Angewandte Chemie

Multiferroic MOFs

DOI: 10.1002/anie.200906660

Multiferroic Materials: The Attractive Approach of Metal–Organic Frameworks (MOFs)

*Guillaume Rogez, Nathalie Viart, and Marc Drillon**

hydrogen bonds · magnetic properties · metal–organic frameworks · multiferroic compounds · solid-state structures

The realization of ever smaller tunable devices is a major challenge in nanoelectronics; as a result, considerable efforts have been devoted to multifunctional materials in the last few years. Multiferroic compounds in which magnetic and electric properties coexist have received much attention. The observation of combined weak ferromagnetism and antiferroelectric order in a metal–organic framework (MOF) from Jain et al. illustrates a new route towards multiferroic systems that significantly differs from usually reported studies.[1]

Multiferroic materials present at least two coexisting orders among the electric, magnetic and/or elastic ones. The most appealing combination to date involves electric and magnetic orders, as it opens great perspectives in terms of applications, especially in the field of spintronics.[2] A clear distinction has to be made between systems exhibiting independent electric and magnetic orders and those featuring a magneto-electric coupling, both of which are promising in terms of applications. The former allows, for example, the conception of a four-state memory,[3] but the greatest promise is likely to be held by magneto-electric compounds, for they give access to a new type of control of magnetization by an electric field in spintronics devices.[4]

The heart of the problem currently is to find examples of multiferroic/magnetoelectric materials. One option is, of course, to combine the properties of two separate materials, one being ferromagnetic, the other ferroelectric, in a nanostructured composite material.[5] The coupling between both, which allows their mutual control, is usually carried out indirectly through strain by magneto- and electro-striction, which results in slow switching and fatigue phenomena. Intrinsic multiferroics are thus highly desirable, although, as mentioned by Jain et al., electric and magnetic orders tend to be mutually exclusive. Indeed, the presence of d electrons of transition metal ions, which are required to stabilize ferromagnetism, inhibits hybridization with the p orbitals of the surrounding oxygen anions, and thus displacement of the cations necessary for the establishment of a ferroelectric order.[6]

Intrinsic multiferroic materials, which are scarce, are generally classified according to the mechanism responsible for ferroelectricity: in proper ferroelectrics, spontaneous polarization appears as being itself the order parameter, whereas in improper ferroelectrics, it only appears as a by product in a phase transition governed by another order parameter.[7] For the former, the magnetic and electric orders are usually due to distinct cations, and the magnetoelectric coupling is generally weak. The prototypical compound is $BiFeO_3$ (BFO), in which 3d electrons of the iron(III) cations are responsible for magnetization, whereas ferroelectricity originates from a structural instability caused by the hybridization between the oxygen 2p and the empty bismuth 6p orbitals. Exhibiting both an antiferromagnetic order (unfortunately for applications) and a ferroelectric state at room temperature, BFO has the most remarkable features reported to date. As for the latter property, the ferroelectricity may result from phase transitions of different natures: either nonpolar lattice distortions in geometric multiferroics , such as in $YMnO_3$, or long-range ordering of charges ($LuFe_2O_4$) or spins ($TbMnO_3$) in electronic and magnetic ferroelectrics, respectively.

In this scenario, which is mainly covered by oxides, a few hybrid or molecule-based materials are currently emerging. Coordination polymers have been recently tailored to show both electric and magnetic ordering. Cyanide-bridged compounds have been investigated in particular, as it is well known that the cyanide ligand facilitates efficient magnetic coupling between metal ions. Electric ferroic order is promoted either by the use of chiral ligands[8] or by a subtle balance between vacancies and lattice distortions, as pointed out for the ferroelectric ferromagnet rubidium manganese hexacyanoferrate.[9] Cyanide-bridged clusters and chains that associate ferroelectricity and slow magnetization relaxation (single-molecule magnet or single-chain magnet behavior) have also been reported.[10]

MOFs have long been at the forefront in hybrid materials, as they provide an impressive number of applications, such as gas storage, exchange or separation, drug delivery, catalysis, optics, and magnetism.[11] In turn, such hybrid nanoporous structures in which metal ions or polymetallic clusters are embedded in an organic framework have not been considered

---

[*] Dr. G. Rogez, Prof. N. Viart, Dr. M. Drillon
Institut de Physique et Chimie des Matériaux de Strasbourg
UMR CNRS-UdS 7504
23, rue du Loess, BP 43, 67034 Strasbourg cedex 2 (France)
Fax: (+33) 3-8810-7250
E-mail: drillon@ipcms.u-strasbg.fr

for multiferroics purposes until recently.[12] The series of compounds $(Me_2NH_2)[M(HCOO)_3]$ (M = Mn, Co, Ni, Fe) reported by Jain et al. illustrates the last achievements in this new route towards multiferroics.[1]

