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Effect of Al substitution on magnetocaloric effect in $La_{0.57}Nd_{0.1}Sr_{0.33}Mn_{1-x}Al_xO_3$ ($0.0 \leq x \leq 0.30$) polycrystalline near room temperature

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ABSTRACT

We have investigated the effect of aluminum (Al) doping on the magnetic and magnetocaloric properties of $La_{0.57}Nd_{0.1}Sr_{0.33}Mn_{1-x}Al_xO_3$ (LNSMAO) ($0.0 \leq x \leq 0.3$). The Curie temperature T_C of the prepared samples is found to be strongly dependent on the aluminum content and it spans between 238 K and 342 K. It has been analyzed by using two methods: a linear extrapolation of $M(T)$ to zero magnetization and the thermodynamic model. With an increasing Al concentration, a systematic increase in the values of magnetic entropy is observed. The magnitude of the isothermal magnetic entropy ($|\Delta S_M|$) at the FM Curie temperature increases from 2.31 J/kg K for $x = 0$ to a maximum value of 3.58 J/kg K for $x = 0.3$ for a magnetic field change of 10 kOe. Moreover, the relative cooling power (RCP) increases from 23 J/kg to 68 J/kg, respectively. Large magnetic entropy changes upon the application of a low magnetic field and a wide temperature range of T_C suggest that these materials can be used as candidates for magnetic refrigerants.

1. Introduction

Magnetic refrigeration based on the magnetocaloric effect (MCE) has attracted a great deal of interest in the prospect of an energy-efficient and environment-friendly alternative to the common vapor-cycle refrigeration technology in use today [1–3].

Magnetic materials contain two energy reservoirs; the usual phonon excitations connected to the lattice degrees of freedom and magnetic excitations connected to the lattice spin of freedom. These two reservoirs are coupled by the spin–lattice (in other words – magnetoelastic) interactions. An externally applied magnetic field can strongly affect the spin degree of freedom that results in the MCE. Historically, many ferromagnets concerning second-order transition were investigated in an attempt to achieve large magnetocaloric effect (MCE), of which the rare-earth elemental gadolinium Gd was used as a prototypical refrigerant because of near room temperature ferromagnetic transition ($T_C = 293$ K) and a large magnetic entropy change ($|\Delta S_M^{max}| = 13.3$ J/kg K for $\Delta H = 7$ T), due to a high spin value ($S = 5/2$ for Gd) [4].

Nonetheless, because of the high price of Gd (~$4000/kg), its usage as an active magnetic refrigerant (AMR) in magnetic refrigerators is limited. Therefore, the search for a new working substance at low prices and large MCE becomes a main research topic in this field. At present, besides some possible candidates, such as $Gd5(Si_{1-x}Ge_x)_4$ [4], $MnAs_{1-x}Sb_x$ [5], $MnFeP_{1-x}As_x$ [6], $Tb_{1-x}Gd_xAl_2$ [7] and RM_2 (where R = rare earth, M = Al, Co, Ni) [5,8–12], the hole-doped manganites with the general formula $Ln_{1-x}A_xMnO_3$ (Ln = trivalent rare earth, A = divalent alkaline earth) with perovskite structure should be one of the most promising materials because they present numerous advantages such as the low production costs, the ease of shaping and preparation, the tunable T_C and the chemical stability [13].

In this context, several studies have been performed on the effects of the substitution in the Ln-site [14,15], however, only a few studies have been reported in the substitution effects in the Mn-site [16,17] especially the presence of the non-magnetic ion in this Mn-site which influences the magnetotransport, the MR and the MC properties of the material. In fact, it has been revealed that $La_{1-x}Sr_xMnO_3$ based manganite materials, modulated by Mn-site substitution with Cr, Cu, Ni, Co, Fe etc., present a large isothermal entropy change upon an application of a magnetic field around the ordering temperature T_C [18–21].

To gain more insight into this aspect, we have studied the effect of the non-magnetic ion Al^{3+} substituted in the Mn-site on new magnetocaloric material $La_{0.57}Nd_{0.1}Sr_{0.33}MnO_3$ which might has properties applicable at room temperature.

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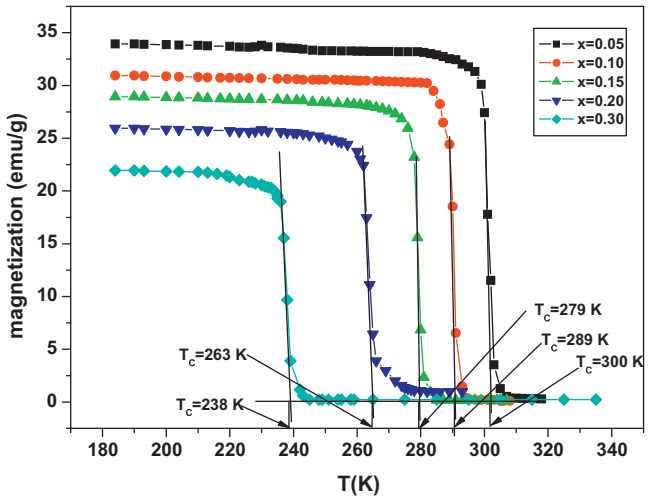

Fig. 1. Variation of the magnetization M vs. temperature for $La_{0.57}Nd_{0.1}Sr_{0.33}Mn_{1-x}Al_xO_3$ samples at 0.05 T for $x = 0.05$, 0.1, 0.15, 0.2 and 0.3.

