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Magnetocaloric effect in $La_{1-x}Na_xSrMn_2O_{5+\delta}$ (with x = 0.1, 0.2 and 0.3)

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Abstract. The present paper is aimed to analyze the effects of sodium substitution on the magnetic entropy change between $La_{0.9}Na_{0.1}SrMn_2O_{5+\delta}$ and $La_{0.8}Na_{0.2}SrMn_2O_{5+\delta}$ polycrystalline samples. Evaluation of the potential magnetocaloric effects is sought through identifying the magnetic entropy change ΔS_M, which was basically determined from the magnetic field dependences of magnetization at different temperatures $M(H,T)$ near T_C. Interestingly, the substitution of a small amount of Na in $La_{1-x}Na_xSrMn_2O_{5+\delta}$ nanocrystalline samples (with $x = 0.1$, 0.2 and 0.3) reduced the maximum magnetic entropy $|\Delta S^M_{Max}|$ from $2.2\,J\,kg^{-1}\,K^{-1}$ (for $x = 0.1$) to $0.8\,J\,kg^{-1}\,K^{-1}$ (for $x = 0.3$) for a field change $\Delta H = 5\,T$. The relative cooling power (RCP) decreases with increasing Na content reaching $53.13\,J\,kg^{-1}$ for $x = 0.3$ ($\Delta H = 5\,T$), respectively.

1 Introduction

New brownmillerite materials have been extensively investigated not only for the variety of their physical properties but also for their wide potential for application in various industries and processes, including magnetic refrigeration technology which is based on the magnetocaloric effect. Compared to gas compression refrigeration, this technology exhibits significant advantages, such as high efficiency and minimal environmental impact [1,2]. The magnetocaloric effect, which results from the application or removal of a magnetic field to a magnetic material, is characterized by the isothermal entropy change ΔS_M and the adiabatic temperature change ΔT_{ab}. Recently, a large magnetic entropy change was reported for many compounds, such as Gd [3] and $LaSrMn_{2-x}Fe_xO_5$ [4]. Recent research within the magnetic cooling field has, therefore, given increasing attention to the search for new cost-effective materials with larger magnetocaloric effects. In this context, due to their large magnetocaloric effect which is comparable to the entropy change in Gd [5], low-cost, simple-preparation, and high-chemical-stability, new brownmillerite materials have attracted special interest as potential candidates for application in several magnetic refrigeration technologies. However, the magnetocaloric effect properties of these compounds are variable according to the substitution element of the A site. In particular, these properties can be affected by the partial replacement of Mn ions by transition metals such as Fe [4]. The magnetization, Curie temperature T_C, and magnetic entropy change ΔS_M have previously been reported to decrease by the substitution of a high amount of Fe at Mn [4].

In order to understand the impacts of the Na substitution on the magnetocaloric effect, we have studied the magnetic and entropy changes (ΔS_M) of $La_{1-x}Na_xSrMn_2O_{5+\delta}$ with $x = 0.1$, 0.2 and 0.3 samples as a function of temperature.

2 Experimental techniques

Powder samples of $La_{1-x}Na_xSrMn_2O_{5+\delta}$ (with $x = 0.1$, 0.2 and 0.3) were prepared by the ceramic method at high temperature. The detailed preparation procedure and basic physical properties are reported in ref. [4]. DC magnetization measurements on $La_{1-x}Na_xSrMn_2O_{5+\delta}$ were performed by a superconducting quantum interference device (SQUID) magnetometer.

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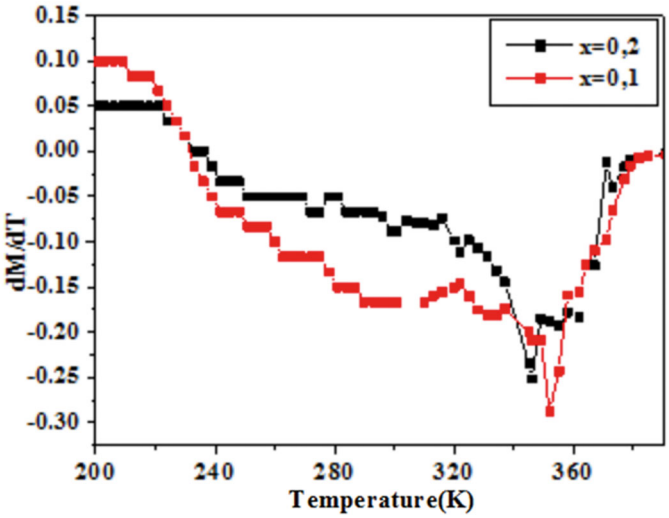

Fig. 1. Temperature dependence of the first derivative of the magnetization for $La_{1-x}Na_xSrMn_2O_{5+\delta}$ (with $x = 0.1$ and 0.2).

