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EFFECTS OF Gd DOPING ON THE MAGNETIC PROPERTIES AND MAGNETOCALORIC EFFECT OF $La_{1.4}Ca_{1.6}Mn_2O_7$

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Abstract. The magnetic properties and magnetocaloric effect near the critical phase transition temperatures of $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ ($x = 0, 0.2$) double layered manganites are analysed. The polycrystalline nanopowders with grain sizes smaller than 30 nm were successfully synthesized by a sol-gel method. The magnetic measurements indicate a canted spin arrangement in $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ double layered manganites and an increased Mn effective magnetic moment in $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$. The investigated manganites show a moderate magnetocaloric effect, with the maximum entropy change located at temperatures near the magnetic transition ones. The Gd doped sample shows larger maximum values of $|\Delta S_m|$ and cooling efficiency than $La_{1.4}Ca_{1.6}Mn_2O_7$. The high RCP(S) values together with the broadened magnetic entropy curves suggest the possibility to use these materials for magnetic refrigeration devices.

Key words: perovskite manganites, magnetic properties, magnetocaloric effect.

1. INTRODUCTION

The double-layered manganites belonging to the Ruddelsden-Popper series have generated considerable interest in the last two decades due to their intriguing properties such as colossal magnetoresistance, charge ordering, anisotropic transport in charge carriers, and the possibility of a short-range magnetic ordering above the 3D ferromagnetic transition temperature [1–9]. The doped $R_{2-2x}A_{1+2x}Mn_2O_7$ perovskites, where R is a rare earth and A an alkaline earth cation, consist of MnO_2 bilayers separated by insulating $(R, A)_2O_2$ rock-salt layers, stacked along the c-axis, leading to a quasi-two-dimensional structure. The R(A) ions can occupy two different sites: a twelve-fold-coordinate site in the middle of the MnO_2 layer, inside the perovskite blocks, and a nine-fold-coordinate site in the rock-salt layer, at the top and bottom of each block. The distribution of the various R(A) cations between these two sites is dependent on the dopant ion size and therefore the physical properties of the layered manganites are sensitive to small changes in composition. Two anisotropic exchange interactions are expected in these manganites, namely an intralayer exchange interaction within the MnO_2 bilayers and an interlayer exchange interaction acting between the perovskite MnO_2 bilayers, which could be the reason for the magnetic transition temperatures [2, 10]. $La_{2-2x}A_{1+2x}Mn_2O_7$ double layered manganites with A = Sr, Ca, or Ba can also exhibit large magnetocaloric effect [9–14]. The substitution of La with rare earth atoms may induce lattice effects and/or change the magnetic interactions with the Mn moments. In this paper the magnetic properties and magnetocaloric effect of $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$ are presented and analysed in relation to previously reported results for $La_{1.4}Ca_{1.6}Mn_2O_7$ [15].

2. MATERIAL AND METHODS

$La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ ($x = 0,\ 0.2$) compounds were prepared as polycrystalline powders by sol-gel method. Suitable amounts of the starting materials $R(NO_3)_3 \bullet xH_2O$ (R = La, Gd), $CaCO_3$ and $Mn(CH_3COO)_2 \bullet 4H_2O$ were dissolved in aqueous polyol solution and thoroughly stirred to achieve a homogeneous transparent solution. The pH was adjusted to a value between 1 and 2 and the gel-type solution was obtained by heating. The gel was dried in air at 300°C and then heated to 900°C in order to remove the organic matter produced during the chemical reactions. The phase purity and the crystal structure of the resulted polycrystalline powders were analysed at room temperature by using a Bruker D8 Advance AXS X-ray diffractometer with Cu *Kα* radiation in the 2θ region 20°–90°. For magnetic measurements the powders were pressed into pellets, heated in air to 500°C for 12 h and slowly cooled to room temperature. The samples morphology was investigated by scanning electron microscopy (JEOL-JSM 5600-LV microscope) equipped with an energy dispersive x-ray microanalysis (EDX) spectrometer (Oxford Instruments, INCA 200 software). A 12 T VSM from Cryogenics was used for magnetization measurements in the temperature range 4.2–500 K and external magnetic field up to 12 T. The magnetic entropy changes were determined from magnetization isotherms, between zero field and a maximum field (H_0) using the thermodynamic relation [16]:

