Significantly large magnetocaloric effect in polycrystalline $La_{0.83}Sr_{0.17}MnO_3$ near room temperature

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A B S T R A C T

We have observed a significantly large magnetocaloric effect near room temperature for polycrystalline ferromagnetic $La_{0.83}Sr_{0.17}MnO_3$ compound. The maximum value of the magnetic entropy change at the vicinity of the paramagnetic to ferromagnetic ordering temperature is about 8.0 J/kg-K in the presence of a 70 kOe external magnetic field. The present study indicates that the magnetic entropy change near room temperature is comparable to (or larger than) that for the suggested refrigerant materials reported earlier.

1. Introduction

In order to avoid the increasing tendency of using environmentally harmful gases in cooling technology, search for environment friendly technologies has been intensed over the past few decades. In this context magnetic cooling technology, based on magnetocaloric effect, gets priority for several beneficial aspects, namely, higher efficiency, environment friendliness, recycling operation etc. In magnetic cooling technology, selection of magnetic refrigerants with large magnetocaloric effect is primarily important. Magnetocaloric effect (MCE) is almost a generic nature of magnetic materials. MCE is the isothermal magnetic entropy change or adiabatic temperature change of a material when it is subjected to an external magnetic field. The study of MCE is important from both fundamental and technological points of view. From the fundamental point of view, magnetic phase diagram can be constructed from the investigation of MCE, which elucidates the nature of the magnetic ground state and its modification with the external magnetic field and temperature [1–5]. On the other hand, from the technological perspectives, the materials with a large magnetocaloric effect are of prior interest for their application as a refrigerant material in magnetic cooling technologies. Another important factor for the cooling technology is the operating region of temperature (in which the material can be used). Generally, the material recognized as suitable refrigerants are those for which the magnetocaloric effect is large either

at the cryogenic temperature region or near room temperature. In recent years, in cooling technologies, the search for room temperature refrigerants has become intensive. In this perspective, numerous research works have been performed in the past two decades [1,6–13]. It is worth mentioning that initially the investigation of MCE was mainly carried out on rare-earth based intermetallic compounds due to their high magnetic moments [1,6,12,13].

However, oxide based compounds, for several beneficial aspects such as better chemical stability and low cost, have attracted more interest in the investigation of magnetocaloric effect [14–30].

As mentioned earlier, the operating temperature range is very important for a good refrigerant material for commercial use. Doped perovskite manganite compounds are represented by the general formula $R_{1-x}B_xMnO_3$ where 'R' is trivalent rare earth element and 'B' is bivalent element of alkaline earth. Depending on the bivalent dopant ion 'B' and the doping concentration 'x', the transition temperature (disorder to order) can be tuned [28,31]. In the manganite family, $La_{1-x}Sr_xMnO_3$ is one of the most well studied compounds. According to the reported phase diagram of the bulk compound for different doping concentration 'x', this compound exhibits many rich physical properties [31]. For the doping concentration $x > 0.17$, the compound exhibits ferromagnetic metallic behaviour whereas for $x < 0.17$ it shows ferromagnetic insulating nature with decreasing temperature [31]. Since the magnetocaloric effect is related with the suppression of the

magnetic randomness with the application of the magnetic field, its maximum value generally appears at the vicinity of the paramagnetic to ferromagnetic transition temperature (Curie temperature, T_C). For this reason most of the ferromagnetic compounds were studied previously [1,28]. On the other hand high resistive property of a material is more beneficial compared to the metallic nature. The insulating materials are superior compared to metals because of low Eddy current loss. Although Eddy current has several applications in modern techniques, it is undesirable in the case of refrigeration [28,32]. Additionally, we should mention here that Relative Cooling Power (RCP) is an important parameter for magnetic refrigeration. RCP of a magnetic material is mathematically estimated by the product of the maximum entropy change (ΔS) with the full width at half maximum (FWHM) of ΔS vs T plot [$= \Delta S_M(T) * \delta T_{FWHM}$]. Large RCP value is essential for the commercial application of any magnetic refrigerant material [33]. Large RCP can be expected at the phase boundary due to the interfacial strain developed between different magnetic phases [14]. Thus search for a material with high magnetocaloric effect near or above room temperature, high RCP value, no hysteresis and no Eddy current loss, i.e, a material with high MCE value, higher operating temperature, no hysteresis and insulating in nature is crucial. In this context we have chosen ferromagnetic insulating $La_{0.83}Sr_{0.17}MnO_3$ compound for the present study with the expectation of large value of the magnetocaloric effect and reasonably large RCP.

