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Large magnetic entropy change in nanocrystalline $Pr_{0.7}Sr_{0.3}MnO_3$

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Nanocrystalline $Pr_{0.7}Sr_{0.3}MnO_3$ sample has been prepared by sol-gel method. The room temperature powder x-ray diffraction data show single phase nature of the sample and confirm the cubic crystal structure with $Fm\bar{3}m$ space group. The average crystallite size is calculated using Scherrer formula, and it is found to be ~25 nm. Transmission electron microscopy image shows that the particles are spherical in shape and the average particle size is ~35 nm. The sample undergoes ferromagnetic ordering at 235 K (T_C) and obeys the Curie–Weiss law in the paramagnetic region. The maximum value of the magnetic entropy change $|\Delta S_M|_{max}$ is ~6.3 J kg^{-1} K^{-1}, and the relative cooling power is ~385 J kg^{-1} for a field change of 50 kOe. The Arrott plot confirms that the magnetic ordering is of second order nature. The experimentally observed magnetic entropy change of the sample obeys Landau theory of phase transition well. © *2010 American Institute of Physics*.
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I. INTRODUCTION

Doped manganites of type $R_{1-x}A_xMnO_3$ (where R=rare-earth and A=alkaline-earth) exhibit exotic phenomena such as colossal magnetoresistance and charge ordering. These have been extensively studied not only because of fundamental interest but also for their potential applications.[1–5] Manganites are relatively easy to synthesize, their magnetic ordering temperatures are tunable by the choice of suitable dopant concentration, and they exhibit large magnetocaloric effect.[6–9] Hence they are considered as promising magnetic refrigerants. In the present work, we study magnetic and magnetocaloric properties of nanocrystalline $Pr_{0.7}Sr_{0.3}MnO_3$ compound. This compound shows large magnetic entropy change at 235 K (T_C), with moderate relative cooling power (RCP). This result is of practical importance because it shows that these compounds could be good working materials for magnetic refrigeration in the intermediate temperature range.

II. EXPERIMENTAL DETAILS

Nanocrystalline $Pr_{0.7}Sr_{0.3}MnO_3$ sample was synthesized using sol-gel method. The crystal structure was determined by powder x-ray diffraction (XRD) at room temperature using Cu K_α radiation (λ=1.5405 Å). The morphology, size, and chemical composition of the sample were examined by scanning electron microscopy attached with the energy dispersive x-ray analysis (EDAX) (FEI, Quanta-200), and transmission electron microscope. The magnetic measurements were performed using vibrating-sample magnetometer (Physical Properties Measurement System (PPMS), Quantum Design) in the temperature range of 5–300 K.

III. RESULTS AND DISCUSSION

The analysis of powder XRD pattern confirms the single phase nature of sample. This sample has cubic crystal structure (space group of $Fm\bar{3}m$) with a cell parameter of $a(=b=c)=0.3662$ nm. The average crystallite size calculated from XRD data using Scherrer formula is ~25 nm. The chemical composition and homogeneity of the sample are confirmed by EDAX. Transmission electron microscopy (TEM) image shows that the particles are nearly spherical in shape and the average particle size is ~35 nm (Fig. 1). The temperature dependence of magnetization measured in an applied field of 100 Oe shows divergence between zero-field-cooled (ZFC) and field-cooled (FC) magnetization (M_{FC}) curve below 240 K, and M_{FC} reaches a maximum value of ~0.43 μ_B/f.u. at 5 K. The sample undergoes paramagnetic to ferromagnetic transition at 235 K while cooling from 300 to 5 K (Fig. 2). The nanocrystalline transition temperature (T_C) is small compared to polycrystalline bulk T_C~250 K of the $Pr_{0.7}Sr_{0.3}MnO_3$ sample.[10] The data follows the Curie–Weiss law from 250 to 300 K. The estimated value for paramagnetic Curie temperature θ_P is 240 K, and the effective magnetic moment, μ_{eff}, is ~4.38 μ_B/f.u. The saturation

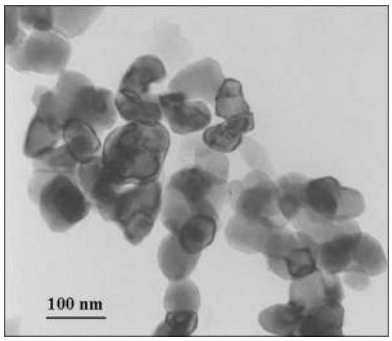

FIG. 1. Transmission electron microscopy image of the nanocrystalline $Pr_{0.7}Sr_{0.3}MnO_3$ sample.

