Original Article

Effect of Mg addition on LaMnO$_3$ ceramic system

García Iván Supelano$^{a,*}$, Aura J. Barón-González$^a$, Armando Sarmiento Santos$^a$, César Ortíz$^a$, Julieth A. Mejía Gómez$^b$, Carlos A. Parra Vargas$^a$

$^a$ Universidad Pedagógica y Tecnológica de Colombia, Tunja 150003, Colombia
$^b$ Universidad Antonio Nariño, Boyacá 150003, Colombia

ARTICLE INFO

Article history:
Received 7 October 2016
Accepted 28 May 2017
Available online 26 August 2017

Keywords:
Magnetic materials
Doped LaMnO$_3$

ABSTRACT

In the present work we report the synthesis of La$_{1-x}$Mg$_x$MnO$_3$ (with $x=0.10$, $0.25$, and $0.50$) polycrystalline samples based on LaMnO$_3$ (LMO) antiferromagnetic with low Neel temperature and insulating behavior. Structure was analyzed by Rietveld fitting of XRD patterns at room temperature by FullProf software, these show that La$_{1-x}$Mg$_x$MnO$_3$ ($x=0.10$, $0.25$, $0.50$) samples crystallize in the space group R-3c. Magnetic and electrical measurements exhibits ferromagnetic and semiconductor like behavior. A decreases of $T_C$ is observed when $x$ doping value increases.

© 2017 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

LaMnO$_3$ (LMO) is an inorganic compound with perovskite structure. It is an A-type antiferromagnetic insulator with a low Neel temperature [1-4]. Depending on the synthesis process, LMO samples can be obtained as thin films [5], monocrystals [3,6] and polycrystalline powders [7]. To prepare stoichiometric LMO ceramics, the synthesis has to be carried out in low partial pressures of oxygen. In contrast, non-stoichiometric LaMnO$_{3÷δ}$ is obtained when the production is made in air [8].

The presence of Mn$^{4+}$ influences the structural and magnetic behavior of LMO samples. For instance, it has been reported that for 12% of Mn$^{4+}$ content, the structure is orthorhombic with antiferromagnetic ordering. Whereas for higher Mn$^{4+}$ content, the structure is rhombohedral or cubic exhibiting ferromagnetism [9].

Partial substitution of lanthanum ions [3,9,10] or Mn ions [11,12] has an effect on the physical properties of LaMnO$_3$ such as structural changes and Mn$^{4+}$/Mn$^{3+}$ ratio. The last one promotes phenomena such as charge and orbital ordering, which are controlled by interaction between electrons from $e_g$ and $t_{2g}$ levels [13].

The aim of this paper is to present the results from the production and characterization of polycrystalline La$_{1-x}$Mg$_x$MnO$_3$ ($x=0.10$, $0.25$, $0.50$).
2. Experimental

Polycrystalline La$_{1-x}$Mg$_x$MnO$_3$ ($x=0.10$, $0.25$, $0.50$) samples were prepared by the usual solid state reaction method from a stoichiometric mixture of high purity La$_2$O$_3$ (99.99%), MgO (99.995%) and MnO$_2$ (99.99%) in air at sintering temperature of $1150^\circ$C by 24 h at 2.5 °C/min of heating and cooling rate. X-ray powder diffraction (XRD) data were collected on PANalytical X’Pert’s X-ray diffractometer with $K_{\alpha}Cu$ radiation at room temperature. XRD patterns were studied by Rietveld method with FullProf software. Surface was analyzed by scanning electron microscopy (SEM) with JEOL JSM-6490LV microscope and elemental analysis (EDS) with EDS Inca Energy 250 analyzer. Magnetization measurements were performed in vibrating magnetometer Versalab and Physical Property Measurements System (PPMS) of Quantum-Design. Electrical resistance measurements were performed with PPMS by using the standard 4-probe method.

3. Results and discussion

XRD patterns for La$_{1-x}$Mg$_x$MnO$_3$ samples are displayed in Fig. 1(a). Based on these diffraction patterns, it can be observed that lanthanum manganites Mg-doped range from 0.25 to 0.50 exhibit the same phase. However, for the samples with $x=0.25$ and 0.5, additional reflections at $2\theta=35.57^\circ$ and $2\theta=36.37^\circ$ are detected. This corresponds to a secondary phase Mn$_3$O$_4$ (peaks marked as $\Delta$).

