ORIGINAL PAPER

# Magnetic and Magnetocaloric Study of Polycrystalline $(1-x)$La$_{0.65}$Ca$_{0.35}$MnO$_3/x$Fe$_2$O$_3$ Composites

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**Abstract** Magnetic and magnetocaloric properties of poly-crystalline $(1-x)$La$_{0.65}$Ca$_{0.35}$MnO$_3/x$Fe$_2$O$_3(0 \leq x \leq 0.09)$ composites were investigated. Our composites were elaborated using the solidstate reaction at high temperature. Polycrystalline La$_{0.65}$Ca$_{0.35}$MnO$_3$ (LCMO) was synthesized using the solidstate reaction at high temperature while for Fe$_2$O$_3$ we used a commercial product. Xray diffraction patterns show that the parent compound La$_{0.65}$Ca$_{0.35}$MnO$_3$ is a single phase without any detectable impurity and crystallizes in the orthorhombic structure with *Pbnm* space group. Magnetocaloric effect of our composite materials in the vicinity of the magnetic transition temperatures was investigated. The maximum of the magnetic entropy change $\left|\Delta S_M^{\max}\right|$ is found to be 6.25, 6.37, 6.18 and 5.87 J kg$^{-1}$ K$^{-1}$ for $x = 0$, 0.03, 0.06, and 0.09 under a magnetic field change of 5 T respectively.

**Keywords** Manganites · Composites · Magnetocaloric effect

## 1 Introduction

Nowadays, the search for new materials with enhanced magnetocaloric effect (MCE) for their utilization in room

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temperature magnetic refrigerators is a very active field of research due to its lower energy consumption and environmental friendly character. The magnetocaloric effect was first discovered by Warburg in 1881 [1], Deby in 1926 [2] and Giauque in 1927 [3] independently pointed out that ultra-low temperature could be reached through the reversible temperature change of param-agnetic salts with the alternation of magnetic field and first foresaw the technological potential of this effect. Magnetic refrigeration near room temperature is of special interest because of its great social effect and econom-ical benefit. The prototype magnetic material available for room temperature magnetic refrigeration is gadolin-ium Gd. At the Curie temperature $T_c$ of 294 K, Gd undergoes a second-order paramagnetic–ferromagnetic transition. The MCE and the heat capacity of Gd have been studied in many research activities [4] Recently, large values of MCE are observed in the perovskite man-ganese oxides [5–10] The research is very interesting in the system La$_{1-x}$Ca$_x$MnO$_3$ which is characterized by rather large values of MCE and adjustable phase transition temperatures [5, 11–13] For La$_{0.65}$Ca$_{0.35}$MnO$_3$ elaborated using the solid–solid reaction method at high temperature, the $\left|\Delta S_M^{\max}\right|$ under an applied field of 5 T reaches 6.2 J kg$^{-1}$ K$^{-1}$, around its Curie tem-perature $T_c = 265$ K [14]. Moreover the presence of magnetic multiphases broadens the $\Delta S_M(T)$ curves and enhances consequently the relative cooling power (RCP) [15–20] In this context, several magnetocaloric studies have been performed recently on composites based on manganites in order to enhance the phys-ical properties comparing to manganites [21–25]. In

our study we elaborated polycrystalline composites based on $La_{0.65}Ca_{0.35}MnO_3$ manganites with $Fe_2O_3$ oxide at several mass fractions and studied the magnetic and magnetocaloric properties of $(1-x)$ $La_{0.65}Ca_{0.35}MnO_3/xFe_2O_3$ with $x = 0, 0.03, 0.06$ and $0.09$.