Table 1. Transition temperature T_C, θ_p, C, μ_{eff}^{exp}, and μ_{eff}^{th} as function of x content for $La_{1-x}Na_xSrMn_2O_{5+\delta}$ ((a) $x = 0.1$ and (b) $x = 0.2$).

	T_C (K)	θ_p (K)	C	μ_{eff}^{exp}	μ_{eff}^{th}
$x = 0.1$	352	358	1.4	3.34	3.25
$x = 0.2$	346	346.6	1.3	3.22	3.22
$x = 0.3$	335	346	1.2	3.09	3.19

3 Results and discussion

The temperature dependencies of the magnetization derivative curves obtained for the samples under an external applied magnetic field of 0.05 T are shown in fig. 1 for $x = 0.1$ and $x = 0.2$. The results revealed a paramagnetic to ferromagnetic transition. The $La_{1-x}Na_xSrMn_2O_{5+\delta}$ system was noted to undergo multiple magnetic phases. On cooling, the parent compound $LaSrMn_2O_5$ exhibited paramagnetic to ferromagnetic (FM) transition at $T_C = 365$ K, and the magnetic decrease in the 200–5 K temperature range was due to the presence of ferromagnetic clusters.

For all our samples, the temperature dependence of the inverse susceptibility χ^{-1} following the Curie Weiss fitted in solid lines (fig. 2). In the paramagnetic region, the relation between χ^{-1} and the temperature T is known to follow the Curie Weiss law, *i.e.*, $\chi = \frac{C}{T-\theta_p}$. The values of the Curie Weiss temperature, θ_p, and the Curie constant, C, could be obtained from the linear fit in the paramagnetic region of the samples. The θ_p followed the same trend of T_C, and its positive values suggested the presence of a ferromagnetic exchange interaction between the nearest neighbors. The values obtained for θ_p were higher than those recorded for T_C. This difference was previously reported to generally depend on the substance and to be associated with the presence of a short range ordered lightly above T_C, which could be related to the presence of a magnetic non-homogeneity or Griffits phases [6].

The Curie constant can be deduced from the fitting of the high temperature linear of χ^{-1} and expressed by the following relation:

$$C = \frac{N_A \mu_B^2}{3k_B} \mu_{eff}^2,$$

where $N_A = 6.023.10^{23}$ mol^{-1} refers to the number of Avogadro number, $\mu_B = 9.274.10^{-21}$ emu is the Bohr magneton, and $k_B = 1.38016.10^{-16}$ erg k^{-1} to the Boltzmann constant. The theoretical effective moment could also be calculated for all samples as follows [7]:

$$\mu_{eff}^{th} = g\sqrt{S(S+1)}.$$

Table 1 summarizes the temperature dependence of C, θ_p, μ_{eff}^{exp}, and μ_{eff}^{th} for an applied magnetic field of 0.05 T. The Curie constant values calculated from the line slopes of the reciprocal susceptibility *versus* temperature curve, χ^{-1} (T) have been used to estimate the experimental effective paramagnetic moment μ_{eff}^{exp}. The μ_{eff}^{exp} values were found to be 3.34 μ_B, 3.22 μ_B and 3.09 μ_B for $x = 0.1$, 0.2 and 0.3, respectively. The differences between the experimental effective paramagnetic moment and the theoretical one can be attributed to the presence of a Griffits phase in the paramagnetic state.

