

Paper published in

Journal of Magnetism and Magnetic Materials

Volume 322, Issue 21, November 2010, Pages 3460-3463

Magnetocaloric effect in $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite

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Abstract

The polycrystalline manganite $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ prepared by an alternative carbonate precipitation route reveals the rhombohedral perovskite structure. Magnetization isotherms measured up to 2 T are used to determine Curie temperature of 332 K by means of Arrott plot. Maximum of magnetic entropy change is found at Curie temperature. The relative cooling power equal to 64 J/kg for 1.5 T magnetic field, is superior as compared to the manganite with the same chemical composition from the sol–gel method.

Keywords: Magnetocaloric effect; Magnetic refrigeration; Manganite; Curie temperature; Arrott plot

1. Introduction

Magnetic refrigeration based on the magnetocaloric effect shows advantages over traditional gas compression technology [1] and [2]. Magnetic entropy change is a parameter achieving relatively high values around the para- to ferromagnetic transition. It is theoretically predicted and experimentally confirmed that the magnetic entropy change is larger for the first than for the second order phase transition. The magnitude of the magnetic entropy change is known to be affected by the microstructure of the material. On the other hand, the relative cooling power (RCP) depends also on the width of transition temperature interval [1] and [2]. The third factor important for the applicability of materials is the critical temperature of the transition, which may be tuned mainly by a chemical composition. This opens a search for

new refrigerants and new preparation methods leading to the stronger magnetocaloric effect. A present paper aims to evaluate the magnetocaloric effect in polycrystalline $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite prepared by the alternative carbonate precipitation method.

2. Samples

Polycrystalline $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ sample was prepared by the carbonate precipitation route. Aqueous solutions (~ 0.2 M) of metal nitrates, $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ were chosen as starting reagents. The concentrations of metal cations in the starting solutions were determined by trilonometric titration. Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, with 15% excess (in the molar ratio to the sum of the moles of cations in the solution) was slowly added to the appropriately mixed solution of the metal nitrates. The precipitate was aged for 24 h under the mother solution, then filtrated and rinsed with a distilled water and ethanol. The powder obtained was dried in air at 80 °C. Carbonate precipitate was converted to $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_{3-\delta}$ by slow heating in the air atmosphere up to 810 °C with the subsequent annealing at this temperature for several hours. Then the powder was grinded in an agate mortar and annealed at 900 °C for 24 h. Finally, the powder was grinded again, pressed into pellets and annealed at 1250 °C for 48 hours in a flowing oxygen atmosphere. According to the XRD analysis, the product has a single phase of rhombohedral perovskite crystal structure with lattice constants $a=0.5470(5)$ nm, $b=0.510(3)$ nm, $c=0.76(2)$ nm. The angle and volume are $90.3(2)^\circ$ and $0.2340(8)$ nm³, respectively. The oxygen deficit δ is equal to 0.01.

3. Magnetic measurements

The magnetic characterization was performed by means of the PPMS system. The temperature dependence of the AC magnetic susceptibility was measured at 10 Oe amplitude, whereas the temperature variation of the field-cooled (FC) and zero-field-cooled (ZFC) magnetization was registered at magnetic fields of 100 Oe. The DC magnetization isotherms were registered in magnetic fields up to 2 T. The magnetic field was applied along the axis of the needle shaped sample.

4. Magnetic results

The dc magnetic susceptibility is a slowly increasing function of temperature up to 270 K, where a maximum is observed ([Fig. 1](#)). It is followed by an abrupt decrease above 320 K and the Curie temperature is found at 331 K, as indicated by the temperature derivative of susceptibility. The relatively narrow maximum in the out of phase component of susceptibility indicates that the energy absorption increases in the same narrow temperature range. The field-cooled (FC) and zero-field-cooled (ZFC) magnetization measured in magnetic field of 100 Oe ([Fig. 2](#)) shows that the irreversibility temperature is as high as 320 K. This reveals the competing magnetic orderings. The temperature variation of the susceptibility and magnetization confirms that the sample is single phase.

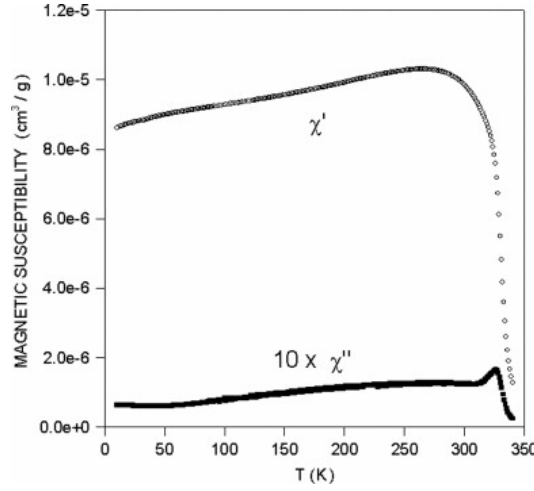


Fig. 1. Temperature variation of the in-phase and out of phase components of AC magnetic susceptibility of $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite.