$$\Delta S_m\left(T,H_0\right)=\frac{1}{\Delta T}\int_0^H\left[M\left(T+\Delta T,H\right)-M\left(T,H\right)\right]dH\,, \tag{1}$$

where ΔT is the temperature increment between measured magnetization isotherms (ΔT = 5K in our case). The magnetic cooling efficiency was evaluated by calculating the relative cooling power (RCP) based on the magnetic entropy change:

$$RCP(S)=-\Delta S_{Max}\left(T,H_0\right)\times\delta T_{FWHM}\,, \tag{2}$$

where ΔS_{Max} represents the maximum magnetic entropy change and δT_{FWHM} its full-width at half-maximum.

3. RESULTS AND DISCUSSION

3.1. Structural and morphological characterization

Figure 1 shows the XRD patterns recorded for the sintered polycrystalline powders and the $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$ pellet.

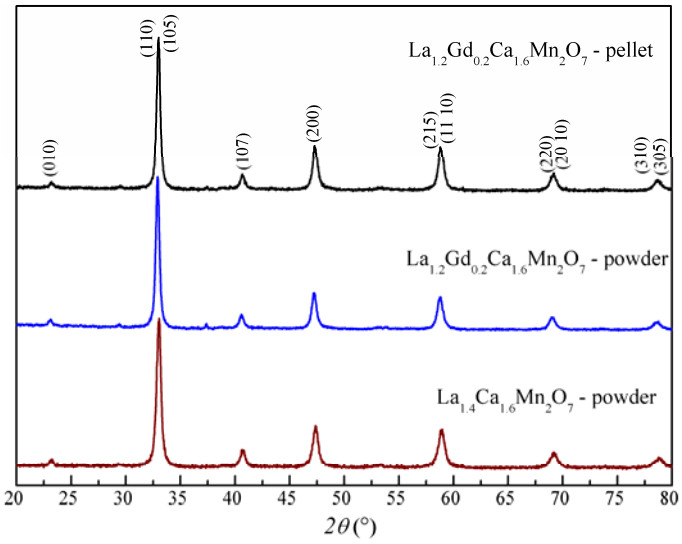

Fig. 1 – XRD patterns of $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ samples at room temperature.

The analysis reveals the $Sr_3Ti_2O_7$-type tetragonal (I4/mmm) perovskite structure of all the samples. The broadened XRD maxima indicate that the crystallite size is in the nanometer range. The values found for the lattice parameters, c/a ratios and crystallite-sizes, listed in Table 1, are typical for $La_{2-2x}A_{1+2x}Mn_2O_7$ perovskites [2, 15, 17].

Table 1

Lattice parameters, c/a ratio and crystallite sizes
estimated from XRD patterns for $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$

x	*a* (Å)	*c* (Å)	*c*/a	Crystallite size (nm)
0.0	3.844(0)	19.176(6)	4.988	22±1
0.2 (powder)	3.849(2)	19.168(8)	4.980	19±1
0.2 (pellet)	3.851(1)	19.195(4)	4.984	20±1

The compositional analysis performed on the pressed pellets by EDX indicated the presence of all elements in quantities closed to the nominal one (within the accuracy of EDX), confirming that there is no loss of any integrated element after the thermal treatment. The surface morphology of the samples has been observed with SEM. Figure 2 (right) shows the granular nature of $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$, with grains sizes smaller than 30 nm that tend to agglomerate.

