	Experiment title: SEARCHING FOR EVIDENCES OF ZENER PAIRS IN Mn2OBO3	Experiment number: 25-01-609
ESRF		

Beamline: BM25A	Date of experiment: from: 13 September 2006 to: 19 September 2006	Date of report:
Shifts: 9	Local contact(s): **Dr. German Rafael CASTRO**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Maria Antonia Señarís Rodriguez
Prof. Dr. Castro García*
Dr Manuel Sánchez Andújar*

Departamento Quimica Fundamental
Facultade de Ciencias
Universidade da Coruña
Campus da Zapateira
15071 A Coruña
Spain

Report:

This set of experiments deals with studies on transition metal oxides with interesting magnetic and transport properties arising form the strong interplay between spin, orbital and charge degrees of freedom of d-electrons, in particular with charge ordering (CO), magnetoresistance and cation ordering. The experiments focused in first place in the Mn-oxyborate Mn_2OBO_3, and were subsequently extended to $Pr_{0.75}Na_{0.25}MnO_3$ Y_2MnCoO_6, $Gd_2SrCo_2O_7$.

Experimental details: The compounds were prepared as polycrystalline powders. The sample was introduced in a capillary of 0.3 mm of diameter to perform high resolution powder diffraction studies in the Spanish BM25A beamline. The wavelength used was $\lambda=0.826096$ Å and the range of scan was 5-60 (2θ) with a step of 0.02º. The HRPD patterns were recorded at room temperature and at 150 K (with a liquid-nitrogen-cooled cryostat). The HRPD patterns were refined by the Rietveld method with the GSAS and Rietan software.

1.- **Mn_2OBO_3**: The aim of this study was to find evidences of Zener pairs in the Mn-oxyborate Mn_2OBO_3 by carefully studying the crystallographic characteristics, in particular the variation of Mn-O distances as function of temperature (80<T(K)300).

The first main difficulty was to find that this kind of experiments as a function of temperature had not been carried out before in this Spanish BM25A beamline, and that a liquid nitrogen cryostat set-up needed to be built up beforehand in quite a manual way.

The second important inconvenience was to find that as the scattering power of the Mn_2OBO_3 compound is low with the experimental conditions of this beamline the signal intensity recorded was very weak.

In view of all these inconveniences and with the aim of optimize the beam time available, we considered it was better to postpone this study, and concentrate in other systems more suitable for the available experimental conditions at the BM25 beamline.

We would like to mention that for future improvements of this beamline, we think that it would be necessary to increase the number of detectors in the powder diffractometer. Different sample environments as liquid-helium-cooled cryostat and a furnace will be also very useful.

2.- $Pr_{0.75}Na_{0.25}MnO_3$: In this tridimensional perovskite it has been reported that a charge-ordering (CO) transition takes place at around $T_{CO} \approx 220$ K [1]. From the structural point of view, the compound shows an orthorhombic symmetry above T_{CO}, while the structure is unknown in the CO state.

To deepen in its structural characterization, we have recorded HRPD patterns at room temperature ($T>T_{CO}$) and at 150 K ($T< T_{CO}$), see figures 1 and 2, respectively.

At RT, we have found that this compound shows an orthorhombic structure (space group: Pnma) with cell parameters a=5.4341 Å b=7.6850 Å c=5.4434 Å, in agreement with the literature [2]. In this structure, there is only one site for the Mn cations that are in an octahedral environment with three different Mn-O bond lengths, see table I.

In the CO state, the diffraction pattern shows small superstructure peaks that could be indexed in monoclinic symmetry (space group: P 21/m) with cell parameters a=10.8588 Å b=7.6766 Å c=5.4432 Å and β=90.066. This symmetry has been reported in other tridimensional manganite perovskites (Mn^{3+} and Mn^{4+} 1:1 ratio) as $Ln_{0.5}A_{0.5}MnO_3$ with CO. In this structure, there are three different crystallographic sites for the transition metal cations. Table II shows the Mn-O bond lengths of the different sites. Taking into account the value of the Mn-O distances, we have obtained that the Mn cation at the Mn(1) site has a +4 valence while those at the Mn(2a) and Mn(2b) sites would have +3 valence. This would imply that in the $Pr_{0.75}Na_{0.25}MnO_3$ compound, the CO state displays a checkboard configuration.

