

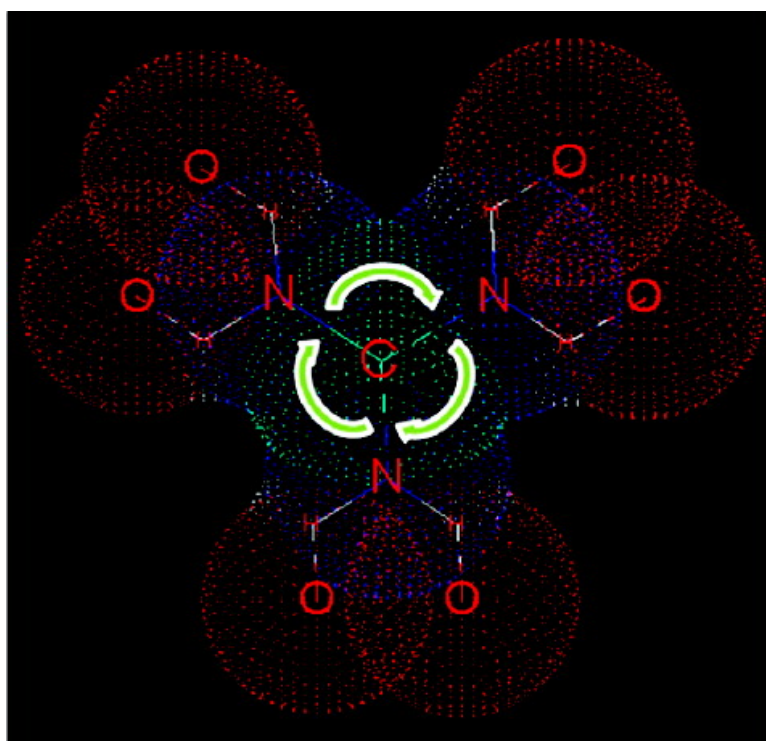
Communication

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## Order–Disorder Antiferroelectric Phase Transition in a Hybrid Inorganic–Organic Framework with the Perovskite Architecture

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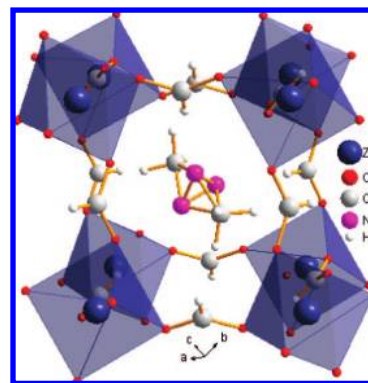
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Materials that exhibit electrical ordering are of great interest because of their technological importance. The high permittivity (dielectric constant [ $\epsilon$ ]) properties<sup>1</sup> of some of these electrically ordered materials have also made them important in development of dielectric resonators and filters for microwave communication systems. Many of these materials are oxides with the perovskite structure, such as lead zirconate titanate (PZT) and BaTiO<sub>3</sub>, which have found applications in an entire set of technologies (actuators, sensors, transducers, memory elements, filtering devices, high performance insulators).<sup>2,3</sup> In the case of PZT, the remarkable electromechanical and electrical properties are associated with the morphotropic phase boundary, which is formed by doping antiferroelectric PbZrO<sub>3</sub> with ferroelectric PbTiO<sub>3</sub> and which occurs for the coexistence of tetragonal (*P4mm* symmetry FT), monoclinic (*Cm* symmetry FM), and rhombohedral (*R3c* symmetry FR) polar distortions of the perovskite structure.<sup>4</sup> These properties are technically important, but concern about the environmental impact of Pb-based systems has spurred considerable interest in the discovery of lead-free ferro/antiferroelectric materials.

