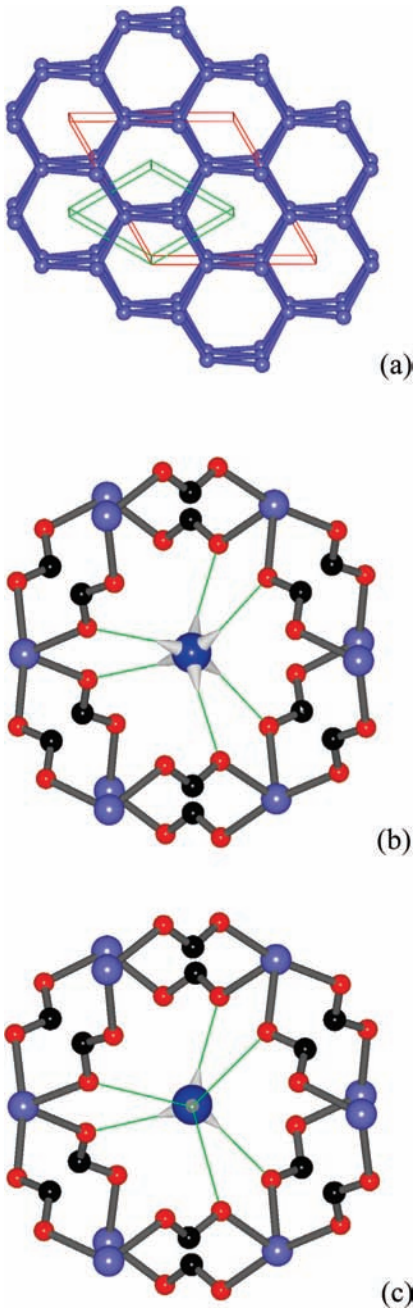

Figure 1. (a) Topological view of the ($4^9 \cdot 6^6$) anionic framework in **1**; spheres are Zn^{2+} and sticks $HCOO^-$. Green and red boxes are unit cells at 290 and 110 K, respectively. (b) One trigonally disordered NH_4^+ cation in the channel at 290 K. (c) One ordered NH_4^+ tetrahedral cation in the channel at 110 K. All views are along the *c* axis. Atom scheme: H, white; C, black; O, red; Zn, blue-violet; N, blue. In (b) and (c), thin green lines are N−H···O hydrogen bonds; H atoms of formate have been omitted.

