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Multiferroic Behavior Associated with an Order−Disorder Hydrogen Bonding Transition in Metal−Organic Frameworks (MOFs) with the Perovskite ABX_3 Architecture

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Single-phase multiferroic materials in which magnetic and electrical ordering coexist are very rare. This is because the two cooperative phenomena require very different molecular interactions that are hard to incorporate in the same compound. In the case of ABX_3 perovskites, for example, the conventional mechanism for ferroelectricity in classical systems such as $BaTiO_3$ involves an off-centering of d^0 cations on the B-site. This is incompatible with magnetic ordering which requires unpaired spins.[1] The d^0 requirement can be circumvented if the electrical ordering can be achieved in a different way. In the classical cases of $BiMnO_3$ and $BiFeO_3$, the electrical ordering is driven by off-center displacements of the lone pair Bi^{3+} ions.[1−3] Similarly, in the case of nickel iodine boracite, $Ni_3B_7O_{13}I$, the first ferromagnetic ferroelectric material to be discovered, the distorted iodine−oxygen octahedron provides the origin for the ferroelectricity.[4] There are, of course, other ways in which ferroelectric ordering can be generated. In nonmagnetic ferroelectrics such as $NaCaF_3$, the driving force involves Coulomb interactions, rather than covalency. On the other hand, in potassium dihydrogen phosphate, KDP, hydrogen-bond ordering leads to ferroelectricity.[5] The present work demonstrates that multiferroic behavior can be achieved in hybrid inorganic−organic framework structures by using a combination of transition metal ions with hydrogen bond ordering.

In recent years there has been remarkable growth in the synthesis of nanoporous hybrid frameworks, usually known as metal−organic frameworks (MOFs), largely due to their potential applications in gas storage and separations, catalysis, nonlinear optics, photoluminescence, magnetic and electronic materials, and so on.[6−11] However, there have been very few reports in the literature on ferroic or multiferroic hybrid frameworks. It is possible for MOFs to exhibit multiferroic properties by combining host lattice magnetic ordering with ferroelectric behavior due to guest or solvent molecule ordering at low temperatures in the nanopores.[12,13] Most of these guest molecules (water, methanol or ethanol), however, have low boiling points and tend to evaporate on approaching room temperature, thereby leading to irreproducible data. Hence it is preferable for a structural driving force that is an inherent property of the lattice to be present to facilitate the electrical ordering. We recently reported a case of antiferroelectric ordering at 160 K in a cation-templated MOF with the ABX_3 perovskite topology, $[(CH_3)_2NH_2]Zn(HCOO)_3$ (DMZnF).[14] In the present communication we show that this same class of materials can become multiferroic when the zinc is replaced by a transition metal ion.

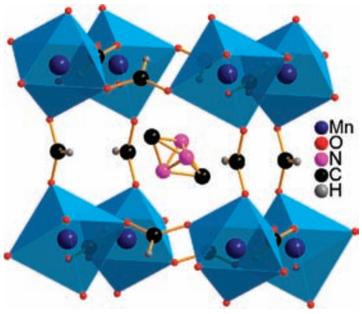

Figure 1. Building block of $[(CH_3)_2NH_2]Mn(HCOO)_3$, DMMnF. The DMA cation (A) is at the center of a ReO_3 type cavity, formed by manganese (B) and formate (X) ions. Nitrogen is disordered over three positions.

Samples of $[(CH_3)_2NH_2]M(HCOO)_3$ (DMMF = dimethylammonium metal formate), where M = Mn (Figure 1), Fe, Co, and Ni, were synthesized under solvothermal conditions at 140 °C. Metal chloride salts (5 mmol) were dissolved in a 60 mL solution of 50 vol % DMF in water, and the solution was transferred into a Teflon-lined autoclave. This was heated for 3 days at 140 °C. The autoclaves were air cooled, and the supernatants were transferred into a glass beaker for room temperature crystallization. Within another 3 day period, cubic colorless crystals for Mn and Fe, red crystals for Co, and green crystals for Ni were obtained. DMFeF has not previously been reported in the literature (see Supporting Information for cif file). In DMMF, the DMA cation at the center of the ReO_3-type cavity is disordered at room temperature with nitrogen distributed over three equivalent positions, as in the analogous zinc system. This is a consequence of disordered hydrogen bonding between the hydrogen atoms of the NH_2 group and the oxygen atoms of the formate framework (N...O $\approx$ 2.9 Å´).