Rietveld analysis (Fig. 1(b-d)) suggests that all the samples crystallize in the rhombohedral R-3c space group. This result differs from that reported by Zhao et al. [14]. They obtained the Pbnm structure for samples with $x=0.05$, 0.10, 0.20, 0.33 and 0.40. This difference can be attributed to different conditions of synthesis. The structural parameters of La$_{1-x}$Mg$_x$MnO$_3$ ($x=0.10$, 0.25, 0.50) were refined by fitting the XRD patterns using the program FullProf (Table 1). Substitution of La with Mg causes changes in the lattice parameters due to smaller Mg ionic radius than La ionic radius.

Fig. 2 shows the scanning electron micrograph (SEM) of La$_{1-x}$Mg$_x$MnO$_3$ ($x=0.10$, $0.25$, $0.50$) samples. These images show that, there is no significant change in the morphology with increasing Mg concentration in LMO. The grain size distributions for each sample are shown in the insets of Fig. 2. For $x=0.1$ the grain size ranges between 3.23 and 1.83 µm, for $x=0.25$ between 2.45 and 1.65 µm, and for $x=0.5$ between 1.93 and 1.13 µm. Hence, it is concluded that in La$_{1-x}$Mg$_x$MnO$_3$ ($x=0.10$, 0.25, 0.50), the Mg substitution at the lanthanum positions induces decreasing of grain size. This result is in agreement with the decreasing of cell volume that is clearly observed from the Rietveld analysis (Table 1). EDS analysis ruled out the presence of other traces elements.

The ZFC-FC M(T) curves of La$_{1-x}$Mg$_x$MnO$_3$ ($x=0.10$, 0.25, 0.50) are illustrated in Fig. 3. The plots evidence the ferromagnetic behavior for all the samples. In order to understand the

![Fig. 1](image-url) - (a) XRD patterns of La$_{1-x}$Mg$_x$MnO$_3$ system. Rietveld analysis for (b) La$_{0.5}$Mg$_{0.5}$MnO$_3$, (c) La$_{0.75}$Mg$_{0.25}$MnO$_3$ and (d) La$_{0.5}$Mg$_{0.5}$MnO$_3$ sample at 300 K.
Table 1 – Structural details of La_{1-x}Mg_xMnO_3 obtained by Rietveld refinement of DRX. La/Mg occupy 6a Wyckoff position (0 0 0), Mn occupy 6b (0 0 0) and O occupy 18e (x 0 ½).

<table>
<thead>
<tr>
<th></th>
<th>La_{0.9}Mg_{0.1}MnO_3</th>
<th>La_{0.75}Mg_{0.25}MnO_3</th>
<th>La_{0.5}Mg_{0.5}MnO_3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lattice parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a = b (Å)</td>
<td>5.334(5)</td>
<td>5.529(4)</td>
<td>5.526(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.354(5)</td>
<td>13.345(3)</td>
<td>13.339(9)</td>
</tr>
<tr>
<td><strong>Statistical parameters of fitting</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_{wp} (%)</td>
<td>6.28</td>
<td>7.27</td>
<td>6.12</td>
</tr>
<tr>
<td>R_f (%)</td>
<td>4.20</td>
<td>5.34</td>
<td>6.04</td>
</tr>
<tr>
<td><strong>Atomic positions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O x</td>
<td>0.44659</td>
<td>0.43746</td>
<td>0.44501</td>
</tr>
<tr>
<td>Cell volume V (Å³)</td>
<td>354.267</td>
<td>353.351</td>
<td>352.784</td>
</tr>
</tbody>
</table>

Fig. 2 – SEM micrographs of (a) La_{0.9}Mg_{0.1}MnO_3, (b) La_{0.75}Mg_{0.25}MnO_3 and (c) La_{0.5}Mg_{0.5}MnO_3.

Table 2 – Data of magnetization: Curie temperature (T_C), remnant magnetization (M_r), coercive field (H_c) and saturation magnetization (M_s).