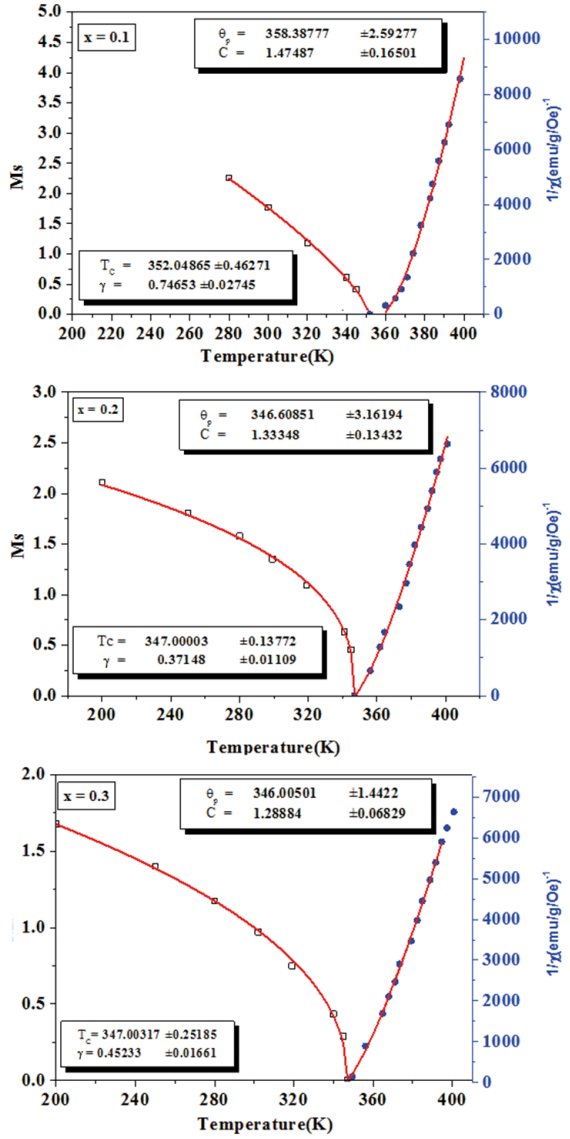

Fig. 2. Spontaneous magnetization and inverse susceptibility *versus* temperature for $La_{1-x}Na_xSrMn_2O_{5+\delta}$ (with $x = 0.1$, 0.2 and 0.3).

Figure 2 shows the spontaneous magnetization M_{sp}, deduced from the magnetization *versus* the applied magnetic field curves obtained for the $La_{1-x}Na_xSrMn_2O_{5+\delta}$ samples at different temperatures revealed a variation of magnetization around the Curie temperature. This indicated that there was a possible large magnetic entropy change associated with the ferromagnetic–paramagnetic transition temperature that occurred at T_C.

The total magnetic entropy change $|\Delta S_M|$ was calculated from magnetization isotherms as a function of temperature and magnetic applied field for all our synthesized samples. According to the thermodynamic theory based on the Maxwell relations, $|\Delta S_M|$ could be evaluated through the following formula:

$$\begin{aligned}\Delta S_M(T,H) &= S_M(T,H) - S_M(T,0)\\ &= \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right)_H dH,\end{aligned} \tag{1}$$

where H_{max} refers to the maximum value of the external magnetic applied field. In practice, for magnetization measurement, this relation can be estimated as follows:

$$|\Delta S_M| = \Sigma_i \frac{M_i - M_{i+1}}{T_{i-1} - T_i} \Delta H_i \tag{2}$$

where M_i and M_{i+1} refer to the experimental values of magnetization measured at temperatures T_i and T_{i+1} under magnetic applied field H_i, respectively [8].

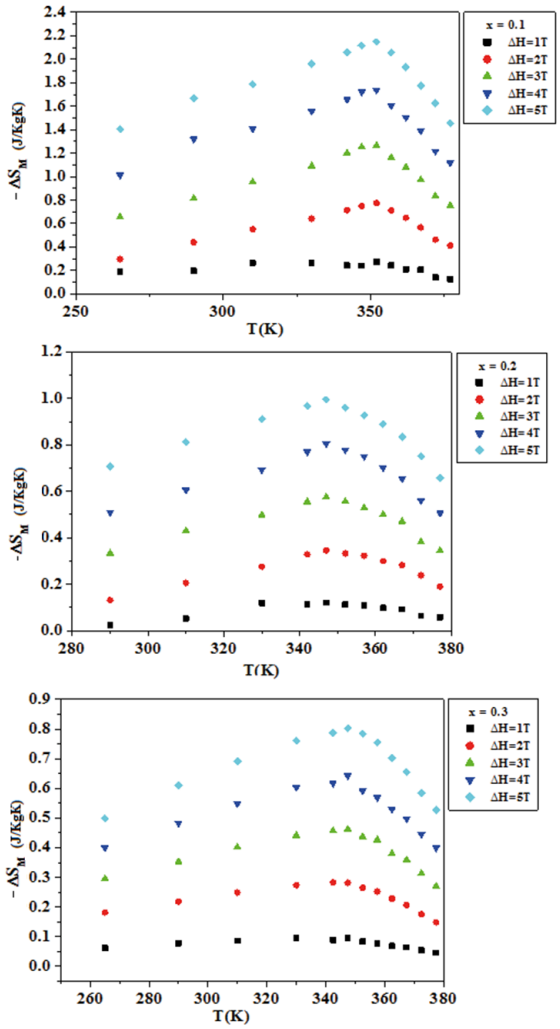

Fig. 3. Temperature dependence of the magnetic entropy change under different amplitudes of change in the magnetic field (from bottom to top $\Delta H = 1\,\mathrm{T}$, $2\,\mathrm{T}$, $3\,\mathrm{T}$, $4\,\mathrm{T}$, and $5\,\mathrm{T}$) for $La_{1-x}Na_xSrMn_2O_{5+\delta}$ (with $x = 0.1$, 0.2 and 0.3).