In the earlier studies it was reported that the phase boundary plays a vital role in the magnetocaloric effect [14]. In this Letter we present the effect of the phase boundary (between ferromagnetic metallic and ferromagnetic insulating phases) on magnetic and magnetocaloric properties of ferromagnetic insulating polycrystalline $La_{0.83}Sr_{0.17}MnO_3$ compound. This compound shows significantly large magnetocaloric effect and relative cooling power. Moreover, the operating temperature region is close to room temperature. These properties indicate the suitability of this compound as a refrigerant for magnetic cooling technology.

2. Sample preparation, characterization and measurements

Polycrystalline $La_{0.83}Sr_{0.17}MnO_3$ compound was prepared by sol-gel processes. For the sample preparation by this route, the starting materials were pre-heated La_2O_3, $Sr(NO_3)_2$ and MnO_2 with purity 99.9%. Appropriate amount of La_2O_3 compound was converted to its nitrate form and dissolved into millipore water. $Sr(NO_3)_2$ was directly dissolved into millipore water and a clear solution was formed. Since MnO_2 is not converted to its nitrate form directly by adding nitric acid, the suitable amount of oxalic acid was added in the mixture of MnO_2 and millipore water by which MnO_2 was converted to manganese oxalate. This manganese oxalate was then dissolved in millipore water in the presence of nitric acid. Finally, all individual clear solutions were mixed properly by using a magnetic stirrer in a beaker and citric acid was added as a chemical ligand. This homogeneous solution was slowly evaporated using a water bath at temperature 80–90 °C until the gel was formed. After gel formation, it was decomposed at slightly higher temperature (~200 °C) and black porous powder was formed. The pelletized powder was further annealed at high temperature (1300 °C) for longer time (36 h) for better crystallization of the compound.

For structural characterization, x-ray diffraction (XRD) study was carried out using a Rigaku-TTRAX-III diffractometer having Cu-Kα radiation of wavelength 1.54 Å. A Quantum Design Superconducting Quantum Interferences Device (SQUID) MPMS-III was employed for the investigation of magnetic and magnetocaloric properties.

3. Results and discussions

X-ray diffraction has confirmed the single phase nature of the compound. We have determined the structural parameters of the compound from Rietveld refined XRD data shown in Fig. 1. This phase
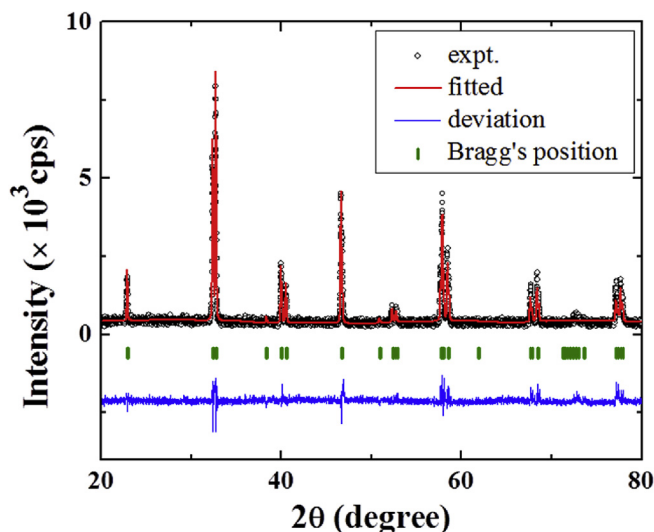

Fig. 1. XRD pattern and Reitveld refinement of the data.

of the material has lattice parameters $a = b = 5.54$ Å and $c = 13.38$ Å with space group R3c. Magnetization as a function of temperature was measured in two different protocols namely Zero Field Cooled (ZFC) and Field Cooled (FC). In case of the ZFC, sample was first cooled down from T = 300 K (paramagnetic state) in the absence of any external magnetic field. After stabilization of the temperature at T = 5 K, external magnetic field was applied and magnetization data were recorded in the warming cycle. Whereas, in case of the FC measurements, external magnetic field was applied from the paramagnetic state (T = 300 K) and the sample was cooled down in the presence of the specified field.