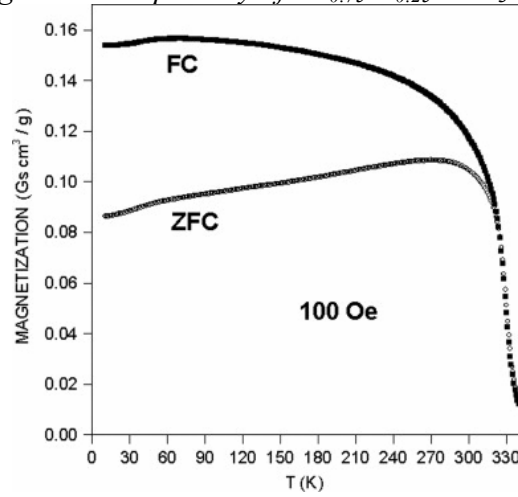


Fig. 2. Temperature variation of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization of $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite.

A fast drop of magnetization occurring in a narrow interval above around Curie temperature suggests that this material may exhibit a high magnetocaloric effect. Therefore, the magnetization isotherms were recorded up to 2 T between 286 and 340 K (Fig. 3) following a method described separately [3] and [4]. At temperatures close to 286 K, magnetization exhibits an abrupt increase below about 1500 Oe, which is followed by a slow approach to saturation. The magnetic moment at 286 K equal to $2.1 \mu_B$ is lower as compared to the theoretical value of $3.75 \mu_B$ and shows that the manganite studied is far from achieving magnetic saturation. On the other hand, temperature variation of magnetization close to 340 K is typical for paramagnetic phases.

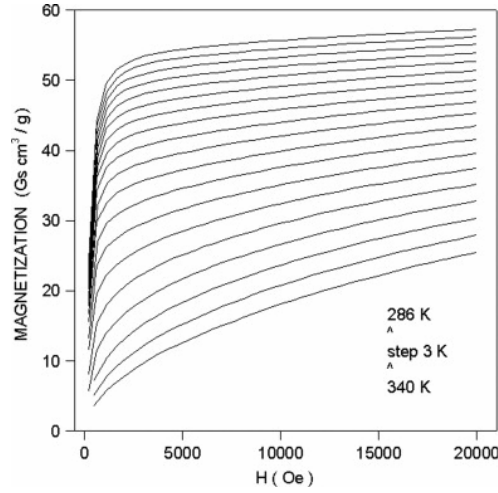


Fig. 3. The DC magnetization isotherms of $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite measured at temperatures between 286 and 340 K, with 3 K step.

The magnetic phase transition is analyzed by means of the so-called Arrott plot based on Landau expansion in vicinity of Curie temperature

$$AM + BH^3 = H \quad (1)$$

where the A and B parameters depend on temperature. The isotherms are plotted in [Fig. 4](#) for temperatures between 286 and 340 K. The positive slope for all curves proves that the ferro-to paramagnetic transition is of the second order [\[5\]](#). Values of the A parameter are determined by fitting to the straight high field fraction of isotherms in [Fig. 4](#) (not shown). The sign change in thermodynamic parameter A indicates the Curie temperature of 332 K ([Fig. 5](#)), which agrees well with values determined from susceptibility data. Additionally, the temperature variation of spontaneous magnetization ([Fig. 6](#)) derived by extrapolation from high field magnetization ([Fig. 3](#)) reveals the same Curie temperature.

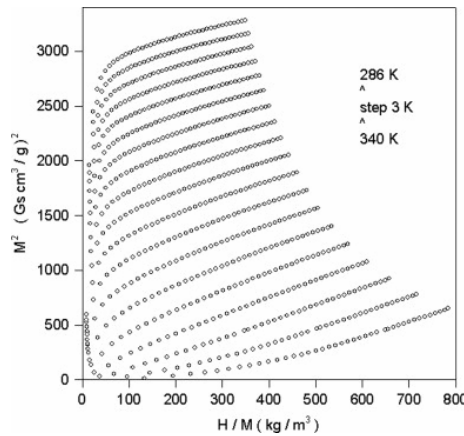


Fig. 4. Arrott plot of M^2 vs. H/M isotherms between 286 and 340 K.

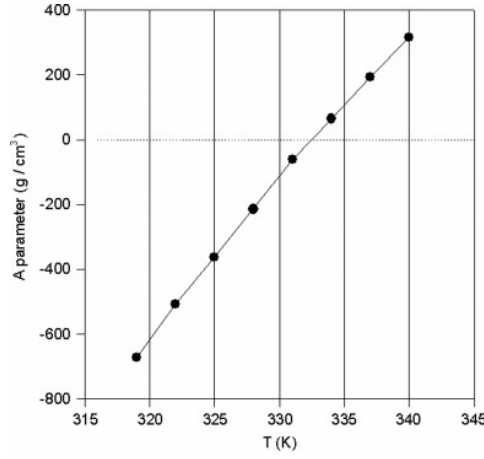


Fig. 5. Thermodynamic parameter A for equation ($AM+BM^3=H$) as a function of temperature for $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite.

