Experimental report

01/03/2016

Proposal: **5-31-2311**

Council: 4/2014

Title: Structural and magnetic characterization in a honeycomb $Ca_2Mn_3O_8$

Research area: Materials

This proposal is a new proposal

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Samples: $Ca_2Mn_3O_8$

Instrument	Requested days	Allocated days	From	To
D1B	1	0		
D20	1	1	14/10/2014	15/10/2014
D2B	1	1	13/10/2014	14/10/2014

Abstract:

$Ca_2Mn_3O_8$ crystallizes in a monoclinic layered structure with infinite sheets of $[Mn_3O_8]^{-4}$ held together by Ca^{2+} atoms alternately stacked along a axis. Moreover, Mn^{4+} atoms octahedrally coordinated by oxygen atoms (MnO_6) share only edges and result in a honeycomb geometry for Mn^{4+} cations.
The magnetic and heat specific characterization show several anomalies could indicate long-range AF order and/or structural distortion into MnO_6 octahedra.
Our aim is to characterize the honeycomb $Ca_2Mn_3O_8$ material by temperature dependent neutron powder diffraction in order to establish the temperature long range order as well as to resolve the magnetic structure in the honeycomb geometry. Moreover, a distortion of MnO_6 octahedral is not discarded below Néel temperature and it could be detectable by means neutron diffraction.
Therefore, according to ILL instruments availability, we need 1 day in D2B and 1 day in D1B or only 1 day in D20

Calcium manganese oxides have received particular attention since they can act as photocatalysts at the anode side. Among these, $Ca_2Mn_3O_8$ shows especially appealing because is found to be an active catalyst for water oxidation as well as for organic matter decomposition[1]

$Ca_2Mn_3O_8$ crystallizes in a monoclinic layered structure with infinite sheets of $[Mn_3O_8]^{-4}$ held together by Ca^{2+} atoms alternately stacked along a axis[2-3]. Moreover, Mn^{4+} atoms octahedrally coordinated by oxygen atoms (MnO_6) share only edges and therefore form octahedral sheets. The presence of ordered cation vacancies (one fourth) in the octahedral sites results in a honeycomb geometry for Mn^{4+} cations in edge sharing MnO_6 ordered layers. The honeycomb lattice is a type of geometry where magnetic atoms are arranged in edge sharing hexagons and there has been much recent interest as they often demonstrate more complex magnetic behaviour. Although not generally appreciated to be frustrated, magnetic ions on honeycomb lattice frequently display nontrivial types of magnetic ordering due to frustration that arises from the presence of strong competition between nearest neighbour and second nearest neighbour magnetic interactions[4] .

We collected diffraction data at high resolution powder diffractometer D2B at 5, 40, 100 and 300 K. Besides, we carried out a temperature dependent neutron powder diffraction with D20 diffractometer.

We have started the refinement of the diffraction data at RT (figure 1). Extra intensity not accounted for the structural model is evident in several reflections at temperature below 70 K (see Figure 2). These contributions to the diffraction pattern are being analyzed by considering that they were magnetic in origin and could be accounted for by the C2/m space group with a propagation vector, k =0, 0.5, 0.

The results of this work will provide the well-defined characteristics of the magnetic and crystal structures of the honeycomb compound $Ca_2Mn_3O_8$.

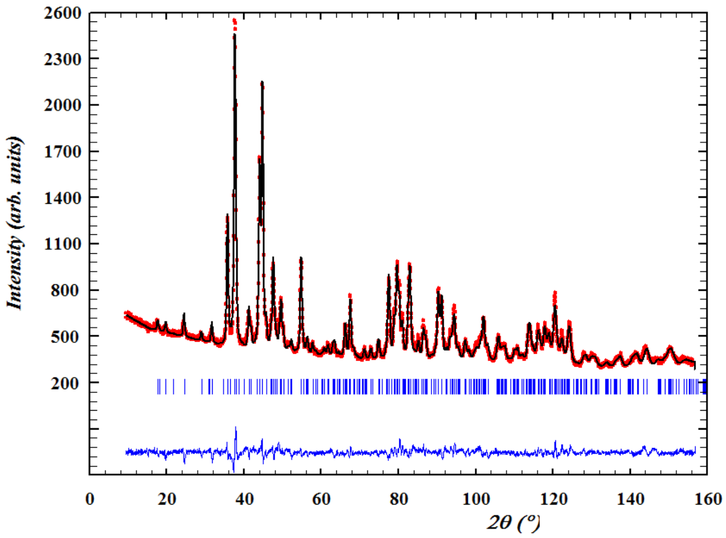

Figure1- Rietveld refinement of neutron diffraction data collected at RT

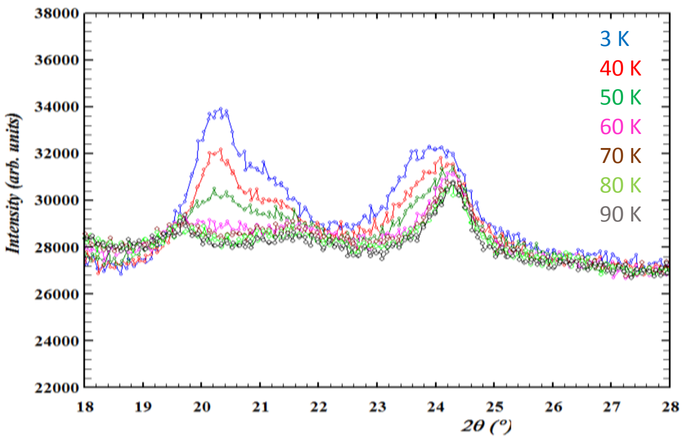

Figure 2- Neutron pattern diffraction at different temperatures.

-1-A. Ramírez et al. Nano Energy 1(2), 282-289 (2012)
-2- Gerald et al. Acta CrystB38, 1795-97 (1982)
-3- White T.R. et al. J. Solid State Chem. 29, 205-214 ,(1979).
-4-O. Smirnova et al J.Am Chem Society 131, 8313-8317, (2009).