## 2 Experiments

### 2.1 Synthesis

The composites $(1-x)La_{0.65}Ca_{0.35}MnO_3/xFe_2O_3(x = 0, 0.03, 0.06$ and $0.09)$ were elaborated in two stages. At first we elaborate $La_{0.65}Ca_{0.35}MnO_3$ sample using the ceramic route at high temperature, stoichiometric amounts of dried $La_2O_3$, $CaCO_3$ and $MnO_2$, with high purity equal to 99, 9 %, according to the following equation:

$$0.325La_2O_3 + 0.35CaCO_3 + MnO_2 \rightarrow La_{0.65}Ca_{0.35}MnO_3$$

$$+ \delta CO_2 + \delta'O_2 \qquad (1)$$
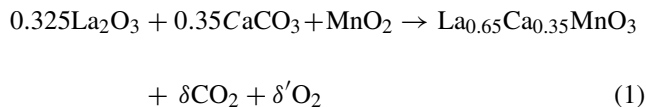
were intimately mixed in an agate mortar for 45 min; the obtained powder was pressed into pellets of about 1 mm thickness and 13 mm diameter and sintered at 1000 °C in air for 24 h. The sample undergoes several cycles of grinding–pelleting–annealing between 1000 and 1200 °C during 48 h for each annealing The obtained sample was characterized by X-ray powder diffraction at room temperature with CuK $\alpha$ radiation Structural analysis was made using the standard Rietveld technique [26, 27]. Secondly we have prepared three composites based on $La_{0.65}Ca_{0.35}MnO_3$ and $Fe_2O_3$ for different mass fractions The composites were prepared by thoroughly mixing 97, 94, and 91 % of $La_{0.65}Ca_{0.35}MnO_3$ with 3, 6 and 9 % of $Fe_2O_3$ respectively, and then were sintered at 1000 °C for 4 h. The microstructure was studied by scanning electron microscope (SEM). The density of the as-produced pellets was measured with a Micrometrics AccuPyc 1330 helium pycnometer. Magnetization measurements versus magnetic applied field up to 5 T were performed using a vibrating sample magnetometer in the temperature range 200–350 K. Magnetocaloric effect $\left|\Delta S_M^{(T)}\right|$ at several magnetic field change up to 5 T were deduced from the $M(H)$ curves at several temperatures.
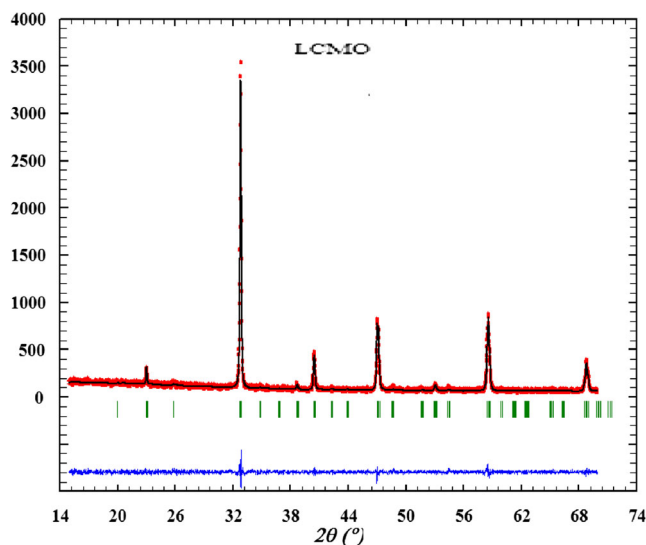


**Fig. 1** X-ray diffraction patterns at 300 K for $La_{0.65}Ca_{0.35}MnO_3$ sample including the observed and calculated profiles as well as the difference profile