Magnetization data were recorded in the warming cycle from 5 to 300 K. Magnetization (ZFC and FC) as a function of temperature for 100 Oe and 10 kOe external magnetic field is shown in Fig. 2. The lower field (100 Oe) magnetization data show a bifurcation between ZFC and FC values in the low temperature region (T < 150 K). In the low temperature region the magnetization values for both ZFC and FC cases decrease for 100 Oe magnetic field (which is not the subject matter of this manuscript). However, for a higher magnetic field (H = 10 kOe) such bifurcation in magnetization disappears. Another point should be mentioned here that the paramagnetic to ferromagnetic transition temperature is close to the room temperature ($T_C = 270$ K). Additionally, near this temperature region no hysteresis was found even at lower values of the magnetic field. Such magnetic behavior motivated us to study the magnetocaloric properties of this compound.

Before doing the magnetocaloric effect measurements, field dependence of the magnetization at a fixed temperature was carried out. The magnetization as a function of the external magnetic field at different fixed temperatures is given in Fig. 3. To measure the magnetization as a function of magnetic field at each temperature, the sample was first cooled down from the paramagnetic state at the specified temperature in the absence of external magnetic field to remove the magnetic history of the previous measurements, if present. From the field dependent magnetization data two points should be mentioned. First, at the low temperatures the sample behaves as a soft ferromagnet. Secondly, there is no magnetic hysteresis due to the magnetic field cycling even at low temperatures. Such reversible behavior (no hysteresis loop) is also another beneficial aspect for a good refrigerant material.

Magnetocaloric entropy change (ΔS) was determined from the magnetic isotherm data using Maxwell's thermodynamic relation, given by,

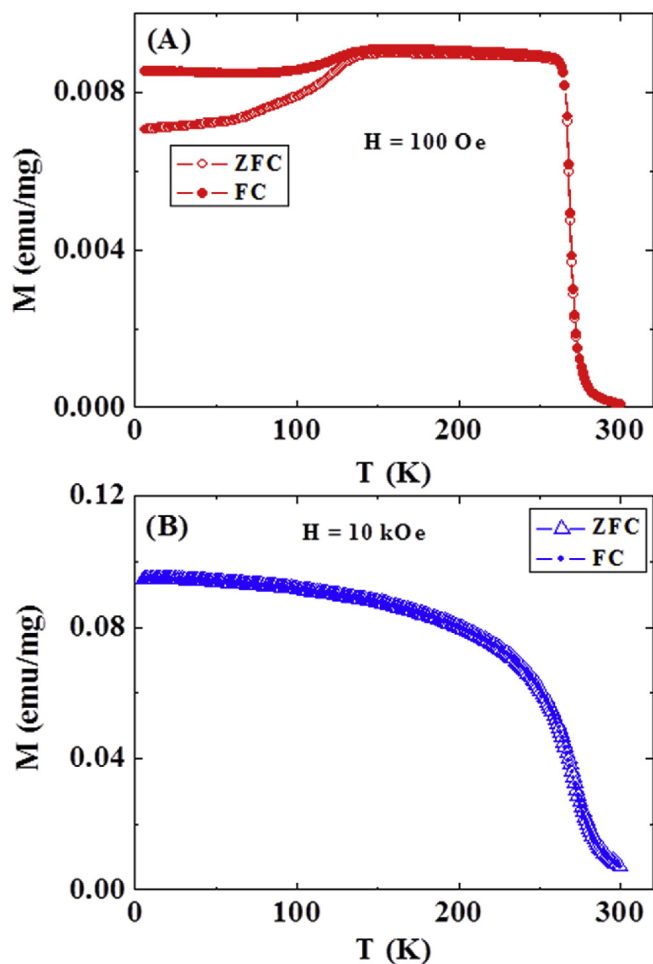$$\Delta S = \int_0^H \left(\frac{\partial M}{\partial T} \right) dH \qquad (1)$$

