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Magnetocaloric effect in $La_{0.67}Sr_{0.33}MnO_3$ manganite above room temperature

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ABSTRACT

The $La_{0.67}Sr_{0.33}MnO_3$ composition prepared by sol–gel synthesis was studied by dc magnetization measurements. A large magnetocaloric effect was inferred over a wide range of temperature around the second-order paramagnetic–ferromagnetic transition. The change of magnetic entropy increases monotonically with increasing magnetic field and reaches the value of 5.15 J/kg K at 370 K for $\Delta\mu 0H=5$ T. The corresponding adiabatic temperature change is 3.3 K. The changes in magnetic entropy and the adiabatic temperature are also significant at moderate magnetic fields. The magnetic field induced change of the specific heat varies with temperature and has maximum variation near the paramagnetic–ferromagnetic transition. The obtained results show that $La_{0.67}Sr_{0.33}MnO_3$ could be considered as a potential candidate for magnetic refrigeration applications above room temperature.

1. Introduction

The entropy of a magnetic material changes when it is subjected to an applied magnetic field. Under adiabatic conditions, the lattice and magnetic parts of the total entropy change by the same amount but with opposite sign [1–3]. In this process there is a temperature change, which is known as the magnetocaloric effect (MCE) [1–3]. Magnetic refrigeration (MR) is based on MCE and has potential as a future cooling technology. Near room temperature (RT) MR is a promising alternative to conventional gas compression refrigeration due to its unique advantages such as high efficiency and minimal environmental impact [1–4]. While refrigeration involves about 15% of the worldwide energy consumption, it has been estimated that MR has the potential to reduce the energy consumption by 20–30% over the conventional vapor compression technology [6]. Therefore, there is an ongoing quest to find suitable materials that have a large enough magnetic entropy change at moderate magnetic fields near room temperature [1–6].

Since the discovery of the colossal magnetoresistance effect, the physical properties of doped perovskite manganites have been studied extensively in view of their complex physics and potential applications [7–9]. Manganites are good candidate materials for MR near RT [1–3,5], where Gadolinium (Gd) is a leading material [1–5]. Although the change of magnetic entropy near RT in some manganites is much higher than in Gd [3] their specific heat is larger so their adiabatic temperature change is relatively smaller. This problem can be eased at higher temperatures, because the adiabatic temperature change is proportional to temperature [1–3]. $La_{1-x}Sr_xMnO_3$ is one of the most attractive manganite families because it has the highest Curie temperature of 370 K at optimum doping $x=0.33$ [7–9]. In this work, we use dc magnetization measurements to study the MCE in a $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) powder sample. Around the Curie temperature, a large magnetic entropy change has been observed and the changes of magnetic entropy and adiabatic temperature at moderate magnetic fields are quite significant. The results suggest that LSMO has potential for magnetic refrigeration above RT.

2. Experiments

The powder samples of LSMO were prepared by the sol–gel method [10]. Stoichiometric amounts of $La(NO_3)_3\cdot 6H_2O$, $Mn(NO_3)_2\cdot 4H_2O$ and $Sr(NO_3)$ were dissolved in water and mixed with ethylene glycol and citric acid (molar ratio of 1:4:3 for cations: citric acid: ethylene glycol). The gel was dried and calcined at 500 °C for 5 h. The resultant powder was then annealed at 1000 °C for 5 h. Structural characterization of the sample was investigated by X-Ray diffraction (XRD using Philips X'Pert PRO X-ray diffractometer equipped with a Cu–K_α X-ray source ($\lambda=1.5406$ Å). Magnetization measurements were performed as a function of field and temperature using a Quantum Design MPMS XL SQUID magnetometer.

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3. Results and discussion

The XRD pattern and the Rietveld analysis using the FULLPROF program [11,12], shown in Fig. 1, confirm that the sample is of single phase with no detectable secondary phases. The crystal structure is rhombohedral with space group $R\bar{3}C$ at room temperature. The refined lattice parameters are $a=5.4879$ Å and $c=13.3622$ Å. The calculated Mn–O bond length and Mn–O–Mn bond angle are $d_{Mn-O}=1.9439$ Å and $\theta_{Mn-O-Mn}=169.93^{\circ}$, respectively. The refined structural parameters are in good agreement with those reported for $La_{0.7}Sr_{0.3}MnO_3$ ($a=5.5039$ Å, $c=13.3553$ Å, $d_{Mn-O}=1.9537$ Å and $\theta_{Mn-O-Mn}=166.351^{\circ}$) [13].

Fig. 2 shows the magnetization σ and its temperature derivative ($d\sigma/dT$) versus temperature in field-cooled mode ($\mu_0H=5$ mT). The sample shows a sharp paramagnetic–ferromagnetic (PM–FM) transition with Curie temperature at 375 K. Fig. 3 shows a plot of the temperature dependence of magnetization of the sample. If one assumes the magnetic moment at temperature T and magnetic field H is given by $m(T,H)=m_{sp}(T)+\chi H$, the spontaneous magnetic moment of the sample at T, $m_{sp}(T)$, can be calculated by fitting the linear part of magnetization at high magnetic field. From the temperature dependence of m_{sp} and χ, shown in the inset of Fig. 2, it can be seen that m_{sp} increases with decreasing temperature and reaches the theoretical value of 3.68 μ_B/Mn expected for fully aligned spin of LSMO at low temperature.