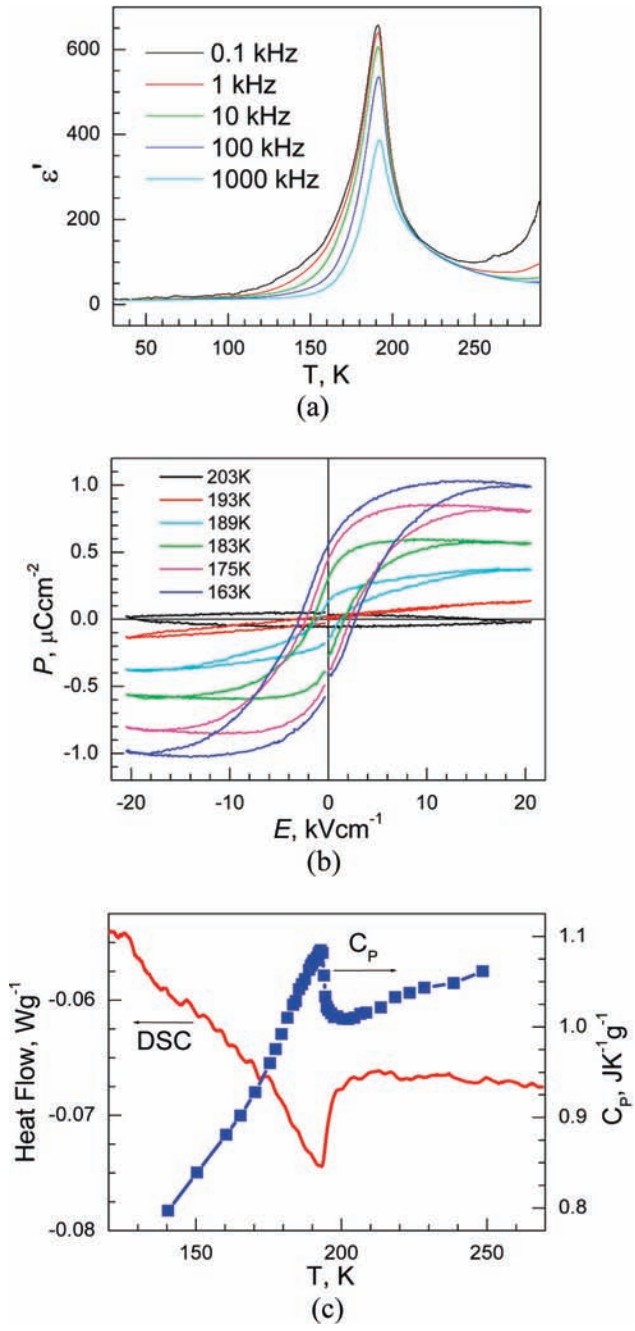

Figure 2. (a) Temperature-dependence of the dielectric permittivity ε' of **1**, with $E \parallel c$. (b) Dielectric hysteresis loops of **1** with $E \parallel c$ at various temperatures. (c) DSC and C_P plots for **1**.

ferroelectricity. The C_6 point group of the LT phase is a subgroup of the D_6 point group of the RT phase in which the twofold axes have vanished, indicating the symmetry breaking and coinciding with a typical ferroelectric type of 622F6 in the Aizu notation.[15]

The temperature dependence of the dielectric permittivity (ε) of **1** was measured on a single crystal of **1** (Figure S3) under an applied electric field $E \parallel c$ with frequencies of 100 Hz to 1 MHz. Indeed, the real component, ε', showed very high dielectric anomaly peaks at 191−192 K (Figure 2a), corresponding to the transition. The peak ε' values are several or tens-fold larger than those at higher and lower temperatures. This is characteristic of a ferroelectric transition. The reciprocal ε' data at 10 kHz between 210 and 260 K fitted the Curie−Weiss law well (Figure S6), affording the Curie constant $C = 5.39 \times 10^3$ K and the Curie−Weiss temperature $T_0 = 181$ K. The C value is comparable to those of ferroelectrics undergoing disorder−order transitions of H-bonding systems, such as KDP and TGS,[1,3] and T_0 is slightly lower than $T_C = 191$ K.

The ferroelectricity was confirmed by the dielectric hysteresis loops of polarization measured with $E \parallel c$ below T_C (Figure 2b). The characteristic loop clearly occurred at 189 K, just below T_C. The spontaneous polarization increased on cooling and reached saturation at 163 K with a remnant polarization (P_r) of 0.68 μC cm^{-2}, a coercive field (E_c) of 2.8 kV cm^{-1}, and a saturation spontaneous polarization (P_s) of 1.03 μC cm^{-2}, all of which are typical for H-bonded ferroelectrics.[1,3] In the LT phase, the shifts

of NH_4^+ cations related to the anionic framework could be considered to create dipoles with ± unit charges separated by these shifts along the *c* axis, from which P_s could be easily estimated as 0.96 μC cm^{-2}, in agreement with the above experimental value.

1 was subjected preliminary differential scanning calorimetry (DSC) and specific heat (C_P) measurements (both in heating mode; Figure 2c). An endothermic peak in the DSC curve and a λ-shaped peak in the C_P data were clearly observed at 192 K, corresponding to the paraelectric−ferroelectric transition. The ΔH and ΔS were estimated as ∼0.7 kJ mol^{-1} and ∼2 J mol^{-1} K^{-1}, respectively. From the Boltzmann equation, $\Delta S = R \ln N$, where R is the gas constant and N is the ratio of the numbers of respective geometrically distinguishable orientations, we obtain $N = 1.3$. This value is less than the value $N = 2$ denoting two discrete states in the disorder phase, indicating the discomplicated disordered−ordered feature of the phase transition.[8a,b] These results confirm the phase transition, though the thermodynamic characteristics need further investigation.

In conclusion, the paraelectric−ferroelectric phase transition at 191 K triggered by the disorder−order transition of NH_4^+ cations in the metal formate framework of **1** has successfully been established. As a large number of magnetic metal formate frameworks templated by various protonated amines have been discovered,[7−9,11,13] the finding of ferroelectricity in **1** opens an avenue to a new class of MOF-based multiferroics, and this research is underway.

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Supporting Information Available: Experimental details, Tables S1 and S2, Figures S1−S6, and CIF files for the two structures in this communication. This material is available free of charge via the Internet at http://pubs.acs.org.

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