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Structural, magnetic, and magnetocaloric properties of Ag-doped in the $La_{0.6}Ca_{0.4}MnO_3$ compound

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ABSTRACT

We present a study of the physical properties of the $La_{0.6}Ca_{0.4}MnO_3$ and $La_{0.6}Ca_{0.3}$ $Ag_{0.1}MnO_3$ powder samples. Our synthesized samples were prepared by sol–gel methods. They crystallize in the orthorhombic perovskite structure with Pnma space group. The substitution of calcium by silver induces an increase in cell volume. The magnetocaloric effect was estimated from the magnetic isotherms. With 10% of Ag doped in the $La_{0.6}Ca_{0.4}MnO_3$, we can observe a significant maximum variation of the magnetic entropy $-\Delta S_{Max}$ and a relative cooling power RCP near room temperature under an applied magnetic field of 5 T. The RCP varied from 221 to 264 J kg−1 under an applied magnetic field of 5 T for $La_{0.6}Ca_{0.4}MnO_3$ and $La_{0.6}Ca_{0.3}Ag_{0.1}MnO_3$, respectively. The comparison of the values, reported in the reference Gd material, underlines that the proposed oxide material has significant advantages for magnetic refrigeration.

1. Introduction

The perovskite manganese oxides with the general formula $Ln_{1-x}A_xMnO_3$, where Ln is a rare-earth and A is a divalent alkaline-earth or a monovalent alkali-metal, are widely studied by several scientific research teams [1–5]. Indeed, these compounds exhibit a variety of phases and rich physical properties. These manganites were subsequently taken essentially in 1993 following the discovery of colossal magnetoresistance (CMR) in thin films of $La_{1-x}Ca_xMnO_3$ [6,7]. This discovery had a highly significant impact not only on the level of fundamental studies but also on industrial applications, such as the manufacture of hard drives with a large storage capacity and read heads. Manganites are also characterized by a magnetocaloric effect (MCE) defined by the warming or cooling of certain magnetic materials in the application or removal of an external magnetic field. Nowadays, the use of MCE technology, as an alternative to magnetic refrigeration, received an immense interest not only due to its strong potential for magnetic refrigeration but also to its capacity to clarify the understanding of its fundamental physical property [8,9]. The Gd possesses excellent magnetic entropy change $-\Delta S_{max}$ values equal to 10. 2 J K^{-1} kg^{-1} [10] and a T_C of 294 K under 5 T, however, unfortunately the Gd is more expensive and oxidizable in air. Accordingly, research studies have focused on the synthesis of new materials at reasonable costs while having these magneto-caloric properties near room temperature. The motivation for the present study in the perovskite manganites stems from the possible utility of large magnetocaloric (MC) properties at low field and room temperature. Tang et al. studied MC effect in a series of bulk perovskites manganites $LaAgMnO_3$ and they found that magnetic entropy change is larger than that of gadolinium [11,12]. Thus, it is possible to use them as the magnetic refrigerants working in quite a large temperature range. From this view-point, the present study examines the silver substitution effect on the magnetic and magnetocaloric effects in $La_{0.6}Ca_{0.4-x}Ag_xMnO_3$ with x = 0.00 and 0.10 prepared by sol-gel methods. We report a material which is endowed with beneficial parameters such as low cost, no corrosion, ease of synthesis, and chemical stability showing a giant magnetocaloric effect near room temperature.

2. Experimental details

$La_{0.6}Ca_{0.4-x}Ag_xMnO_3$ with x = 0.0 and 0.1 samples were prepared by the sol-gel method [13]. We dissolved stoichiometry amounts of La $(NO_3)_3{\cdot}6H_2O$, Ca $(NO_3)_2{\cdot}4H_2O$ and Mn $(NO_3)_2{\cdot}4H_2O$ in the nitric acid HNO_3 and we mixed them to an aqueous citric acid solution $C_6H_8O_7$. Afterwards, a few drops of ethylene glycol $C_2H_6O_2$ were added to the solution as chelating agent. The obtained gel was converted into powder by heating, using a hot plate. The

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sample was then heated at 800 and 900 °C for 24 h at each temperature. This method was chosen since it minimizes the possible Ag evaporation from the system due to the low melting point (961, 8 °C) and the high vapor pressure of Ag_2O. Additionally, it is known for yielding a high degree of homogeneity. The powder is sintered in the pellet of 10 mm of diameter and approximately 2 mm of thickness. Phase purity and homogeneity were determined by X-ray diffraction (XRD) (Cu-Kα radiation λ_{Cu} = 1.5406 Å) at room temperature in the 2θ range of 10–90° with step of 0.02°.

Magnetization measurements of the samples were performed as a function of temperature and applied field using a Quantum Design Vibrating Sample Magnetometer: operated in PPMS systems capable of fields up to 9 T and 14 T.

3. Results and discussions

3.1. Structural properties

Fig. 1 shows the X-ray diffraction (XRD) pattern of $La_{0.6}Ca_{0.4}MnO_3$ and $La_{0.6}Ca_{0.3}Ag_{0.1}MnO_3$ recorded at the room temperature. In order to obtain the structural parameters, the diffraction data were analyzed, using the Rietveld powder diffraction profile fitting technique. All the synthesized samples are single phase with minor traces of Mn_3O_4, crystallizing in orthorhombic symmetry with Pnma space group.

