Journal of Alloys and Compounds 690 (2017) 497–502

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Magnetic and electrical properties induced by the silver in the lanthanum sites of $La_{0.6}Ca_{0.4}MnO_3$ compound

I. Walha*, E. Dhahri

Laboratoire Physique Appliquée, Faculté des Sciences, Université de Sfax, B.P. 1171, Sfax 3000, Tunisia

ARTICLE INFO

Article history:
Received 24 June 2016
Received in revised form
11 August 2016
Accepted 15 August 2016
Available online 18 August 2016

Keywords:
Ferromagnetic transition
Magnetic materials
Electrical resistivity
Magnetoresistive effect

ABSTRACT

Structural, magnetic and electrical measurements were performed to examine the effect of the silver substitution in the lanthanum sites on the physical properties. X-ray diffraction data have been analyzed by Rietveld and show no structural changes induced by Ag doping. Magnetization versus temperature studies have shown that all samples exhibit a magnetic transition from ferromagnetic to paramagnetic phase when temperature is increased. Two transitions ($T\rho_1$ and $T\rho_2$) are observed in the electrical resistivity, the second transition in the resistivity can be attributed to an abnormality characteristic of charge ordering (CO) effect. The electrical resistivity was described by a phenomenological percolation model. The MR increases with increasing applied magnetic field and decreases with the Ag substitution. At room temperature, the magnetorresistance (MR) for lanthanum substitution is about 40% and 55% for the parent compound at a magnetic applied field of 8 T.

1. Introduction

The mixed valence perovskite manganites with the general formula $A_{1-x}B_xMnO_3$ (where A is a rare-earth ion and B is a divalent alkali) have generated interest due to the colossal magnetorresistive (CMR) and magnetocaloric effects as well as their applications in magnetic memory devices and magnetic field sensors [1–4]. The appearance of the ferromagnetic and metallic states in these systems is attributed to the double-exchange effect between the Mn^{3+} and Mn^{4+} ions [5,6], polaronic effects [7] and phase separation [8]. A complete understanding of the physics of the manganites, requires electron-phonon coupling terms to be included in the relevant hamiltonians [9]. Recent studies have shown that the double exchange (DE) interaction, between Mn^{3+} and Mn^{4+} ions, cannot explain alone the behaviors observed in these systems. Other effects play a crucial role for further explanation, such as the average A-site cationic radius $\langle r_A \rangle$ [10–14]. Analysis of charge transport in the ferromagnetic metallic state is essential for clarifying the specific mechanisms responsible for the resistivity behavior. Electron–phonon, electron–electron, electron–magnon scattering and polaronic effects are the major proponents of various conceptions in electrical transport. In order to explain the transport mechanism in the whole temperature range, Li et al. [15] developed a new model based on the phase segregation mechanism [16]. Such model supposes that the materials are composed of paramagnetic and ferromagnetic regions.

In this paper, we have studied magnetic, electrical, and magnetorresitance (MR) properties in $La_{0.6}Ca_{0.4}MnO_3$ and $La_{0.5}Ag_{0.1}Ca_{0.4}MnO_3$ prepared by sol-gel methods. In addition, analysis of the resistivity based on the percolation theory is reported.

2. Experimental

Polycrystalline bulk samples of $La_{0.6}Ca_{0.4}MnO_3$ and $La_{0.5}Ag_{0.1}Ca_{0.4}MnO_3$ were synthesized using sol-gel method and annealed at 950 °C temperature in air. This method is chosen because it minimizes possible Ag evaporation from the system due to the low melting point (961.8 °C) and high vapor pressure of Ag_2O and it is known to give a high degree of homogeneity. The detailed preparation procedure and basic physical properties are reported in Ref. [17]. In order to verify the percentage of Mn^{3+} and Mn^{4+} ions in $La_{0.6}Ca_{0.4}MnO_3$ and $La_{0.5}Ag_{0.1}Ca_{0.4}MnO_3$ and hence the oxygen stoichiometry. The amount of Mn^{4+} ions has been quantitatively checked by chemical analysis (iodometric titration). The crystallographic structure was characterized by X-ray diffraction with Cu K_α radiation ($\lambda = 1.5406$ Å). Magnetic measurements were performed in a VSM magnetometer in an 8T PPMS cryostat from Quantum Design Magneto transport measurements were recorded in the

* Corresponding author.
E-mail address: skander_walha@yahoo.fr (I. Walha).

http://dx.doi.org/10.1016/j.jallcom.2016.08.132
0925-8388/

same instrument (PPMS) in the temperature range from 1.8 to 300 K.