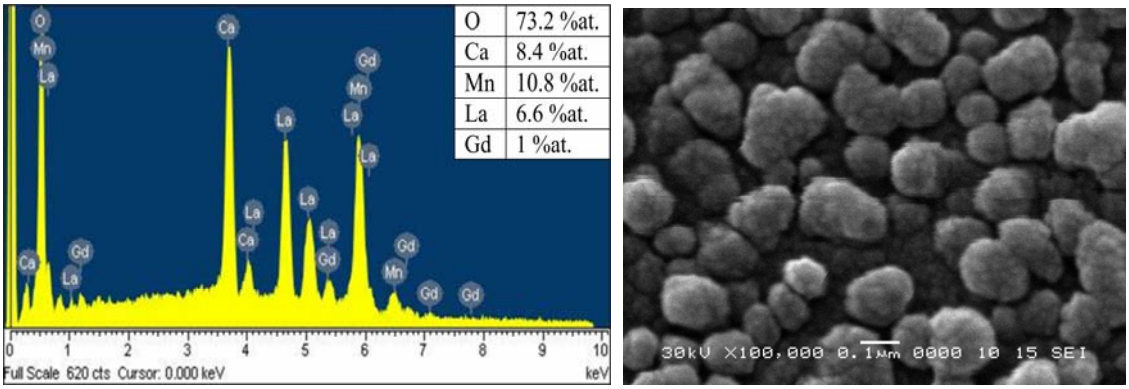

Fig. 2 – EDX data (left) and SEM image (right) of $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$ at room temperature.

3.2. Magnetic properties

In order to analyse the effect of Gd substitution on the magnetic properties, the temperature dependence of the magnetization in zero field cooling (ZFC) and field cooling (FC) modes under a magnetic field of 0.2 T were recorded. Below 50 K the ZFC and FC magnetizations of $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$ (Fig. 3) show a clear splitting, which indicates a spin glass like state. This may be due to frustration of random competing ferromagnetic and antiferromagnetic interactions together with the anisotropy originating from layered structure [18, 19]. Figure 4 shows the M (H) curves at 5 K in magnetic fields up to 12 T for both $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$ and $La_{1.4}Ca_{1.6}Mn_2O_7$. The magnetization of the two samples does not saturate even in magnetic fields of 12 T, at 4 K. This can be due to the absence of true long-range FM coupling due to the small grain size of the samples obtained by the sol-gel method [17]. The magnetic frustration present in $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ manganites is also responsible for the hysteresis effect observed at low temperatures, as showed in the inset of Fig. 4. The reduction of magnetization in low magnetic field (below 2 T) of $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$ indicates the antiparallel alignment of the Gd and Mn magnetic moments. For magnetic fields higher than 2 T the magnetization of the doped sample becomes larger than for the parent manganite. Gd doping can induce distortions and tilting of the MnO_6 octahedra and therefore can reduce the overlap of the Mn and O orbitals, but could also modify the valence state of the Mn ions.

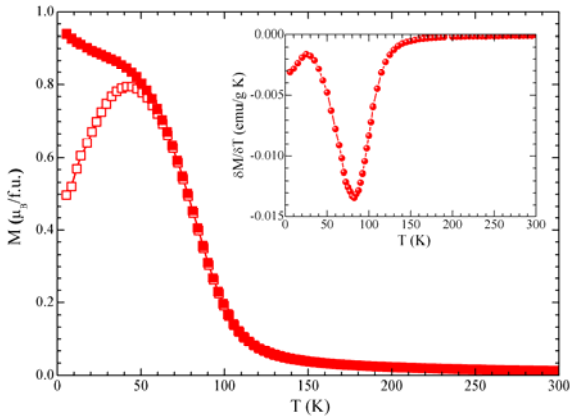

Fig. 3 – Temperature dependence of zero-field cooled and field cooled magnetization in 0.2 T of $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$; the inset shows the |δM/δT| dependence.

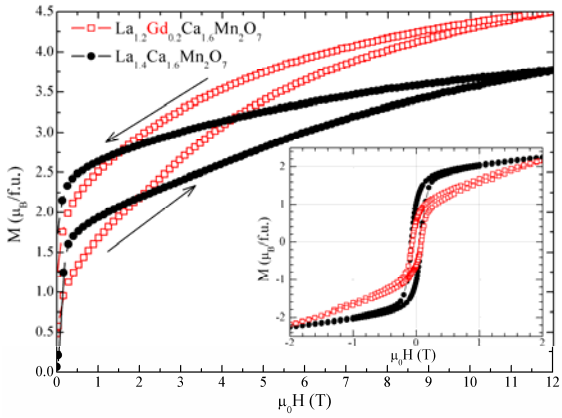

Fig. 4 – Magnetic field dependence of the magnetization at 4 K in fields up to 12 T or $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ manganites.