Fig. 2. (A) and (B) show magnetization as a function of temperatures for different external magnetic field in ZFC and FC protocols.
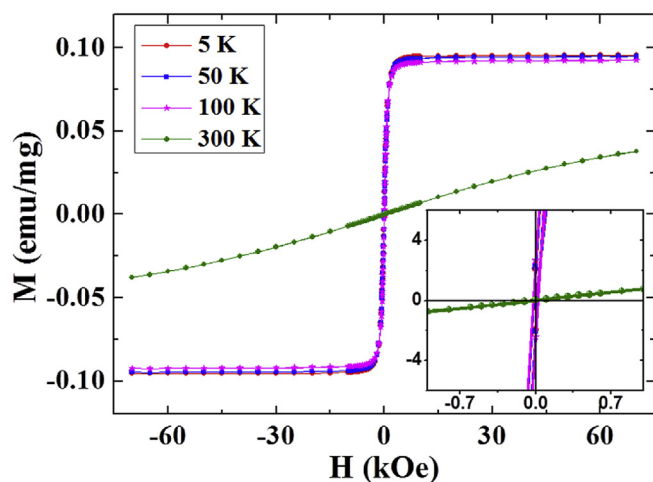

Fig. 3. Magnetization as a function of external magnetic field at different temperatures for La$_{0.83}$Sr$_{0.17}$MnO$_3$ compound. The low field region is shown in the inset.

Temperature dependence of magnetic entropy changes ($-\Delta S(T)$) at different magnetic field is given in Fig. 4. The entropy change ($-\Delta S$) is significantly large and comparable to the other reported refrigerant materials including intermetallic based magnetocaloric materials [1,28]. The isothermal magnetic entropy change and the relative cooling power (which is described in later part) of some selective La-Sr-
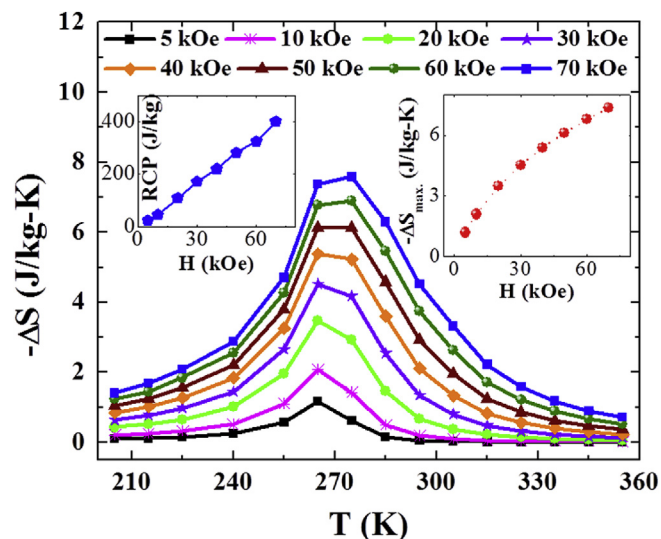

Fig. 4. Magnetic entropy change ($-\Delta S$) as a function of temperature for different external magnetic field. Left inset is the variation of the RCP and right inset indicates the variation of the peak value of the magnetic entropy change with magnetic field.

Table 1
Comparison of $-\Delta S$ and RCP of several *La-Sr-MnO3* FI (ferromagnetic insulator) and FM (ferromagnetic metal) compounds.

