A brief discussion of the magnetocaloric effect in thin films of manganite doped with chromium

G Campillo 1, A I Figueroa 2, O Arnache 3, J Osorio 3, J M Marín Ramírez 3 and L Fallarino 4

1 Facultad de Ciencias Básicas. Universidad de Medellín. Medellín, Colombia
2 Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Spain
3 Grupo de Estado Sólido, Instituto de Física. Facultad de Ciencias Exactas y Naturales. Universidad de Antioquia, Calle 70 No. 52-21, Medellín, Colombia
4 Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Bautzner Landstrasse 400, 01328 Dresden, Germany

E-mail: gecampillo@udem.edu.co

Abstract. In this work we report on the magnetocaloric effect of La$_{2/3}$Ca$_{1/3}$MnO$_3$ (LCMO) and La$_{2/3}$Ca$_{1/3}$Mn$_{0.94}$Cr$_{0.06}$O$_3$ (LCMCrO) manganite thin films grown by DC magnetron sputtering on LaAlO$_3$ (100) substrates. X-ray diffraction shows that both doped and undoped films crystallize in the orthorhombic structure. Magnetic measurements show a decrease in both the Curie temperature, $T_C$, and the saturation magnetization, $M_S$, for the LCMCrO sample. The change in the magnetic entropy ($\Delta S_m$) was extracted from hysteresis loops at different temperatures around the ferromagnetic to paramagnetic transition, displaying a maximum of entropy change ($\Delta S_{m\text{max}}$) near $T_C$ in both films. Moreover, a shift in $(\Delta S_{m})_{\text{max}}$ toward temperatures above $T_C$ with increasing magnetic field and a broadening of the entropy change curve were observed. Results of refrigeration cooling power show a lower efficiency for LCMCrO. In order to obtain a local insight into the magnetic interactions of these films, measurements of X-ray absorption spectroscopy and X-ray magnetic circular dichroism (XMCD) were performed. XMCD suggests that an antiferromagnetic coupling between Mn$^{3+}$ - Mn$^{3+}$ is favored with Cr$^{3+}$ incorporation, which reduces the Mn $L_2,3$ XMCD signal and results in a decrease of $M_S$ and $(\Delta S_{m})_{\text{max}}$ in LCMCrO films.

1. Introduction

In the magnetic refrigeration technology, the magnetocaloric effect (MCE) has been recently explored as a promising property of some solid magnetic materials [1,2] since it is a low cost environment-friendly refrigeration process compared to the traditional one. It is defined as the thermal response of a magnetic material to an external magnetic field. The MCE is associated to the change of the magnetic entropy $\Delta S_{m}$, which originates in the coupling of atomic magnetic moments. Manganite oxides are among the potential materials to be employed in magnetic refrigeration due to their MCE values in a wide range of temperatures and their low cost for fabrication [2]. La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) thin films in particular have shown an increase in the refrigeration efficiency, which is a key property for the development and design of refrigerant materials at the nanoscale [3]. Properties of manganite compounds display a great variety of magnetic phases with a series of charge, spin and orbital ordering.
phenomena [4]. LCMO exhibits a paramagnetic (PM) to ferromagnetic (FM) phase transition, with a high Curie temperature $T_C$ for $x = 0.33$, La$_{0.67}$Ca$_{0.33}$MnO$_3$. From the theoretical point of view, the magnetic and transport properties of manganites have been traditionally interpreted in terms of the double exchange (DE) mechanism [4], which involves hopping of $e_g$ electrons between transition metal ions Mn$^{3+}$ and Mn$^{4+}$ via the oxygen atom. Thus, the competition between different magnetic phases depends on the valence states of the Mn atoms. However, such DE model does not provide a full picture of the mechanisms governing all the physical properties of these compounds.

Mn-site substitution with trivalent metals in LCMO has been the focus of several studies [5], aiming at investigating the role of the dopant in the balance of Mn$^{3+}$ and Mn$^{4+}$ interactions. Doping at the Mn site has shown a clear effect in the FM transition and, as a consequence, in the magnetocaloric behavior of LCMO. Studies of partial substitution at the Mn site have explored how to control the magnetic entropy change and have provided insight into the physical properties of these materials [6]. Cr is the ideal element of choice due to the similar ionic radius and electronic structure to that of Mn, if we compare Cr$^{3+}$ and Mn$^{4+}$. Even though different studies have shown a weak coupling between Mn and Cr spins in a wide range of Mn/Cr relative occupancy, it has been challenging to elucidate the real interaction between Mn and Cr ions. In fact, these interactions have been object of current research topics [7,8].