3.- Y_2MnCoO_6: This perovskite compound is a candidate to show magnetodielectric properties, as the parent compound $YMnO_3$ [3]. Although, the structure of the Y_2MnCoO_6 compound has been reported, the cation charge distribution is still an open question. To clarify this point, we try to obtain information about the charge of Y and the transition metal cations by the bond valence sum and maximum entropy method, for which precise diffraction data are very important.

[1] J. Hejtmanek, Z. Jirak, J. Sebek, A. Strejc, M. Hervieu, J. Appl. Phys. 89 (2001) 7413.

[2] D. P. Kozlenko, Z. Jirak, I. N. Goncharenko, B. N. Savenko, J. Phys.: Condens. Matter 16 (2004) 5883.

[3] U. Adem, A. A. Nugroho, A. Meetsma, and T. T. M. Palstra Phys. Rev. B 75 (2007) 014108.

In figure 3, we show the powder diffraction pattern of this compound and the corresponding Rietveld refinement. We have obtained a monoclinic cell (space group: P21/n) with cell parameters a= 5.2256 Å b= 5.5814 Å c= 7.4610 Å and β=90.158, in agreement with the literature [4]. Also, we have to note that the Co/Mn cations order in the structure, see inset figure 3.

On the other hand, we have estimated the charge of Y and transition metals cations by the bond valence sum method. Surprisingly, we have found that the valence state of the transition metal cations is less than 3+ while for the Y cations it is higher than 3+. To explain this result, we suggest that the Y^{3+} cation provokes a distortion of the oxygen electron cloud towards the Y^{3+} cation. To confirm this fact it is necessary to analyze the electron density (ED) maps. In this context and with the obtained high resolution powder diffraction pattern, we carried out a maximum entropy method study that allowed us to obtain an ED map. As shown in figure 4, the ED map shows clear evidences of the electron distortion around the oxygen anions due to the rather high acidity of the Y^{3+} cation.

4.- **$Gd_2SrCo_2O_7$**: This compound is a n=2 member of the Ruddesden-Popper series. Previous structural studies have shown that this compound has the $Sr_3Ti_2O_7$-type structure (space group: I4/mmm) with cell parameters $a_t \approx 3.85$ Å and $c_t \approx 19.4$ Å [5], even if more recent electron diffraction results introduce doubts about this assignment [6].

The here obtained synchrotron diffraction patterns showed nevertheless another tetragonal structure (space group: P4$_2$/mnm) with cell parameters of a ≈ 5.37 Å c ≈ 19.35 Å. These cell parameters and space group had been described for other n=2 Ruddlesden-Popper compounds, like for example $Ga_2BaMn_2O_7$ [7], $HoSr_2Mn_2O_7$ and $YSr_2Mn_2O_7$ [8].

In figure 5, we show the Rietveld refinement of this powder diffraction pattern.

Also, very interestingly, according to the obtained results the $Gd_2SrCo_2O_7$ compound presents a cation ordering where the divalent and bigger Sr^{+2} cation ($^{XII}\Gamma_{Sr}+2 = 1.44$ Å) selectively prefers the 12-coordinated site while the smaller and trivalent Gd^{+3} cation $^{IX}\Gamma_{Gd}+3 = 1.107$ Å) prefers the 9-coordinated sites, as it frequently occurs in RP phases, see figure 6.

On the other hand, the cobalt ions are in a distorted octahedral environment, where there are five different Co-O bond lengths: two apical Co-O(1,2) bond lengths (along the c direction) and three equatorial Co-O(3,4,5) bond lengths (in the ab plane). In addition to the distorted octahedral environment, the [CoO$_6$] octahedra are tilted, resulting in a reduction of the Co-O-Co angle from 180º in contrast with the conventional structure S.G. I4/mmm.

[4] I. O. Troyanchuk, D. D. Khalyavin, J. W. Lynn, R. W. Erwin, Q. Huang, H. Szymczak, R. Szymczak, M. Baran, J. Appl. Phys. 88 (2000) 360.
[5] L. Siwen, R. Yufang, J. Solid State Chem. 114 (1995) 286.
[6] M. Sanchez Andujar, Doctoral thesis, University of A Coruña, 2003.
[7] N. Kamegashira, H. Satoh, T. Mikami, J. Alloys Comp. 311 (2000) 69.
[8] P. D. Battle, J. E. Millburn, M. J. Rosseinsky, L. E. Spring, J. F. Vente, Chem. Mat. 9 (1997) 3136.

