MS32 Advanced techniques to disclose Structure-Property Relationships

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Structural investigations of a magnetoelectric plastic-crystal by complementary in situ multi-constraint (T, P, E) SC-XRD experiments

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Abstract

Materials presenting a coupling between two ferroic orders, such as ferroelectricity and (anti)ferromagnetism, are of particular interest owing to their high potential for applications in memory devices [1]. Therefore, there is an important research effort to design new multiferroic materials with improved magnetoelectric coupling. Molecule-based materials are particularly appealing to achieve magnetoelectric coupling since the versatility of each molecular components offers the possibility to tune the physical properties [2].

On the other hand, plastic crystalline molecular materials have attracted significant interest in the past few years because the solid-solid phase transition from the ordered crystal phase to the disordered plastic-crystal phase (PC) is generally accompanied by large enthalpy/entropy variations [3]. Recent investigations have been carried out on so-called ferroelectrics PC where the PC-crystal transition is associated to the para-ferroelectric transition giving rise to barocaloric, electrocaloric and multicaloric effects [4].

The ferroelectric PC triethylmethylammonium tetrabromoferrate (III) reported in 2012 by H. Chai et al [5] is particularly attractive as the para-ferroelectric transition, taking place around 355K, is accompanied by a change in the magnetic properties. At room temperature, $[(Et_3NMe)^+(FeBr_4)^-]$ crystallizes in polar space group P63mc and presents a structural transition leading to a new ferroelectric phase around 170K. More recently, we observed a colour change from dark red to yellow as function of temperature. The structural properties at the origin of this wide range of physical properties, especially the ferroelectricity, are almost unexplored. Indeed, $[(Et_3NMe)^+(FeBr_4)^-]$ shows an important disorder, complicating the atomic structure determination of the cationic part. To overcome these difficulties, we investigated the structural behaviour of this compound by in situ X-ray diffraction in different non-ambient conditions. First, we explored the phase diagram from room temperature to 5K and we quenched the room temperature phase at low temperature. Then, we performed in situ SC-XRD under pressure from ambient pressure to 4.5 GPa. Both experiments, at low temperature and under pressure, evidence an absence of correlation between the structural phase transition and the colour change. Finally, thanks to the new experimental setup we develop in our lab, we realized an in situ SC-XRD under a static electric field of 2kV/mm. All these non-routine measurements allowed us to have a better description of the cationic part disorder of $[(Et_3NMe)^+(FeBr_4)^-]$. This is a first step to establish structure-properties relationships of this multifunctional material.

References

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