Wang et al.[14,15] have shown that DMMnF, DMCoF, and DMNiF are canted weak ferromagnets with T_c values of 8.5, 14.9, and 35.6 K, respectively. They have also shown that, for DMCoF and DMNiF, spin reorientation takes place at 13.1 and 14.3 K, respectively. All of the samples show hysteresis loops below their critical temperatures. Using the model developed by Rushbrook and Wood for a Heisenberg antiferromagnet on a simple cubic lattice and/or the molecular field theory for antiferromagnetism, the magnetic coupling parameters J were

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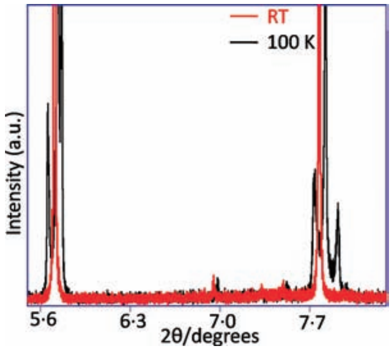

Figure 2. PXRD pattern for DMMnF, collected at the Advanced Photon Source, ANL (λ = 0.608 Å´, BM-11).

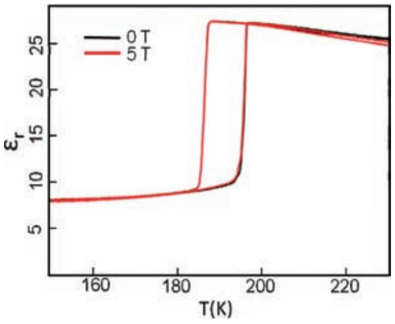

Figure 3. Dielectric constant of DMMnF as a function of temperature with no magnetic field and with that of 5 T. The measurements were done at 1 kHz, using an amplitude of 1 V.

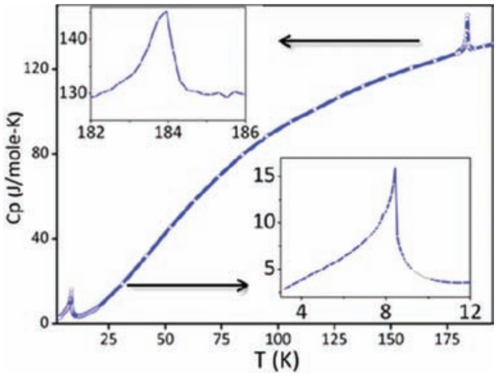

Figure 4. Heat capacity of DMMnF as a function of temperature. The anomalies relating to electrical ordering and magnetic ordering are clearly visible.

estimated to be −0.23/−0.32, −2.3, and −4.85 cm^{-1} for Mn, Co, and Ni, analogues respectively. Their *J* values indicate that the dominant superexchange mechanism is antiferromagnetic. Wang et al. also suggested that the spin canting in these compounds may originate from the noncentrosymmetric character of the three-atom formate bridge, CHOO$^-$.[15,16] In the present work, we have confirmed the findings of Wang et al. and also found that DMFeF is ferromagnetic below 20 K. It is important to note that it is possible to synthesize other weak ferromagnets simply by changing the central amine cation.[17]

Powder X-ray diffraction (PXRD) data for all samples gave clear indications of a phase change between room temperature and 100 K (Figure 2). The PXRD peaks for the DMMFs at 100 K are shifted to higher angles compared with those at room temperature as a consequence of lattice contraction on cooling, and the main peaks in the PXRD pattern showed splitting associated with a lowering of symmetry. Single crystal X-ray data were collected for DMMnF at 110 K, well below the transition temperature, but because of twinning it has not yet been possible to solve and refine the structure to a satisfactory standard. However, we are confident that the unit cell of the low temperature structure is monoclinic with cell dimensions a = 14.451(8) Å, b = 8.376(3) Å, c = 8.952(4) Å, β = 120.88(1)°. The monoclinic unit cell has been confirmed for all the samples by low temperature powder X-ray diffraction (see Supporting Information).