In order to determine the magnetic moment of the Mn atoms in $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ manganites, the temperature dependence of the reciprocal susceptibility was recorded above room temperature. As shown in Fig. 5, in the temperature range 400–500 K the magnetic susceptibility of $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$ obeys a Curie-Weiss law with the Curie constant C ≈ 6.65 emu·K/mol. According to additional law of magnetic susceptibilities and supposing that the Gd^{3+} effective moment is given by its free ion value, the contribution of Mn ions to the Curie constant was estimated to about 5.07 emu·K/mol. Assuming that only Mn^{3+} and Mn^{4+} ions are present, their content was calculated to be about 41 % and 59 %, respectively. The partial substitution of trivalent La^{3+} by divalent Ca^{2+} is balanced by the conversion of Mn valence states between Mn^{3+} and Mn^{4+} and the creation of oxygen vacancies as well. Therefore the ionic structure of the Gd doped sample can be expressed as $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_{7-\delta}$. Considering the charge neutrality of the manganite we estimate for the oxygen vacancies a value of δ = 0.7.

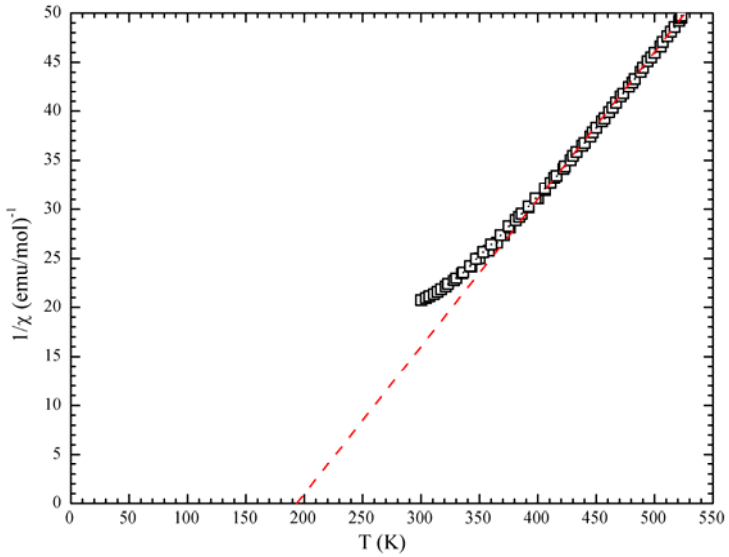

Fig. 5 – Temperature dependence of the reciprocal susceptibility of $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$.

3.3. Magnetocaloric effect

The temperature dependences of the magnetic entropy changes, ΔS_m, for $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ (x = 0, 0.2), in magnetic fields of 2 T and 4 T, were determined from magnetization isotherms using relation (1). As shown in Fig. 6, a moderate magnetocaloric effect can be observed over a broad temperature range. The maxima values of $|\Delta S_m|$ are located at temperatures very close to the magnetic transition ones and the peaks

are nearly symmetrical around their maximum values, which is in general characteristic of a second order magnetic transition [20]. The broadening of the magnetic entropy change toward high temperature can be attributed to the short-range magnetic order still present. The maximum values of $|\Delta S_m|$ are rather small compared to the values reported for similar manganites [14, 16, 20, 21], which is expected considering that even in 4 T the magnetization of the samples is far from the saturation value.

