

MS15-O5 Structure–property relationships in multiferroic metal–organic frameworks at high pressure

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Dense metal–organic frameworks (MOFs) show promise for a new generation of multiferroic materials,¹⁻³ which have technological importance in sophisticated multistate devices. MOFs present several advantages over already known multiferroic ceramic materials, such as increased framework flexibility, a vast chemical diversity, and numerous host–guest interactions. These characteristics could lead to increased ferroelectric responses and guest-tuned multiferroic properties. However, so far the study of multiferroic MOFs is in its infancy, and a much greater understanding of the structure–property relationships is needed in order to direct the design of functional multiferroic MOFs.

The dense MOF families of ammonium metal formates, $[\text{NH}_4][\text{M}(\text{HCOO})_2]$, and dimethylammonium metal formates, $[(\text{CH}_3)_2\text{NH}_2][\text{M}(\text{HCOO})_3]$, have shown great potential for multiferroic behaviour.^{3,4} The metal cations in the MOF—connected via organic ligands—provide the magnetic property, while the guest cation in the framework pore yields the ferroelectric response; host–guest interactions may then lead to coupling between the two ferroic parameters. Both these families of MOFs contain disordered A-site cations, which order in a preferential direction at low temperature (below 250 K) to create a switchable uniaxial electric dipole [Fig. 1]. Hydrogen bonding between the A-site cation and the formate linker, which connects the metal cations, provides a way to couple the electric and magnetic ordering.

In this study, we use high-pressure conditions in order to evoke electric and magnetic ordering in dense MOFs, which have already shown multiferroic behaviour at low temperature and ambient pressure. Investigating the structural evolution under pressure is important for determining the way chemical pressure (*i.e.* how different sizes of chemical components can mimic the effect of hydrostatic pressure) should be used in order to obtain desirable ferroelectric and ferromagnetic properties at ambient conditions.

References

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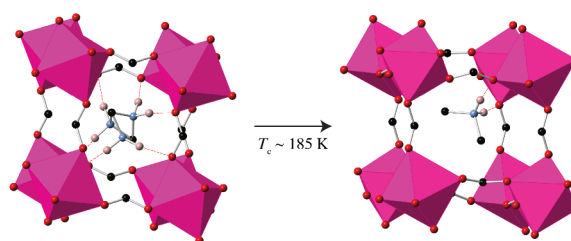


Figure 1. Ferroelectric phase transition of $[(\text{CH}_3)_2\text{NH}_2][\text{Mn}(\text{HCOO})_3]$ induced upon cooling from ambient temperature to below 185 K, creating a uniaxial electric dipole.⁵ Hydrogen bonds are shown in dotted red lines, and octahedral coordination about Mn^{2+} is represented by polyhedra.

Keywords: metal–organic framework, high pressure, multiferroic