2. Experimental

Polycrystalline samples of $La_{0.57}Nd_{0.1}Sr_{0.33}Mn_{1-x}Al_xO_3$ ($0.0 \le x \le 0.3$) prepared by conventional solid-state reaction method were taken from the same batches used in a previous work [22]. Room temperature X-ray diffraction measurement showed that the samples are single phase perovskite rhombohedral (space group $R\bar{3}c$) structures. The magnetization (M) vs. temperature (T) and magnetization vs. magnetic field (H) curves were measured by using a Foner magnetometer equipped with a super-conducting coil. Magnetization of the samples was measured in an isothermal regime under an applied magnetic field varying from 0 to 10 kOe. In the vicinity of Curie temperature, isothermal M (H) curves were obtained by steps of 5 and 2 K. The temperature steps were smaller near T_C and larger further away.

3. Results and discussion

3.1. Magnetization investigation

In order to analyze the effect of Al substitution on the Curie temperature, two methods have been used to determine T_C:

(i) The first one is a linear extrapolation of M (T) to zero magnetization. The Curie temperature T_C of the samples defined as the temperature corresponding to the inflection point of the M (T) curve. Fig. 1 shows the temperature dependence of magnetization for the LNSMAO ($0.05 \le x \le 0.30$) samples during cooling and warming measured under $\mu_0 H = 500$ Oe and T_C data extracted by extrapolation are shown in it. The obtained values of Curie temperature T_C are 300, 289, 279, 263 and 238 K, respectively, for $x = 0.05$, 0.10, 0.15, 0.20 and 0.30.

(ii) The second method is based on the thermodynamic model: Amaral et al. [23,24] discussed the magnetic properties of manganites in terms of the Landau theory of phase transitions. Here, the magnetic energy MH has been included in the expression of Gibb's free energy as given by:

$$F(T, M) = F_0 + \frac{1}{2}AM^2 + \frac{1}{4}BM^4 - MH$$

where A and B, known as Landau coefficients, depend both on pressure P and temperature T and provide information about magnetoelastic coupling and electron–electron interaction [23–26]. The last term in the equation describes the energy of spins which is expected to be slowly varying with temperature. On the other hand, the coefficient A shows negative and positive values below and above T_C respectively.

By assuming equilibrium condition of Gibb's free energy: $(\delta F/\delta M) = 0$, the magnetic equation of state is obtained as: $AM + BM^3 = H$. In this equation, M is the experimentally measured mass magnetization and equal to $M_S + M_i$, where M_S is the spontaneous and M_i is the true magnetization caused by the application of the field H.

Thus, by plotting the experimental data in the form, $A + BM^2 = H/M$, the temperature dependence of the parameters A and B can be extracted, from which the transition point T_C and the temperature dependence of M_S below T_C can be determined.

In order to gain a deeper understanding of the magnetic properties and to confirm the ferromagnetic behavior at low temperatures, we plotted the magnetization vs. the applied magnetic field (from 0 to 10 kOe) obtained at various temperatures for the LNSMAO samples ($x = 0.05$ and 0.20) in Fig. 2. We have not shown the M (H) data of the other samples since they have a similar behavior. These curves provide evidence of a close relationship between the magnetization M and the applied magnetic field H. Below T_C, the magnetization M increases sharply with magnetic applied field for ($H < 0.5$ kOe) and then saturates above 1 kOe. The saturation magnetization shifts to higher values with decreasing temperature. When the temperature approaches T_C, the magnetization change

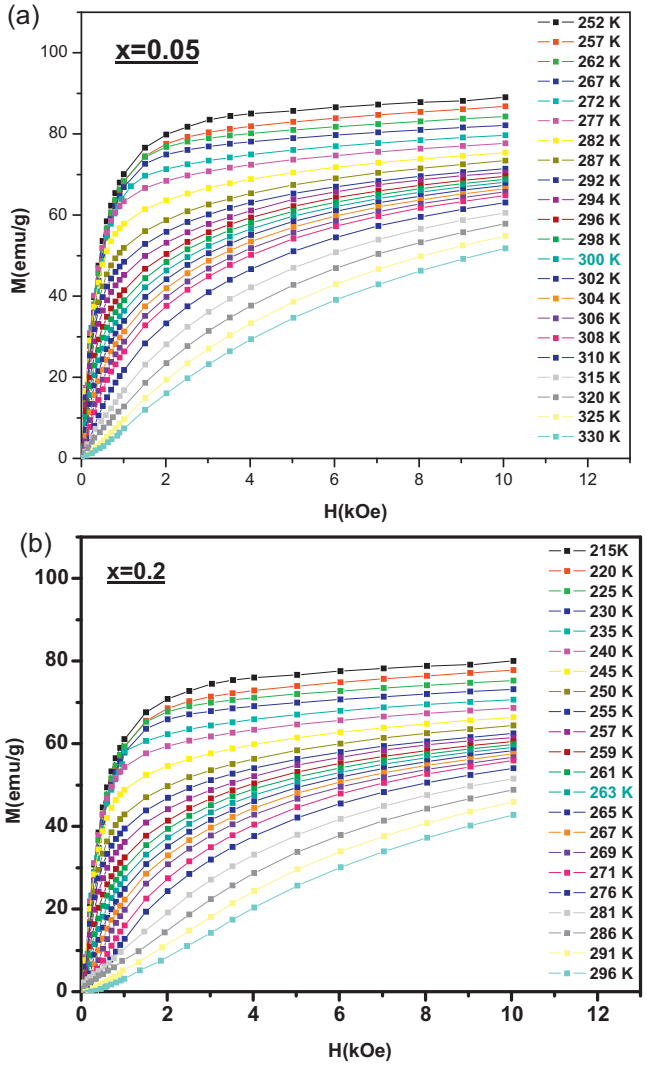

Fig. 2. Isothermal magnetization for $La_{0.57}Nd_{0.1}Sr_{0.33}Mn_{1-x}Al_xO_3$ samples measured at different temperature around T_C for: (a) $x = 0.05$, (b) $x = 0.2$.