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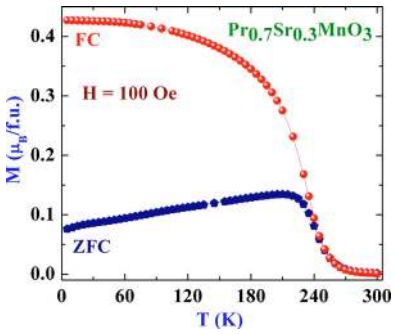

FIG. 2. (Color online) Temperature variation of ZFC and FC magnetizations in 100 Oe applied magnetic field.

magnetization computed from M-H data at 5 K is ~3.1 μ_B/f.u. (Fig. 3). The magnetic entropy change is calculated from magnetization isotherms [Fig. 4(a)] using the Maxwell's relation. The change in magnetic entropy associated with the magnetic field change can be written as

$$|\Delta S_M| = \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right) dH, \quad (1)$$

where H_{max} is the maximum external magnetic field. The calculated maximum value of the magnetic entropy change $|\Delta S_M|_{max}$ is ~6.3 J kg^{-1} K^{-1} for field change from 0 to 50 kOe [shown in Fig. 4(b)], which is large compared to that obtained for other manganite materials.[11] For the application point of view, the RCP is an important parameter in determining the cooling efficiency and is defined as

$$RCP = |\Delta S_M| \times \delta T_{FWHM}, \quad (2)$$

where δT_{FWHM} is the full width at half maximum of $|\Delta S_M|$ versus T curve.[12] The calculated RCP value is 385 J kg^{-1} for 50 kOe field change, which is comparable to that in bulk $Pr_{0.63}Sr_{0.37}MnO_3$, which has $|\Delta S_M|$ value of 8.5 J/kg/K for 50 kOe field variation.[9] It is of importance to note that the hysteresis is negligible near and below T_C (and very feeble at 5 K) because of the second order nature of the magnetic phase transition in this system. Indeed care must be taken when one deals with materials that exhibit first order magnetic transition giving rise to large thermal hysteresis in the vicinity of this magnetic transition such as $Gd_5Si_2Ge_2$ or charge ordered $Pr_{0.5}Sr_{0.5}MnO_3$ manganites.[13]

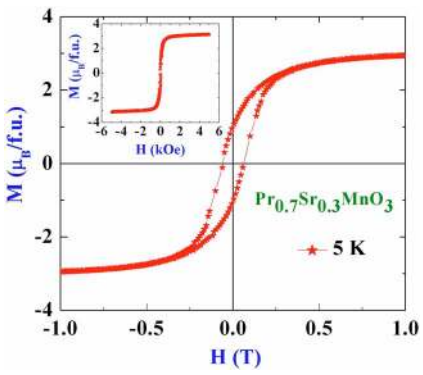

FIG. 3. (Color online) Field dependence of magnetization at 5 K for the nanocrystalline $Pr_{0.7}Sr_{0.3}MnO_3$ sample.