Figures 3 show the temperature dependence of the magnetic entropy change under several applied magnetic fields for $La_{1-x}Na_xSrMn_2O_{5+\delta}$ samples with $x = 0.1$, 0.2 and 0.3. These samples exhibited large magnetocaloric effects around the magnetic transition temperature, and the magnitude of $|\Delta S|$ increased non-linearly to reach a maximum with increasing the applied magnetic field. The maximum magnetic entropy change observed, Max $|\Delta S_{\mathrm{M}}^{\mathrm{Max}}|$, was found to be $2.21\,\mathrm{J\,kg^{-1}\,K^{-1}}$, $1\,\mathrm{J\,kg^{-1}\,K^{-1}}$ and $0.8\,\mathrm{J\,kg^{-1}\,K^{-1}}$ in a magnetic field change of $5\,\mathrm{T}$ for $x = 0.1$, 0.2 and $x = 0.3$ respectively.

The magnetic cooling efficiency of a magnetocaloric material was evaluated by considering the relative cooling power (RCP) [9] given by

$$\mathrm{RCP} = -|\Delta S_{\mathrm{M}}^{\mathrm{Max}}| \times \delta T_{\mathrm{FWHM}},$$

where δT_{FWHM} is the full-width at half maximum of the magnetic entropy change curve. The $|\Delta S_{\mathrm{M}}^{\mathrm{Max}}|$ and RCP values corresponding to a magnetic field of $5\,\mathrm{T}$ obtained for $x = 0.1$, 0.2 and 0.3 Na content are summarized in table 2. The results illustrated in table 2 present a comparison between the magnetocaloric effect performances of our samples and those of other samples reported in the literature. The results indicated that our RCP for the $La_{1-x}Na_xSrMn_2O_{5+\delta}$ sample was about 25% of the one reported for pure Gd [10] with $\Delta H = 5\,\mathrm{T}$. The magnetocaloric effect performances of the other samples were noted to decrease (*i.e.* $|\Delta S_{\mathrm{M}}^{\mathrm{Max}}|$ and RCP values decrease) when we had a substitution of a small amount of Na (see table 2). Table 2 also shows that the values achieved in our work are in good agreement with previous reports in the literature [11]. In particular, the authors have shown that the substitution of a small amount of Na in $La_{1-x}Na_xSrMn_2O_{5+\delta}$ system strongly reduced the maximum entropy decrease $|\Delta S_{\mathrm{M}}^{\mathrm{Max}}|$ from 2.2 to $0.8\,\mathrm{J\,kg^{-1}\,K^{-1}}$ ($\Delta H = 5\,\mathrm{T}$) for $x = 0.1$ and 0.3 samples, respectively.

Table 2. Maximum entropy change $|\Delta S_M^{Max}|$ and relative cooling power (RCP) occurring at the Curie temperature T_C and at a magnetic field $\Delta H = 5\,T$ for $La_{1-x}Na_xSrMn_2O_{5+\delta}$ (with $x = 0.1$, 0.2 and 0.3) samples compared to several materials considered for magnetic refrigeration.

	T_C	$\lvert\Delta S_M^{max}\rvert$ (J/kg K)	δT^{FWHM} (K)	ΔH (T)	RCP (J/kg)	Ref.
$La_{0.9}Na_{0.1}SrMn_2O_{5+\delta}$	352	2.2	47.025	5	103	This work
$La_{0.8}Na_{0.2}SrMn_2O_{5+\delta}$	346	1	58.18	5	58	This work
$La_{0.7}Na_{0.3}SrMn_2O_{5+\delta}$	335	0.8	66.42	5	53	This work
Gd	293	9.5	–	5	410	[10]
$LaSrMn_{0.8}Fe_{0.2}O_5$	345	0.75	97	5	73	[4]
$La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$	260	3.1	–	5	192	[11]

In our case, the reduction of magnetocaloric properties in our samples, *i.e.* the decrease of T_C, $|\Delta S_M^{Max}|$ and RCP values, with the increase of Na content can be explained qualitatively by the ferromagnetic double exchange interaction between the Mn^{3+} and Mn^{4+} ions dominating in the ferromagnetic cluster phase. On the other hand, the antiferromagnetic super-exchange interaction between the Mn^{3+} - Mn^{3+} or Mn^{4+} - Mn^{4+} ions dominated in the antiferromagnetic matrix.

4 Conclusion

Magnetic measurements show that all compounds presented a second-order PM-FM phase transition with a decrease in magnetization magnitude and in Curie temperature T_C. A decrease in the maximum magnetic entropy $|\Delta S_M^{Max}|$ and relative cooling power (RCP) was also observed upon the substitution of a high amount of Na. This can be explained by the reduction of the Mn^{3+}/Mn^{4+} ratio, which led to the decrease of double exchange (DE) interaction.

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