Much of the recent attention in this field has been focused on developing devices based upon well-established inorganic compounds such as KH<sub>2</sub>PO<sub>4</sub> (KDP), BaTiO<sub>3</sub>, PZT, and LiNbO<sub>3</sub>;<sup>3</sup> consequently, reports of new electrically ordered systems have remained sparse. However, the significant increase in interest in hybrid inorganic–organic framework materials during the past decade is now opening up new possibilities. Much of the focus has been on nanoporous frameworks, often known as metal organic frameworks or MOFs, which mainly have potential applications in catalysis, separation techniques, and gas storage.<sup>5–8</sup> There is also a recent report of a room temperature, hybrid ferroelectric based upon the use of homochiral ligands during the synthesis.<sup>9</sup> Also of interest is the equally recent observation of a ferroelectric ordering transition in the porous coordination polymers [Mn<sub>3</sub>(HCOO)<sub>6</sub>](H<sub>2</sub>O)(CH<sub>3</sub>OH) and [Mn<sub>3</sub>(HCOO)<sub>6</sub>](C<sub>2</sub>H<sub>5</sub>OH).<sup>10</sup> The methanol and ethanol are loosely bound guest molecules in the pores, and ordering of these molecules results into net polarization. The growing emphasis on dense hybrid systems that have a much wider range of applications in areas such as magnetism, photoluminescence, and nonlinear optics<sup>11,12</sup> raises the intriguing possibility of finding a hybrid framework for which electrical ordering is an inherent property of the crystal structure and not dependent upon guest molecules in pores. The present work reports a hybrid system with the perovskite architecture which exhibits a ferroic transition between paraelectric and antiferroelectric states.

[(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]Zn(HCOO)<sub>3</sub>, **1**, was synthesized in a reaction between zinc chloride and water in dimethylformamide, DMF. In a typical synthesis, 5 mL of DMF, 0.5 mL of water, and 1 mmol



**Figure 1.** Crystal structure of **1**. It has the same architecture as an ABX<sub>3</sub> perovskite, with A = (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup>, B = Zn<sup>2+</sup>, and X = HCOO<sup>−</sup>.

of zinc chloride were heated overnight in a Teflon lined autoclave at 125 °C. In situ hydrolysis of DMF produces formic acid and dimethyl ammonium cation, which are the building blocks for **1**.

Overnight synthesis followed by slow (3–4 h) cooling to room temperature results in the formation of branched structures that consist of needle-shaped crystals. Longer, room temperature crystallization over a period of a few months produced perfect cube-shaped transparent crystals. Synthesis conditions have been optimized, and the synthesis of **1** is reproducible as a pure single phase compound. An analogue of **1** was first prepared in 1973,<sup>13</sup> but its relationship to the perovskite structure was not recognized until 2005.<sup>14</sup> The structure of **1** at room temperature, as shown in Figure 1, was confirmed by single-crystal X-ray diffraction.

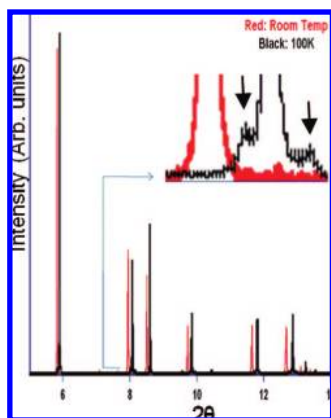
We were struck by the observation that the dimethylammonium cation at the center of the ReO<sub>3</sub>-type cavity in **1** is disordered with nitrogen apparently existing in three different possible positions. This is a consequence of disordered hydrogen bonding between the hydrogen atoms of the NH<sub>2</sub> group and oxygen atoms from the formate framework (N···O ~ 2.9 Å). The knowledge that hydrogen bonding of this type can lead to ferroelectric (e.g., in KDP) or antiferroelectric (as in NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, ADP) transitions when ordering takes place on cooling led us to examine the dielectric and phase transition behavior in this system.

The first evidence of a phase transition was noted when we saw splitting of spots while attempting to collect single-crystal X-ray data at liquid nitrogen temperatures. Unfortunately, it was not possible to index the low temperature data set due to complex twinning. However, synchrotron X-ray powder data collected on beamline 11-BM at the Advanced Photon Source gave clear indications of a phase change. As shown in Figure 2, peaks at 100 K were shifted to higher angles compared with the room temperature data as a consequence of lattice contraction on cooling. More

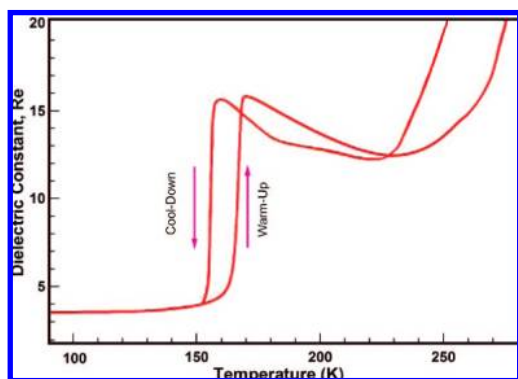
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**Figure 2.** Synchrotron powder patterns collected with a wavelength of 0.608 Å at the APS; red data: room temperature, black data: 100 K.

