Experimental report

04/11/2019

Proposal: CRG-2531 **Council:** 4/2018

Title: Study of the nuclear and magnetic structure of the new quadruple perovskite (TbMn3)Mn4O12

Research area:

This proposal is a new proposal

Main proposer: Marine VERSEILS

Experimental team: Marine VERSEILS

Local contacts: Vivian NASSIF

Samples: (TbMn3)Mn4O12

Instrument	Requested days	Allocated days	From	To
D1B	2	2	08/09/2018	10/09/2018

Abstract:

Experimental report of proposal CRG-2531

Objective and expected results: In the framework of the search for new functional materials suitable for electronic devices, $(AMn_3)Mn_4O_{12}$ compounds with quadruple perovskite structure have attracted a great deal of interest as they present some fundamental issues as magnetically induced polarization. Recently, we reported the synthesis and characterization of a new ferroelectric compound $(YMn_3)Mn_4O_{12}$ characterized by *I2/m* symmetry at room temperature lowering to the non-centrosymmetric space-group *Ia* below 200 K. In analogy with the parent compound $(LaMn_3)Mn_4O_{12}$, the Yttrium-based compound displays the same antiferromagnetic ordering of manganese ions on the octahedrally coordinated B-sites but at higher temperature. Surprisingly, no long-range magnetic ordering of the manganese square-planar A'-sites, usually observed at lower temperature was detected by means of neutron powder diffraction. However, a clear anomaly is visible in the magnetization curve between 50 and 70K, where the long-range ordering of the A' sites should lie. Interestingly the magnetic anomaly matches the temperature of stabilization of a spontaneous polarization, observed thanks to pyrocurrent measurements. Our purpose is now to investigate the possible peculiar scenario of ferroelectricity induced by a short-range (maybe spin-glass) behavior, and in particular the influence of the size and electronic configuration of the A-cations on the competition between the interactions. The new $(TbMn_3)Mn_4O_{12}$ compound was synthesized for this purpose as the ionic radius of Tb^{3+} lies between the ones of La^{3+} and Y^{3+}. Noteworthy is the presence of unpaired f- electrons, representing a further degree of freedom in principle capable to induce different properties of the system. The purpose of this experiment was to solve the nuclear and magnetic structures of $(TbMn_3)Mn_4O_{12}$ and to seek for hints of a short-range magnetic order. We expect to confirm a scenario in which the length of the magnetic correlations responsible for the ordering of the manganese on the A' sites decreases with the ionic radius of the atom on the A sites. Our preliminary X-rays powder diffraction data indicated the monoclinic symmetry (*I2/m*) to be present at room-temperature and from magnetization measurements we expected three magnetic transitions, likely due to the magnetic ordering of B-sites, A'-sites and Tb^{3+} ions at 84, 33 and 9 K, respectively.

Measurements performed: The experiment was successfully performed on ~350 mg of powder at several temperature (300, 100, 50, 20, and 1.5 K) at the D1B beamline with two wavelengths λ_1= 1.28 Å and λ_2= 2.52 Å chosen for an accurate determination of the nuclear and magnetic structure, respectively.

Results: i) The small quantity of sample was confirmed to be sufficient thanks to the good crystallinity of the phase. ii) We performed a preliminary Lebail fit of the nuclear structure at 300 K on the λ_1= 1.28 Å pattern and using the expected *I2/m* monoclinic space-group. As we can see on figure 1, this structure roughly accounts for the main peaks of the quadruple perovskite structure but several peaks remain unexplained. The unexplained peaks at 2θ = 30.5 and 39.5 ° could be supposedly attributed to some magnetic impurity phases (alpha-Mn2O3, Mn3O4…) but we know from our preliminary X-rays diffraction measurements that their quantities can hardly exceed 5% of the sample. Moreover, at 2θ = 28, 35 and 37.5 ° we see additional peaks, systematically at the left of the main reflections of to the monoclinic *I2/m* quadruple perovskite structure. iii) On Figure 2, we have reported the patterns obtained at different temperatures (300, 100, 50, 20 and 1.5K) using the λ_2 = 2.52 Å wavelength. At 100K, we can see additional intensity on top of the main nuclear Bragg peaks at 28, 50, 58, 64,66, 72,73 and 79°, which indicates a first magnetic order with **k**= (0,0,0). At 50 K, we can see additional intensity on top of the nuclear Bragg peaks at 48.5 and 50° which account for a new magnetic phase with no change of the propagation vector. This could account for a real transition toward a new magnetic space group between 100 and 50 K or simply a reorientation of the

spins with no change of the magnetic symmetry. At 20K, new peaks appear at 20, 30 and 45° indicating a different magnetic order with a non-zero propagation vector occurring between 50 and 20K. Finally, at 1.5K we see additional intensity at 20 and 45° and a new peak at 35°. It is not clear now if the peak at 35° was already existing at 20 K or not. In any case, the low temperature results indicate that a change in the magnetic structure also occurs between 20 and 1.5 K, has expected form our measurements of the magnetization.