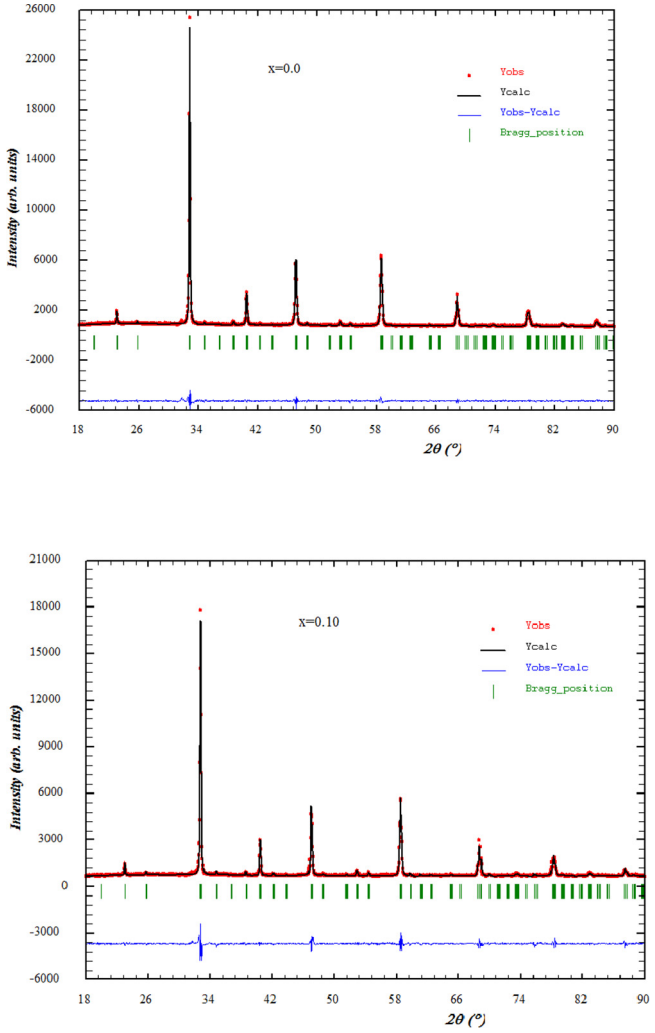

Fig. 1. Rietveld refinement of X-ray diffraction data (XRD) for the samples $La_{0.6}Ca_{0.4-x}Ag_xMnO_3$($x$ = 0.0 and 0.1): experimental data in red, calculated data in black, difference between them in blue and Bragg positions in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The measured and calculated (refined) X-ray diffraction patterns and positions of Bragg reflections for the $La_{0.6}Ca_{0.4-x}Ag_xMnO_3$ samples with x = 0.0 and 0.1 are measured in Fig. 1. The refinement results for all our samples are listed in Table 1. We observe that the substitution of calcium by silver induces an increase of the cell parameters and the unit cell volume compared to the parent compound $La_{0.6}Ca_{0.4}MnO_3$. This increase is ascribed to the average ionic radius $\langle r_A \rangle$ of A site whose increase is caused by a substitution of large Ag^+ (1.28 Å) ions for smaller Ca^{2+} (1.18 Å) ions [14].

3.2. Magnetic properties

Fig. 2 reveals the zero-field-cooled (ZFC) and the field-cooled (FC) magnetization curves taken at 0.05 T with the data recorded during warming up. The magnetization curves exhibit a typical transition to the Curie temperature T_C of a ferromagnetic state at a low temperature and to a paramagnetic state at a high temperature.

The curves M (T) – ZFC and M (T) – FC have a common part, for high temperatures, wherein the variations in magnetization with temperature are overlaid and reversible. At low temperatures, the behavior is irreversible with a low divergence between M (T) – ZFC and M (T) – FC. The temperature corresponding to the separation between M (T) – ZFC and M (T) – FC is called the thermo magnetic irreversibility temperature and it is equal to the Curie temperature Tc. The values of the Curie temperature are determined by considering the abscissa point of intersection of the tangent with the temperature axis at the inflection point in the curve M (T).

The FC regime magnetization values are higher than those recorded in the ZFC mode when the temperature decreases; this difference is explained by the applied magnetic field, which favors double exchange interactions [15]. This separation may also be assigned to the presence of a canted spin state in our sample at low temperature. The evolution of dM/dT versus temperature (T) measured at an applied magnetic field of 0.05 T is reported in Fig. 2. The analysis gives evidence of the presence of one peak attributed to the ferromagnetic-paramagnetic transition at the Curie temperature (Tc). The $La_{0.6}Ca_{0.4}MnO_3$ and $La_{0.6}Ca_{0.3}Ag_{0.1}MnO_3$ undergo a paramagnetic to a ferromagnetic phase transition at T_C of 269 and 267 K, respectively. In order to study the magnetic behavior above T_C in our samples, we indicated in the inset of Fig. 2 the thermal evolution of inverse susceptibility $\chi - 1$ obtained from magnetization measurements in a field of 0.05 T. The adjustment of the $\chi - 1$ curve as a function of temperature in the paramagnetic domain (above Tc) leads to effective magnetic moment values which are greater than those calculated. In the paramagnetic phase, both samples exhibit a linear behavior in accordance with the Curie-Weiss law:

Table 1
Refinement results for the samples $La_{0.6}Ca_{0.4-x}Ag_xMnO_3$($x$ = 0.0 and 0.1).

Compounds	$La_{0.6}Ca_{0.4}MnO_3$	$La_{0.6}Ca_{0.3}Ag_{0.1}MnO_3$
Space Group	Pnma	Pnma
a (Å)	5,463(3)	5,472(7)
b (Å)	7,697(6)	7,724(1)
c (Å)	5,450(4)	5,459(4)
V (Å^3)	229,212	230,778
$\langle r_A \rangle$ (Å)	1,201	1,211
$\langle rB \rangle$ (Å)	0,602	0,59
χ^2	1,6	2,1