The Banerjee criterion has been frequently used to check the nature of the magnetic phase transition in manganites [14–16]. According to this criterion, the positive or negative slope of μ_0H/σ versus σ^2 (Arrott plot) curves indicates whether the magnetic phase transition is second order or first order. As can be seen from Fig. 4, near the paramagnetic–ferromagnetic phase transition, μ_0H/σ versus σ^2 curves clearly exhibit positive slope in the entire σ^2 range, which confirms the second-order nature of the transition. According to the mean field theory, near the transition point, μ_0H/σ versus σ^2 should show a series of parallel lines at various temperatures and the line related to T_C should pass through the origin [14,15]. The Arrott plot curves shown in Fig. 4 are not linear, which indicates the mean field theory is not valid for LSMO. In fact, the critical isotherm is closer to $H\propto M^5$ than $H\propto M^3$.

The change of magnetic entropy of a magnetic material has the largest value near a phase transition, where the magnetization changes rapidly with temperature [1–3]. Therefore, a large

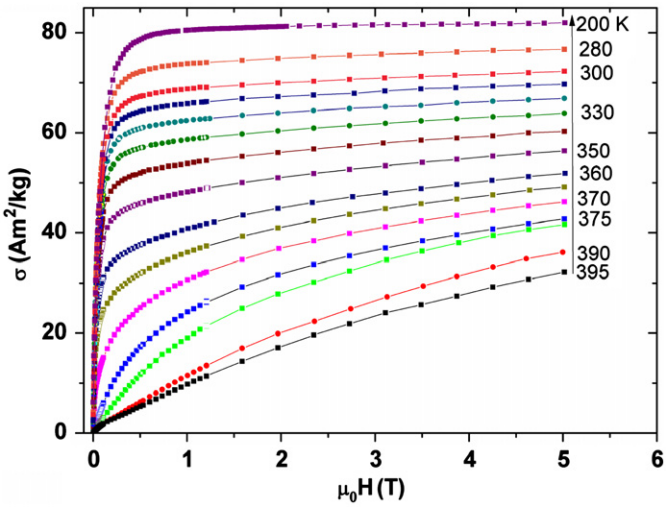

Fig. 3. Magnetization curves of the sample at different temperatures.

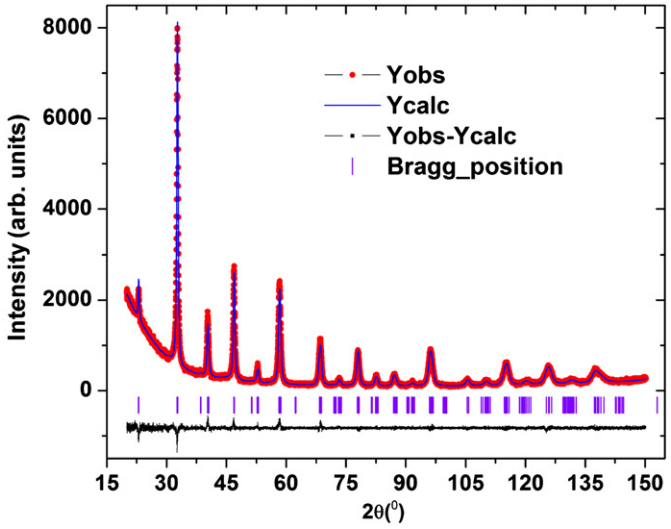

Fig. 1. X-ray diffraction pattern and the corresponding Rietveld refinement of the sample.

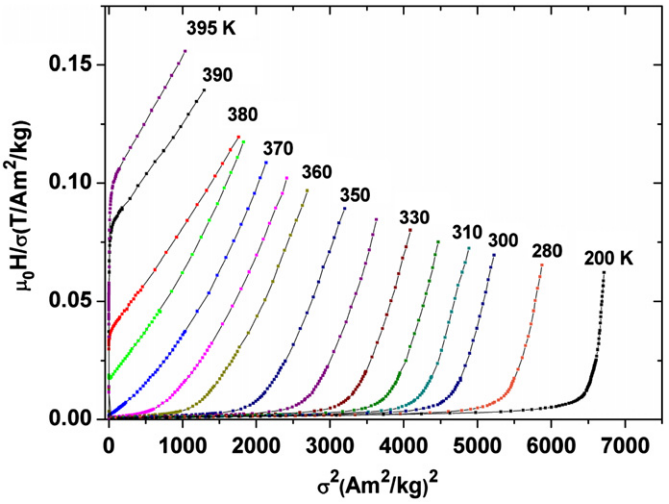

Fig. 4. Arrott plot (μ_0H/σ versus σ^2) of the sample at different temperatures.

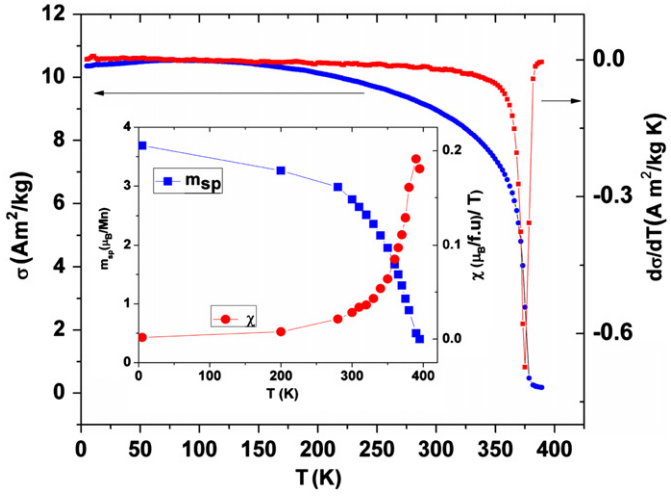

Fig. 2. Field cooled magnetization of the sample and its temperature derivative as a function of temperature at applied field of 5 mT. Inset shows the temperature dependence of spontaneous magnetization and magnetic susceptibility.