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<tr>
<td><strong>Citation</strong></td>
<td>Kumar, V. S., Chukka, R., Chen, Z., Yang, P., Chen, L. (2012). Strain dependent magnetocaloric effect in La0.67Sr0.33MnO3 thin-films. AIP Advances, 3(5), 052127-.</td>
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<td><strong>Date</strong></td>
<td>2013</td>
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<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10220/10952">http://hdl.handle.net/10220/10952</a></td>
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Strain dependent magnetocaloric effect in La$_{0.67}$Sr$_{0.33}$MnO$_3$ thin-films

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(Received 2 April 2013; accepted 13 May 2013; published online 20 May 2013)

The strain dependent magnetocaloric properties of La$_{0.67}$Sr$_{0.33}$MnO$_3$ thin films deposited on three different substrates (001) LaAlO$_3$ (LAO), (001) SrTiO$_3$ (STO), and (001) La$_{0.7}$Sr$_{0.3}$Al$_{0.65}$Ta$_{0.35}$O$_9$ (LSAT) have been investigated under low magnetic fields and around magnetic phase transition temperatures. Compared to bulk samples, we observe a remarkable decrease in the ferromagnetic transition temperature that is close to room temperature, closely matched isothermal magnetic entropy change and relative cooling power values in tensile strained La$_{0.67}$Sr$_{0.33}$MnO$_3$ films. The epitaxial strain plays a significant role in tuning the peak position of isothermal magnetic entropy change towards room temperature with improved cooling capacity.

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There has been a passionate search for the materials exhibiting magnetocaloric effect (MCE), which would meet the prospect of efficient magnetic cooling near room temperature. The motivation essentially comes from the fact that the refrigerants that are greenhouse gases can successfully be replaced by environmental friendly solids with higher efficiency. The magnetocaloric materials (MCM) that have been investigated so far cover a very wide spectrum of material families, some of them include elemental Gd,¹ Laves Phases,²,³ Gd$_5$(Si,Ge)$_4$ family,⁴,⁵ manganites,⁶ amorphous alloys,⁷,⁸ and other materials in the form of thin-films⁹,¹⁰ and superlattices.¹¹,¹² In a broader perspective, these materials are categorized into those exhibiting first order phase transitions (FOP) and second order phase transitions (SOPT). Even though materials with SOPT are preferred for practical purposes, both the categories attract the attention from the fundamental point of view. Majority of the studies on MCE in bulk materials, mainly demonstrate the effects of different parameters like, structure, chemical composition, chemical substitution and nature of phase transitions on MCE, by means of direct and indirect measurements. More details on different materials and models studied to understand the above mentioned effects on MCE are summarized in the recent review article.¹³ In spite of the tremendous amount of work that has gone into the understanding and finding out potential MCMs in bulk, very few attempts have been made to explore the magnetic refrigeration (MR) properties in thin-film systems, which can be used in functional micro scale devices for refrigeration. The earlier attempts in the investigation of MCE for thin-films and multilayer/superlattices, show the results of magnetic entropy change associated with (i) chemical doping effecting the para-to-ferromagnetic phase transition temperature ($T_C$); (ii) field induced martensite transformations;¹⁰ and (iii) interfacial effects in thin-film heterostructures such as Co/Cr and LSMO/SRO superlattices.¹¹,¹²

Apart from the parameters listed above, another parameter which influences the $T_C$ and hence the MCE in case of thin-films is the epitaxial strain. In this article, we report the tuning of the
FIG. 1. AFM images of 20 nm-thick LSMO films grown on (a) LAO (b) LSAT and (c) STO substrates with the representative area and height being 2 \( \mu m \times 2 \mu m \) and the height profile mentioned in nm, respectively. The reciprocal space mapping around the pseudocubic (002) reflections of LSMO films on (d) LAO substrates and (e) STO substrates.

magnetic phase transition temperature and accordingly temperature and field dependent change in magnetic entropy resulting from substrate induced strain on the La\(_{0.67}\)Sr\(_{0.33}\)MnO\(_3\) (LSMO) films, around the magnetic phase transition temperatures and at low fields. We observe that the substrate (STO) induced tensile strain not only helps to decrease the \( T_c \) remarkably and brings it nearer to the room temperature but also improves the MCE and cooling capacity of the material (LSMO).