In this work, we explore the MCE in La$_{2/3}$Ca$_{1/3}$MnO$_3$ (LCMO) and La$_{2/3}$Ca$_{1/3}$Mn$_{0.94}$Cr$_{0.06}$O$_3$ (LCMCrO) manganite thin films with a thickness of 260 nm, grown on LaAlO$_3$ (LAO) substrate. The magnetic entropy change has been analyzed by magnetization measurements up to 10 kOe. The local electronic and magnetic properties have been studied by element selective X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD), which provide unparalleled information about the magnetic interactions between Cr and Mn ions in LCMO and LCMCrO films, beyond conventional macroscopic magnetometry [9-11]. These results have been correlated to the MCE properties of the LCMCrO films and would provide further understanding of materials with potential application in magnetic refrigeration.

2. Experimental

LCMO and LCMCrO films with a thickness of 260 nm were grown on (100)-LAO single-crystal substrates by dc magnetron sputtering under identical deposition conditions. X-ray diffraction (XRD) and rocking curves were obtained using a Bruker D8 diffractometer using incident Cu-Kα1 radiation. Magnetometry measurements were performed in a Quantum Design SQUID – VSM evercool. Zero field cooling (ZFC) curves of magnetization as a function of temperature were measured while warming up in 500 Oe after cooling at 0 Oe. The magnetic field was applied in the plane of the sample. XAS and XMCD spectra at the Mn L$_{2,3}$ edges were measured using a bending magnet and a VLS-PGM monochromator with fixed exit slit and refocusing mirror. The XMCD signal was obtained by applying a magnetic field of 10 kOe along the X-ray beam direction at a temperature of 80 K. The angle of incidence of the X-rays was 60° with respect to the sample surface normal. XMCD was recorded using the difference of XAS spectra measured at fixed helicity by flipping the magnetic field orientation. XANES spectra at the Mn K edges were performed at room temperature. Acquisition was performed with a nine-element Ge fluorescence detector in quick-EXAFS mode using the monochromatic beam of the Si(111) crystal.

3. Results and discussion

Figure 1(a) shows the indexed XRD pattern for the LCMCrO film, with the (h00) LAO substrate and (0k0) LCMCrO film reflections. A single orthorhombic phase was identified in the Cr-doped films. The lattice parameters for LCMO and LCMCrO films were calculated as 0.3847(3) nm and 0.3875(9) nm, respectively. Cr-doping of the film results in a slight increase of lattice parameter with respect to LCMO and that reported for bulk LCMCrO (0.3857 nm [12]). A rocking curve was recorded around the (020)
peak at $\sim 23.5^\circ$ in order to check the degree of orientation of the LCMCrO film, as shown in Fig 1(b). The full-width at half-maximum (FWHM = $\Delta \theta$) was obtained from fits using Gaussian and Lorentzian functions, which yielded values of 0.237° and 1.347°, respectively. These results suggest that there are two regions having different degrees of orientation: i) the narrow peak corresponds to a highly oriented interfacial region close to the substrate, and ii) the wider peak to a more distorted region away from it. The co-existence of two crystallographic phases is influenced by the presence of Cr, which contributes to structural disorder in the manganite. This intrinsic disorder can be related to strain effects due to the compression on the film by the substrate. Despite strain effects and mismatch with the substrate, relaxation in the 260 nm thick LCMCrO film is evident.

Figure 1(c) shows the temperature dependence of the ZFC magnetization of LCMO and LCMCrO films, performed under an applied field of 500 Oe. Both LCMO and LCMCrO samples show a PM - FM phase transition, with a Curie temperature, $T_C$, of 228 K and 192.5 K, respectively, as calculated from the minimum of the first derivative of the $M(T)$ curve. The saturation magnetization $M_S$, as obtained from hysteresis loops at low temperature, is estimated to be 545 emu/cm$^3$ and 132 emu/cm$^3$ for LCMO and LCMCrO, respectively. A clear decrease in both $T_C$ and $M_S$ is found for the LCMCrO sample. However, whereas $M_S$ reduction is close to 80% for the LCMCrO film, its $T_C$ is only about 15% lower than that for the undoped LCMO sample. These results evidence a strong influence in the FM ordering as consequence of the Cr doping on these manganite films. The magnetic transition in LCMCrO is less sharp than that for LCMO, and it extends both above and below $T_C$. An increased transition width and a lower $M_S$ at low temperature are signatures of a reduction in magnetization possibly because of increasing antiferromagnetic order in the system.