A few MOFs have been shown to stabilize ferromagnetism or weak ferromagnetism,[13] and accordingly they are good candidates for obtaining multiferroics. A key issue is the observation of a net magnetic moment at quite high temperature because of the rather low efficiency of the bridging organic ligands (mainly carboxylates and polypyridines) for mediating exchange coupling. This intrinsic drawback can be bypassed by using an organic radical.[14] Alternatively, a compromise between the size of the ligand and the strength of the exchange coupling can be sought.[15]

Reports of MOFs showing an electric ferroic ordering are rather scarce. The main strategies involve either a chiral ligand[16] or a bridging ligand that is sufficiently flexible to induce the crystallization of the system in a polar point group.[17] Following these developments, MOFs appear to be an appealing way to combine magnetic and electric orders within a single structure. In 2006, Cui et al. described a new porous ferrimagnet, $[Mn_3(HCOO)_6]$ ($T_N = 8.0$ K); the pores of this structure can be filled in by ethanol, giving rise to ferroelectric behavior.[12] The ordering of the guest solvent molecules in the pores is the source of the ferroelectric transition observed at 165 K. Unfortunately, this first multiferroic MOF suffers from the tendency of the guest solvent molecules to escape at room temperature, inducing a loss of the electric properties.

A step further was recently taken by Jain et al., who first described an antiferroelectric dimethylammonium zinc formate (DMAZnF) in which the electric order at 160 K results from the hydrogen bond ordering of the dimethylammonium cation (DMA^+). Unlike the previous system, DMA^+ is not a guest molecule but part of the perovskite structure at the center of the ReO_3-type cavity formed by the MO_6 units and formate ions (Figure 1). In that sense, the origin of the electric ordering can be assumed to be intrinsic, and moreover not dependent on solvent contents.[18]

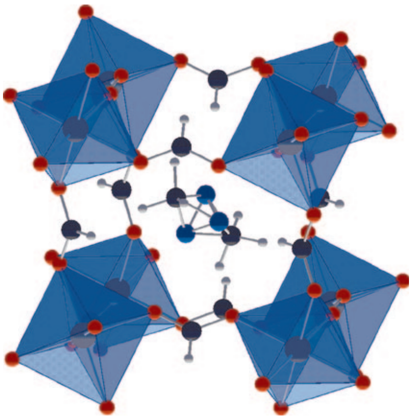

Figure 1. View of the perovskite structure of DMAFeF, showing the FeO_6 octahedra and the DMA^+ cations. N blue spheres, C black, H gray, O red; nitrogen atoms are distorted over three positions. (Adapted from Ref. [1]).

The authors subsequently demonstrated that this antiferroelectric behavior was also present in the Mn, Co, Ni, and Fe magnetic analogues, which thus constitute the first series of multiferroic MOFs. The non-collinear magnetic ordering that occurs below $T_N = 8.5$ K to 35.6 K, depending on the transition metal ion,[15,19] coexists with the antiferroelectric order, which develops at a higher temperature (170 K).[1] Although the hydrogen bond ordering mechanism responsible for the electric ordering has already been reported in the ferroelectric potassium dihydrogen phosphate (KDP), in the present case it is involved in multiferroics for the first time. Although the antiferroelectric transition has an order–disorder character rather than a displacive one, these MOF multiferroics can probably be referred to as proper ferroelectrics, such as $BiFeO_3$ and $BiMnO_3$, the only difference being that the transition relies on hydrogen bonds instead of covalent bonds.

Careful investigation of the paraelectric/antiferroelectric transition by means of heat-capacity measurements shows that important fluctuations probably occur, as only 10% of the expected entropy is involved at the transition temperature. Upon cooling the sample below the electric ordering temperature, the system is only partly ordered and its behavior looks like a spin ice in magnetic systems.

Finally, it should be noted that the magnetic ordering temperature is still far too low to predict immediate applications, and the electric transition is unaffected by the application of a magnetic field, which indicates that there is probably no magnetoelectric coupling, thus limiting their practical use. However, MOF-based compounds offer very attractive perspectives as model intrinsic multiferroic systems, because ligand, metal ion, and organic cation can be varied almost at will. Now that the ideas have been laid down and the feasibility demonstrated, new compounds will no doubt soon be tailored and developed to overcome these difficulties, thereby taking advantage of the richness of MOF chemistry.