Conclusion: The experiment was successful as we obtained patterns of high quality with a small quantity of sample. A preliminary Lebail fit in the quadruple perovskite *I2/m* monoclinic space group highlights that the expected structure is not the correct one for describing the phase, even at room temperature, despite the main peaks are correctly recovered. Indexing of the pattern is required in order to proceed with the nuclear and magnetic structure analysis. A rapid observation of the evolution of the patterns as a function of the temperature account for 3 or maybe 4 different magnetic phases. The system first enters (between 300 and 100 K) into a magnetic phase that does not break the symmetry of translation (**k** = (0,0,0)). Then the translation is broken by a new magnetic order between 50 and 20 K. As expected from preliminary results and by comparison with similar compounds, these two orders could correspond to the ordering of the B and A' sites, respectively. Our data show that two changes occur in the magnetic phase between 100 and 50K and between 20 and 1.5 K. The latter could be either simple spin reorientations or additional intermediate magnetic orders.

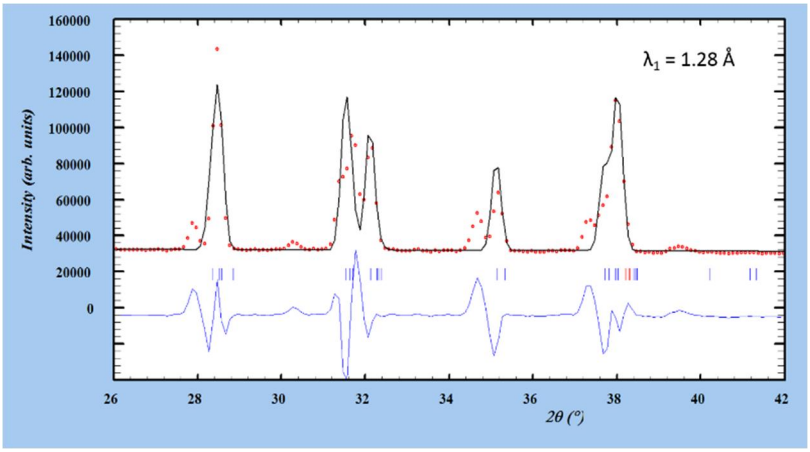

Figure 1: Red circles: experimental neutron diffraction pattern taken at 300K on the $(TbMn_3)Mn_4O_{12}$ powder sample using a wavelength λ_1= 1.28 Å.

Black line: Calculated Lebail fit in the *I2/m* monoclinic space group using the Fullprof software implemented in winPLOTR.

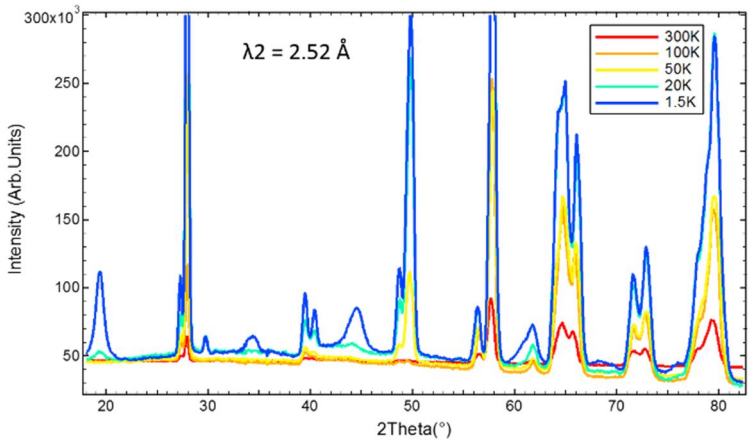

Figure 2: Experimental neutron diffraction patterns obtained at 300, 100, 50, 20 and 1.5K on the $(TbMn_3)Mn_4O_{12}$ powder sample using a wavelength λ_2= 2.52 Å.

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