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ScienceDirect
Journal of Magnetism and Magnetic Materials 320 (2008) e19–e21
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Preparation and structural study of $LaMnO_3$ magnetic material

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Available online 10 March 2008

Abstract

We report the crystallographic parameters of $LaMnO_3$ obtained from X-ray diffraction data and electronic properties predictions using the density functional theory (DFT). $LaMnO_3$ was prepared by the citrate precursor method (CPM). The initial solution was 0.1 M of each cation and the citrate nitrate relation was one. The solution was dried at 373 K; the yielded foam was annealed at 873 K and then was characterized by X-ray diffraction. Diffraction peaks show that the space group is R-3c (#167) with $a = b = 5.523$ Å and $c = 13.324$ Å (rhombohedrally distorted perovskite). Structural results of the Rietveld method have a matching of 97% with that obtained from the Structure Prediction Diagnostic Software. DFT calculation reveals a half-metallic character and its magnetic moment is about $2.0\,\mu_B$.

Keywords: $LaMnO_3$ perovskite; Density of states; Rietveld refinement

1. Introduction

At the last time metal oxides with transition elements have a great research interest because these materials are associated to important advances in Solid State Physics and Chemistry. Perovskite oxides display special attention due to their particular electrical, magnetic, catalytic and superconductive properties that can be taken in advantage to technological and basic materials science investigations. These properties have motivated structural, electronic and magnetic ordering studies which have allowed to verify some of the fundamental rules of magnetic interactions [1,2]. The study of $LaMnO_3$ perovskite is interesting because exhibits colossal magnetoresistance and a complex magnetic behavior [3–5]. This work presents the structural and electronic properties of samples prepared by CPM.

2. Experimental and calculation method

$LaMnO_3$ perovskite samples were prepared by the citrate complex precursor method from lanthanum oxide (La_2O_3), hexahydrated manganese nitrate ($Mn(NO_3)_2 \cdot 6H_2O$) and monohydrated citric acid $C_6H_8O_7 \cdot H_2O$. Precursor dissolution was prepared adding under continuous stirring stoichiometric amounts of lanthanum nitrate and manganese nitrate dissolutions to citric acid dissolution. Then this dissolution was subjected to gelling and drying process at 373 K. The ratio of citric acid concentration to metallic ions concentration (c/n) was 1 and the concentration of each ion was 0.1 M. The obtained foam was heated until 873 K at 10 K/min and then calcined at this temperature during 1 h.

XRD pattern of $LaMnO_3$ powder was recorded in a Phillips diffractometer (model PW1710) using the Cu Kα radiation. Analysis was carried out at 2θ between 20° and 60° with a scanning step of 0.04° and a step time of 2 s. Rietveld refinement was made by means of GSAS code and its graphic interface EXPGUI, using the structural parameters of the ABO_3 rhombohedral perovskite family.

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0304-8853/$ - see front matter
doi:10.1016/j.jmmm.2008.02.052

Ab-initio full-potential linearized plane wave (FP-LAPW) calculations with spin-polarization were carried out by the wien2k code [6–8], with the generalized gradient approximation (GGA) [9]. The spin-polarized DOS were obtained for the experimental lattice constants. The muffin-tin radii, in Å, were 1.3229, 0.9736 and 0.8626 for La, Mn and O, respectively. RMT × KMAX = 8.0 and 85 k-points over the irreducible Brillouin zone were used. These two last parameters were selected from graphs of total energy versus them. The values were taken where the graph started a "plateau". The maximum angular momentum inside the muffin-tin sphere was $l = 10$.

3. Results and discussion

Fig. 1 shows the result of Rietveld refinement. The continuous curve corresponds to the pattern calculated and the symbols represent the XRD diffractogram. The peaks Bragg location is shown as vertical lines. The curve in the lowest part of figure is the difference between experimental pattern and the calculated one. This pattern is characteristic of perovskite structure with a rhombohedral distortion R3-CH, space group R-3c (#167), which has still been found with doping [10]. Results are in good agreement with ones found with SPuDS Software [11]. The discrepancy factors were: $R_p = 8.1\%$, $R_{wp} = 9.1\%$, $R_{exp} = 8.02\%$, $R_{Bragg} = 3.18\%$ and $\chi_2 = 1.21$. The lattice parameters were $a = 5.520(1)$ Å, $c = 13.559(4)$ Å, $\alpha = \theta = 90^\circ$ and $\gamma = 120^\circ$. The atomic positions and occupancy are shown in Table 1.