As expected, this phase change is associated with a dielectric (ϵ_r) anomaly. Dielectric constant measurements were carried out on single crystals of DMMnF, DMFeF, and DMCoF as well as on a powder sample of the nickel phase. The dielectric constant of DMMnF shows a clear anomaly close to 185 K on cooling (Figure 3). A clear hysteresis of ~10 K was seen when compared with the transition on heating. The shape of the dielectric plot suggests that DMMnF is undergoing a paraelectric to antiferroelectric phase transition with ϵ_r values of approximately 25 and 9, respectively. This is a result of the structural phase transition due to the ordering of the nitrogen atoms. No other dielectric anomaly was observed while cooling the sample down to 1.8 K. The transition is of an order−disorder nature, rather than displacive, and the shape resembles the antiferroelectric transition for $NH_4H_2PO_4$ (ADP).[18] Similar hydrogen bond ordering is responsible for the ADP phase transition, which is at ~148 K. The dielectric constants for the paraelectric phases of DMFeF, DMCoF, and DMNiF were found to be approximately 45, 50, and 30, respectively; their transition temperatures on cooling were found to be 160, 165, and 180 K, respectively. As expected from their similar structures and the origin of the disorder, the shapes of the anomalies are essentially the same for the other three analogues.

The dielectric constant findings were corroborated by specific heat measurements. The measurements were carried out on 20−30 single crystals by immersing them inside N-grease on a Quantum Design PPMS sample holder. The measurements were performed several times to ensure reproducibility, and appropriate backgrounds were measured before each experiment. The specific heat of DMMnF, which was measured as a function of temperature from 1.8 to 300 K, shows clear anomalies at 183 and 8.4 K corresponding to the transitions leading to electrical and magnetic ordering, respectively (Figure 4). Both of the transition temperatures are in agreement with dielectric and magnetic susceptibility measurements. The area under the C_p/T curve at ~183 K yielded a value for ΔS of 0.9 J/mol·K. For a complete order−disorder transition ΔS is expected to be given by R ln(N) where N is the number of sites in the disordered system. For N = 3, ΔS would therefore be 9.1 J/mol·K, which is almost an order of magnitude larger than the observed value. This suggests that the transition is more complex than a simple 3-fold order−disorder model. It appears that as the sample is cooled through the transition, the compound becomes only partly ordered and the long-range ordering takes place over a broad range of temperatures. The strength of the magnetic field neither affected the antiferroelectric transition nor altered the heat capacity significantly (see Supporting Information, Figure 1); we therefore conclude that there is no magnetoelectric coupling associated with this phase transition.

Detailed studies of the specific heat changes for DMMF (M = Mn, Co, Ni) through the magnetic phase transition show that

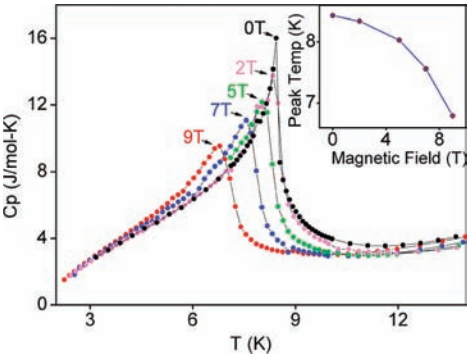

Figure 5. Effect of magnetic field on the magnetic phase transition in DMMnF on cooling.

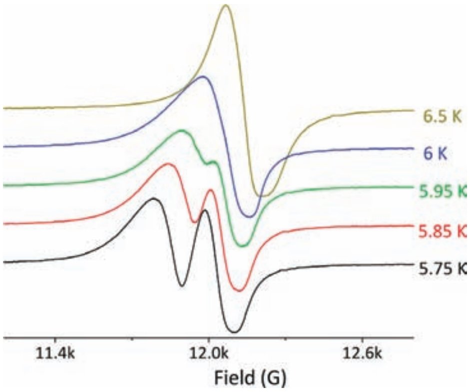

Figure 6. Temperature dependence of Q-Band EPR spectra of DMMnF.