<table>
<thead>
<tr>
<th>Doping x</th>
<th>T_C (K)</th>
<th>M_r (emu/g) at 5 K</th>
<th>H_c (Oe) at 5 K</th>
<th>M_s (emu/g) at 5 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>157</td>
<td>1.53</td>
<td>15</td>
<td>79.35</td>
</tr>
<tr>
<td>0.25</td>
<td>106</td>
<td>5.86</td>
<td>43</td>
<td>49.59</td>
</tr>
<tr>
<td>0.5</td>
<td>73</td>
<td>3.05</td>
<td>137</td>
<td>20.88</td>
</tr>
</tbody>
</table>

Influence of Mg doping at La site, the Curie temperature (T_C) change of the samples (T_C determined by the minimum value of the derivative of magnetization as a function of the temperature in the ZFC curve) is shown in the inset of Fig. 3. The values of T_C were found to decrease with Mg content.

The M vs H hysteresis plot of La_{1-x}Mg_xMnO_3 (x = 0.10, 0.25, 0.50) at 5 and 50 K (Fig. 4(a and b)) indicate ferromagnetic behavior at low temperatures. Whereas at 300 K (Fig. 4(c) the behavior is paramagnetic.

La_{1-x}(Ca, Sr)_xMnO_3 samples exhibit similar behavior [9]. In this work, the content of Mn^{4+} increases as x value increases. Mn–O–Mn bond angle values were found to be 164° approximately. Mn–O bond length values range between 1.92 Å and 1.96 Å. Furthermore, there is colossal magnetoresistance (CMR) which is observed only for values of Mn–O bond length below 1.97 Å. In our study, Mn–O–Mn bond angle values lie between 162.8(6)° and 164.2(5)°. The values of Mn–O bond length are around 1.969(6) Å. However, CMR was not observed.

Log R is plotted in Fig. 5 as a function of the inverse of the absolute temperature. Samples with x = 0.10, 0.25 and 0.50
present a linear behavior, first and second exhibit an inflection at 139 K and 197 K, above \( T_C \). It suggests that samples have a normal semiconductor behavior. Semiconducting behavior also occurs in the sample with \( x = 0.05 \) [2]. Inset in Fig. 5 shows electrical resistance as a function of the temperature, at applied field of \( H = 0 \), and \( H = 1 \) kOe. For sample with \( x = 0.10 \), resistance increases while the temperature decreases, there is no evidence of magnetoresistance. A similar behavior was found in the other samples.

For this system, based on LMO, the results suggest that previously values of Mn–O–Mn bond angles and Mn–O bond lengths are the reason why the La\(_{1-x}\)Mg\(_x\)MnO\(_3\) \( (x = 0.10, 0.25,\) and \( 0.50 \) ) system present ferromagnetism and does not present CMR.

Comparing the present results with those reported by Zhao et al. [14], the \( T_C \) obtained is in the same order of magnitude, which permitted to conclude that the better doping value of \( x \) is around 0.1. Table 2 listed the values of \( T_C \).

4. Conclusions

Polycrystalline La\(_{1-x}\)Mg\(_x\)MnO\(_3\) \( (x = 0.10, 0.25, 0.50) \) samples were synthetized by solid state reaction method. The system crystallize in rhombohedral structure (R-3c) at room temperature. The inclusion of Mg in the system, induce interactions which arise the ferromagnetic phase at low temperature. The system present a decrease of \( T_C \) when the doping increases. The electrical Response have semiconductor behavior, in which the resistance is proportional the inverse of the temperature. Results suggest that this behavior is due to the strong influence of Mn–O–Mn bond angles and Mn–O bond lengths values.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

To Institut de Ciència de Materials de Barcelona (CSIC), Dr. Carlos Frontera and Dr. Bernat Bozzo. This work was supported by the Gobernación de Boyacá (N° 733 Colciencias).

References


[14] Zhao JH, Kunkel HP, Zhou XZ, Williams G. Magnetic and transport properties, and the phase diagram of hole-doped \( \text{La}_{1-x}\text{Mg}_x\text{MnO}_3 \) \((x \leq 0.4)\). J Phys: Condens Matter 2001;13:9349.