Epitaxial LSMO films were grown by pulsed laser deposition using a KrF excimer laser on three different types of substrates, (001) LAO, (001) LSAT and (001) STO substrates, which provide lattice mismatch of \(-2\%\), \(-0.05\%\) and 0.9\%, respectively. These films were deposited at 780 °C, under an oxygen pressure of 27 Pa. The laser energy and repetition rates used were 1.5 J/cm\(^2\) and 5 Hz, respectively. The surface morphology was characterized by atomic force microscopy (Asylum Research MFP-3D) and high resolution reciprocal space mappings (RSM) and x-ray reflectivity studies were carried out at Singapore Synchrotron Light Source (\( \lambda = 1.5406 \) Å). The RSMs were plotted in reciprocal lattice units (r.l.u) of the substrates. The x-ray reflectivity measurements reveal that these films are of 20 nm thick. Magnetic properties of the LSMO thin-films were measured by Quantum Design MPMS in the temperature range around the respective phase transition temperatures and in the field range of 0 to 1.5 T. The magnetocaloric effect was determined from the magnetic isotherms recorded at different temperatures using the Maxwell equation

\[
\Delta S_m(T, H) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_{H} dH.
\]

To estimate magnetic entropy change (\( \Delta S_m \)), the above integration was numerically approximated to the equation

\[
\Delta S_m(T, H) = \frac{M(T, H) - M(0, T)}{T \lambda} \Delta H,
\]

where \( M(T, H) \) and \( M(0, T) \) are the magnetization values at temperatures \( T_{i+1} \) and \( T_i \), respectively for a magnetic field interval of \( \Delta H \). It is worth emphasizing here that the change in magnetic entropy depends on the temperature derivative of change in magnetization rather than the individual value of magnetization itself. Hence, while determining the \( \Delta S_m \) values, we have followed this strategy to eliminate the temperature independent substrate contribution, instead of individually eliminating it from the magnetic isotherms at different temperatures.

Fig. 1(a)–1(c) show the AFM images for \( \sim 20 \) nm thick LSMO films grown under optimal growth conditions on LAO, LSAT and STO, respectively. These images clearly indicate that all films are atomically smooth. LSMO in its bulk form is a rhombohedral distorted pervoskite with a pseudocubic
lattice parameter of 3.87 Å. Therefore, the LSMO films grown on LAO and STO substrates exhibit in-plane compressive and out-of-plane tensile strain and out-of-plane compressive and in-plane tensile strain, respectively. Because of the small lattice mismatch, films grown on LSAT show weak out-of-plane tensile strain. From the RSMs, we estimated the out-of-plane lattice constants for these films grown on LAO, STO and LSAT to be 4.02, 3.872 and 3.908 Å, respectively, meaning that all the films are strained. A typical off-axis RSM and clear Laue oscillations around the film peak for LSMO film on LAO and STO substrates are shown in Fig. 1(d) and 1(e) evidencing that these films have identical in-plane positions, and are coherently strained and further indicating the high quality, good crystallinity and smooth surfaces of these films.

MCE in a material is evaluated either by the isothermal change in magnetic entropy ($\Delta S_m$) or by the adiabatic change in temperature ($\Delta T$). The isothermal change in magnetic entropy is determined by indirect methods, whereas the adiabatic change in temperature is measured directly. For a material to be a good magnetic refrigerant, large value of $\Delta S_m$ and a broad $\Delta S_m$ vs T curve are preferred along with a second order phase transition.

