J MATER RES TECHNOL. 2017;xxx(xx):xxx–xxx

Available online at www.sciencedirect.com

jmr&t
Journal of Materials Research and Technology
www.jmrt.com.br

Original Article

Effect of Mg addition on $LaMnO_3$ ceramic system

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ARTICLE INFO

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

Keywords:
Magnetic materials
Doped $LaMnO_3$

ABSTRACT

In the present work we report the synthesis of $La_{1-x}Mg_xMnO_3$ (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 $La_{1-x}Mg_xMnO_3$ ($x = 0.10$, 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.

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 $LaMnO_{3+d}$ 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 $La_{1-x}Mg_xMnO_3$ ($x = 0.10$, 0.25, 0.50).

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http://dx.doi.org/10.1016/j.jmrt.2017.05.012

2. Experimental

Polycrystalline $La_{1-x}Mg_xMnO_3$ ($x = 0.10$, 0.25, 0.50) samples were prepared by the usual solid state reaction method from a stoichiometric mixture of high purity La_2O_3 (99.99%), MgO (99.995%) and MnO_2 (99.99%) in air at sintering temperature of 1150 °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 $K_{\alpha\text{-}Cu}$ 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 $La_{1-x}Mg_xMnO_3$ 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 $2\theta = 35.57°$ and $2\theta = 36.37°$ are detected. This corresponds to a secondary phase Mn_3O_4 (peaks marked as Δ).

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 $La_{1-x}Mg_xMnO_3$ ($x = 0.10$, 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 $La_{1-x}Mg_xMnO_3$ ($x = 0.10$, 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 $La_{1-x}Mg_xMnO_3$ ($x = 0.10$, 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 $La_{1-x}Mg_xMnO_3$ ($x = 0.10$, 0.25, 0.50) are illustrated in Fig. 3. The plots evidence the ferromagnetic behavior for all the samples. In order to understand the

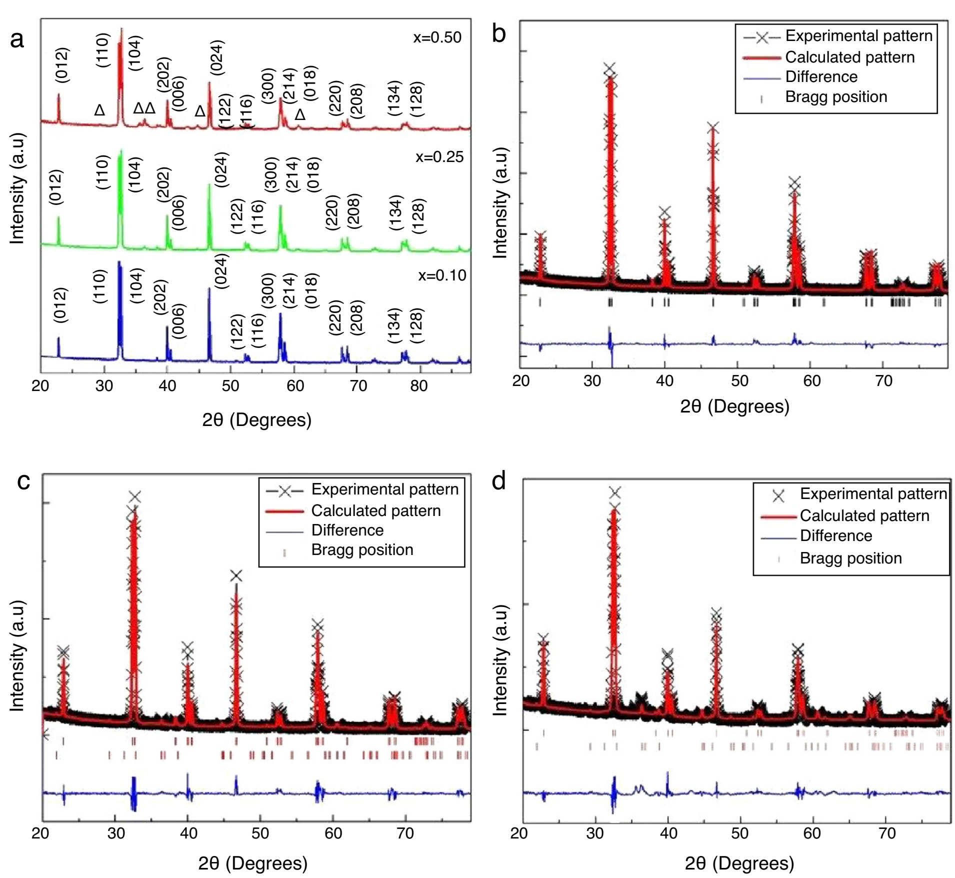

Fig. 1 – (a) XRD patterns of $La_{1-x}Mg_xMnO_3$ system. Rietveld analysis for (b) $La_{0.9}Mg_{0.1}MnO_3$, (c) $La_{0.75}Mg_{0.25}MnO_3$ and (d) $La_{0.5}Mg_{0.5}MnO_3$ sample at 300 K.