Experimental report

05/08/2016

Proposal: 5-31-2369 **Council:** 10/2014

Title: Crystal and magnetic structure of the new double perovskites Ba1+xLa1-xMnSbO6 with 0.1<x<0.7 containing Mn2+/Mn3+ mixtures.

Research area: Materials

This proposal is a new proposal

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Samples: Ba1.1La0.9MnSbO6
Ba1.2La0.8MnSbO6
Ba1.3La0.7MnSbO6
Ba1.4La0.6MnSbO6
Ba1.6La0.4MnSbO6
Ba1.7La0.3MnSbO6
Ba1.5La0.5MnSbO6

Instrument	Requested days	Allocated days	From	To
D2B	3	2	14/09/2015	16/09/2015

Abstract:

Double perovskites Ba1+xLa1-xMnSbO6 with 0.1<x<0.7 were synthesized by conventional ceramic method in air atmosphere as polycrystalline powders. These perovskites belong to the I2/m monoclinic space group. By doping BaLaMnSbO6 with Ba2+, we force Mn to be in a mixture of Mn2+ and Mn3+. This is supported by magnetization measurements performed in a SQUID with indications of the presence of Mn3+. Magnetic behavior of Mn containing double perovskites with Mn2+/Mn3+ has been explained either assuming that Zener double exchange is established or uncompensated antiferromagnetic interactions between Mn2+ (S=5/2) and Mn3+ (S=2) conducting to ferromagnetic behavior. We expect in this project to study the crystal and magnetic structure of the title double perovskites and to understand their magnetic behavior as a function of temperature.

CRYSTAL AND MAGNETIC STRUCTURE OF THE NEW DOUBLE PEROVSKITES $Ba_{1+X}La_{1-X}MnSbO_6$ WITH 0.1<X<0.7 CONTAINING Mn^{2+}/Mn^{3+} MIXTURES

1) Introduction.

Double perovskites with composition $A_2BB'O_6$ have been the focus of interest since Sr_2FeMoO_6 was synthesized, due to its CMR effect at room temperature with a high curie temperature ($T_C \approx 400$ K) **[1].**
Possible existence of CMR was investigated previously in double perovskites AA'BB'O6, with A=Ca, Sr and Ba; A'= Ln; B= magnetic 3d transition metal ion and B'=4^{th}, 5^{th} rows transition metal ions or diamagnetic ion, like Sb^{5+} **[2,3]**. Also, doped system in A or A' cations have been studied by different authors because this can allow change on the properties of the samples just with varying the composition **[4,5]**. In a previous work, the undoped $BaLaMnSbO_6$ was synthesized and its structural and magnetic properties were analyzed **[6]**.
In this work, we just focus in preparing and characterizing the doped system of double perovskites $Ba_{1+x}La_{1-x}MnSbO_6$ with 0.1<x<0.7 which contains a mixture of oxidation states (Mn^{2+}/Mn^{3+}). This mixture decrease the difference of charge between B and B', so it is interesting because the increase of disorder is related with a decrease in charge and this could have influence on the properties. Neutron Powder Diffraction data let us to obtain a complete study of crystal and magnetic structure that allow to understand the magnetic behavior and comprehend the connection between crystal structure and physical properties of the system.

2) Experimental.

Neutron Powder Diffraction (NPD) patterns were collected in the D2B powder diffractometer (λ= 1.594 Å) at 300 K and 4K for all samples, and D1B powder diffractometer (λ=1.28 Å) at different temperatures. The measurements were performed with an angular range from 0° to 159.95° with steps of 0.05°. Structure refinement of NPD patterns were performed by the Rietveld method using the FullProf Suite refinement program **[7]**. A Thompson-Cox-Hastings pseudo-Voigt convoluted with axial divergence asymmetry shape function was used to obtain a good fit for experimental data.

3) Results and discussion.