In Fig. 2(a), magnetization of LSMO/LSAT, LSMO/STO and LSMO/LAO, measured along the in-plane (100) direction under a magnetic field of 50 Oe is plotted as a function of temperature in the temperature range 250–350 K. The inset of Fig. 2(a) shows the temperature dependent magnetization of the LSMO/LAO measured along (100) direction, under a field, $H = 50$ Oe, down to 135 K and the para-to-ferrromagnetic transition in this sample is spread over a wide temperature range unlike those of LSMO on LSAT and STO and the same has been clearly shown in the inset. The ferromagnetic transition temperatures for LSMO/LSAT ($T_C \sim 321$K) and LSMO/STO ($T_C \sim 312$K) have been estimated from the derivative of the temperature dependent magnetization curves measured along (100) direction. These values of $T_C$ are greatly suppressed from the $T_C$ of bulk $\sim 370$ K. The $T_C$ for LSMO/STO is further reduced compared to that of LSMO/LSAT and tending towards room temperature. The temperature dependent isothermal change in magnetic entropy determined from the in-plane magnetic isotherms M(H) measured in the temperature range 316–326 K and by using
representing the peak position of $\Delta S_m$ vs T curve, very much coincides with the $T_C$ ($\sim 321$ K). This is because the maximum change in the spontaneous magnetization occurs at $T_C$ that in turn is reflected in the change in magnetic entropy at that temperature. The peak position remains the same with increasing field, mainly due to the close lattice match between LSMO and LSAT results in retaining the second order nature of phase transition exhibited by LSMO. To observe the response of magnetic entropy change at low fields and around the $T_C$, the LSMO/LSAT sample is subjected to a maximum field of 1.5 T, and the temperature range is confined to 5 K above and below $T_C$. The maximum value of $\Delta S_m$ obtained is 1.47 J/kg K for $\Delta H = 1.5$ T and it is slightly higher compared to LSMO thin-films$^9$ reported earlier but less than that of LSMO/SRO superlattices.$^{12}$

The large spread in the $T_C$ for LSMO/LAO consequently results in a broad distribution of the peak in the temperature dependent $\Delta S_m$. Hence we have reported the isothermal magnetic entropy change exhibited by the substrate induced strain for LSMO/LSAT and LSMO/STO films only. Keeping in view of the thickness of the film ($\sim 20$ nm), the broad $T_C$ can be attributed to the inhomogeneity present in the sample. It is also known that LSMO thin-films on LAO can have coexistence of stable ferromagnetic (FM) and anti-ferromagnetic (AFM) phases depending on the thickness of the film and the epitaxial strain, induced by the mismatch of the substrate, and the FM phase can be driven more towards AFM phase with the increase of $c/a$ ratio.$^{14}$ Because the film in the present case is thin, it may be possible that the sharpness of $T_C$ has been influenced by the competition between the existing FM and AFM phases in LSMO film. This value of film thickness has been chosen for all the three thin-films so as to demonstrate the effect of substrate induced strain on MCE, as the thin-films with higher thickness may be relaxed.$^{15}$ As described before, our objective is to demonstrate the influence of substrate induced strain on MCE around the phase transition temperatures. So a comparison of isothermal magnetic entropy change between less compressive, nearly lattice matched LSMO/LSAT and tensile strained LSMO/STO thin-films around the respective phase transition temperatures has been made.

The temperature dependent isothermal change in magnetic entropy determined from the in-plane magnetic isotherms $M(H)$ measured in the temperature range 304–320 K, at temperature intervals of 2 K, are shown in Fig. 3(a), for LSMO/STO at $\Delta H = 1.5$ T. Compared to the temperature dependent $\Delta S_m$ behavior exhibited by LSMO/LSAT, the same curves for LSMO/STO are broader without considerable change in the peak value of $\Delta S_m$ and moreover the temperature corresponding to the peak has no deviation from the $T_C$ ($\sim 312$ K). Neither hysteresis in the magnetic isotherms nor any shift in the peak position of $\Delta S_m$ with the field is observed for LSMO/STO, confirming the second order nature of phase transition. Besides reduction in the $T_C$ and broadening of the $\Delta S_m$ vs T peak, presence of second order phase transition is an added advantage for magnetic refrigeration (MR) from the application point of view. The LSMO/STO sample is subjected to a maximum field of 1.5 T, and the temperature range is confined to 8 K above and below $T_C$. The maximum value of $\Delta S_m$ is 1.54 J/kg K for $\Delta H = 1.5$ T and it is almost the same as that of LSMO/LSAT. The $\Delta S_m$ values are 1.32, 1.1, 0.88 and 0.56 J/kg K for $\Delta H = 1.2$, 0.9, 0.6 and 0.3 T, respectively. These curves are more symmetric and difference between the $(\Delta S_m)_{\text{Max}}$ of any two consecutive curves is more uniform compared to those of LSMO/LSAT. The later feature is clearer in the $\Delta S_m$ vs H curves.

