

Multiferroic metal organic frameworks with perovskites structure

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Summary. — Hybrid inorganic-organic or Metal-Organic Frameworks (MOFs) are compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous. More formally a MOF is a coordination network with organic ligands containing potential voids. Most of the efforts on this materials have been focused on discovering porous MOFs for gas storage applications, such as hydrogen and carbon dioxide. But not much attention has been payed to other physical properties for which oxides are usually known, like multiferroic behavior. A review of the scientific community works on these nanoporous hybrid frameworks, will be given, showing how, due to the large tunability of their pore size, unprecedented properties and applications can be exploited. Moreover filling their cavities with proper materials, allows to tune their optical, electronic, or magnetic properties by guest interactions. Second-Harmonic Generation (SHG) is proposed as optical technique to confirm a paraelectric-ferroelectric phase transition under the critical temperature for multiferroic metal organic frameworks with perovskites structure.

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1. – Introduction

The interest of the scientific community working on the synthesis of nanoporous hybrid frameworks, usually known as metal-organic frameworks (MOFs), is mainly due to the large tunability of their properties, acting on the material pore size, or ranging the inorganic/organic ratio, or changing the metal ions and/or organic ligands, even maintaining the same structure topology.

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In general, hybrid porous solids result from the reaction between organic and inorganic species in order to build up three-dimensional frameworks whose skeleton contains both organic and inorganic moieties only linked by strong bond. Such hybrid structures differ from classical inorganic porous solids in the contrast between the bonds within the framework, which are mainly covalent for the organic part; ionocovalent for the inorganic one.

Historically, in the first hybrid frameworks [1-5] the inorganic part contained either isolated polyhedra or small clusters, like in coordination chemistry. That is why these solids were named coordination polymers. Increasing the control in their syntheses process, it was shown that these hybrid solids could possess inorganic parts with a larger dimensionality, giving rise to chains (1D), layers (2D) and even inorganic frameworks (3D). Compared to inorganic frameworks, MOFs show several advantages [1]: a) the existence of inorganic and organic moieties in MOFs allows hydrophilic and hydrophobic parts to coexist within the pores, leading to a control of the adsorption properties; b) while in inorganic moieties only few cations can participate in the framework, MOFs can accept almost all the cations of the classification, at least those which are di-, tri- or tetravalent, including rare earths, providing a huge number of possibilities for creating new materials; c) due to the large choice of functionalized organic linkers which can be associated with the inorganic parts, the possibility of creating new materials tends towards infinity; d) during the syntheses the dimensionality of the inorganic subnetwork strongly depends on the temperature of the reaction. The increase of the inorganic dimensionality favours the onset of long-range interactions and therefore, the appearance of physical properties usually encountered in dense solids. This introduces a new field of potential applications beside the usual properties of porous solids (fluids separation and storage, catalysis). On the other hand, such a variability increases once more the possibilities for the creation of new solids. These are only some of the advantages of hybrids towards inorganic frameworks. For the moment only one disadvantage appears: their weak thermal stability which excludes the possibility of any high-temperature application.

Cheetham *et al.* propose in [6] a simple but systematic classification of this class of materials, and explore the chemical and geometrical factors that influence their formation, highlighting their potential applications in areas such as gas separations and storage, heterogeneous catalysis, and photoluminescence. Their use in absorption and separation process is allowed by their highly porosity: low-density materials are good deals for gas storage capacities, including hydrogen and methane. Even if the total hydrogen adsorption capacity of the MOF materials is not as high as one can expect (as pores are too large and molecules prefer to adsorb at surfaces), this capacity can be increased by using interpenetrating networks [7,8] or by using lightweight hybrid materials with smaller cavities, such as magnesium formate [9]. Their use in catalytic applications seemed the first place generally inferior to conventional zeolitic materials, due to their relative instability, their lack of strong acidity, and their relatively costly synthesis. However, the scientific research pointed out advantages like a) the easiness with which they can be functionalized, post-synthesis, b) the possibility to tune the pore size over a wide range and c) the manner in which enantiomerically pure chiral frameworks can be created [10]. There is also considerable interest in the optical properties of hybrid frameworks on account of their tunability and their capacity to incorporate a wide range of metal ion and organic ligand chromophors.

