

## Application for beam time at ESRF – Experimental Method

### *Crystal structure determination of the $[CH_6N][M(CH_2O)_3]$ multiferroic material*

#### **Proposal Summary (should state the aims and scientific basis of the proposal) :**

The development and the characterization of new materials, are key challenges in chemistry and physics. Recently, metal organic frameworks (MOFs) have received much attention and among those in particular porous materials with multiferroic properties [1]. MOFs are typically synthesized by reacting an organic ligand with a metal salt under solvo-thermal conditions or by slow evaporation or diffusion techniques. The chemical nature of the ligand plays a crucial role, influencing for example the structure of the network[2]. The latter may also be governed by a template molecule, e.g. protonated amines. Such a molecule, remaining as a guest in the cavities of the framework, can introduce functionalities such as ferroelectricity in coexistence with magnetism [3]. Our studies are focused on the specific materials represented by compounds of the family  $ABX_3$ , where A is a cation (methylamines) M is a divalent transition metal ( $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ) and X formate as the organic ligand. The goal of this proposal is to study the structural properties of such perovskite-like metal-organic compounds through the application of four different points of targeted temperatures, in order to determine and refine the crystal structures, and in a second step of our project to be able to explain the magnetic properties of the system.

#### **Scientific background:**

In preliminary measurements carried out on the compound  $[CH_6N][Co(CH_2O)_3]$ , the structural, magnetic and dielectric properties have been investigated by variable-temperature single crystal diffraction, magnetic susceptibility measurements, dielectric constant in the form of relative permittivity and pyroelectric current measurements. These analyses reveal a structural phase transition at *ca.* 220 K correlated with electric order, which coexist with magnetic order below 6 K. The phase transition implies a symmetry change of the space group from  $Pnma$  at room temperature (RT) to  $P2_1/c$  at low temperature (LT) resulting in a reorientation of the methylammonium ions in the pores and a small distortion of the framework. The existence of a spontaneous polarization

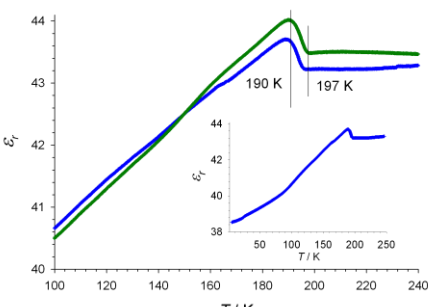


Figure 1. Relative permittivity as a function of temperature (green curve on cooling and blue curve on warming). The inset shows a detail of the temperature range explored from 5 to 300 K. The measurement was done on a pellet sample at 10 kHz.

(see below figure 3) is not compatible with the LT centrosymmetric space group; however the presence of

defects in the crystal after the structural phase transition may be the physical origin of the observed phenomenon. Cryomagnetic studies have shown an overall antiferromagnetic coupling with a long range ferromagnetic order below 6 K due to a non-compensation of a non-collinear antiferromagnetic structure. The dielectric constant in the form of relative permittivity ( $\epsilon_r$ ) has been explored from 5 to 300 K, showing basically a constant value from 250 K to 197 K, where an abrupt increase of signal is observed, from 43.3 at 196 K to a maximum value of 43.7 at 190 K, obtained from the cooling curve. After this anomaly, the relative permittivity decreases linearly achieving a value of 38.5 at 5 K (see Figure 2). No significant

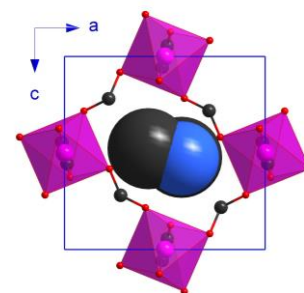


Figure 2. View along the c-axis of  $[CH_6N][Co(CH_2O)_3]$  crystal structure.

hysteresis was observed in the permittivity curve between the transitions on cooling and on heating ( $\Delta T$

close to 1 K). Nevertheless, a clear change is noticed in the path followed on cooling and on warming, with a difference in the relative permittivity ( $\Delta\epsilon_r$ ) of 0.3 at RT.