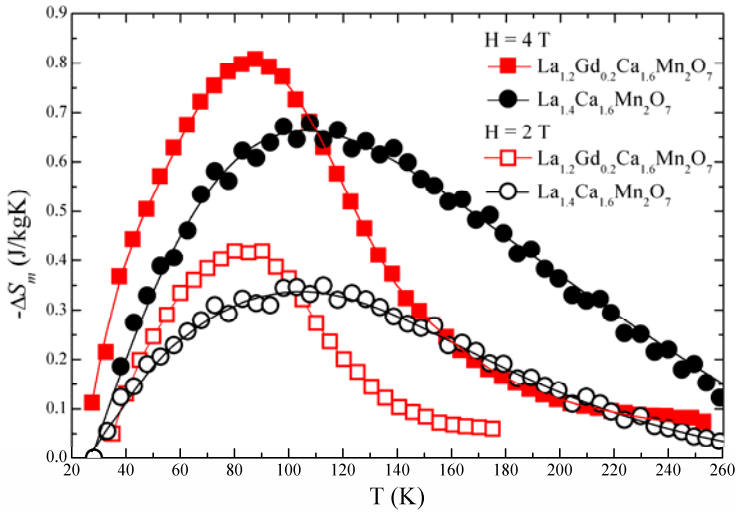

Fig. 6 – Magnetic entropy change for $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ manganites.

In order to evaluate the magnetic cooling efficiency, the RCP(S) values were calculated by using relation (2). However, the RCP alone is not sufficient for considering a material for magnetic refrigeration applications [22]. First, from an application point of view, a different way of calculating the useful RCP value was proposed, i.e. the maximal area of the product $\Delta S \times (T_{hot} - T_{cold})$, where T_{hot} and T_{cold} are the hot and cold working temperatures, respectively [23]. If we consider the typical working temperature range ±25 K around the transition temperature for magnetic refrigerators ($T_{hot} - T_{cold} = 50$ K), then the useful RCP values of the samples are greatly reduced. The magnetocaloric properties of the investigated samples are presented in Table 2. The Gd doped sample shows larger maximum values of $|\Delta S_m|$ than $La_{1.4}Ca_{1.6}Mn_2O_7$. The significant improvement of the magnetic entropy changes is probably due to the larger magnetization of $La_{1.4}Gd_{0.2}Ca_{1.6}Mn_2O_7$ for magnetic fields higher than 2 T. Even though the RCP(S) values for the Gd doped sample are lower, the useful cooling efficiency calculated as $\Delta S_{Max} \times 50$ K are higher.

Table 2

Magnetocaloric properties of $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ manganites under magnetic field changes of 2 T and 4 T

	$La_{1.4}Ca_{1.6}Mn_2O_7$		$La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$	
	ΔB = 2 T	ΔB = 4 T	ΔB = 2 T	ΔB = 4 T
T_{max} (K)	106	107	83	86
$\|\Delta S_{Max}\|$ (J/kgK)	0.34	0.66	0.42	0.81
δT_{FWHM} (K)	139	154	72	93
RCP(S) (J/kg)	47.3	101.6	30.2	75.3
$\Delta S_{Max} \times 50$ K (J/kg)	17	33	21	40.5
RCP(S)/ΔB (J/kgT)	23.6	25.4	15.1	18.8
$\Delta S_{Max} \times 50$ K /ΔB (J/kgT)	8.5	8.3	10.5	10.1

4. CONCLUSIONS

Polycrystalline double layered manganites $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ (x = 0.0, 0.2) were synthesized by a direct sol-gel method. The partial substitution of La with Gd ions does not change the crystal structure, but increases the inter-layer lattice distortion causing the reduction of the exchange interaction strength. There are clear differences between FC and ZFC magnetizations at low temperatures indicating a spin-glass like behaviour, which may be due to frustration of random competing ferromagnetic and antiferromagnetic interactions together with the anisotropy originating from layered structure. The magnetic measurements support the picture of a canted spin arrangement in $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ double layered manganites and indicate an increased Mn effective magnetic moment in $La_{1.2}Gd_{0.2}Ca_{1.6}Mn_2O_7$. Also the Gd doped sample shows larger maximum values of $|\Delta S_m|$ located at temperatures near the magnetic transition one and higher cooling efficiency than $La_{1.4}Ca_{1.6}Mn_2O_7$. The high RCP(S) values together with the broadened magnetic entropy curves and the absence of magnetic hysteresis at temperature higher than 70 K suggest the possibility to use $La_{1.4-x}Gd_xCa_{1.6}Mn_2O_7$ double layered manganites for magnetic refrigeration devices.

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