Experimental report

18/09/2017

Proposal: **5-31-2474** **Council:** 4/2016

Title: Crystal and magnetic structures ofiron layered polyanions compounds

Research area: Materials

This proposal is a new proposal

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Samples: Sr4Fe2O6(SO4)
Ca4Fe5.5O6S4

Instrument	Requested days	Allocated days	From	To
D2B	3	3	27/08/2016	30/08/2016

Abstract:

The potential of perovskite systems and derivatives to accommodate oxyanions (Carbonates, phosphates, borates…) which leads to the design of new materials with exotic physical properties is very high and attractive.

We have investigated the Sr-Fe-O-S system focusing our attention on the Ruddlesden-Popper family. The RP3 related compound Sr4Fe2O6(SO4) has been stabilized as powder ceramic and is derivative of the RP3 phase: Sr4Fe3O10 in which substitution of SO4 groups for FeO6 octahedra occurs in the central perovskite layer (shown by TEM analysis and X-ray diffraction). Similar phenomenon has been previously reported for iron oxycarbonate.

In the same approach, another oxyanions compound, the compound Ca4Fe5.5O6S4 has been stabilized as polycrystalline powder. It is characterized by an orthorhombic symmetry Cmcm (11.1;11.2 and 17.5Å) and can be described as alternating FeO4S2 (top shared) and FeO2S4 (edge shared) octahedral layers. This new compound exhibits complex magnetic behavior in a large temperature range with three transitions as visible in the ZFC curve.

Crystal and magnetic structures of iron layered polyanions compounds

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The potential of perovskite systems and derivatives to accommodate oxyanions (Carbonates, phosphates, borates…) which leads to the design of new materials with exotic physical properties is very high and attractive. Two systems have been considered

1-

The compound $Sr_4Fe_{2.5}O_{7.25}(SO_4)_{0.5}$ have been stabilized as powder ceramic. Powder neutron diffraction, realized on D2B at 500K (to avoid the presence of magnetic peaks), allowed to determine precisely the position of (SO_4^{2-}) tetrahedron within the intergrowth. Fourier differences have been done to underline the residual electronic density indicating the positions of sulfur atoms (figure 1). Positions, occupancies and anisotropic thermal displacements of every atom have been refined (figure1). The resulting structural model presented figure 2 can be depicted as a derivative compound from the RP3 phase where 50% of the octahedra of the central layer of the perovkite bloc, are substituted for sulfate groups. The sequence $SrO/SrFeO_{2.5}/Sr(Fe_{0.5}(SO_4)_{0.5})O_{1.25}/SrFeO_{2.5}$ is then observed. The environment of Fe(1) atoms can be described as a pyramid, the sixth oxygen neighbor O(3) sits further apart (Fe(1)-O(3) =2.371(9) Å) - the off centering of the iron from the midpoint of the “octahedral” being a direct evidence. Within the central layer, no long range order have been detected between Fe(2) pyramids and SO_4^{2-} tetrahedron. Most of the sulfate groups share basal corners with Fe(2) pyramids. They have the peculiarity to possess at least 2 “free” oxygen corners (the apical O(3’)) like it is reported for $Na_3Fe(SO_4)_3$ for instance.

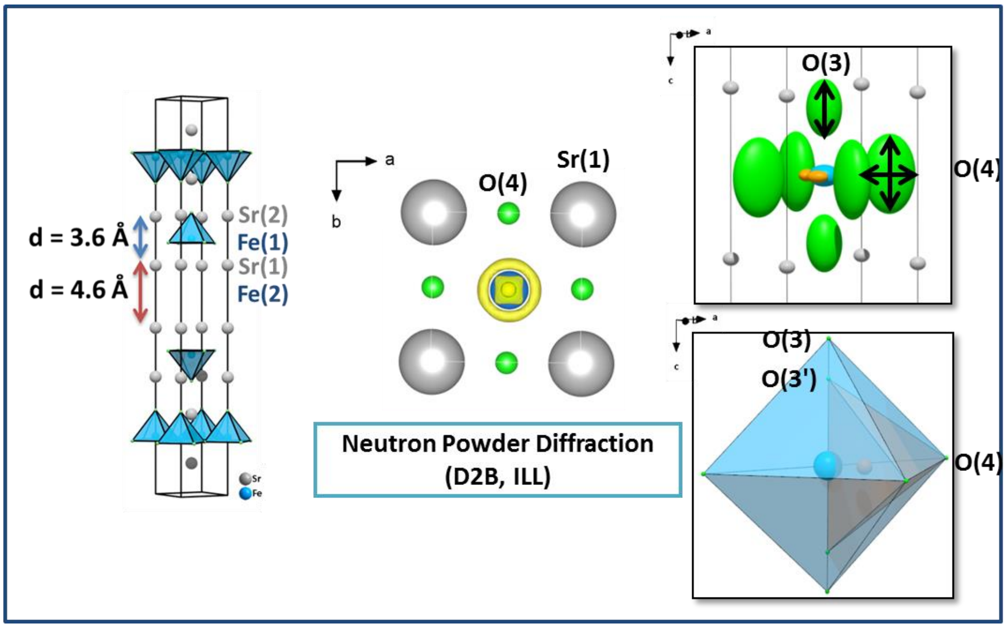

Figure 1: **Difference Fourier map between NPD observation and calculation considering the structure $Sr_4Fe_{2.5}O_{7.25}(SO_4)_{0.5}$ with S at the B site. Illustration of thermal ellipsoid for O(3) and (O4) atoms at the end of NPD refinement. Illustration of iron pyramid and sulfate tetrahedron sharing the same O(4) with the splitting of O(3) atoms.**