Fig. 3(b) shows the field dependent isothermal change in magnetic entropy for LSMO/LSAT and LSMO/STO in the field range 0–1.5 T, around the respective ferromagnetic phase transition temperatures. The field dependent curves for LSMO/LSAT, determined at very close temperatures, except the two curves at $T_C \pm 0.5$ K, almost coincide with one another and represent a linear growth of the $(\Delta S_m)_{\text{Max}}$ with field. On the other hand, the two curves at temperatures 320.5 and 321.5 K that are very close to $T_C$, show non-linear behavior at fields greater than 1 T. But as far as the low field behavior is concerned, we see a gradual increase of the $(\Delta S_m)_{\text{Max}}$ with field. In general, the height of the peak $(\Delta S_m)_{\text{Max}}$ at a particular temperature grows with the magnetic field, which does not follow the same law throughout the field range. All the field dependent $\Delta S_m$ curves of LSMO/STO follow a non-linear growth of the $(\Delta S_m)_{\text{Max}}$ starting from the low filed region. The $(\Delta S_m)_{\text{Max}}$, can be expressed in a power law with respect to field ($H^p$) but in the present case, the field is so week that the power law becomes invalid because it has been realized that the exponent ‘n’ itself is field dependent at low fields and it reaches its mean filed limit, $n = 2/3$, when the fields are high enough.$^{16}$
Another important parameter to evaluate the efficiency of MR of any magnetic material is Relative Cooling Power (RCP), which is defined as the product of \((\Delta S_m)_{\text{max}}\) and the corresponding Full width at Half Maximum (FWHM) of the \(\Delta S_m\) vs T curve and given by the following equation. \[ \text{RCP} = (\Delta S_m)_{\text{max}} \times \delta T_{\text{FWHM}}. \] This equation highlights the significance of having a large \(\Delta S_m\) value, a peak in \(\Delta S_m\) and distribution of peak of \(\Delta S_m\) vs T curve, which is reflected by means of \(\delta T_{\text{FWHM}}\). In other words, lack of well defined \(T_C\) and hence a peak in \(\Delta S_m\) for LSMO/LAO can be pointed out and relatively broader peaks in LSMO/STO compared to those of LSMO/LSAT can be quantified by the definition and values of RCP, respectively. A comparison between the field dependence of RCP values calculated for LSMO/LSAT and LSMO/STO is made in the inset of Fig. 3(b). The RCP value of LSMO/STO (50.16 J/kg) is greater than that of LSMO/LSAT (34.24 J/kg) under the field of \(H = 1.5\) T and interestingly, LSMO/STO films have predominantly greater RCP values throughout the field range. In fact, the RCP value for LSMO/STO obtained here is as high as the RCP for bulk LSMO\(^{17}\) under the same field with an appreciable reduction in the \(T_C\). This comparison clearly demonstrates that the substrate induced strain is conducive to improve the cooling efficiency of the material in the thin-film form.

To summarize, the role of substrate induced compressive and tensile strain in the LSMO thin-films on the isothermal entropy change and the cooling capacity has been highlighted and the possibility of achieving a near room temperature MCM with RCP as high as bulk samples is demonstrated in LSMO/STO thin-films.

ACKNOWLEDGMENTS

This work was supported by the Singapore National Research Foundation under CREATE program Nanomaterials for Energy and Water Management. V. S. Kumar is very thankful to Dr. Wang Baomin, Mr. Chen Weigang and Dr. You Lu for the helpful discussions and support in carryout thin-film deposition experiments with PLD.