The MCE response of the LCMCrO film was studied by measurements of isothermal magnetization curves as a function of field, $M(H)$, at different temperatures near $T_C$, Fig. 2(a). $M(H)$ curves reach saturation above 2 kOe. All isotherms were recorded at intervals of 1 K and measured by sweeping the external magnetic field from 10 kOe down to remanence.

In a magnetic material, the magnetic entropy change, $\Delta S_H$, in response to an external magnetic field can be determined from temperature and field dependent magnetization measurements following the Maxwell equation [2]:

$$\Delta S_H(T, \Delta H) = \int_0^{H} \frac{\partial M(T, H)}{\partial T} dH.$$  

From $M(H)$ measurements at different temperatures at small discrete field values, $\Delta S_H$ is approximately

$$\Delta S_H(T, \Delta H) = S_H(T, H) - S_H(T, 0) = \sum_i \frac{M(T, H) - M(T, 0)}{T_{i+1} - T_i} \Delta H,$$

(1)

where $M(T, H)$ and $M(T, 0)$ are the magnetization values at temperatures $T_{i+1}$ and $T_i$, respectively. The temperature dependent isothermal magnetic entropy change $\Delta S_H$ for the LCMCrO film was calculated from Eq. (1) and its temperature dependence near $T_C$ is plotted in Fig. 2(b). $\Delta S_H$ for the LCMCrO film exhibits a maximum $(\Delta S_H)_{max}$ near $T_C$, but the temperature at which this peak appears
shifts slightly towards higher values above $T_c$ as the field increases. Such a displacement reaches $\sim 210$ K at 10 kOe, the maximum magnetic field applied. Similarly, $(\Delta S_M)_{\text{max}}$ changes from 0.035 mJ/cm$^3$K at 500 Oe up to 0.62 mJ/cm$^3$K at 10 kOe. The inset of Fig. 2(b) shows the temperature dependence of $\Delta S_M$ for the LCMO sample. In this case, the displacement of $(\Delta S_M)_{\text{max}}$ shifts with increasing $H$ from 230 K up to 238 K at 10 kOe and $(\Delta S_M)_{\text{max}}$ increases from 1.7 mJ/cm$^3$K up to 6.4 mJ/cm$^3$K.

An efficient refrigerant material satisfies both conditions of having a high $\Delta S_M$ value and a broad $\Delta S_M(T)$ curve. The magnetic capacity of a magnetocaloric material can be evaluated by considering the magnitude of $(\Delta S_M)_{\text{max}}$ and its full-width at half maximum ($\delta T_{\text{FWHM}}$). The product of the $\Delta S_M$ peak and the $\delta T_{\text{FWHM}}$ ($\delta T = T_2 - T_1$) is the relative cooling power (RCP). The RCP values at various intervals of magnetic fields were estimated for LCMO and LCMCrO samples. The RCP for the LCMCrO sample was found to be lower than that for LCMO, which translates in a reduction of $\sim 85\%$ in efficiency at 10 kOe for the former. This result is in agreement with the reduction in magnetization due to Cr-doping in the manganite, as well as with a possible increase of antiferromagnetic order that affects $(\Delta S_M)_{\text{max}}$.

In order to provide further insight into the local magnetic interactions of the LCMCrO system and their role in its MCE properties, qualitative analysis of XAS and XMCD measurements at the Mn $K$ and $L_{2,3}$ edges were performed. XAS and XMCD measurements at the Mn $L_{2,3}$ edges on the LCMO and LCMCrO films are shown in Fig. 3(a) and 3(b), respectively. Changes in the electronic structure of LCMCrO are evident from the XAS spectra. In particular, an increase of the features related to Mn$^{3+}$.
sites (peak A in Fig. 3(a)) is observed, which can be interpreted as incorporation of \(\text{Cr}^{3+}\) onto \(\text{Mn}^{4+}\) sites in the LCMO structure. X-ray absorption near edge (XANES) spectra at the Mn K depicted in Fig. 3(c) show a similar increase in the \(\text{Mn}^{3+}\) character with Cr doping. The amplitude of the XMCD signal plotted in Fig. 3(b) is proportional to the projection of the net magnetization of Mn along the X-ray beam. A decrease in the Mn \(L_{2,3}\) XMCD signal for the LCMCrO film compared to the pure LCMO sample suggests that an antiferromagnetic (AFM) coupling between \(\text{Mn}^{4+} - \text{Mn}^{4+}\) is favored by \(\text{Cr}^{3+}\) incorporation into the lattice. As a result, AFM interactions between Mn and Cr ions are also favored.

