Magnetocaloric effect and magnetic refrigeration in La$_{0.7}$Ca$_{0.15}$Sr$_{0.15}$Mn$_{1-x}$Ga$_x$O$_3$ (0 $\leq$ $x$ $\leq$ 0.1)

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Abstract. In this paper we report magnetic and magnetocaloric effect (MCE) properties for La$_{0.7}$ (CaSr)$_{0.3}$Mn$_{1-x}$Ga$_x$O$_3$ ($x$ = 0, 0.025, 0.05, 0.075 and 0.1) manganites. Our compounds were prepared by sol-gel method and characterized by X-ray diffraction and magnetization measurements. The temperature dependence of the magnetization $M(T)$ reveals a decrease of $M$ with increasing Ga content. The same behavior was observed for the Curie temperature $T_C$. MCE was calculated according to the Maxwell relation based on magnetic measurements. The magnetic entropy change ($\Delta S_M$) reaches a maximum value which decreases with increasing Ga content. It is found to decrease from 5.15 J/kgK for $x$ = 0 to 1.86 J/kgK for $x$ = 0.1 under an applied magnetic field of 5T. So, the studied samples could be considered as good materials for magnetic refrigeration for a large temperature interval near room temperature.

Keywords. Manganites, Magnetocaloric Effect, Magnetic refrigeration, Relative cooling power.

1 Introduction

The magnetocaloric effect is defined as the response of a magnetic material to an applied magnetic field and is apparent as a change in its temperature. It was discovered by Warburg [1] in 1881 and is intrinsic to all magnetic materials. In the case of ferromagnetic material, the material heats up when it is magnetized and cools down when the magnetic field is removed out. The magnitude of the MCE of a magnetic material is characterized by the adiabatic temperature change $\Delta T_{ad}$ or by the isothermal magnetic entropy change $\Delta S_M$ due to a varying magnetic field. The nature of the MCE in a solid is the result of the entropy variation due to the coupling of the magnetic spin system with the magnetic field [2].

Magnetic refrigeration is a method of cooling based on the MCE. The heating and cooling caused by a changing magnetic field are similar to the heating and cooling of a gaseous medium in response to compression and expansion. It has been shown later that the heating and cooling in the magnetic refrigeration process are proportional to the size of the magnetic moments and to the magnetic applied field. That is why research on magnetic refrigeration has been exclusively conducted on heavy rare-earth elements and their compounds [3, 4]. Among the rare-earth metals, gadolinium was found to show the highest MCE [4]. Since, the cost of this metal as a magnetic refrigerant is quite expensive (~4000 $/kg), further efforts to discover new materials exhibiting large MCE in response
to low applied field, are of significant importance. Among them, perovskite-type manganese oxide materials [5-11] having large MCEs are believed to be good candidates for magnetic refrigeration at various temperatures.

The manganite parent compound, LaMnO$_3$, is an antiferromagnetic insulator (AFI) characterized by a super exchange coupling between Mn$^{3+}$ sites facilitated by a single $e_g$ electron subjected to strong correlation effects. Substitution on La$^{3+}$ ion by a divalent or a monovalent ion results in a mixed valence states of Mn ($\text{Mn}^{3+}$ and $\text{Mn}^{4+}$), where $\text{Mn}^{4+}$ lacks $e_g$ electron, and hence the itinerant hole associated with $\text{Mn}^{3+}$ ion may hop to $\text{Mn}^{4+}$. The hopping is favorable only when the localized spins of these ions are parallel and this is the essence of double exchange (DE) mechanism [12] which is expected to explain the ferromagnetic metallic nature of manganites below metal–insulator transition temperature TMI. Millis et al. [13] stressed that the physics of manganites is dominated by the interplay between a strong electron–phonon coupling $e_g$ via Jahn–Teller effects and large Hund’s coupling effect that optimizes the electronic kinetic energy by the formation of ferromagnetic.

It is interesting to note that, when compared with Gd (the most used material for magnetic refrigeration) and other candidate materials, the manganites are more convenient to prepare and exhibit higher chemical stability, as well as the higher resistivity that is favorable for lowering eddy current heating. In addition, they have much smaller thermal and field hysteresis than any rare earth and 3d-transition metal based alloy. Moreover, this material is the cheapest among the existing magnetic refrigerants. These superior features may make it more promising for future magnetic refrigeration technology.

In this context we devoted this paper to develop magnetic and MCE results of La$_{0.7}$Ca$_{0.15}$Sr$_{0.15}$Mn$_{1-x}$Ga$_x$O$_3$ manganite compounds ($0 \leq x \leq 0.1$).