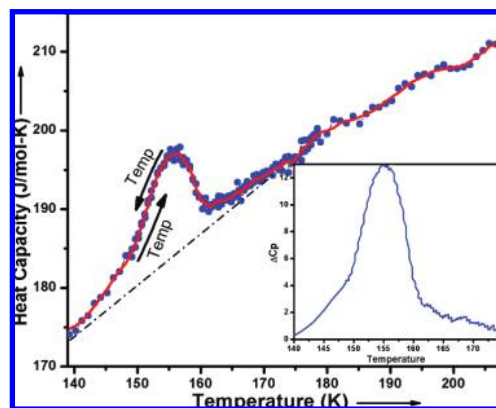


**Figure 3.** Dielectric constant of **1** measured as a function of temperature.

importantly, at 100 K, the main peaks also had weak satellites due to the formation of a superlattice (features indicated by arrows, see inset in Figure 2). Although the features are weak, our conclusion is supported by the observation of analogous features on all the other peaks. This observation is consistent with ordering of the NH<sub>2</sub> hydrogen atoms. It has not yet been possible to solve the structure of low temperature phase from the limited amount of data available.

In order to determine if this phase transition is accompanied by a dielectric anomaly, as expected for a perovskite,<sup>4</sup> the dielectric constant ( $\epsilon$ ) of **1** was measured as a function of temperature. We used a pellet as single crystals were too small to make silver paste contacts;  $\epsilon$  showed a clear anomaly around 160 K (Figure 3), in agreement with the synchrotron data. The maximum value of  $\epsilon_r$  (real part of  $\epsilon$ ) was found to be rather sample dependent, ranging from about 15 to 120, but the transition temperature was essentially reproducible. There was a clear hysteresis of about 10 K, its magnitude decreasing with slower temperature scan rates. The shape of the dielectric plot around 160 K furnishes clear evidence that **1** becomes antiferroelectric below 160 K on cooling.<sup>15</sup> The shape resembles the antiferroelectric transition for ADP (at 148 K).<sup>16</sup>

In order to probe the transition mechanism, we measured the specific heat of **1** over the temperature range of 1.8–300 K. A clear anomaly is seen around 156 K, in both the increasing and decreasing temperature scans (Figure 4). The shape of the curve points to a second-order transition. The area under the Cp/T curve yielded a value of  $\Delta S$  for the phase transition of 1.1 J/mol·K. For an order–disorder transition,  $\Delta S = R \ln(N)$ , where  $N$  is the number



**Figure 4.** Heat capacity of **1** as function of temperature. The inset shows the change in Cp related to the phase transition.

of sites for the disordered system. However, for  $N = 3$ , the value of  $\Delta S$  should be 9.1 J/mol·K, that is, almost an order of magnitude larger than the observed value. Clearly the transition is much more complex than a simple 3-fold order–disorder model. The structure of the low temperature phase clearly holds the key for explaining the transition mechanism. It will require neutron diffraction studies on a deuterated sample and NMR studies to sort it out. This is in our future plans.

In conclusion, we report an order–disorder type electrical ordering at 156 K in **1**. **1** also falls into the category of high dielectric constant material with an  $\epsilon_r$  value of 15. This type of electrical ordering associated with an order–disorder phase transition is unprecedented in hybrid frameworks and opens up an exciting new direction in rational synthetic strategies to create extended hybrid networks for applications in ferroic-related fields. Our results have led to new insights into this exciting family of structures exhibiting the unusual ferroic behavior. We are now actively exploring transition metal analogues of **1** that exhibit multiferroic properties.

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