In 2009 Tan *et al.* [11] published a study of the anisotropic mechanical properties of inorganic-organic framework, with different dimensionalities, showing how this anisotropy is directly correlated with the underlying crystalline structures. Using the

nanoindentation technique to measure anisotropy, they show how the elastic anisotropy of the polymorphic hybrid frameworks was found to be large compared with their plastic anisotropy, and how the presence of strong covalent bonding coupled with weaker intermolecular bonding (*e.g.* hydrogen bonds) within the same hybrid framework can give rise to highly directional mechanical responses. In the same paper, they incorporate the MOFs elastic modulus and hardness into a materials selection map: in comparison with other common engineering materials, they show how their mechanical properties are to some extent intermediate between those of purely organic and non-metallic inorganic solids. Also from a mechanical point of view, the wide diversity of chemical and structural variations, that can be achieved for hybrid frameworks, allows to tune their mechanical properties to match specific applications in the field of the nanospace engineering [12].

2. – Perovskite MOFs

Particularly interesting are MOFs with the perovskite ABX_3 architecture [13]. Hybrid perovskites of general formula $(CH_3)_2NH_2M(HCOO)_3$ have a ReO_3 -type cage made up of formate and metal ions. The perovskite topology ABX_3 can be recognized from the analogy $A=(CH_3)_2NH_2$, $B=Mn$ and $X=(HCOO)_3$. The metal ions sit at the corners of the cubes and are connected to each other via coordination bonding with oxygen of the formate ion. The dimethylammonium cation is located at the center of this cavity. The amine hydrogen atoms make hydrogen bonds with the oxygen atoms of the metal formate framework. Because of this hydrogen bonding, the nitrogen of the ammonium cation is disordered over three equal positions at room temperature. Cooling down these materials below a critical temperature (~ 180 K) leads to a lowering in symmetry, a result of the ordering of nitrogen atoms.

Exciting physical properties, like colossal magnetoresistance, ferroelectricity and superconductivity, have been discovered in this family of MOFs in the past years. Recently, Loi *et al.* [14] reported an electron-hole diffusion length exceeding 1 μ m in these materials, that is an important step towards highly efficient and cheap solar cells. However, most of the research on these materials is still focused on their ferroelectrics and multiferroics properties, as they exhibit the coexistence of magnetic and ferroelectric ordering [15, 16]. Jain *et al.*, reported about an antiferroelectric ordering at 160 K in $[(CH_3)_2NH_2]Zn(HCOO)_3$ (DMZnF) [17]. Moreover, by replacing Zn by Mn, a multiferroic phase may be eventually obtained [18].

3. – Second-Harmonic Generation

Second-Harmonic Generation (SHG) is the nonlinear optical process in which an optical wave at frequency 2ω is generated by an incident wave of frequency ω . As an even-order nonlinear optical effect, it is non-vanishing only in non-centrosymmetric media. In the case of ferroelectrics, the inversion symmetry breaking characterizing the ferroelectric phase causes the SHG signal. On the contrary, if the paraelectric state is centrosymmetric, no SHG occurs. In this respect SHG is an ideal probe of the ferroelectric-to-paraelectric phase transition. The SHG source in the wave equation is given by the nonlinear contribution to the total polarization of the material $P = P_L + P_{NL}$, where the induced second-order optical polarization $P_{NL}(2\omega)$ is given by

$$(1) \quad P_i(2\omega) = \epsilon_0 \chi_{ijk}^{(2)} E_j(\omega) E_k(\omega).$$