Compound	Property	Magnetic field (kOe)	$-\Delta S$	RCP (J/ kg)	Reference
La$_{0.88}$Sr$_{0.12}$MnO$_3$	FI	70	6.0	372	[28]
La$_{0.865}$Sr$_{0.135}$MnO$_3$	FI	70	4.4	330	[28]
La$_{0.845}$Sr$_{0.155}$MnO$_3$	FI	70	6.7	670	[28]
La$_{0.83}$Sr$_{0.17}$MnO$_3$	FI	70	7.6	402	Present study
La$_{0.815}$Sr$_{0.185}$MnO$_3$	FM	70	7.1	533	[28]
La$_{0.8}$Sr$_{0.2}$MnO$_3$	FM	70	7.9	395	[28]

MnO3 based materials are given in Table 1. Importantly, the maximum entropy change is observed near the room temperature which is important from technological perspectives. Additionally, the relative cooling power (RCP) of this material is significantly large. RCP is generally defined as the product of maximum value of $-\Delta S$ and the temperature span at its half value (full width at half maxima, T$_{FWHM}$). Large value of the RCP is one of the standard parameters for recognizing a refrigerant material. We should mention that other two compounds in Table 1 and Fig. 5 with comparable RCP and operating temperature are metallic in nature. But our compound is insulating and thus the Eddy current loss is suppressed in this material. This is an important factor for MCE applications.

In order to explore the origin of this large magnetocaloric effect, we have compared magnetic entropy change as a function of the doping concentration 'x' for several reported compounds which are given in Fig. 4. Data were taken from ref. [28] except for the x = 0.17 compound. Our compound (x = 0.17) lies on the phase boundary and the value of $-\Delta S$ is quite large. Such behaviour is possibly due to the effect of two different competing phases. The influence of the phase boundary (canted magnetic state) on the inverse magnetocaloric effect of polycrystalline La$_{0.125}$Ca$_{0.875}$MnO$_3$ and La$_{0.17}$Ca$_{0.83}$MnO$_3$ compounds was reported earlier where large inverse magnetocaloric effect was observed in case of the La$_{0.125}$Ca$_{0.875}$MnO$_3$ compound [14]. Authors explained that since the compound having Ca-0.875 doping concentration is close to the phase boundary, magnetocaloric effect was quite large compared to the Ca-0.83 compound due to the influence of the phase boundary [14]. Such observation of large value of the RCP close to the phase boundary may be attributed to the interfacial strain developed
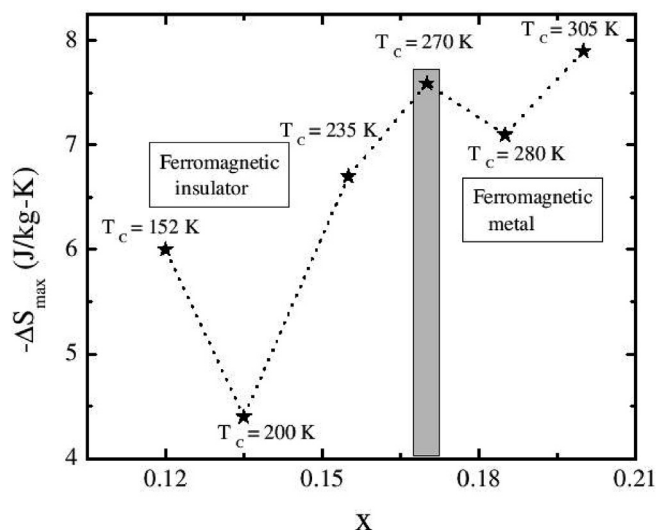
Fig. 5. Variation of $-\Delta S_{max}$ with the doping concentrations 'x' at 70 kOe magnetic field. The shaded region indicates the phase boundary between the two different phases. Data are collected (except in the shaded region for x = 0.17) from ref. [28].

between the different types of magnetic phases.

Overall, we find a significantly large value of magnetic entropy change, a large value of RCP and no hysteretic nature in ferromagnetic insulator polycrystalline $La_{0.83}Sr_{0.17}MnO_3$ compound. Thus, this material may be considered as a suitable refrigerant material for the magnetic cooling technology.

4. Conclusions

To summarize, the present study shows that significantly large magnetocaloric effect and RCP was observed near the vicinity of the room temperature for the ferromagnetic insulating polycrystalline $La_{0.83}Sr_{0.17}MnO_3$ compound. Additionally, no hysteresis effect was found in magnetic isotherms. The broadening of the peak of the magnetic entropy change resulting in the large RCP was analyzed considering the phase boundary effect between two competing phases. The material might find application in magnetic cooling technology.

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