Fig. 2 shows the DOS and it is clearly observed that the spin up channel evidences a continuous characteristic through the Fermi level, while the DOS spin down shows an insulator behavior with a gap of 3.5 eV. Materials that present this exotic effect are known as half-metallic [12].

From Fig. 2b–d, it is evident that Mn spin up channel is responsible by the conductor behavior. Mn spin up is present in the energy interval −1.8 to 0.6 eV, and 0.8 to 4.0 eV. The Mn spin down channel shows contribution above Fermi level (FL), from 0.2 to 4.0 eV. A incipient presence of O is detected through the Fermi level. More contribution of oxygen to DOS corresponds to the low energy levels from −8.0 to −3.0 eV for both spin up and down configurations. La levels are observed above the FL between 1.0 and 2.1 eV. These (O and La) have no direct influences on the conductor or half-metallic behavior of material. On the other hand, we observe that Mn is the main magnetic element of the system.

The calculated magnetic moment (MM) value was $2.0\,\mu_B$. This result is in agreement with the characteristic of half-metallic systems, which MM corresponds to an integer value for effective number of Bohr magneton. In Fig. 3 we can examine the contribution of particular levels to the density of states, and conclude that all Mn-d with spin up polarization (z^2, $x^2y^2{+}xy$, $xz{+}yz$) contribute to the conductor character. It is too perceived that all Mn-d spin down orbitals have insulator behavior.

Table 1
Structural parameters of $LaMnO_3$ found by Rietveld analysis of XRD data

Atom		Ox	x	y	z	B	Occ
La	6a	3	0	0	0.25	0.23	0.99
Mn	6b	3	0	0	0	0.07	1.04
O	18e	−2	0.5	0	0.25	0.7	1.04

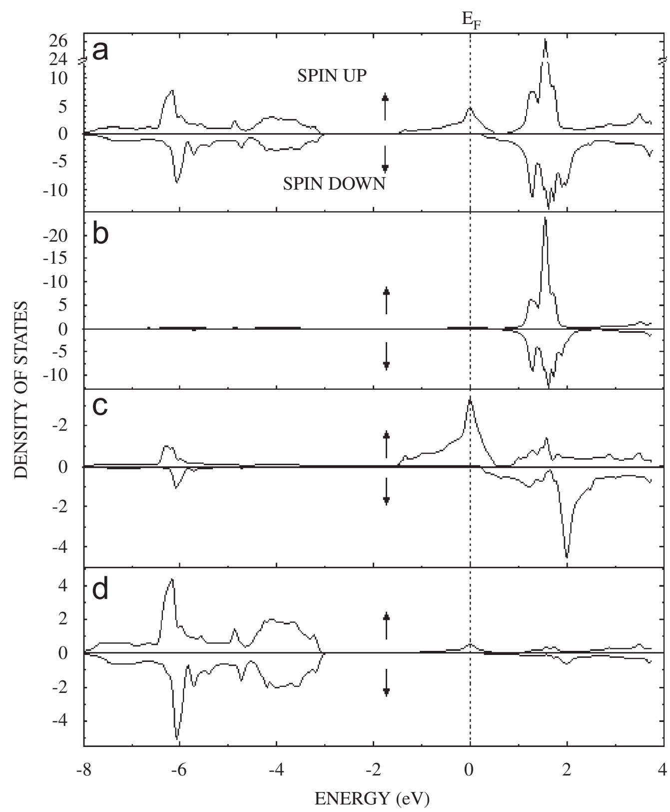

Fig. 2. Total and partial DOS.