At 300 K, the structures were refined in the monoclinic I 2/m space group, taking as starting structural model the one of undoped $BaLaMnSbO_6$ according to X-Ray Powder Diffraction (XRPD) refinements made previously. XRPD patterns showed notable changes in the peaks at higher angles values along the series. When all the XRPD and NPD patterns were first refined with the monoclinic space group, the *a* and *b* cell parameters were more similar among them and β tends to 90° with increasing x. For that reason, a set of space groups of a higher symmetry were explored, and the best results could be obtained with the tetragonal I 4/m space group. The Rietveld refinement of the RT NPD patterns for x=0.2 and x=0.7 are shown in Fig. 1a and b, showing that $Ba_{1+x}La_{1-x}MnSbO_6$ belongs to the space group I 2/m for x≤0.2 and space group I 4/m for x≥0.3.
At 4 K for $Ba_{1+x}La_{1-x}MnSbO_6$, the same I 2/m symmetry for 0.1≤x≤0.2 and I 4/m symmetry for x≥0.3 were found; also, the system $Ba_{1+x}La_{1+x}MnSbO_6$ present new peaks at low angles in 2θ, as shown in Fig. 2a, b and c, and this is evidence of the magnetic long range order (LRO) which start to vanish with increasing x values. Rietveld refinements of NPD data at 4K were done with crystal and magnetic structures using an antiferromagnetic cell with propagation vector K=0 and just are shown for x=0.2 and x=0.7 with the respective magnetic cell in the Fig 3a, b, c and d. NPD patterns for x=0.2 were collected in the temperature range T=8-300K in D1B powder diffractometer with the aim to obtain information about the magnetic moments. The sequential NPD patterns are shown in Fig 4, and shows extra peaks at low Bragg angles and this is proof of a LRO magnetic structure below ≈18K and it is in line with magnetic measurements that were made before.
In the Table 1, it is possible to observe a very low B cation anti-site disorder (ASD) in the samples that increase together with x.

4) Conclusions.

NPD data shows for samples with x≤0.2 that $Ba_{1+x}La_{1-x}MnSbO_6$ crystallize in the monoclinic space group I 2/m, while the samples with 0.3≤x≤0.7 crystallize in the tetragonal space group I 4/m. The Volume presents a non-monotonic behaviour and it is probably due to two phenomena: *i)* the doping with a bigger <A> cation and *ii)* the increase oxidation state of Mn^{2+} to Mn^{3+} . The double perovskites were obtained with a higher order degree in B and B' cations which decreases slightly with Ba doping. NPD data shows the appearance of new peaks at low angles at 4K and this is indicative of magnetic long range order which is given by two antiferromagnetic sublattices with a net component of the total magnetic moment that gives a weak ferromagnetic behavior.

5) References.

[1] K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, *Nature,* **395** (1998) 677.
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[3] M.C. Viola, M.C. Viola, M.J. Martínez-Lope, J.A. Alonso, J.L. Martínez, J.M. De Paoli, S. Pagola, J.C. Pedregosa, M.T. Fernández-Díaz, R.E. Carbonio, Chem. Mater. 15 (2003) 1655–1663.
[4] G. Popov, M. Greenblatt, and M. Croft, Phys. Rev. B 67 (2003), 024406.
[5] M.T. Haque, H. Satoh, N. Kamegashira, Journal of Alloys and Compounds 408–412 (2006) 1205–1209.
[6] M. C. Blanco, J.M. De Paoli, S. Ceppi, G. Tirao, V.M. Nassif, J. Guimpel, R. E. Carbonio, Journal of Alloys and Compounds 606 (2014) 139–148.
[7] J. Rodríguez-Carvajal, Physica B 192 (1993) 55.

6) Figures and Tables.

