EPJ Web of Conferences **75**, 04006 (2014)
DOI: 10.1051/epjconf/ 201475 04006

Magnetocaloric effect and temperature coefficient of resistance of $La_{0.85}Ag_{0.15}MnO_3$ epitaxial thin films obtained by polymer-assisted deposition

R. Cobas Acosta[1,a], S. Muñoz-Pérez[1,2], J. M. Cadogan[1], W.D. Hutchison[1] and M. C. Ridgway [2]

[1]School of Physical, Environmental and Mathematical Sciences, The University of New South Wales, Canberra, ACT 2610, Australia
[2]Department of Electronic Materials Engineering, Research School of Physics and Engineering, Australian National University, Canberra, ACT 0200, Australia

Abstract. We report the magnetocaloric effects and temperature coefficient of resistance (TCR) of $La_{0.85}Ag_{0.15}MnO_3$ epitaxial thin films grown on single-crystal substrates of $LaAlO_3$ (001) and $SrTiO_3$ (001) using the chemical solution approach of polymer-assisted deposition (PAD). The film thicknesses are in the range 30-35 nm. Magnetocaloric effects, with entropy changes of -2.14 J/kg.K, in the case of the $LaAlO_3$ substrate and -2.72 J/kg.K for the $SrTiO_3$ substrate, (corresponding to a magnetic field variation of 2T) were obtained at room temperature. The refrigeration capacity at this field variation reached large values of 125 J/kg and 216 J/kg, indicating that these films prepared by PAD have the potential for microcooling applications. The temperature coefficient of resistance has been calculated from the resistivity measurements. A maximum TCR value of 3.01 % K^{-1} was obtained at 309 K, which shows that these films also have potential as uncooled thermometers for bolometric applications.

1 Introduction

There has been an increase in the demand for localized cooling and temperature stabilization of micro and opto-electronic devices [1-3] since (i) the number of components in an integrated circuit continues to increase, and (ii) modern devices demand ever smaller chips at an accelerated pace. The manufacture of micro-systems using magnetic refrigeration technology seems to be a promising alternative for thermo-electric microcooler applications [3, 4]. In this context, high quality and inexpensive thin films suitable for magnetic refrigeration applications near room temperature could play an important role in the development of these micro-refrigeration devices.

Magnetic refrigeration technology (MRT) is based on the magnetocaloric effect exhibited by magnetic solids upon application of an external magnetic field [5]. Using magnetic refrigeration has two considerable advantages: (i) high cooling efficiency and (ii) it avoids the use of ozone-depleting or global-warming gases.

The keys issues in using magnetic refrigeration at room temperature are: (i) find a suitable material that produces a large entropy and temperature change when it undergoes a magnetization–demagnetization process, by means of relatively low $\mu_0\Delta H$ between 1 and 2 T, and (ii) obtain samples with high chemical stability at low cost, resulting from an easy and scalable sample preparation route.

In the present work, high quality epitaxial thin films of $La_{0.85}Ag_{0.15}MnO_3$ (LAMO) have been grown on (001)-oriented $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) single-crystal substrates, using a cost-effective method. The magnetocaloric effects and temperature coefficient of resistance of the films have been investigated. The magnetic entropy changes extracted from the isothermal magnetization and resistivity curves are reported in the temperature range from 100 to 330 K, for $\mu_0\Delta(H)$ = 1, 2, 3 and 5 T.

2 Results and Discussion

The films were prepared by the chemical solution approach of polymer-assisted deposition following a procedure previously reported [6]. The film thicknesses were determined to be in the range 30-35 nm as shown in the inset of fig. 1. The crystal structure of the films was analyzed by x-ray diffraction using a PANalytical X'Pert PRO Extended MRD diffractometer. The x-ray patterns exhibited only the (00*l*) diffraction peaks from the LAMO structure, indicating that the films grew epitaxially on both the LAO and STO substrates. The out-of-plane ($a_\perp$) lattice parameters were estimated from the

[a] Corresponding author: R.CobasAcosta@adfa.edu.au

(002) reflections (see Fig. 1) and are in good agreement with the results from the reciprocal space maps recorded around the (103) reflection [6].

