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Magnetocaloric effect and critical behavior in Fe-doped $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$ manganites

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ABSTRACT

In this paper we report on the magnetocaloric effect and critical behavior of $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$ ($x=0$, 0.05, 0.1 and 0.2) manganites. The samples were prepared by the sol-gel method. X-ray diffraction patterns indicate that the Fe-doped manganites crystallize in a single phase with the rhombohedral structure. The Curie temperature decreases monotonously from 355 K to 100 K as the Fe concentration increases from 0 to 0.2. The maximum values of isothermal entropy change ($-\Delta S_{T,max}$) are found to be 1.66, 0.59, 0.79 and 0.42 J/kg K under a magnetic field change of 3 T for $x=0$, 0.05, 0.1 and 0.2, respectively. Although the $-\Delta S_{T,max}$ maxima are low, the manganites still exhibit significant refrigeration capacity (39–163 J/kg). The critical behaviors of the manganites have been studied by means of modified Arrott plot, Widom scaling and Kouvel-Fisher methods. The obtained critical exponents indicate that the Fe-doping level has significant influences on the critical behavior of the phase transition in the Fe-doped manganites.

1. Introduction

Magnetic refrigeration is considered as a promising cooling technology due to its higher energy efficiency and less impact on environment when comparing with traditional method based on gaseous compression. During the last few years, there has been a great deal of research on magnetocaloric materials for room temperature refrigeration. The studies mainly focused on the magnetocaloric effect (MCE) which is an intrinsic property of magnetic materials. The MCE is defined as the thermal responses (heating or cooling) of magnetic solids during the application or removal of external magnetic field. Commonly, the MCE is considered as the entropy change of the system in an isothermal process on applying field.

It has been found that many magnetic materials exhibit large MCEs near the transition temperatures [1–7]. The perovskite manganites with a common formula of $Ln_{1-x}A_xMnO_3$ (Ln represents trivalent rare-earth elements such as La, Pr, Nd, Sm, etc., and A stands for divalent alkaline-earth cations such as Ca^{2+}, Sr^{2+}, Ba^{2+}, etc.) also show significant MCE and tunable Curie temperature (T_C) near room temperature. Such manganites have been widely investigated due to the observation of colossal magnetoresistance (CMR) [8]. In recent years, the $Ln_{1-x}A_xMnO_3$ manganites have attracted renewed attention because of their possible applications in magnetic refrigeration [9–15].

For a ferromagnetic material, the maximum MCE is normally observed at T_C where the magnetic phase transition takes place. The large MCE originates from the sharp change of magnetic order accompanying the occurrence of transition. Therefore, the study of the critical behavior of phase transition is necessary and important to understand the intrinsic magnetocaloric property in a magnetocaloric material. In $Ln_{1-x}A_xMnO_3$ perovskite manganites, the origin of large MCE and CMR has been widely interpreted by means of the double-exchange (DE) mechanism [16] and the Jahn-Teller distortion related to strong electron-phonon interaction [17]. The critical behavior in the DE mechanism was first described with long-range mean-field theory (MFT) [18,19]. Later, Motome and Furulawa pointed out that the critical behavior in such manganites should be ascribed to short-range 3D-Heisenberg model (3D-HM) [20]. Currently, four kinds of different theoretical models, which are mean-field theory, 3D-Heisenberg model, 3D-Ising model, and tricritical mean field theory, are used to describe the critical behaviors in manganites. Nevertheless, the critical exponents for manganites are dependent on the use of different experimental tools and the values may cover all the universality classes even for the similar systems [21–26]. In the present work, we investigate the magnetocaloric properties and the critical behaviors by means of modified Arrott plot, Widom scaling and Kouvel-Fisher methods for $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$ ($x=0$, 0.05, 0.1 and 0.2) manganites.

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2. Experimental

Manganites with nominal compositions of $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$ (x=0, 0.05, 0.1 and 0.2) were prepared by the sol-gel method. La_2O_3 (99.99 wt%), $Sr(NO_3)_2$ (99.9 wt%), $Fe(NO_3)_2 \cdot 9H_2O$ (99 wt%) and $Mn(NO_3)_2$ aqueous solution (50 wt%) were used as raw materials. La_2O_3 was dissolved in nitric acid to obtain nitrate solution. The four kinds of nitrates with stoichiometric moles together with citric acid were mixed in deionized water (the molar ratio of cations: citric acid is 1:1.2). The gel was obtained after drying 48 h at 70 °C. The obtained gel was calcined at 250 °C for 2 h, and subsequently annealed at 800 °C for 4 h. The freely cooled powders were used in the structural and magnetic measurements. The structures of the samples were characterized by means of X-ray diffraction (XRD) with Cu-Kα radiation (λ=1.54056 Å). Magnetization measurements were carried out using a Quantum Design VersaLab magnetometer.

