Experimental report

05/09/2018

Proposal: **CRG-2473**

Council: 4/2017

Title: Exploring the magneto-structural correlations on Double Salt MagneticIonic Liquids: Dimim[Fe(ClxBrx-1)4] (0<x<1)

Research area:

This proposal is a new proposal

Main proposer: **Imanol DEL VALLE**

Experimental team: Palmerina GONZALEZ IZQUIERDO

Local contacts: Oscar Ramon FABELO ROSA

Samples: Dimim[Fe(ClxBrx-1)4]

Instrument	Requested days	Allocated days	From	To
D1B	3	2	16/04/2018	18/04/2018

Abstract:

D1B 16-17/04/2018

Experimental report CRG-2473

Magnetic ionic liquid (MILs) based on imidazolium cation and tetrahaloferrate ion present several non-covalent interactions such as hydrogen bonds, halogen-halogen (between the nearest metal complex anions) or anion-π (between the anion and cation) interactions. These materials can show several phase transitions from room temperature and interesting magnetic phenomena at low temperatures like a three-dimensional (3D) magnetic ordering. Furthermore, a complete picture of its magnetic behaviour is still missing, being extremely sensitive to temperature cooling rate effect. Therefore, using suitable rates of cooling from room temperature solid state, different ordered crystalline phases can be obtained with different magnetic behaviours. Recently, we have investigated two new MILs based on imidazolium salts and metal halides, named Dimim[$FeCl_4$] and Dimim[$FeBr_4$] (Dimim: 1,3-dimethylimidazolium), which are isostructural at room temperature but present different nuclear and magnetic structures at low temperature. Furthermore, the chloride compound presents two different structures at low temperature depending on the cooling process. In this experiment, we plan to study the crystal and magnetic structure of a series of new DSMILs (Double Salt Ionic Liquids) with 3D antiferromagnetic ordering with the chemical formula Dimim[$Fe(Cl_xBr_{1-x})_4$], x ranging from 0.95 to 0.025.

Initially, high flux neutron diffraction on D1B was performed. About 3 g of the samples with 5, 15, 50 and 80% of bromide were milled and placed in a cylindrical vanadium container. The procedure was similar for all samples: they were quenched in liquid nitrogen and placed inside the cryostat at 100 K. After this, we collected data at 1.8 (1.3 for the sample with 5% of bromide, using two vacuum pumps), 10 and 220 K. For the samples with 5 and 15% of bromide, the low temperature patterns were measured again to see the difference between the quenched and the relaxed phases. Data was acquired also while heating up from 10 to 220 K (except 50% of bromide) and from 1.5 K to 10 K for 5 and 80% of bromide, in order to follow the evolution of the magnetic peaks. This evolution is shown in Figure 1. For the compound with less bromide content, the background increases considerably at low angles with decreasing temperature, which does not occur with the sample with 80% of bromide. Likewise, this phenomenon was observed in the chloride parent, but not in the bromide parent. From the diffraction patterns, we can see that the magnetic peak appears around 5 K and 3 K for 5 and 80% bromide content, respectively. In the intermediate compositions, there is not 3D magnetic order above 1.5 K, according to specific heat measurements. This can be seen In Figure 2, where the low temperature patterns at 1.8 and 10 K of all the samples are shown. No magnetic peaks are observed at in the 15% bromide sample, and a small one appears at 50%. Furthermore, as the bromide content is increased, the background at low angles for the ordered phase disappears apart from 50%.

The nuclear structure for the sample with low bromide content at low temperature (quenched) fits to the parent structure, as expected, for the quenched phase. Nevertheless, at 220 K, the structure has not completely transited to the room temperature phase, and this mixture of phases is maintained when lowering again the temperature gradually. This mixture of phases can be seen in Figure 3, where the patterns at 1.3 (quenched and relaxed) and 220 K are shown. When increasing the temperature after quenching, new peaks appear at 22° and 46°, which remain after lowering again the temperature. The fit to the mixture to the low and room temperature phases of the chloride parent is also shown in Figure 3. For the samples with high content of bromide, it is not possible to fit the data to the structure of the parent MIL, so higher resolution data is needed or deuterated the phases to complete the study.

