Experimental report

01/03/2016

Proposal: **5-24-549** **Council:** 4/2014

Title: Structural transition and thermochromic study of faceted hexagonal prisms and nanoparticles of 4H-SrMnO3.0 with different morphologies

Research area: Materials

This proposal is a new proposal

Main proposer: **Aúrea VARELA**

Experimental team: Maria HERNANDO GONZALEZ
Angel MAZARIO FERNANDEZ

Local contacts: Maria Teresa FERNANDEZ DIAZ

Samples: SrMnO3
nanoSrMnO3

Instrument	Requested days	Allocated days	From	To
D2B	2	2	14/10/2014	16/10/2014
D1B	1	1	13/10/2014	14/10/2014

Abstract:

4H-SrMnO3 bulk material presents a colour transition at temperature close to 140 K, the origin of such colour transition remains unknown. Besides, the influence of the morphology and particle size in the optical properties of this material has not been investigated yet.

We have prepared nanoparticles and faceted microcrystals of 4H-SrMnO3. Whereas the former undergoes a similar colour transition than bulk material, the latter does not manifest it. Our results from ED and Raman show a structural change from hexagonal to orthorhombic symmetry at temperature < 170 K. DSC analysis reveals a second structural transition at around 275 K. These results show the complex structural behaviour of this system when morphology and particle size are involved; a detailed structural study as a function of temperature is mandatory in order to establish whether the optical properties are associated or not to the structural ones. It is worth stressing for the first time 4H-SrMnO3 nanoparticles have been isolated showing significant variations in their magnetic behaviour when compared to bulk material.A complete characterization of this sample is required to understand this complex behaviour.

The structural and magnetic properties of $SrMnO_3$ bulk material have been extensively studied. It crystallizes in a 4H-structure type [1] formed by two pairs of face-sharing $[MnO_6]$ octahedra joined by corners (space group $P6_3/mmc$ a=5.454 Å, c=9.092 Å). Bulk $SrMnO_3$ exhibit two AFM transitions at 350 and 278 K [2], [3] corresponding to the AFM interactions of the Mn^{4+} in face-sharing octahedra and the three dimensionalization of this AFM order with the AFM coupling through the cubic corner-sharing units.

Although the structural and magnetic properties of this material have been studied in some extension, their optical properties are hardly known. In this sense, very little attention has been paid to study thermochromism in the few ceramic materials that show this interesting phenomenon. This is the case of $SrMnO_3$ perovskite which presents a colour transition at temperature close to 140 K [4]. Several studies (XRD, NPD, ED and spectroscopic techniques) were focused in finding the origin (structural or magnetic) of this change in colour.

In order to understand the optical properties as well as to determine the possible influence of the morphology and particle size in magnetic and optical properties we collected neutron powder diffraction (NDP) data for the micro and nano $SrMnO_3$ at RT, 250, 170, 125, 95 and at 70 K on the high resolution powder diffractometer D2B.

NPD patterns for Micro-sized $SrMnO_3$ crystals show the presence of a number of $(hk\ell)$ Bragg reflections with odd ℓ indices forbidden in $P6_3/mmc$ space group (figure 1). Even at RT, two additional peaks around 2θ = 72.6 and 78.9 º are clearly visible. This feature was attributed to a subtle structural distortion from hexagonal ($P6_3/mmc$) to orthorhombic ($C222_1$) symmetry. A peculiar variation in the intensity of both peaks with the temperature is observed. From 298 K, the intensity of both reflections increases when temperature decreases reaching a maximum at T ~ 125 K. From this value to 70 K, the intensity remains almost constant.

The refinement of the NPD data was performed using the structural parameters of the orthorhombic cell as starting model. The refinement results show that both anionic and cationic sublattices are fully occupied within the experimental error. From this results, Mn-O(11)/(12)-Mn angles result a clear signature of the structural distortion degree. These results seem to indicate that the orthorhombic distortion is gradually increased from 298 to ~ 125 K. The maximal distortion degree of Mn-O-Mn angles that occurs at temperature close to 125 K, without any regular phase transition, modifies the electronic structure of $SrMnO_3$ and originates the observed color-change.