## 3 Results and Discussion

The X-ray diffraction (XRD) patterns of the parent compound $La_{0.65}Ca_{0.35}MnO_3$ have been recorded at room temperature; the data have been refined using Rietveld's profile-fitting method. Figure 1 shows the X-ray diffraction patterns at 300 K for $La_{0.65}Ca_{0.35}MnO_3$ sample including the observed and calculated profiles as well as the difference profile .Our parent compound is single phase without
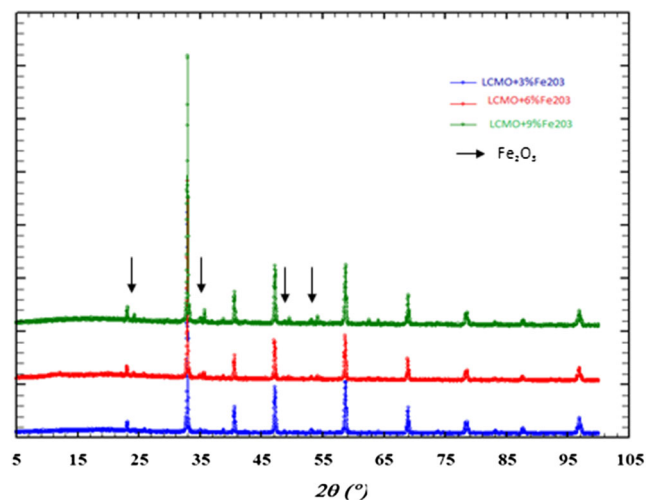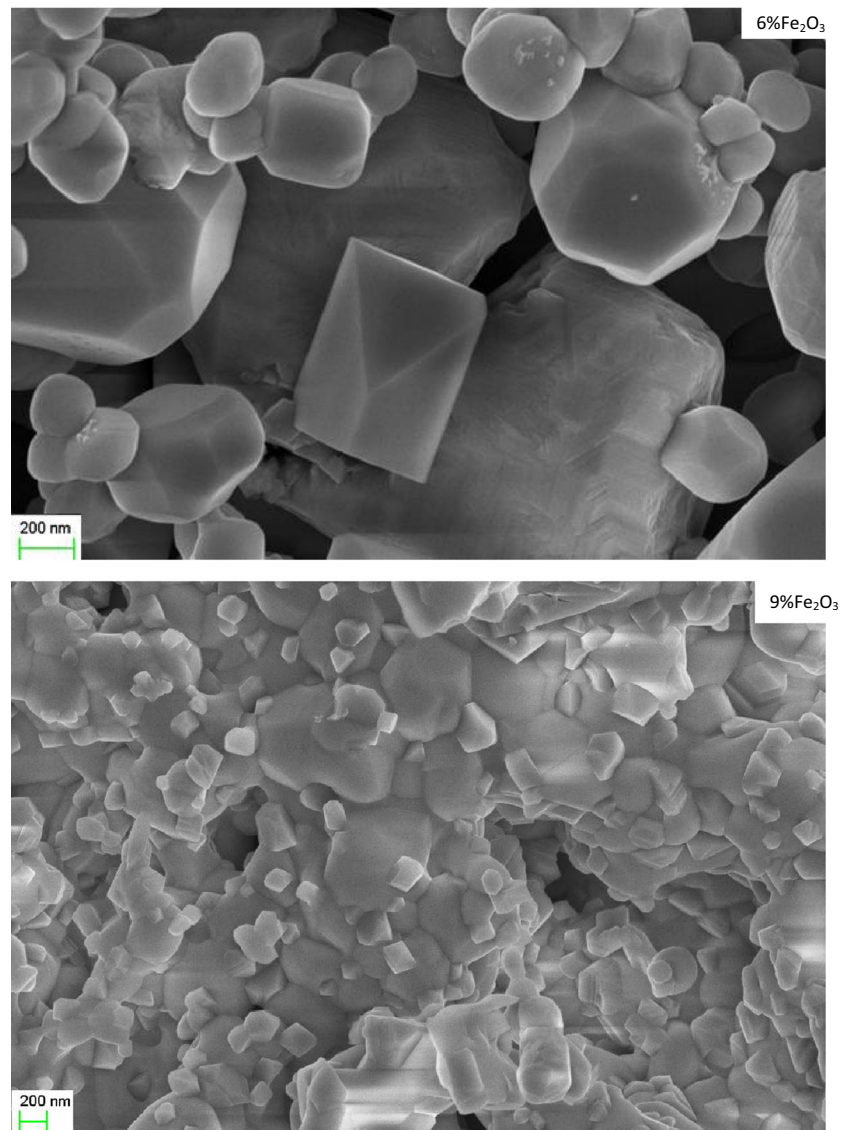