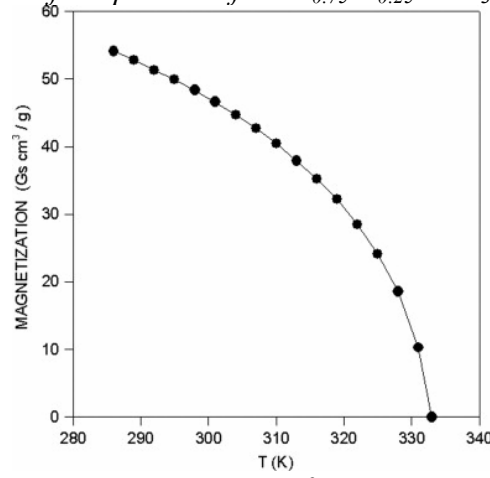


Fig. 6. Spontaneous magnetization of $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite as a function of temperature.

5. Magnetocaloric effect

The magnetic entropy change ΔS was calculated from magnetization isotherms for magnetic fields of 0.5, 1, 1.5 and 2 T following the standard procedure [2], [3] and [4]. The negative values of ΔS achieve a minimum located close to the Curie temperature (Fig. 7) and shifts from 328 to 331 K, when magnetic field raises from 0.5 to 2 T. The ΔS minimum appears about 15 K below a temperature reported for the $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite prepared, by the sol–gel method reported by Guo et al. [6]. Absolute values of ΔS increase roughly proportionally to magnetic field strength and achieve a maximum of -2 J/kg K at 2 T field. For the magnetic field of 1.5 T, the ΔS values are about 15% higher than for the $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite prepared by the sol–gel method [6].

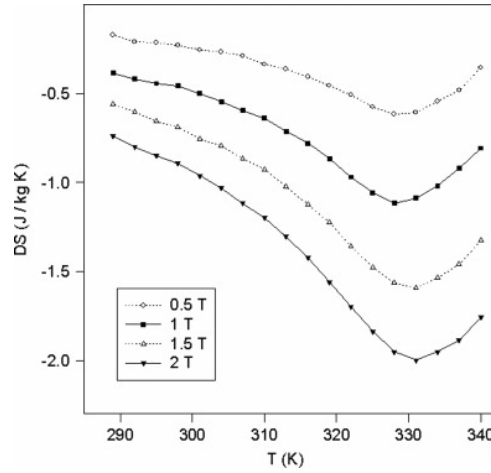


Fig. 7. Magnetic entropy change around the Curie temperature for $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite.

Due to technical reasons, the magnetization isotherms could be measured only up to 340 K. Thus, a DS width at half minimum DT (Fig. 7) can be cautiously estimated, taking into account its asymmetry and assuming that it is the same as for the sol-gel prepared manganite of [6]. A temperature width of the low temperature section of DS peak at half minimum located below minimum is roughly twice broader than the interval of high temperature section above minimum (Fig. 3 in [6]). This assumption is additionally justified by the same asymmetry ratio observed for similar $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ manganite (Fig. 6 in [3]). This in turn allows to evaluate the so-called cooling efficiency RCP(S) as

$$\text{RCP(S)} = -\text{DS}_{\text{MAX}} \text{ DT} \quad (2)$$

Taking DT equal to 40 K and DS_{MIN} of 1.6 J/kg K, one arrives to $\text{RCP(S)} = 64$ J/kg for 1.5 T magnetic field. On the other hand, for the $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite prepared by the sol-gel method [7], corresponding width at half minimum DT is about 41 K resulting in the RCP(S) about 55 J/kg, as estimated from Ref. [6]. Moreover one may notice that, the RCP(S) of the sample studied is larger than for similar $\text{La}_{0.72}\text{Sr}_{0.28}\text{MnO}_3$ manganite, which exhibits the DS minimum around the Curie temperature of 364 K [7]. A width of para- to ferromagnetic transition and of DT peak is known to increase with raising atomic disorder. This in turn enhances the cooling power of material. The almost equal DT width shows indirectly that both the carbonate precipitation and sol-gel methods supply manganites with similar degree of disorder.

The present study of the $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ manganite shows that the carbonate precipitation route produces samples exhibiting the stronger magnetocaloric effect than for the sol-gel method. This enables an application of the manganite studied even above the room temperature. The strontium doped lanthanum manganites are known to suppress the Curie temperature down to room temperature or below when decreasing Sr content [2] and [4]. This is accompanied by an enhancement of magnetic entropy change. Therefore, a reduction of Sr content towards about 0.2 enables to tailor a manganite applicable for magnetic refrigeration around the room temperature.

Acknowledgements

Work supported in parts by Ministry of Science and Higher Education (PL) and CGRI (BE) within the Scientific Cooperation Wallony – Poland.

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