Experimental report

05/09/2018

Proposal: 5-31-2580 **Council:** 4/2017

Title: Searching the influence of the organic group in the magnetic interaction mechanisms of MILs based on imidazolium tetrahalureferrates family

Research area: Materials

This proposal is a new proposal

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Samples: 1,2,3 trimethyl imidazolium tetrahaloferrate TrimimFeX4 (X = Cl and Br)

Instrument	Requested days	Allocated days	From	To
D2B	2	2	15/06/2018	17/06/2018

Abstract:

Magnetic ionic liquids (MILs) are molten salts formed entirely of ions, which have a melting point below 100 ºC. The great variety of possible combinations of anions and cations makes them a huge potential field of development of smart materials with a primary focus in Materials Science. Actually, we are studying the influence of the organic group in the magnetic interaction mechanisms of MILs based on imidazolium tetrahalureferrates family. Specifically, the dependence of the Neel temperature (TN) as a function of the size of the radicals of the imidazolium cation. We have synthetized other two members of this family with a three-dimensional magnetic ordering because the trend is not clear. We have performed a preliminary investigation of the thermal properties (by differential scanning calorimetry) and the crystal and magnetic structure (by neutron powder diffraction) of TriminFeX4. Therefore, in this proposal we ask for 2 days at D2B high resolution diffraction instrument to obtain accurate magnetic structure characterization and phase transitions

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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 behavior 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[FeCl4] and Dimim[FeBr4] (Dimim: 1,3-dimethylimidazolium), which are isostructural at room temperature (phase **II**) but present different nuclear and magnetic structures at low temperature (the bromide compound does not transit). Furthermore, the chloride compound presents two different structures at low temperature depending on the cooling process (called **Ia** for the quenched phase and **Ib** for the relaxed phase). In this experiment, we plan to study the crystal and magnetic structure of a series of new deuterated DSMILs (Double Salt Ionic Liquids) with 3D antiferromagnetic ordering with the chemical formula Dimim[Fe(ClxBr1-x)4], x ranging from 0.95 to 0.025, with the methyl groups of the Dimim molecule deuterated.

High resolution neutron powder diffraction patterns (D2B) with λ = 1.5945 Å were obtained for the samples with 2.5, 5, 10, 60 and 75% of bromide content, at 3 K, after quenching in liquid nitrogen, and room temperature (10 scans, 25 step/scan, 750000 counts/step). The sample with 60% bromide was also measured at 50, 100 and 150 K in order to follow the evolution of the structure with temperature. The diffraction patterns for this sample are shown in Figure 1. Likewise the hydrogenated samples measured in D1B, the samples with low bromide content fit to the same structures than the chloride parent at low and high temperature (see Figure 2, a and b). Nevertheless, as we increase the bromide content, the structure at room temperature fits to phase II (see Figure 2, c), but the compound transits to a new phase in the low temperature regime. In order to solve this new phase, single crystal diffraction is needed.

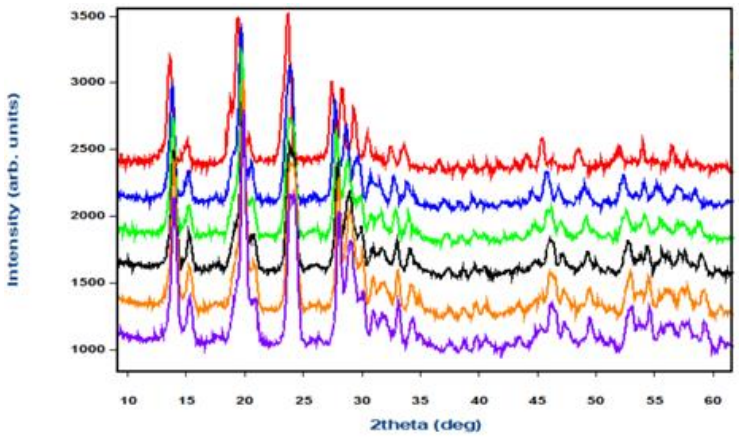

Figure 1: diffraction patterns at 3 (purple), 50 (orange), 100 (black), 150 (gren), 200 (blue) and 300 K (red) for the sample with 60% bromide content.