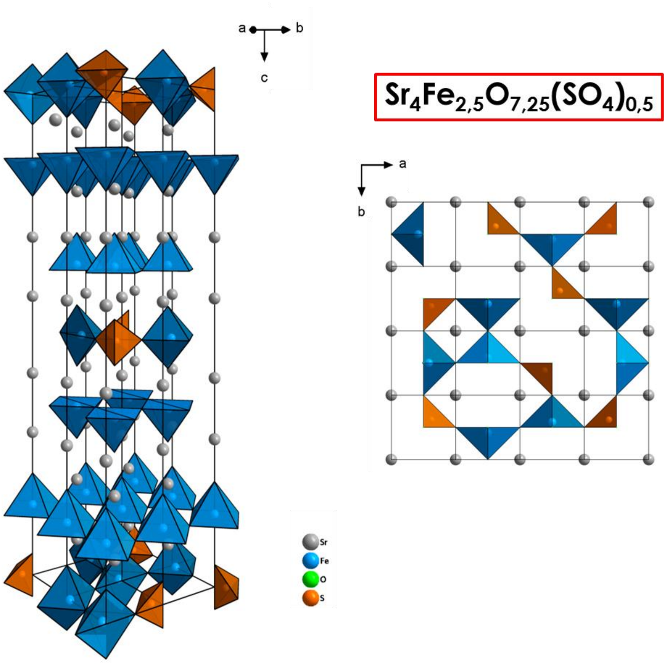

Figure 2 **: Atomic structure of $Sr_4Fe_{2.5}O_{7.25}(SO_4)_{0.5}$ oriented along the c axis (left side) and its projection on (001) (right side).**

The magnetic structure has been determined (at 5K) and corresponds to an antiferromagnetic G type one (in agreement with Goodenough rules). To index and fit all the magnetic peaks correctly, the magnetic propagation vector (1/2,1/2,0) has been used together with the Γ3 irreducible representation (among three possibles) (figure 3). It is of interest to note that the spins are lying in the basal plane contrary to the carbonate compound $Sr_4Fe_2O_6(CO_3)$ for which the spins have 3 spatial components. In our compound, thanks to the thermal evolution of iron magnetic moments, the T_N has been estimated at 400K.

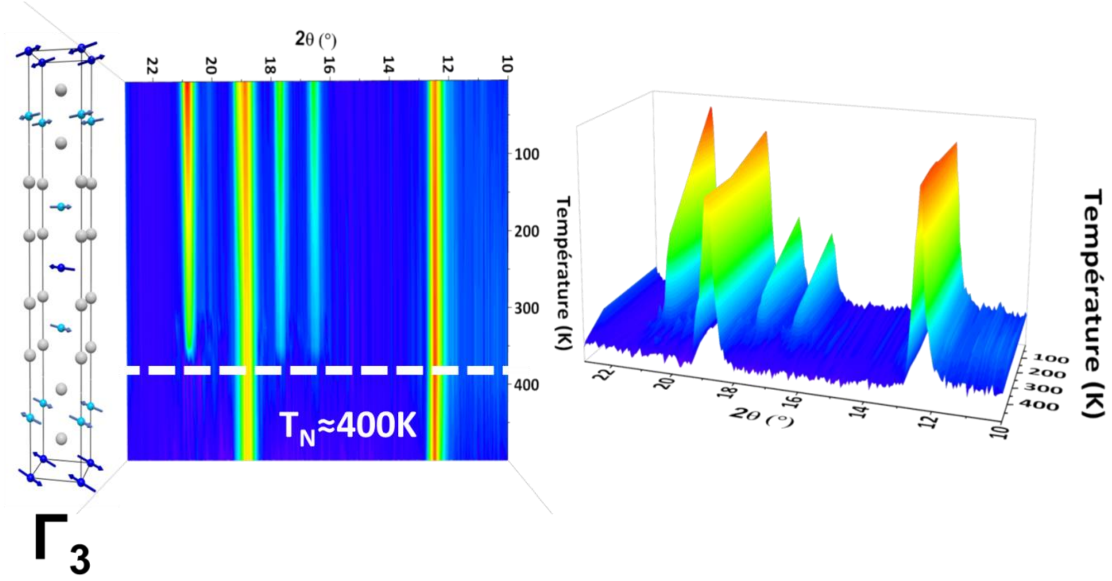

Figure 3 **: Magnetic structure of the compound $Sr_4Fe_{2.5}O_{7.25}(SO_4)_{0.5}$. Temperature dependence of the neutron diffractograms of the compound $Sr_4Fe_{2.5}O_{7.25}(SO_4)_{0.5}$ over a range from 5 to 500K.The angular range extends from 10 to 23°.**

2-

The first analyses of $Ca_4Fe_{5.5}O_6S_4$ have been focused on high temperature data set (T>350K) for which a paramagnetic behaviour is expected taking into account the previous X(T) experiments. Nevertheless, the applied diffraction nuclear model (Cmcm 11.1*11.2*17.5A^3) can not fit the whole collected neutron diffraction data pattern since some extra peaks become unidentified even considering a magnetic contribution (Figure 1).