This difference is intimately related with the temperature dependence on the formation of domains. The shape of the signal suggests the occurrence of a ferroelectric phase transition at *ca.* 190 K. This anomaly

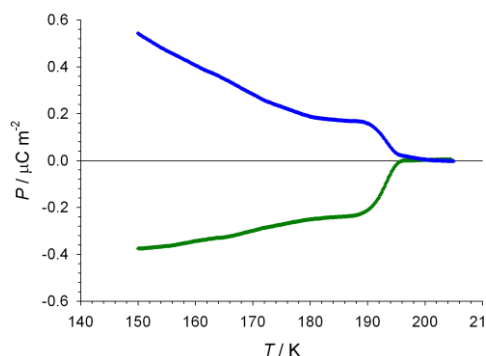


Figure 3. Temperature dependence of the estimated spontaneous polarization obtained integrating the pyroelectric current curves. The different colours on both figures correspond to opposite directions of the electric field applied during cooling down (blue dots for +100 V and green dots for -100 V).

occurs near the same temperature range as that observed in the specific heat measurement (*ca.* 220 K). The difference in temperature between both measurements could arise from the different nature of the sample: being powder for the dielectric measurements, where the measurement depends strongly on the connection between grains, and single crystals for the specific heat. The occurrence of a global polarization was shown by means of pyroelectric current measurements (*see Figure 3*). The spontaneous polarization derived from the pyroelectric current measurements decreased monotonically with increasing temperature from  $0.55 \mu\text{C}\cdot\text{m}^{-2}$  at 150 K to  $0.18 \mu\text{C}\cdot\text{m}^{-2}$  at 180 K (*see Figure 3*). In the temperature range from 180 K to 190 K the polarization presents a plateau with a negligible decrease of signal. After this point, the polarization decreases suddenly, reaching a zero value at *ca.* 200 K, which is in agreement with the result observed in the permittivity curve and in the specific heat measurements.

#### **Experimental technique(s), required set-up(s), measurement strategy, sample details (quantity...etc) : Beamline(s) and beam time requested with justification :**

The aim of this proposal is to investigate the temperature dependence of  $[\text{CH}_6\text{N}][\text{M}(\text{CH}_2\text{O})_3]$  compounds, where M is  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ , in order to obtain a good structural model and performing a reasonable refinement for each pattern. For this purpose, we intend to collect High-resolution powder diffraction (HRPD) data at the BM25A beam line within four specific temperature points. An amount of 200 mg of each sample is estimated. Considering the time required for setting up the sample environment for the three different samples and in order to obtain a high average statistic, we estimate that *ca.* 5h for each compound may be necessary, that is, 2 days for the complete structural studies. A cryostat device is required for carrying out the measurement at low temperature.

#### **Results expected and their significance in the respective field of research :**

The demanded beam time for investigating this family of compounds, reinforced by basic and preliminary studies, represents the opportunity to complete our work on this subject and to support the ab-initio calculation in which it is predicted an interesting magnetic behaviour. Furthermore, a previous single crystal X-ray diffraction experiment has been performed, but without satisfying results because with decreasing temperature the crystal formed a multiple component twin, precluding the correct structure determination. In fact, the twin indexation and integration implemented in *CrysAlis Pro* program has not permitted to acquire a reasonable model at low temperature. Consequently, for the just discussed reasons, the use of the synchrotron radiation will help us to characterize and to perform the best structural refinement for each powder samples.

#### **References**

- [1] R. J. Kuppler, D. J. Timmons, Q.-R. Fang, J.-R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang, H.-C. Zhou, *Coordination Chemistry Reviews*, **2009**, 253, 3042-3066
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- [3] Z.W. Bin Zhang, K. Inoue, H. Fujiwara, T. Otsuka, H. Kobayashi, M. Kurmoo, *Inorg. Chem.*, **2007**, 46, 437–445