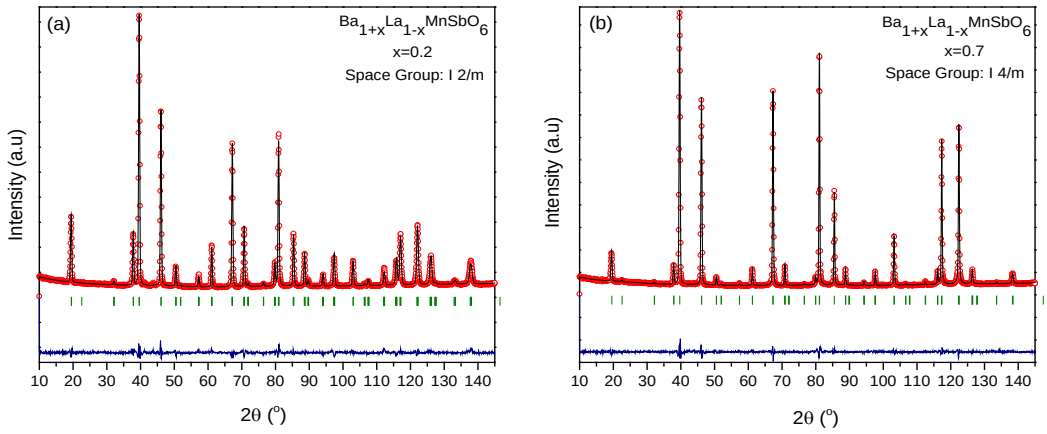

Fig. 1. Observed (red dots), calculated (black full line), Bragg reflections (vertical green bars) and difference (blue bottom line) for NPD patterns at 300K after the refinement of the crystal structure of $Ba_{1+x}La_{1-x}MnSbO_6$ for **a)** x=0.2 and **b)** x=0.7.

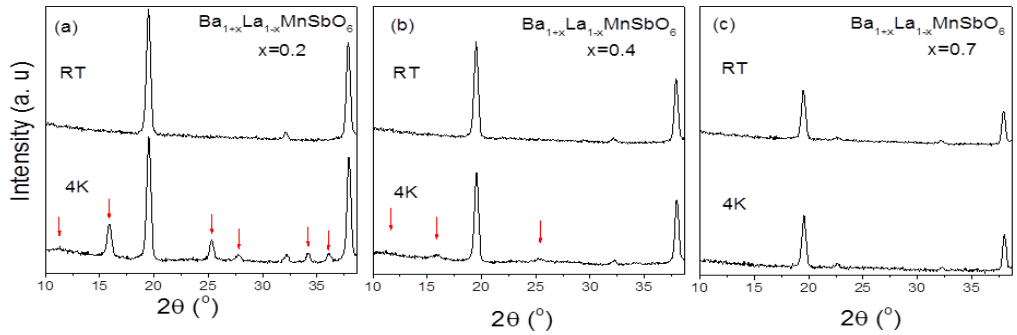

Fig 2. Comparison between NPD data at 4K and 300K for **a)** x=0.2, **b)** x=0.4 and **c)** x=0.7. (arrows corresponds to long range magnetic order reflections).