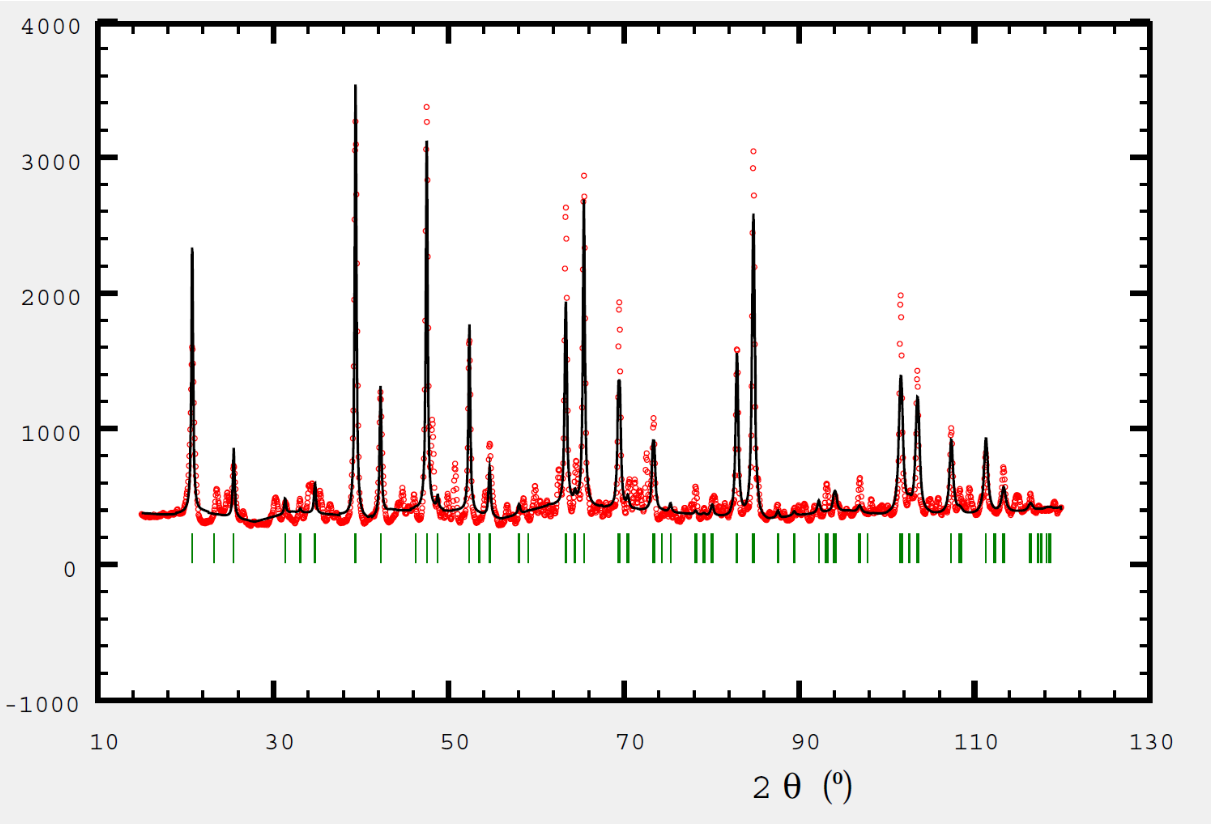

Figure 1 Rietveld analyses at 400K

In fact a complementary TEM analysis (ED + EDS) to detect possible secondary phases has highlighted a modulated lattice (Figure 2) sensitive under electron beam and that needs to work in a 4D superspace formalism to solve the fine structure.

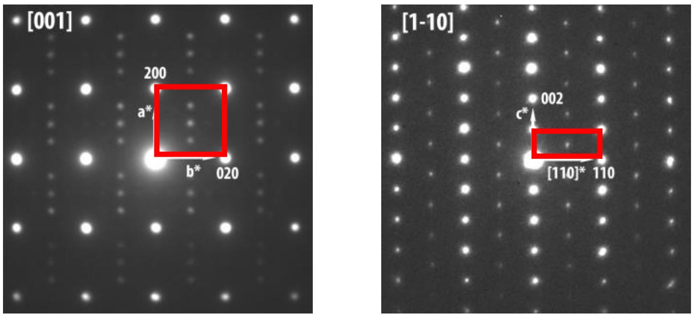

Figure 2 : expected Cmcm unit cell (red box) with extra dots

This work is still in progress.