2 Experimental details

Polycrystalline samples La$_{0.7}$Ca$_{0.15}$Sr$_{0.15}$Mn$_{1-x}$Ga$_x$O$_3$ ($0 \leq x \leq 0.1$) were prepared by sol–gel technique. Citric acid was used as a gelling agent for La, Ca, Sr and Mn ions, and the obtained gel was subjected to successive heat treatments at 600 °C for 4h. After that, the microcrystalline powder was pelletized, pressed into disks and sintered at 900 °C for 48h in air. A final heat treatment was performed at 1000 °C for 12h in air. The crystal structure of the bulk samples was determined by an X-ray diffractometer (XRD) with CuKα radiation. XRD data were refined by means of the Rietveld method using the FullProf refinement program [14]. The magnetic measurements versus temperature were performed using extraction magnetometer (Néel Institute-Grenoble) for high and low temperatures. The magnetization curves were obtained under a magnetic applied field up to 5 T in the temperature range 100-400 K, the MCE results were calculated according to the Maxwell relation using isothermal magnetic measurements.

3 Results and discussions

Structural results and phase identification, carried out by the X-Ray diffraction, were discussed in previous work [15]. We have found that all samples crystallize in the rhombohedral structure (R-3C space group) and that the unit cell parameters are not affected with enhanced Ga doping.

Temperature dependence of magnetization ($M$–$T$) measured at 0.05 T for La$_{0.7}$Ca$_{0.15}$Sr$_{0.15}$MnO$_3$ ($x = 0$) is shown in Figure 1. The $M$–$T$ curve exhibits a $PM$–$FM$ phase transition. The Curie temperature ($T_C$), defined by the minimum in $dM/dT$, has been found to be $T_C = 336.5$ K.
Fig. 1 Left axes: temperature dependence of magnetization measured at $\mu_0H = 0.05\ T$, for $x = 0.0$. Right axes: temperature dependence of $dM/dT$, for $x = 0.0$. Inset: isotherm magnetization curve $M–H$ at 5 K for $x = 0.0$ with field up to 5 T; the solid line is the linear fitting for the saturated magnetization.

The inset of Figure 1 shows the isothermal magnetization measured at 5 K. With the increase of the applied magnetic field, the magnetization increases sharply, and then tends to saturate as $\mu_0H \geq 1.5\ T$. The saturated magnetization ($M_S$) can be obtained from an extrapolation of the high field $M–H$ curve to $H = 0$, and the obtained $M_S = 3.14\ \mu_B$ is close to the theoretical value of $M_S = 3.3\ \mu_B$.

The effective magnetic moment was calculated to be $\mu_{\text{eff}} = 4.59\ \mu_B$ using the relation $\mu_{\text{eff}} = 2\ \sqrt{S(S+1)}\mu_B$, $g = 2$ is the Lande factor and $S$ is the magnetic spin. According to Rhodes–Wohlfarth criterion [16], the degree of itinerancy can be determined from the ratio of $\mu_{\text{eff}}$ to $M_S$. The ratio is close to one for the localized moment whereas it is larger than one for the itinerant moment. Here, the ratio of 1.39 for La$_{0.7}$Ca$_{0.15}$Sr$_{0.15}$MnO$_3$ ($x = 0$) implies that the electrons possess an itinerant character.

Temperature dependence of magnetization for La$_{0.7}$Ca$_{0.15}$Sr$_{0.15}$Mn$_{1-x}$Ga$_x$O$_3$ ($0 \leq x \leq 1$) ($M–T$) measured at 0.05 T is shown in Figure 2. The $M–T$ curve exhibits a $PM–FM$ phase transition. The Curie temperature has been determined to decrease from $T_C = 336.5\ K$ for $x = 0$ to $T_C = 244.5\ K$ for $x = 0.1$.

Fig. 2 Variation of the magnetization $M$ vs. temperature $T$ for La$_{0.7}$Ca$_{0.15}$Sr$_{0.15}$Mn$_{1-x}$Ga$_x$O$_3$ compounds ($x = 0.0, 0.025, 0.05, 0.075$ and $0.10$) at 0.05T.
Temperature dependence of magnetization ($M-T$) measured at 0.05 $T$ for La$_{0.7}$Ca$_{0.15}$Sr$_{0.15}$MnO$_3$ ($x = 0$) is shown in Figure 2. The $M-T$ curve exhibits a PM–FM phase transition. The Curie temperature ($T_C$), defined by the minimum in $dM/dT$, has been determined to be $T_C = 336.5$ K. Figure 3 shows the isotherms recorded in the applied field range of 0–5 $T$ for $x = 0.0$ and 0.05. It is similar to other manganite compounds [17, 18] the $M(H)$ curves reach saturation values at high magnetic fields which is considered as a result of the rotation of the magnetic domains under the action of the magnetic applied field.

![Figure 3](image_url)

Fig. 3 Isothermal magnetization for La$_{0.7}$Ca$_{0.15}$Sr$_{0.15}$Mn$_{1-x}$Ga$_x$O$_3$ ($x = 0$ and 0.05) samples measured at different temperatures.