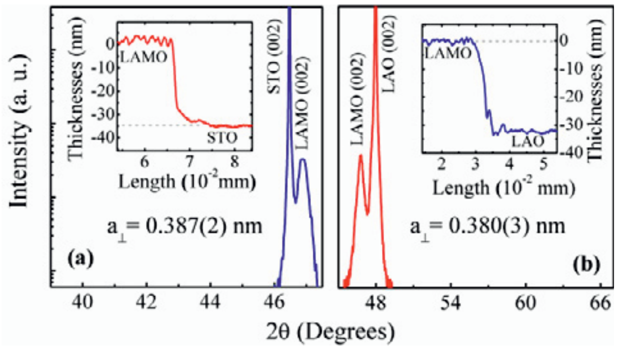

Figure 1. X-ray pattern recorded around the (002) reflection for (a) LAMO/LAO and (b) LAMO/STO. Inset: Thicknesses determined with a Bruker DektakXT stylus profiler.

The magnetic entropy change ΔS_M (T,H) of a material upon application of an external magnetic field (H) is given by the thermodynamic Maxwell relation

$$\Delta S_M(T,H) = \mu_0 \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH \qquad (1)$$

where M(T, H) is the isothermal magnetization measured at successive magnetic field and temperature intervals.

Figure 2a shows the LAMO/LAO isothermal magnetization curves measured at selected temperatures between 100 and 314 K after subtracting the substrate's contribution. From the magnetization curves (using Eq. (1)) we derived the magnetic entropy change caused by the variation of the magnetic field from zero to 1, 2 and 3T (see Fig. 2b). Figure 3 shows the results for LAMO/STO at the same $\mu_0\Delta H$ variations in the temperature window between 100 K and 330 K.

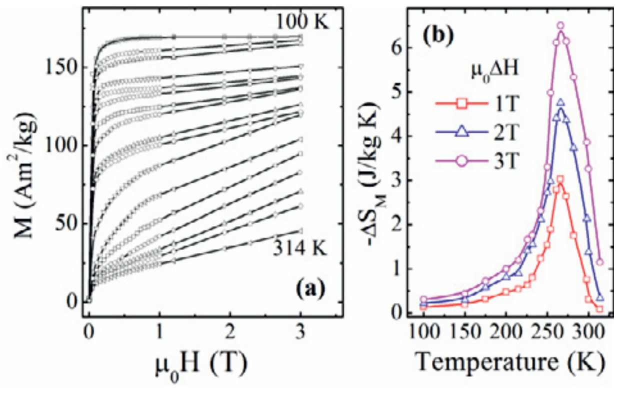

Figure 2. (a) Isothermal magnetization curves of LAMO/LAO at different temperatures as a function of applied magnetic field. (b) Magnetic entropy change at a magnetic field variation of 1, 2 and 3 T as a function of temperature.

A broad uniform peak in the entropy change occurs close to the Curie temperature. According to Eq. (1) the largest entropy change is expected close to the ferromagnetic transition temperature, where the magnetization increases rapidly and the change $(\partial M/\partial T)_H$ attains a maximum value. Therefore, the peak positions follow the same trend observed in the derivative -dM/dT of the isothermal magnetization curves (not shown).

The maximun entropy change of ΔS_M^{max} = -6.50 J/kg.K occurs at 273 K for LAMO/LAO with $\mu_0\Delta H$ = 3T (see fig. 2b). For LAMO/STO a sizable entropy change of -3.95 J/kg.K is achieved at 290 K; see also fig. 3a and table 1. It is interesting to note that for $\mu_0\Delta H$ = 1T, the entropy change value of -3.03 J/kg.K for LAMO/LAO is close to that observed in Gd. This result is relevant because it encompasses the operational temperature range of a magnetic refrigerant. Furthermore, the magnetocaloric effect in both samples occurs inside the temperature range required for commercial applications (see fig. 2b and 3b). A working temperature range of 45 K around room temperature was estimated from the full-width at half maximum (FWHM) for LAMO/STO at $\mu_0\Delta H$ = 1T. The magnetic cooling efficiency or relative cooling power (RCP) in each case can be calculated considering the product ΔS_M^{max}(H) × δT_{FWHM}. RCP values were obtained in the range 70 – 324 J/kg, in good agreement with the best data reported for doped manganites at the corresponding field [6].