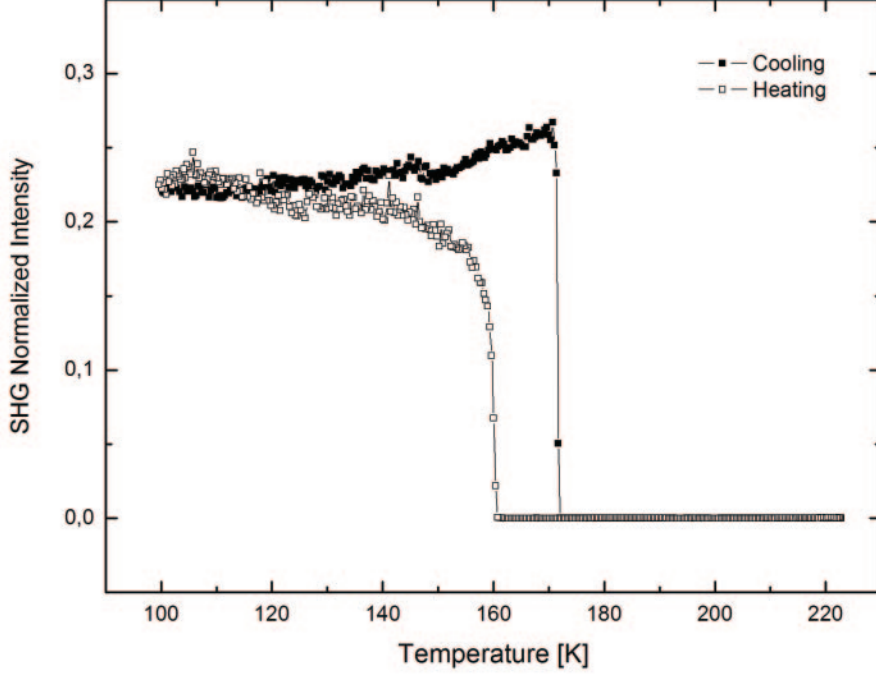


Fig. 1. – SHG signal temperature dependence for $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}(\text{HCOO})_3$, $\lambda_{SHG} = 650$ nm, $\lambda_{FUND} = 1300$ nm, $E_{fund} = 3.00 \mu\text{J}$ at 1300 nm, ramp rate=1 K/min. An hysteresis is visible even in absence of any external applied field. The paraelectric-ferroelectric phase transition takes place at $T_C^c = 160$ K. While the ferroelectric-paraelectric appears $T_C^h = 172$ K.

In eq. (1) ϵ_0 is the static dielectric constant, $E(\omega)$ is the incoming electric field and $\chi_{ijk}^{(2)}$ are the components of the second-order susceptibility tensor $\chi^{(2)}$. The sum over repeated indices is understood. What is actually measured in an SHG experiment is the SHG intensity I_{SHG} , which is given by

$$(2) \quad I_{SHG} \propto |P(2\omega)|^2.$$

Once the crystalline axis is known in detail, the susceptibility tensor elements can be probed by using different polarization combinations of both the input polarization of the fundamental beam and the output polarization of the second-harmonic beam.

Second-harmonic generation on hybrid perovskites can give information on the material phase transition. As expected for the perovskite cubic symmetry, the SHG signal is zero at room temperature. At low temperature a SHG signal, easy to be detected, appears. This shows that below a given temperature the inversion symmetry is broken and second-harmonic generation may take place. To probe the paraelectric-to-ferroelectric transition, a temperature scan from 100 K to 220 K was carried out. Exemplary results are reported in fig. 1.

For each measurement, the temperature is increased and then decreased, with a temperature ramp rate of 1 K/min. A very significant change in the critical temperature T_C is evident. The critical temperature upon heating the sample is found to be $T_C^h = 172$ K,

whereas upon cooling is $T_C^c = 160$ K. Those values are found to be quite reproducible in the range ± 5 K from sample to sample. Moreover, it is interesting to note that the shape of the two transitions is also very different. Upon heating, the SHG signal increases quite linearly before having an extremely sharp cut-off. On the contrary, upon cooling, the transition looks smoother and the SHG signal still increases when the sample temperature is further decreased. The hysteretic behavior suggests the presence of a glass-like phase transition [19].

4. – Conclusions

The paraelectric-ferroelectric phase transition of metal organic frameworks with perovskites structure is demonstrated by the second-harmonic generation technique. The analysis show how the material undergoes from a high-temperature phase that behaves as an ordinary dielectric to a low-temperature phase that has a spontaneous polarization. It is also worth noting that intrinsic hysteretic behaviours driven solely by temperature have been recently reported in analogous systems [20]. The microscopic origin of this is still unclear. Therefore, once the intrinsic nature of the observed hysteresis is asserted, this point must be further investigated both experimentally and theoretically. In order to understand whether the inversion symmetry breaking is homogeneous all over the sample or if the formation of domains occur, SHG microscopy will be carried out.

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