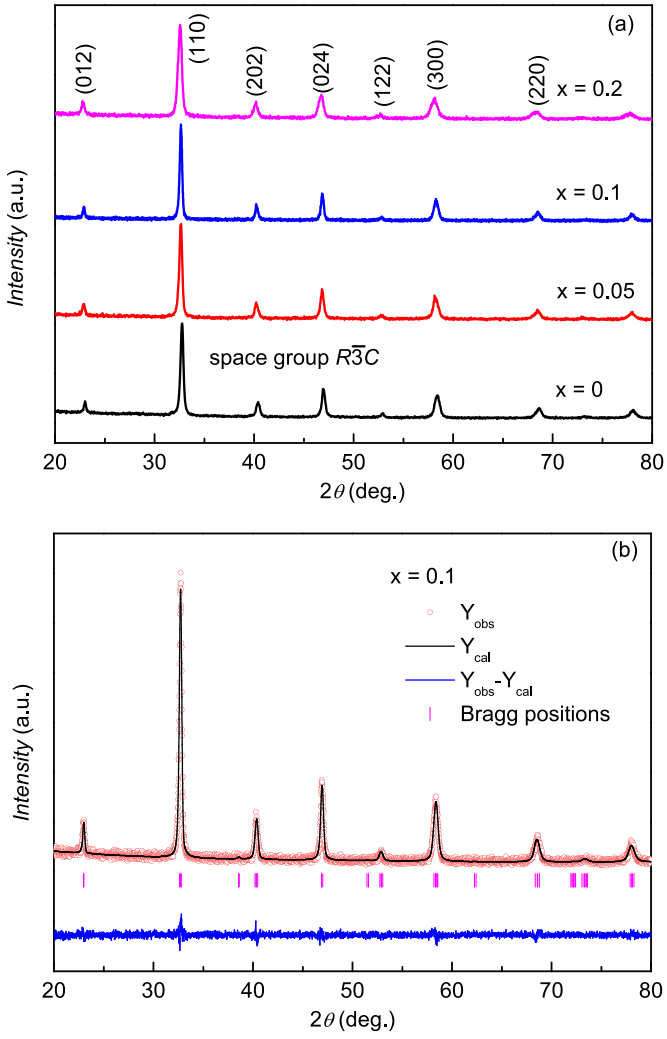

Fig. 1. (a) Powder XRD patterns for $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$ manganites with x=0, 0.05, 0.1 and 0.2. (b) Refined XRD pattern for x=0.1. Red circles: experimental data. Black line: calculated pattern. Pink ticks: positions of the Bragg reflections for the main phase. Blue line: difference between the experimental and calculated patterns. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Structural

Fig. 1(a) shows the XRD patterns measured at room temperature for $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$ manganites with x=0, 0.05, 0.1 and 0.2. The Bragg reflections indicate that all the manganites crystallize in a single phase with rhombohedral structure (space group $R\bar{3}c$). It means that with the Fe-doing up to 20 at% the crystalline structure remains unchanged in $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$. Rietveld refinements of the XRD patterns have been performed using FULLPROF program [27]. As an typical example, the refined XRD pattern for x=0.1 is shown in Fig. 1(b). The resulting lattice parameter and the corresponding agreement factors are summarized in Table 1 for all the studied manganites. An expansion in lattice is observed in the Fe-doped manganites, especially for x=0.2, the unit cell volume increases by about 1% when comparing with that of the Fe-free manganite. Besides, it is found that with an increase of Fe content from 0 to 0.2, the bond angle of Mn/Fe–O–Mn/Fe decreases from 169.67 to 164.88° while the bond length of Mn/Fe–O increases from 1.943 to 1.959 Å.

The crystallite sizes (D_S) of the studied manganites have been evaluated using the Deby-Scherer equation:

$$D_S = \frac{K\lambda}{\beta\cos\theta} \quad (1)$$

where K is the so-called shape factor, taking as 0.89, λ is the wavelength of Cu K_α radiation, β and θ are the full width of the Bragg diffraction peak at half maximum and the corresponding angle, respectively. The D_S has been estimated as the average value for the results of the (012), (110) and (202) peaks in each sample. The D_S values are found to be 25, 24, 31 and 20 nm for x=0, 0.05, 0.1 and 0.2, respectively.

3.2. Magnetic and magnetocaloric properties

Fig. 2(a) shows the magnetization as a function of temperature

Table 1
Values of lattice constants (a and c), unit cell volume (V), coordinate of O(18e) site (x), Mn/Fe–O-Mn/Fe bond angle, Mn/Fe–O bond length, profile factor (R_p), weighted profile factor (R_{wp}), global chi-square (χ^2), Bragg factor (R_{Bragg}) and crystallographic factor (R_F) for $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$ manganites with x=0, 0.05, 0.1 and 0.2.

Parameters	x=0	x=0.05	x=0.1	x=0.2
a (Å)	5.465 ± 0.001	5.469 ± 0.001	5.468 ± 0.001	5.483 ± 0.002
c (Å)	13.449 ± 0.003	13.449 ± 0.005	13.450 ± 0.003	13.493 ± 0.007
V (Å^3)	347.8 ± 0.1	348.3 ± 0.2	348.3 ± 0.1	351.4 ± 0.2
x of O(18e) site	0.465 ± 0.003	0.451 ± 0.002	0.460 ± 0.002	0.453 ± 0.003
Mn/Fe–O–Mn/Fe bond angle (°)	169.67 ± 0.07	168.71 ± 0.11	167.11 ± 0.08	164.88 ± 0.12
Mn/Fe–O bond length (Å)	1.943 ± 0.004	1.945 ± 0.005	1.948 ± 0.004	1.959 ± 0.004
R_p (%)	4.57	6.63	8.98	6.15
R_{wp} (%)	5.82	8.60	11.6	7.90
χ^2	1.01	1.30	1.16	1.17
R_{Bragg} (%)	3.42	2.81	4.54	2.62
R_F (%)	3.69	3.27	4.72	2.21

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