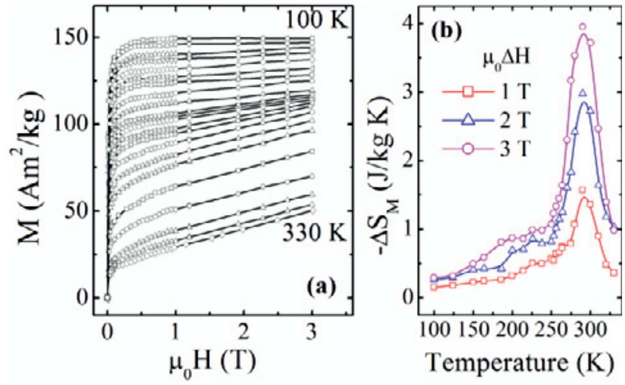

Figure 3. (a) Isothermal magnetization curves of LAMO/STO at different temperatures as a function of applied magnetic field. (b) Entropy change for a field variation of 1, 2 and 3 T as a function of temperature.

Table 1. Relative cooling power and the maximum magnetic entropy change for both films.

LAMO/LAO $\mu_0\Delta H$(T)	-ΔS_M^{max}(273 K) (J/kg.K)	RCP (J/kg)
1	3.03	106
2	4.75	216
3	6.50	324
LAMO/STO $\mu_0\Delta H$(T)	-ΔS_M^{max}(290 K) (J/kg.K)	RCP (J/kg)
1	1.57	70
2	2.98	125
3	3.95	165

The differences in the peak position and the magnitudes of ΔS_M (T, H) in LAMO films grown on LAO and STO substrates are related to differences in the strain relaxation mechanisms. Similar results were observed in the colossal magnetoresistance (CMR) properties, where the LAMO/LAO films also display the most negative CMR values. The LAMO magnetic and CMR properties were strongly modified by the type of substrate, due to different strain relaxation mechanisms [6].

These similarities suggest that there is a physical mechanism that connects the magnetic entropy change and CMR. Indeed, Xiong *et al.* [7] have established an interesting relationship between magnetic entropy change and resistivity ρ(T, H) for the manganites:

$$\Delta S \sim \mu_0 \int_0^H \left[\frac{\partial \ln(\rho)}{\partial T}\right]_H dH \qquad (2)$$

In order to make the same comparison for LAMO/LAO magnetic entropy changes as a function of temperature for $\mu_0\Delta H$ =1, 2, and 5 T were calculated from the resistivity measurements using Eq. (2). The results are shown in Fig. 4a. Figure 5a shows the same study performed on LAMO/STO with the same magnetic field variations. The results are summarized in table 2.

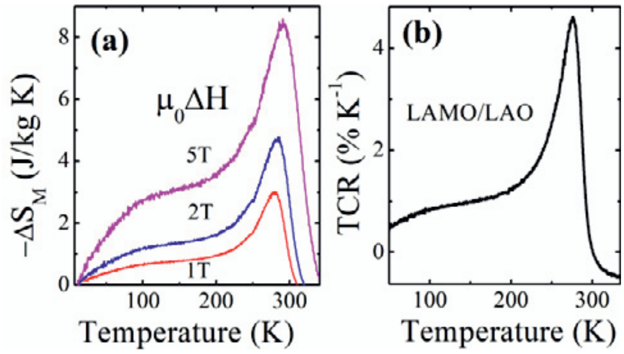

Figure 4. (a) Entropy change for field variations of 1, 2 and 5 T as a function of temperature for LAMO/LAO. (b) Temperature coefficient of resistance.