**Fig. 2** X-ray diffraction patterns at 300 K for our three composites $(1-x)La_{0.65}Ca_{0.35}MnO_3/xFe_2O_3$ with 0.03;.06 and 0.09

**Fig. 3** SEM images of $(1-x)La_{0.65}Ca_{0.35}MnO_3/xFe_2O_3$ for $x = 6$ and $9$ %



any detectable impurity and crystallizes in the orthorhombic structure with *Pbnm* space group. Figure 2 shows the X-ray diffraction patterns at 300 K for our three composites $(1-x)La_{0.65}Ca_{0.35}MnO_3/xFe_2O_3$ with $x = 0.03$, 0.06, and 0.09. As we can observe on this figure, there is no interaction between the parent compound and $Fe_2O_3$ oxide.

### 3.1 Microstructural Analysis

To investigate the microstructural properties of our synthesized samples, XRD and SEM analyses were jointly used. With MAUD software, the model line broadening selected was "popa LB" combined with the isotropic model size–strain. The instrument broadening was corrected using the XRD pattern of a Si standard. Figure 3 shows the SEM image obtained for the composites $(1-x)La_{0.65}Ca_{0.35}MnO_3/xFe_2O_3$, (x = 6 and 9 %). The SEM image shows that the $Fe_2O_3$ oxide occupies the grain boundary of $La_{0.6}Ca_{0.35}MnO_3$.

### 3.2 Magnetic and Magnetocaloric Properties

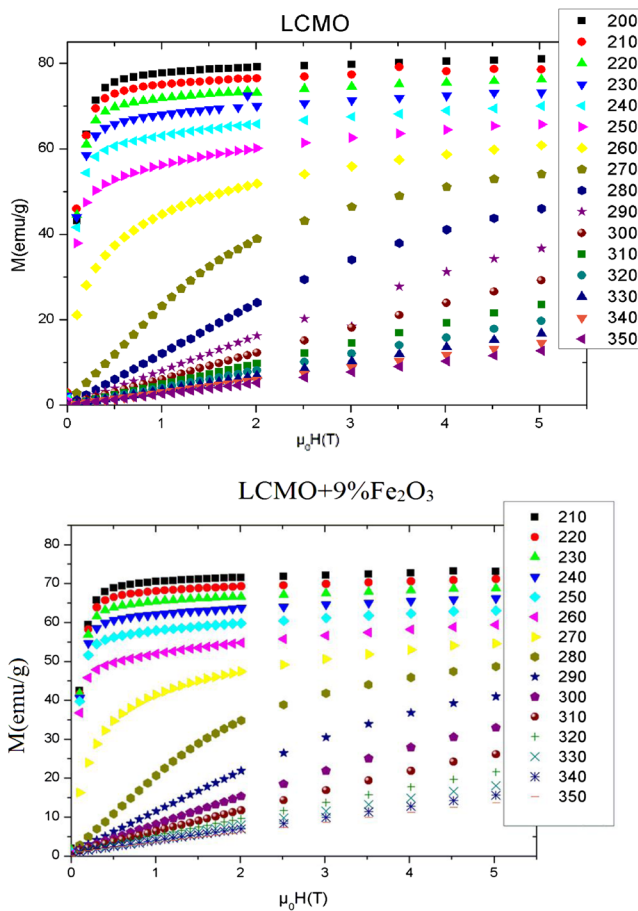We performed magnetization measurements versus magnetic applied field up to 5 T at several temperatures