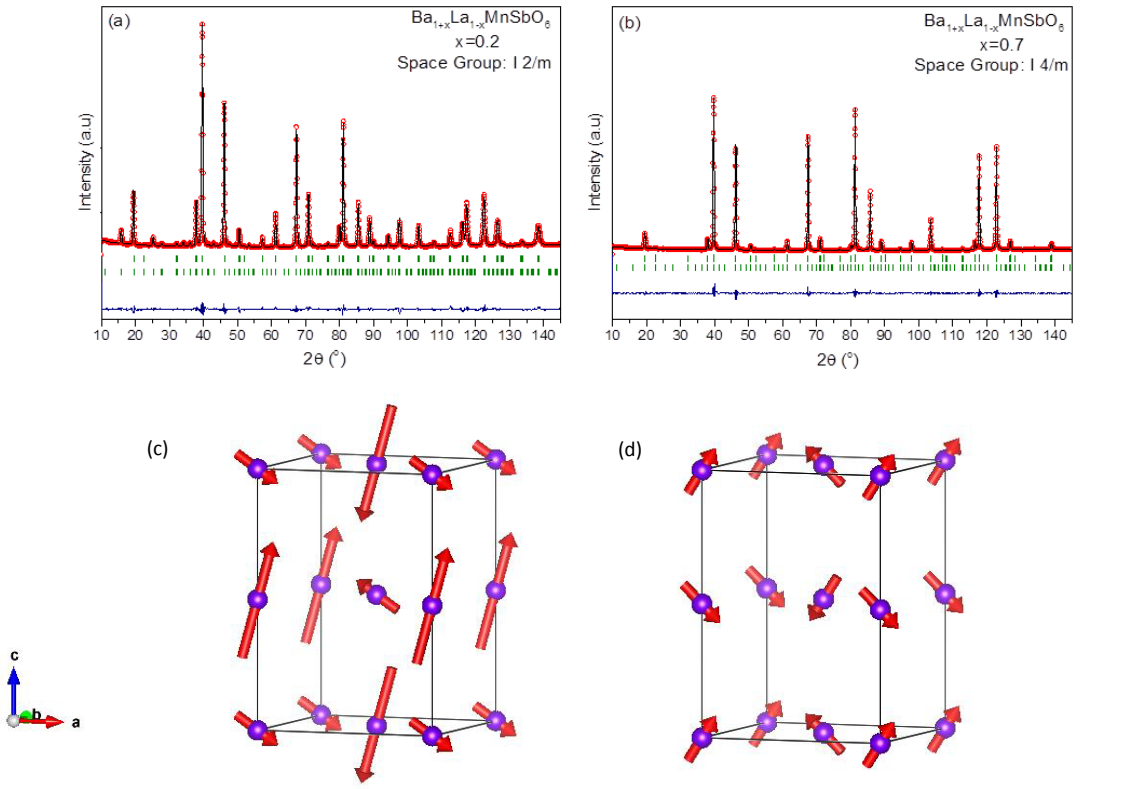

Fig. 3. Upper panel: NPD data refinement at 4 K for **a)** $Ba_{1.2}La_{0.8}MnSbO_6$ and **b)** $Ba_{1.7}La_{0.3}MnSbO_6$. Lower panel: Magnetic cell for 4K NPD data. The arrows represent the effective magnetic moments for **c)** $Ba_{1.2}La_{0.8}MnSbO_6$ of 2d (mainly Mn^{2+}) and 2a (mainly Sb^{5+}) octahedral sites and **d)** $Ba_{1.7}La_{0.3}MnSbO_6$ of 2a (mainly Mn^{2+}) and 2b (mainly Sb^{5+}) octahedral sites.

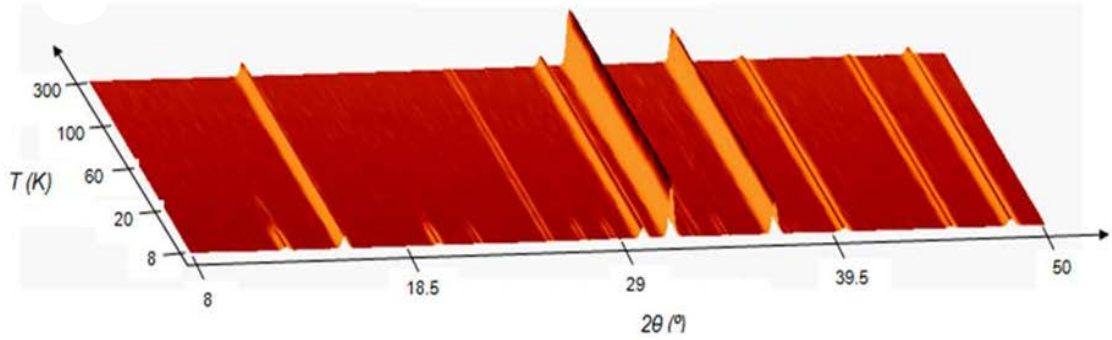

Fig 4. Thermal evolution of the NPD pattern for $Ba_{1.2}La_{0.8}MnSbO_6$ with λ=1.28 Å.

x	Wyckoff Site	B site - Mn/Sb	B´ site - Mn/Sb
0.1	2d/2a	0.976(5) / 0.024(5)	0.05(8)/0.94(8)
0.2	2d/2a	0.968(4)/0.032(4)	0.040(6)/0.960(6)
0.3	2a/2b	0.976(2)/0.024(2)	0.024(3)/0.976(3)
0.4	2a/2b	0.952(2)/0.048(2)	0.048(3)/0.952(3)
0.5	2a/2b	0.920(2)/0.080(2)	0.080(3)/0.920(3)
0.6	2a/2b	0.872(3)/0.128(2)	0.120(3)/0.880(3)
0.7	2a/2b	0.840(1)/0.160(1)	0.152(2)/0.848(2)

Table 1. Occupations for B and B' site for different doping levels.