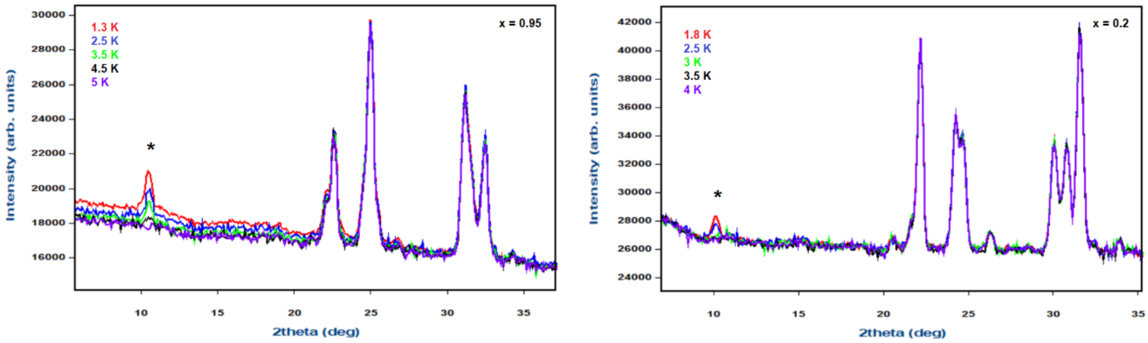

Figure 1: evolution of the magnetic peaks (*) with temperature for the samples with 5% (left) and 80% bromide (right).

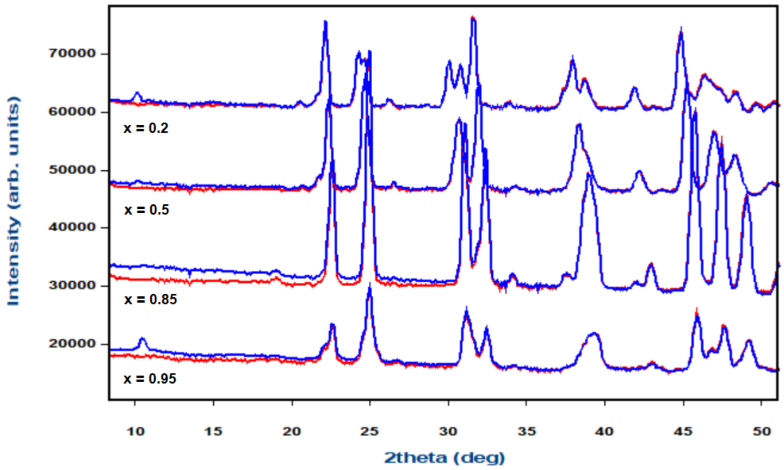

Figure 2: Diffraction patterns at 1.8 (blue) and 10 K (red) for all the measured samples.

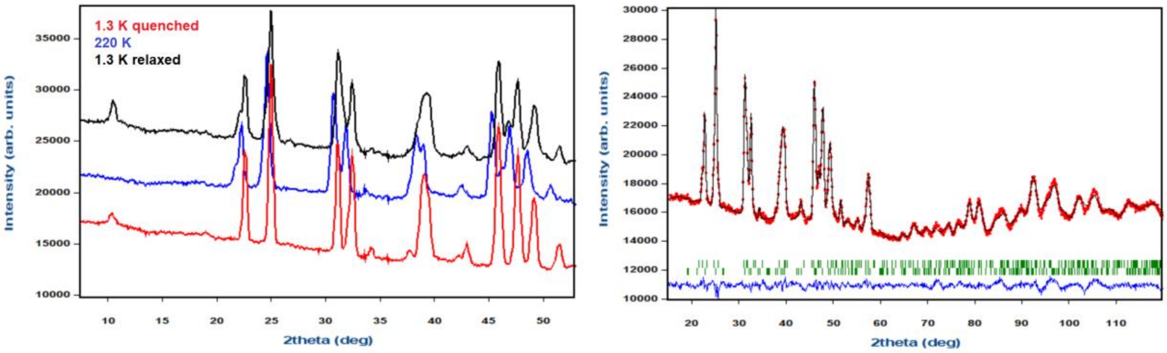

Figure 3: (Left) Diffraction patterns of the sample with 5% bromide content at 1.3 K after quenching, 220 K and 1.3 K after annealing. (Right) Rietveld refinement to a mixture of the quenched and relaxed phases of the chloride parent. Observed (red points) and calculated (black solid line) powder diffraction pattern of the low temperature pattern after annealing. Positions of the Bragg reflections are represented by vertical green bars for both phases. The observed-calculated difference pattern is depicted as a blue line at the bottom of the figure.