3. Results and discussions

In order to obtain structural parameters, the diffraction data were analyzed, using the Rietveld powder diffraction profile fitting technique. All the samples synthesized are single phase, crystallizing in orthorhombic symmetry with Pnma space group. Fig. 1 shows the X-ray diffraction (XRD) pattern of $La_{0.6}Ca_{0.4}MnO_3$ and $La_{0.5}Ag_{0.1}Ca_{0.4}MnO_3$ recorded at room temperature. The values of Bragg factor and χ^2 shown in Table 1 indicate the goodness of our refinement results. Lanthanum substitution by silver implies a small increase in the average ionic radius $\langle r_A \rangle$ values which caused by a difference between Ag^{+} (1.28 Å) ions radii and La^{3+} (1.21 Å) ions radii [18]. The rare earth substitution induces a decrease of the cell parameters and the unit cell volume compared to the parent compound $La_{0.6}Ca_{0.4}MnO_3$ which can be explain by the electrical charge equilibrium equation in which the Mn^{4+} content increase above 40% with average ionic radius ($<rMn^{4+}> = 0.53$ Å) smaller then Mn^{3+} ($\langle r\ Mn^{3+} \rangle = 0.65$ Å).

Fig. 2 shows magnetization curves taken at 0.05 T applied magnetic field and the temperature dependence of electrical resistivity for $La_{0.6-x}Ag_xCa_{0.4}MnO_3$ with $x = 0.0$ and 0.10. All the samples present an insulator state ($d\rho/dT < 0$) at high temperature.

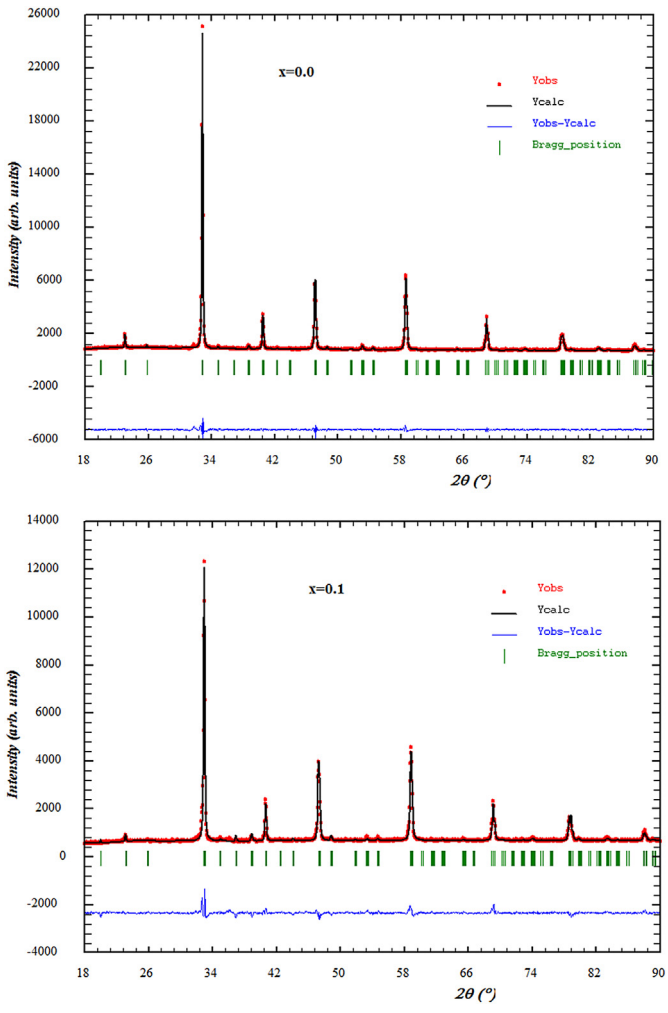

Fig. 1. Rietveld refinement for the samples $La_{0.6-x}Ag_xCa_{0.4}MnO_3$ with $x = 0$ and 0.10: experimental data in red, calculated data in black, difference between them in blue and Bragg positions in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Refinement results for the samples $La_{0.6-x}Ag_xCa_{0.4}MnO_3$ with $x = 0$ and 0.10.