Table I: Values of the Mn-O bond lengths obtained at room temperature in the $Pr_{0.75}Na_{0.25}MnO_3$ compound

Mn-O(1)	1.960(1) Å
Mn-O(2a)	1.955(1) Å
Mn-O(2b)	1.949(1) Å
Mn-O(1)	1.960(1) Å

Table II: Values of the Mn-O bond lengths obtained at 150 K in the $Pr_{0.75}Na_{0.25}MnO_3$ compound

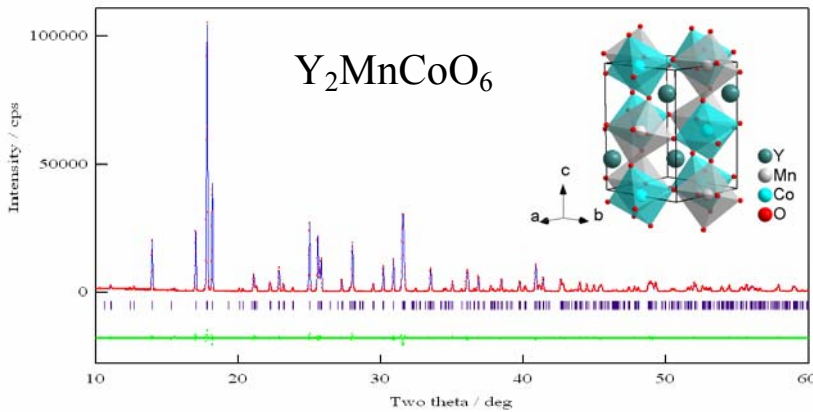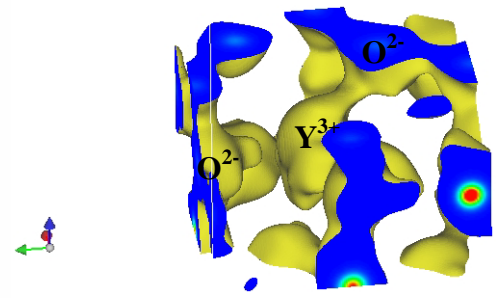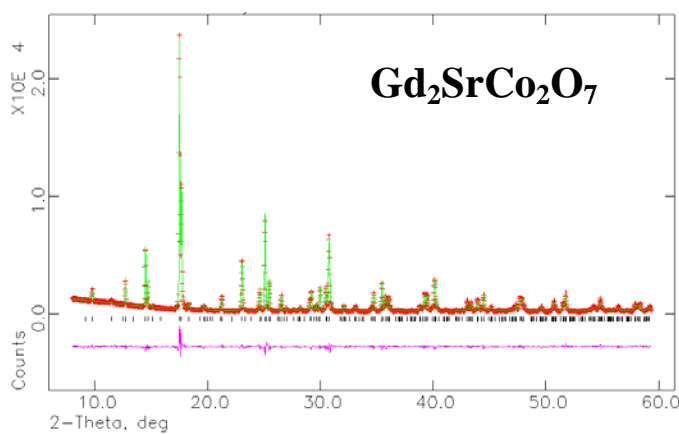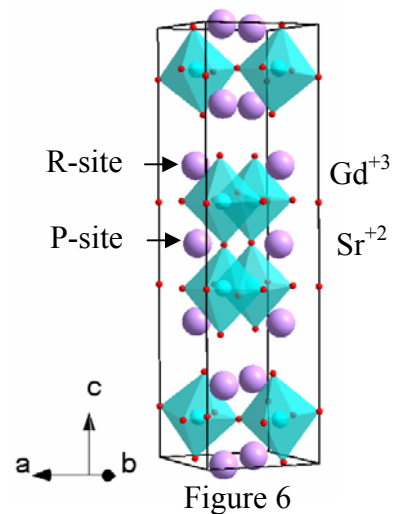|			
Mn(1)-O(5)	1.859(39)	Mn(2a)-O(7)	1.973(42) x2
Mn(1)-O(4)	1.930(6)	Mn(2a)-O(6)	1.978(42) x2
Mn(1)-O(8)	1.992(41)	Mn(2a)-O(1)	1.993(15) x2
Mn(1)-O(2)	2.006(9)		
Mn(1)-O(6)	2.007(44)	Mn(2b)-O(5)	1.896(40) x2
Mn(1)-O(5)	1.859(39)	Mn(2b)-O(3)	1.920(6) x2
		Mn(2b)-O(8)	2.014(37) x2

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6