**Fig. 4** Magnetic field dependence of magnetization up to 5 T at several temperatures for $La_{0.65}Ca_{0.35}MnO_3$ and $0.91La_{0.65}Ca_{0.35}MnO_3/0.09Fe_2O_3$

in the range 200–350 K for the parent compound $La_{0.65}Ca_{0.35}MnO_3$ and the three composites $(1-x)$ $La_{0.65}Ca_{0.35}MnO_3/xFe_2O_3$ ($x = 3, 6,$ and 9 %). Figure 4 shows the magnetic field dependence of magnetization up to 5 T at several temperatures for $La_{0.65}Ca_{0.35}MnO_3$ and $0.91La_{0.65}Ca_{0.35}MnO_3/0.09Fe_2O_3$. At low temperatures, the magnetization $M$ increases sharply with magnetic applied field for $H < 0.5$ T and then saturates above 1 T. This result confirms well the ferromagnetic behavior at low temperatures of our composites. The magnetic entropy change $\Delta S_M(T)$ has been deduced from the isothermal magnetization measurements. It can be evaluated according to Maxwell's relations, using the following equation:

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^{H\,max} \left(\frac{\partial M}{\partial T}\right)_H dH \tag{2}$$

where $H_{max}$ is the maximal value of the magnetic applied field. In practice the relation is approximated as [19, 20]:

$$\Delta S_M(T,H) = \sum_i \frac{M_{i+1}(Ti, H) - M_i(Ti, H)}{T_{i+1} - T_i} \Delta H_i \tag{3}$$

where $M_i$ and $M_{i+1}$ are the experimental values of magnetization measured at temperatures $T_i$ and $T_{i+1}$ respectively, under a magnetic field $H_i$. Figure 5 shows the variation of $-\Delta S_M$ as a function of temperature at different magnetic field changes for our composites. As expected, $-\Delta S_M$ reaches its maximum around the transition temperature and increases with the magnetic applied field change. At 5 T, the maximal value of the magnetic entropy change $\left|\Delta S_M^{max}\right|$ is found to be 6.25, 6.37, 6.18, and 5.87 J kg$^{-1}$ K$^{-1}$ for $x = 0.00, 0.03, 0.06,$ and 0.09 respectively. We do not notice a significant effect of the mass fraction of $Fe_2O_3$ oxide on the maximum of $\Delta S_M(T)$ while temperature of this maximum is shifted to high values. From a cooling perspective, it is important to consider the refrigeration capacity which depends on both the magnetic entropy change and its temperature dependence. The magnetic cooling efficiency of a magnetocaloric material can be evaluated through the relative cooling power (RCP) defined as follows:

$$\mathrm{RCP} = \left|\Delta S_M^{max}\right| \times \delta T_{\mathrm{FWHM}} \tag{4}$$

were $\delta T_{\mathrm{FWHM}}$ is the full with at half maximum of the $\Delta S_M(T)$ curve. The RCP value is found to be 272.6, 255, 219.4, and 208.6 J kg$^{-1}$ for $x = 0, 3, 6,$ and 9 % respectively, under a magnetic field change of 5 T. The RCP decreases with increasing the $Fe_2O_3$ amount in our composites.