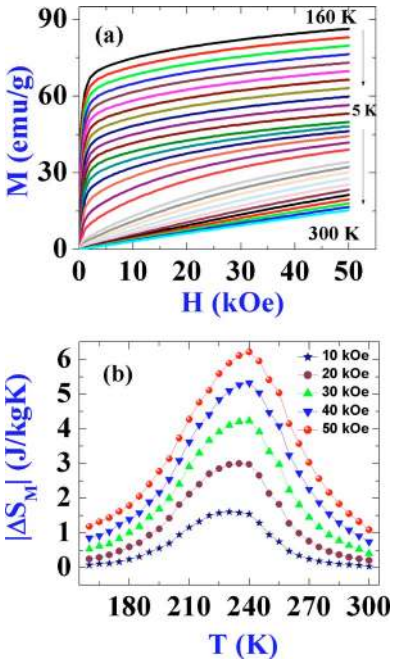

FIG. 4. (Color online) (a) Magnetization vs field (M-H) isotherms measured at a temperature interval of 5 K between 160 and 300 K. (b) The temperature dependence of the magnetic entropy change ΔS_M of the nanocrystalline $Pr_{0.7}Sr_{0.3}MnO_3$ for different field changes.

Applying Landau theory of phase transition, we attempted to understand the temperature dependence of the magnetic entropy change of the sample. The Gibbs free energy can be written as

$$G(T,M) = G_0 + \tfrac{1}{2}AM^2 + \tfrac{1}{4}BM^4 - HM, \quad (3)$$

where coefficients A and B are temperature-dependent parameters containing the magnetoelastic coupling and electron condensation energy.[14] In equilibrium condition at T_C, the magnetic equation of state can be expressed as

$$\frac{H}{M} = A + BM^2. \quad (4)$$

In order to check the nature of phase transition, we have plotted H/M versus M^2 (Arrott plot). Figure 5(a) shows a positive slope, which means a second order phase transition as suggested by Banerjee criterion.[15] The magnetic entropy change can be obtained from the Gibbs free energy relation,

$$\Delta S_M(T,H) = -\tfrac{1}{2}A'(T)M^2 - \tfrac{1}{4}B'(T)M^4, \quad (5)$$

where A′(T) and B′(T) are the temperature derivatives of the expansion coefficients. The temperature dependence of parameters A and B is obtained from the linear region of the Arrott plot of H/M versus M^2 for different temperatures [inset of Fig. 5(a)]. Using parameters A and B determined from the experimental data, ΔS_M are calculated from Eq. (5) and are shown as solid lines in Fig. 5(b). It is clear from the results obtained based on proposed model, fit well with the experimental data on magnetic entropy change. So the temperature dependence of the magnetic entropy change is understood within the framework of Landau theory.

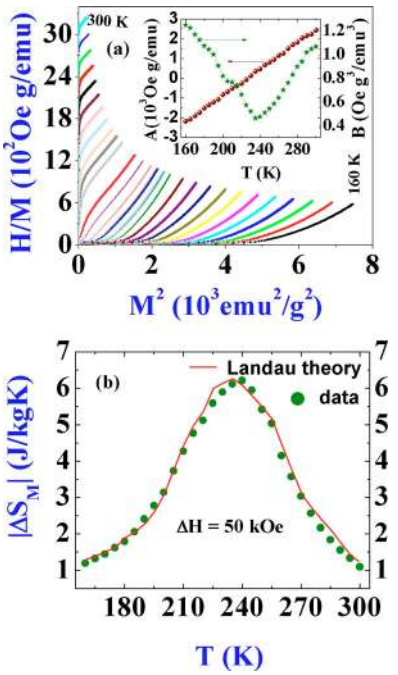

FIG. 5. (Color online) (a) Arrott plot of M^2 vs H/M for $Pr_{0.7}Sr_{0.3}MnO_3$ sample. Inset shows the temperature dependence of A and B parameters. (b) The calculated and experimental values of magnetic entropy change vs temperature.

IV. CONCLUSION

Nanocrystalline $Pr_{0.7}Sr_{0.3}MnO_3$ sample of ~35 nm particle size has been synthesized by sol-gel method. The ferromagnetic transition temperature for this nanomanganite is ~235 K, whereas for the bulk counterpart it is ~250 K. It shows large magnetocaloric effect (MCE) close to T_C, the maximum magnetic entropy change observed is ~6.3 J kg^{-1} K^{-1} for a field change of 50 kOe, and the corresponding RCP is ~385 J/kg^{-1}. The observed temperature dependence of ΔS_M is in accordance with Landau theory.

ACKNOWLEDGMENTS

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