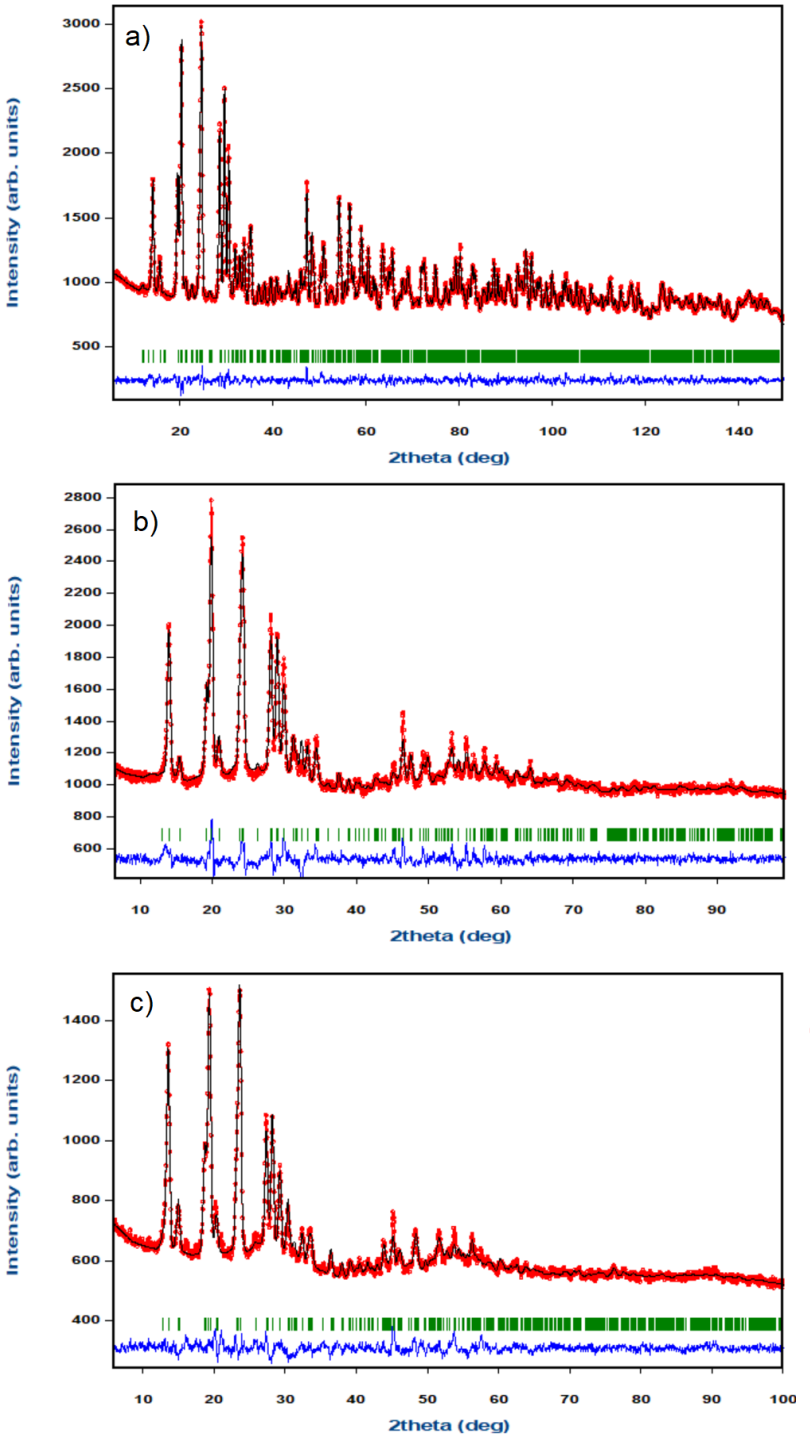

Figure 2: Rietveld refinement to the sample with 2.5% of bromide at 3 K to the phase **Ia** (a), at room temperature to the phase **II** (b) and to the sample with 75% of bromide at room temperature to the phase **II** (c). Observed (red points) and calculated (black solid line) powder diffraction pattern 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.