## 4 Conclusion

We have studied the magnetocaloric effect in composites with general formula $(1-x)(La_{0.65}Ca_{0.35}MnO_3)/x(Fe_2O_3)$ with $x = 0, 3, 6$ and 9 % prepared by solid–solid reaction. The presence of the $Fe_2O_3$ oxide has no great effect on the physical properties of LCMO compound. The Curie temperature remains unchanged ($T_c \approx 270$ K). The maximum of the magnetic entropy $\left|\Delta S_M^{max}\right|$ values are not very affected by the oxide amount while the RCP decreases. The full width at half maximum $\delta T_{\mathrm{FWHM}}$ of the $\Delta S_M(T)$ curves is $\approx 40$ K around $T_c$ for all the samples.
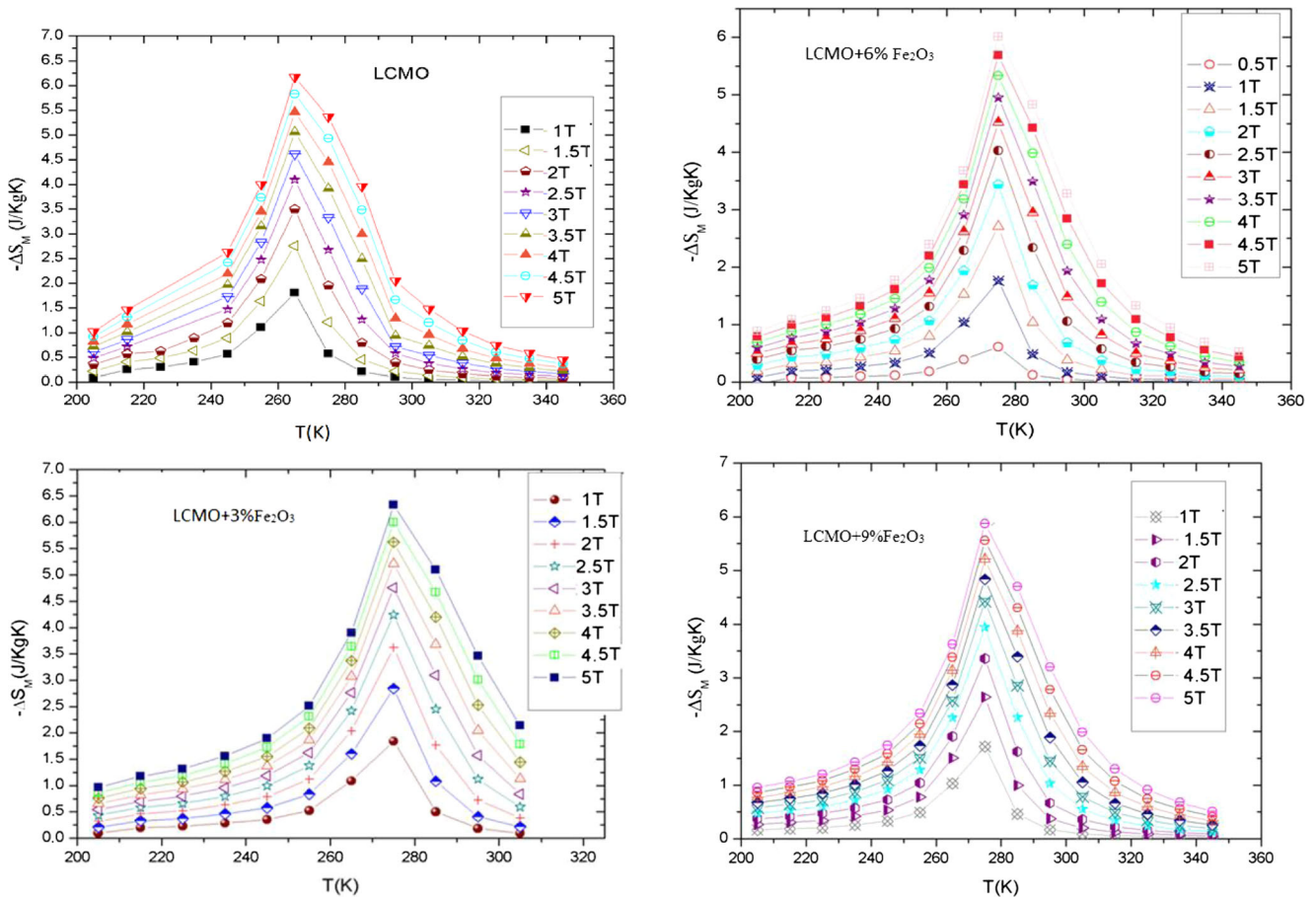
**Fig. 5** Temperature dependence of the magnetic entropy change, $-\Delta S_M$, at several magnetic field changes for our composites

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