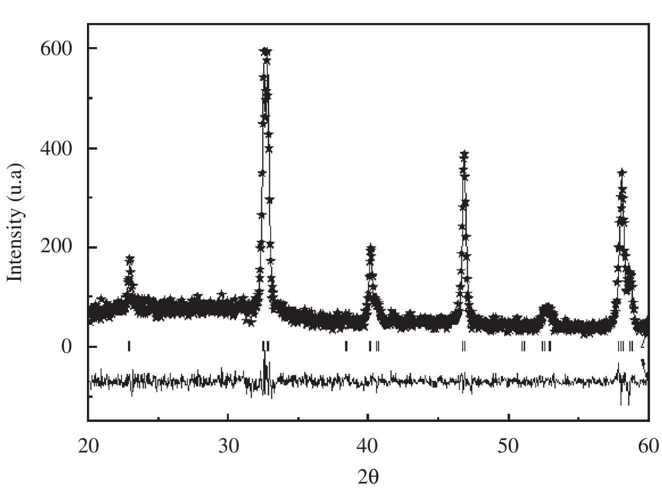

Fig. 1. XRD pattern for $LaMnO_3$ perovskite. Symbols correspond to the experimental data and continuous one is the obtained by Rietveld refinement. Lowest curve represents the difference between experimental and calculated patterns.

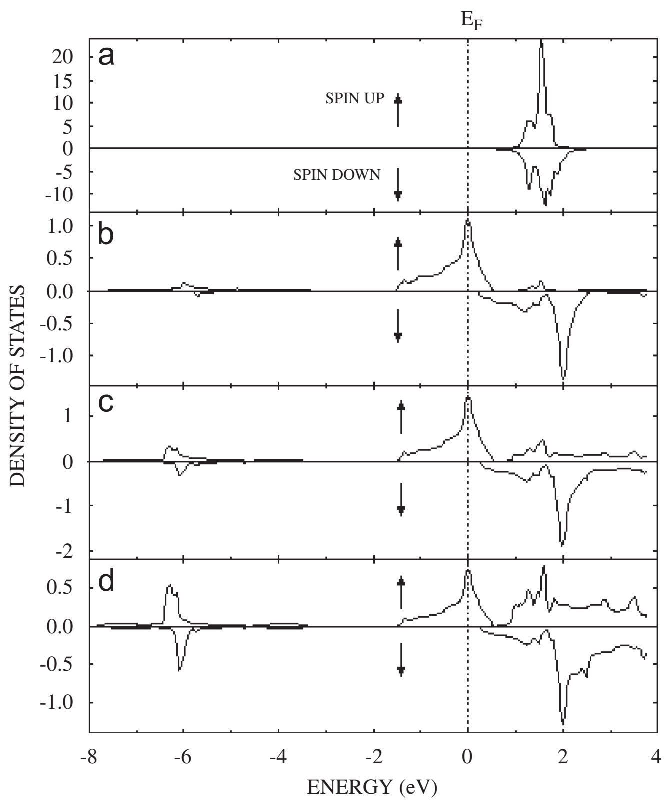

Fig. 3. Partial DOS for up and down spin-polarizations.

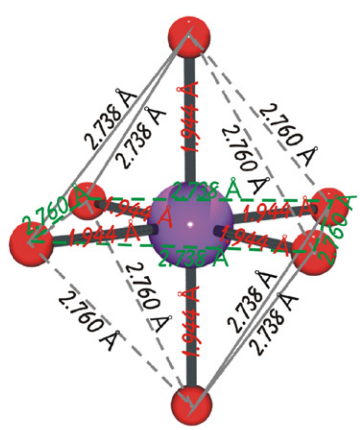

Fig. 4. The MnO_6 distorted octahedron. There are two equilateral triangles of 2.760 Å. Mn-atom is located at center of a rectangle of 2.760 × 2.738 Å. The bond length Mn–O is 1.944 Å.

In contrast, La-f orbitals are not important to MM. Our results are in agreement with reports which reveal a half-metallic behavior for the ferromagnetic $LaMnO_3$ in the cubic phase [13]. Additionally, a Jahn–Teller distortion of the MnO_6 octahedron is presented in cubic phase [13,14] but the rhombohedrally distorted perovskite, studied in this work, is a consequence of the breaking of the symmetry. Then, a mix between e_g and t_{2g} orbitals is caused. Fig. 4 shows the deformed octahedron.

4. Conclusions

$LaMnO_3$ was synthesized by CPM, and XRD data reveal that crystallizes in R-3c space group. Experimental lattice parameters are up to 97% in accordance with the theoretical SPuDS values. Density functional theory (DFT) calculation reveals the half-metallic character with conductor behavior due to Mn spin up carriers and a MM of 2.0 μ_B.

Acknowledgments

This work was partially supported by COLCIENCIAS (Project 1101-06-17622), DIB, and Centro de Excelencia en Nuevos Materiales (Contract 043-2005). Authors thank Dr. Peter Blaha for special support.

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