The Banerjee criterion has been frequently used to check the nature of the magnetic phase transition in manganites [19, 20]. According to this criterion, the positive or negative slope of $\mu_0H/M$ versus $M^2$ (Arrott plot) curves indicates whether the magnetic phase transition is second order or first order. As can be seen on Figure 4 near the paramagnetic–ferromagnetic phase transition, $\mu_0H/M$ versus $M^2$ curves clearly exhibit a negative slope in the entire $M^2$ range for $x = 0$, which confirms the first-order nature of the transition, and a positive slope for $0 < x \leq 0.1$, which confirms the second-order nature of the transition. According to the mean field theory, near the transition point, $\mu_0H/M$
versus $M^2$ should show a series of parallel lines at various temperatures and the line related to $T_C$ should pass through the origin [19, 20].

Since a sharp PM–FM transition occurs around $T_C$, which possibly implies a large magnetic entropy change near room temperature, we performed a measurement of MCE of the present materials.

The isothermal magnetic entropy change $\Delta S_M(T)$, which is associated with the magnetocaloric effect, can be calculated from measurements of magnetization as a function of the magnetic applied field and temperature (indirect measurement technique of the magnetocaloric effect). According to the classical thermodynamics theory, the magnetic entropy change produced by varying the magnetic field from 0 to $\mu_0 H_{\text{max}}$ is given by Maxwell relation [21]

$$\left(\frac{dM}{dT}\right)_{P,H} = \left(\frac{dS}{dH}\right)_{P,T}$$

(1)

The magnetic entropy change can be rewritten as follows [22]:

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\[ \Delta S_M(T, \mu_0 H) = \int_0^{H_{\text{max}}} \left( \frac{\delta M(\mu_0 H_{\text{max}}, T)}{\delta T} \right) \mu_0 dH \]  

(2)

The integral in eq. 2 corresponds to the area enclosed between isothermal magnetization curves \( M(H, T) \) and \( M(H, T+\delta T) \). \( \delta T \) is the temperature difference between two isotherms. The magnetic entropy change was determined by integrating numerically eq. 2 and the obtained results are given in Figure 5.

![Figure 5](image)

**Fig. 5** The temperature dependence of the magnetic entropy change under different magnetic fields for \( \text{La}_{0.7}\text{Ca}_{0.15}\text{Sr}_{0.15}\text{Mn}_{1-x}\text{Ga}_x\text{O}_3 \) (\( x = 0.0 \) and 0.1) compounds.

It is worth noting that all the samples exhibit a maximum entropy change \( \Delta S_{\text{max}} \) around their Curie temperature \( T_C \) [23-25]. It can be seen from Figure 5 that \( \Delta S_{\text{max}} \) decreases from 5.15 to 1.86 J/kgK when increasing \( Ga \) content from 0 to 0.1, for an applied field of 5 T. The sharp ferromagnetic-paramagnetic phase transition for \( x = 0, 0.025 \) and 0.05 indicates a first order transition and would promisingly imply a high entropy change. However the rest of the samples exhibit a second order transition.

Moreover, the Relative Cooling Power (RCP) is given by [26]:
\[ RCP = -\Delta S_{\text{max}} x \delta T_{\text{FWHM}} \quad (3) \]

where \( \delta T_{\text{FWHM}} \) is the full-width at the half maximum of the entropy change curve (Figure 6).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6}
\caption{Magnetic entropy change, for 2T of magnetic field change, obtained for the La_{0.7}Ca_{0.15}Sr_{0.15}Mn_{1-x}Fe_{x}O_3, (0 \leq x \leq 0.1) system.}
\end{figure}

The variation of the RCP values as a function of the fractional composition \( x \), for a magnetic applied field of 2 T, is shown in Figure 7. The RCP values vary between 83 and 118 J/kg.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig7}
\caption{Variation of the RCP factor as a function of the fractional composition (\( x \)).}
\end{figure}

Refrigerants with a wide working temperature span and high RCP are in fact very beneficial to magnetic cooling applications.

3 Conclusion

In this work we have introduced Ga substitution with small amount at the \( B \) site in La_{0.7}Ca_{0.15}Sr_{0.15}MnO_3 manganites. It is shown that the substitution of \( Mn \) by \( Ga \) element doesn’t influence the structural properties. Moreover, variation of the \( Mn/Ga \) ratio has the following effects:

- The curie temperature, which is also the working point of a magnetic refrigerant, decreases from 336 to 253 K in the composition range 0 < \( x \) < 0.1.
The magnetic entropy change is maximal in compound La$_{0.7}$Ca$_{0.15}$Sr$_{0.15}$Mn$_{1-x}$Ga$_x$O$_3$ with $x = 0$. The maximal value decreases with increasing Ga content.

The La$_{0.7}$Ca$_{0.15}$Sr$_{0.15}$Mn$_{1-x}$Ga$_x$O$_3$ manganites exhibit important values of Relative Cooling Power RCP.

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