These results evidence a strong influence of Cr-doping in the FM ordering of these manganite films. Substitution of \(\text{Cr}^{3+}\) onto \(\text{Mn}^{3+}\) sites yields important interactions associated with chemical bonding in these structures, such as FM interactions via superexchange, DE coupling, or AFM interaction at the \(\text{Cr}^{3+}\)-O-\(\text{Mn}^{4+}\) bonds. There is, for instance, a competition between FM and AFM interactions in Cr-doped manganites. The decrease in magnetization is very likely to be a consequence of an increase in AFM interactions between \(\text{Cr}^{3+}\)-\(\text{Mn}^{4+}\) and \(\text{Cr}^{3+}\)-\(\text{Cr}^{3+}\) ions. Such a behavior would explain the decrease in MCE and the reduction of ~85% in the efficiency at 10 kOe observed in LCMCrO.

4. Conclusions

In summary, we have studied the magnetocaloric properties in \(\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3\) and \(\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{0.96}\text{Cr}_{0.04}\text{O}_3\) manganite thin films growth on \(\text{LaAlO}_3\) (100) substrates. Macroscopic and microscopic magnetic measurements, as well as local electronic structure investigated by XAS at the Mn K and \(L_{2,3}\) edges, revealed that FM interactions are affected by Cr-doping, which is reflected in their magnetocaloric properties. A wider magnetic ordering transition, accompanied by a decrease in \(T_c\), XMCD signal at the Mn \(L_{2,3}\) and \(M_5\) at low temperature reveals a reduction in the net magnetization in the LCMCrO film. An increase in AFM order in the system is the most likely scenario to explain these observations. As \(\text{Cr}^{3+}\) incorporates into the LCMO lattice, an increase in the \(\text{Mn}^{3+}\) character would favor AFM coupling between \(\text{Mn}^{4+} - \text{Mn}^{3+}\), \(\text{Cr}^{3+}\)-\(\text{Mn}^{4+}\) and \(\text{Cr}^{3+}\)-\(\text{Cr}^{3+}\) ions, which, at the same time, results in a reduction of \(M_S\), \((\Delta S_m)_{\text{max}}\) and affects the MCE in LCMCrO films.

Acknowledgements

Beamtime at the Advanced Light Source beamline 6.3.1 and Diamond Light Source beamline B18, including the support from the beamline staff, are acknowledged. J.M.M. acknowledges Colciencias for his Ph.D. fellowship. This work was supported by: the Solid State Group – GES Sustainability Strategy 2018-2019 CODI – Universidad de Antioquia and the Project 800 of Vicerectoría Investigaciones of Universidad de Medellín.

References

[1] V.K. Pecharsky, K.A. Gschneidner, A.O. Tsokol, Rep. Prog. Phys. 68 (2005) 1479; O. Taoreed, et al.; AIP Advances 6, (2016) 105009.
[2] A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and Its Applications* (IOP Publishing Ltd, Bristol and Philadelphia, 2003).
[3] X. Moya, et al.; Nature Mat. 12 (2013) 52-58.
[4] E. Dagogot, *Colossal magnetoresistive Oxides*, editado por Y. Tokura, Gordon and Breach Sciences Publishers, New York, 2000; C. Zener, Phys. Rev. 81, 4, (1951) 440.
[5] A. Barnabe, et al.; Appl. Phys. Lett. 71, 3907 (1997); Vanitha, et al.; J. Solid State Chem. 137 (1998) 365; O. Arnache, D. Giratá, A. Hoffmann, Phys. Rev. B 77, (2008) 214430.
[6] A. Marzouki-Ajmi, et al.; J. Magn. Magn. Mater. 433 (2017) 209-215.
[7] C. Shang, et al.; Physica B 502 (2016) 39.
[8] Abdessalem Dhahri, Sobhi Hcini, Aref Omri, Lamjed Bouaziz, J. Alloy. Compd. 687 (2016) 521.
[9] H. Terashita, et al.; Phys. Rev. B 85 (2012) 104401.
[10] A. I. Figueroa, et al.; Superlattices Microstruct. 87 (2015) 42.
[11] Vladimir I. Grebennikov, et al.; J. Magn. Magn. Mater. 440 (2017) 79.
[12] F. Rivadulla, et al.; Phys. Rev. B 62 9 (2000) 5678.