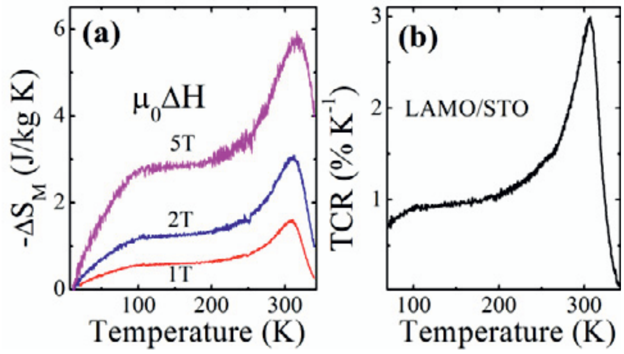

Figure 5. (a) Entropy change for field variations of 1, 2 and 5 T as a function of temperature for LAMO/STO. (b) Temperature coefficient of resistance.

Table 2. Relative cooling power and the maximum magnetic entropy change for both films.

	$\mu_0\Delta H$ (T)	T (K)	$-\Delta S_M^{max}$ (J/kg.K)	TCR (% K^{-1})
LAMO/LAO	1; 2; 5	280	2.96; 4.67; 8.52	4.65
LAMO/STO	1; 2; 5	309	1.56; 3.03; 5.83	3.01

As expected, a deviation in the ΔS_M(H,T) curves occurs in the temperature range below 250 K, where the system is in an almost saturated ferromagnetic state [8]. However, the of ΔS_M^{max} from resistivity is in good agreement with the values obtained from the magnetization curves in the temperature region $\Delta T \sim \delta T_{FWHM}$, during the establishment of ferromagnetic order.

In addition, we also report the temperature coefficient of resistance (TCR) calculated as $(1/R)(dR/dT)$x100% which is important for infrared applications and temperature controlled resistance devices [6]. The maximum TCR values are 4.65% K^{-1} at 280 K and 3.01% K^{-1} at 309 K, for LAMO/LAO (Fig. 4b) and LAMO/STO (Fig. 5b) respectively. These values are slightly higher than those reported in manganite thin films being considered for bolometric applications, in which the TCR coefficient in the 1–3 % K^{-1} range [9].

4 Conclusions

In summary, we have studied the magnetocaloric effect of $La_{0.85}Ag_{0.15}MnO_3$ epitaxial thin films grown on single crystal substrates of $LaAlO_3$ and $SrTiO_3$ using polymer-assisted deposition. The substantial values observed for the coefficients RCP, TCR and for ΔS_M in both films are particularly remarkable because they occur below and around room temperature. This suggests that silver-doped manganite epitaxial thin films obtained via PAD are good candidates for use in magnetic micro-refrigeration technology and they also have the potential to enable the fabrication of high sensitivity bolometers at room temperature.

Acknowledgements

This work was supported by the University of New South Wales. A portion of this work was performed at the ACT node of the Australian National Fabrication Facility.

References

1. X. Fan, G. Zeng, Ch. LaBounty, J. E. Bowers, Appl. Phys. Lett. **78**, 1580 (2001).
2. H. S. Cao, H. J. Holland, C. H. Vermeer, S. Vanapalli, P. P. P. M. Lerou, M. Blom, H. J. M. ter Brake, J. Micromech. Microeng. **23,** 065022 (2013).
3. S. Kim, S. Ghirlanda, C. Adams, B. Bethala, S.N. Sambandam, S. Bhansali, Int. J. Energy Res. **31**, 717(2007).
4. A. M. Pereira, J. C. Soares, J. Ventura, J. B. Sousa, J. P. Araujo, J. C. Oliveira, J. Nanosci. Nanotechnol. **10**, 2590 (2010).
5. P. Debye, Ann. Phys. **81**, 1154 (1926).
6. R. Cobas, S. Muñoz-Pérez, J. M. Cadogan, T. Puig, X. Obradors, Appl. Phys. Lett. **99**, 083113 (2011).
7. C. M. Xiong, J. R. Sun, Y. F. Chen, B. G. Shen, J. Du, Y. X. Li, IEEE Trans. Magn. **41**, 122 (2005).
8. A. Goyal, M. Rajeswari, R. Shreekala, S. E. Lofland, S. M. Bhagat, T. Boettcher, C. Kwon, R. Ramesh, T. Venkatesan Appl. Phys. Lett. **71**, 2535 (1997).
9. F. Yang, L. Méchin, J. M. Routoure, B. Guillet, R. A. Chakalov, J. Appl. Phys. **99**, 024903 (2006).