Received: November 25, 2009

---

[1] P. Jain, V. Ramachandran, R. J. Clark, H. D. Zhou, B. H. Toby, N. S. Dalal, H. W. Kroto, A. K. Cheetham, *J. Am. Chem. Soc.* **2009**, *131*, 13625–13627.

[2] R. Ramesh, N. A. Spaldin, *Nat. Mater.* **2007**, *6*, 21–29.

[3] M. Gajek, M. Bibes, S. Fusil, K. Bouzehouane, J. Fontcuberta, A. Barthélémy, A. Fert, *Nat. Mater.* **2007**, *6*, 296–302.

[4] Y.-H. Chu, L. W. Martin, M. B. Holcomb, M. Gajek, S.-J. Han, Q. He, N. Balke, C.-H. Yang, D. Lee, W. Hu, Q. Zhan, P.-L. Yang, A. Fraile-Rodríguez, A. Scholl, S. X. Wang, R. Ramesh, *Nat. Mater.* **2008**, *7*, 478–482.

[5] H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, R. Ramesh, *Science* **2004**, *303*, 661–663.

[6] N. A. Hill, *J. Phys. Chem. B* **2000**, *104*, 6694–6709.

[7] S.-W. Cheong, M. Mostovoy, *Nat. Mater.* **2007**, *6*, 13–20.

[8] H.-R. Wen, Y.-Z. Tang, C.-M. Liu, J.-L. Chen, C.-L. Yu, *Inorg. Chem.* **2009**, *48*, 10177–10185.

[9] S.-i. Ohkoshi, H. Tokoro, T. Matsuda, H. Takahashi, H. Irie, K. Hashimoto, *Angew. Chem.* **2007**, *119*, 3302–3305; *Angew. Chem. Int. Ed.* **2007**, *46*, 3238–3241.

[10] a) C.-F. Wang, Z.-G. Gu, X.-M. Lu, J.-L. Zuo, X.-Z. You, *Inorg. Chem.* **2008**, *47*, 7957–7959; b) C.-F. Wang, D.-P. Li, X. Chen, X.-M. Li, Y.-Z. Li, J.-L. Zuo, X.-Z. You, *Chem. Commun.* **2009**, 6940–6942.

[11] a) G. Férey, A. K. Cheetham, *Science* **1999**, *283*, 1125–1126; b) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040–2042; c) C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem.* **2004**, *116*, 1490–1521; *Angew. Chem. Int. Ed.* **2004**, *43*, 1466–1496; d) S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; e) J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4748–4758; *Angew. Chem. Int. Ed.* **2005**, *44*, 4670–4679.

[12] H. Cui, Z. Wang, K. Takahashi, Y. Okano, H. Kobayashi, A. Kobayashi, *J. Am. Chem. Soc.* **2006**, *128*, 15074–15075.

[13] a) N. Guillou, C. Livage, M. Drillon, G. Férey, *Angew. Chem.* **2003**, *115*, 5472–5475; *Angew. Chem. Int. Ed.* **2003**, *42*, 5314–5317; b) A. Demessence, A. Mesbah, M. François, G. Rogez, P. Rabu, *Eur. J. Inorg. Chem.* **2009**, 3713–3720.

[14] D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira, J. Veciana, *Nat. Mater.* **2003**, *2*, 190–195.

[15] X.-Y. Wang, Z.-M. Wang, S. Gao, *Chem. Commun.* **2008**, 281–294.

[16] a) Q. Ye, Y.-M. Song, G.-X. Wang, K. Chen, D.-W. Fu, P. W. Hong Chan, J.-S. Zhu, S. D. Huang, R.-G. Xiong, *J. Am. Chem. Soc.* **2006**, *128*, 6554–6555; b) W. Zhang, R.-G. Xiong, S. D. Huang, *J. Am. Chem. Soc.* **2008**, *130*, 10468–10469.

[17] Q. Ye, T. Hang, D.-W. Fu, G.-H. Xu, R.-G. Xiong, *Cryst. Growth Des.* **2008**, *8*, 3501–3503.

[18] P. Jain, N. S. Dalal, B. H. Toby, H. W. Kroto, A. K. Cheetham, *J. Am. Chem. Soc.* **2008**, *130*, 10450–10451.

[19] X.-Y. Wang, L. Gan, S.-W. Zhang, S. Gao, *Inorg. Chem.* **2004**, *43*, 4615–4625.