On the other hand, the refinement of the NPD data of nano-$SrMnO_3$ sample (figure 2) shows that the symmetry reduction from hexagonal to orthorhombic ($C222_1$) only takes place at temperature close to 170 K. This transition temperature is clearly lower than that found for the micro-sample (~ 340 K). Furthermore, even at 70 K, the orthorhombic distortion degree, assessed by the Mn-O-Mn angle value between Mn_2O_9 dimer units, is lessened compared to the micro sample one. This may be the reason why a color-change is not observed at low temperature (77 K).

A detailed structural discussion has been submitted to Inorganic chemistry.

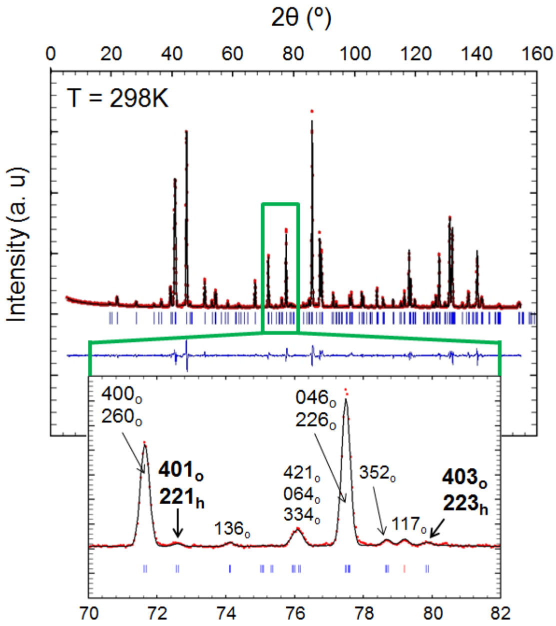

Figure 1. Observed (red), calculated (black) and difference profile (blue) of NPD pattern for micro sample at RT. The enlargement shows 221_h and 223_h forbidden reflections in $P6_3/mmc$ space group. They correspond to 401_o and 403_o in the new orthorhombic cell ($C222_1$), respectively. h and o subindices indicates hexagonal and orthorhombic symmetry, respectively.

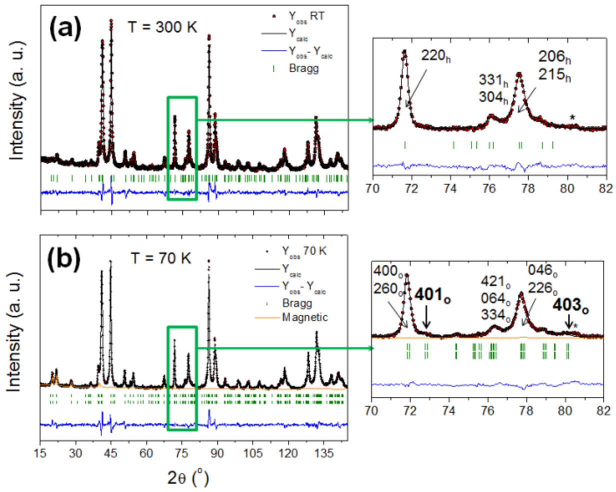

Figure 2. Observed (red), calculated (black), magnetic contribution (orange) and difference profile (blue) of NPD pattern for nano sample at **(a)** RT and **(b)** 70 K. Green ticks represent the contribution from the nuclear and the magnetic scattering. The enlargements show the NPD pattern $70 \leq 2\theta \leq 82$ º region.

[1] T. Negas and R. S. Roth, *J. Solid State Chem.,* **1970**, *1*, 409.

[2] P.D. Battle, T.C. Gibb and C.W. Jones, *J. Solid State Chem*. **1988**, *74 (1)*, 60-66.

[3] B. L. Chamberland, A. W. Sleight and J. F. Weiher, *J. Solid State Chem.* **1970**, *1(3-4)*, 506-511.

[4] J. Heiras, E. Pichardo, A. Mahmood, T. López, R. Pérez-Salas, J. M. Siqueiros, O. Blanco and M. Castellanos, *J. Phys. Chem. Solids* **2002**, *63*, 591-595.