Samples	x = 0.00	x = 0.10
a (Å)	5.463 (3)	5.444 (7)
b (Å)	7.697 (6)	7.670 (1)
c (Å)	5.450 (4)	5.434 (8)
V (Å^3)	57.341	56.741
$<r_A>$ (Å)	1.201	1.208
Bragg factor	3.6	4.83
χ^2	1.6	1.94

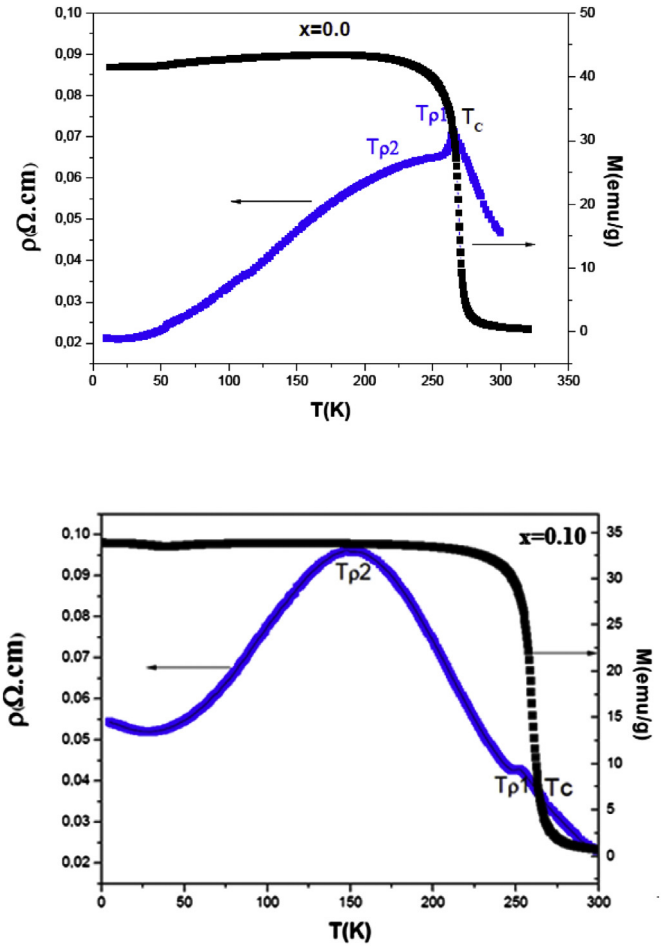

Fig. 2. Temperature dependence of magnetization under magnetic applied field of 0.05 T and electrical resistivity under zero field for the samples $La_{0.6-x}Ag_xCa_{0.4}MnO_3$ with $x = 0$ and 0.10.

For the sample $La_{0.5}Ag_{0.1}Ca_{0.4}MnO_3$, the Paramagnetic (PM)–Ferromagnetic (FM) temperature transition (T_C) was estimated to be $T_C = 262$ K. The electrical resistivity measurements shows that the resistivity reaches a peak indicating a Metal Insulator Transition (MIT) around $T\rho_1 = 260$ K followed by $T\rho_2 = 160$ K. The first electrical transition from insulator to metallic state is in agreement with the results found from magnetic measurements which yields Tc = 260 K. The coincidence of T_C and $T\rho_1$ is an indicator of the good quality of this sample with negligible grain boundary effects which was initially explained within the framework of the double exchange (DE) mechanism, which successfully linked the onset of metallicity with the establishment of ferromagnetism. This value is