T_c decreases from 8.4 to 6.7 K on increasing the magnetic field from 0 to 9 T (Figure 5). This is consistent for the predominantly antiferromagnetic behavior of these systems. Low temperature Q-Band EPR spectra for DMMnF (Figure 6) have shed further light on the magnetic phase transition. Measurements were made on single crystals of DMMnF to find if this magnetic transition was accompanied by a structural phase transition, since our PXRD facility did not enable us to reach these temperatures. As seen in Figure 6, the single EPR peak clearly splits into two, implying two differently oriented domains below ~6 K. Thus the magnetic transition is accompanied by a structural change as well.

In conclusion, we report four multiferroic metal organic frameworks, $((CH_3)_2NH_2)M(HCOO)_3$, with M = Mn, Fe, Co, and Ni, which belong to the ABX_3 type perovskite family with $A = [(CH_3)_2NH_2]^+$, $B = M^{2+}$, and $X = HCOO^-$. The dimethylammonium cation is dynamically disordered in the rhombohedral paraelectric phase, and the transition to the monoclinic antiferroelectric phase involves hydrogen bonded ordering of the DMA cations at temperatures in the range 160−185 K. On further cooling, these materials become magnetically ordered (8−36 K), and below these temperatures the antiferroelectric order coexists with weakly ferromagnetic order. Our findings illustrate a new approach to the creation of systems exhibiting multiferroic behavior whereby electrical order involves hydrogen bonding. These results suggest a highly promising new mechanism for this important behavior and opens up fresh opportunities for production of lead-free multiferroic structures tailored for specific technological applications.

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Supporting Information Available: Crystallographic information file of DMFeF, the effect of magnetic field on the structural phase transition, and X-ray powder diffraction plots. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Hill, N. A. *J. Phys. Chem. B* **2000**, *104*, 23.
(2) Lebeugle, D.; Colson, D.; Forget, A.; Viret, M.; Bataille, A. M.; Gukasov, A. *Phys. Rev. Lett.* **2008**, *100*, 227602.
(3) Moreira dos Santos, A.; Parashar, S.; Raju, A. R.; Cheetham, A. K.; Rao, C. N. R. *Solid State Commun.* **2002**, *122*, 49.
(4) Ascher, E.; Rieder, H.; Schmid, H.; Stossel, H. *J. Appl. Phys.* **1966**, *37*, 1404.
(5) Slater, J. C. *J. Chem. Phys.* **1941**, *9*, 16.
(6) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191.
(7) Cheetham, A. K.; Rao, C. N. R.; Feller, R. K. *Chem. Commun.* **2006**, 4780.
(8) Cheetham, A. K.; Rao, C. N. R. *Science* **2007**, *318*, 58.
(9) Tan, J. C.; Merrill, C. A.; Orton, J. B.; Cheetham, A. K. *Acta Mater.* **2009**, *57*, 3481.
(10) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
(11) Rowsell, J. L. C.; Yaghi, O. M. *Microporous Mesoporous Mater.* **2004**, *73*, 3.
(12) Cui, H.; Zhou, B.; Long, L. S.; Okano, Y.; Kobayashi, H.; Kobayashi, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3376.
(13) Cui, H. B.; Wang, Z. M.; Takahashi, K.; Okano, Y.; Kobayashi, H.; Kobayashi, A. *J. Am. Chem. Soc.* **2006**, *128*, 15074.
(14) Jain, P.; Dalal, N. S.; Toby, B. H.; Kroto, H. W.; Cheetham, A. K. *J. Am. Chem. Soc.* **2008**, *130*, 10450.
(15) Wang, X. Y.; Gan, L.; Zhang, S. W.; Gao, S. *Inorg. Chem.* **2004**, *43*, 4615.
(16) Wang, X. Y.; Wang, Z. M.; Gao, S. *Chem. Commun.* **2008**, 281.
(17) Wang, Z. M.; Zhang, B.; Otsuka, T.; Inoue, K.; Kobayashi, H.; Kurmoo, M. *Dalton Trans.* **2004**, 2209.
(18) Gough, S. R.; Ripmeester, J. A.; Dalal, N. S.; Reddoch, A. H. *J. Phys. Chem.* **1979**, *83*, 664.

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