

Room-temperature large magnetocaloric effect in perovskites $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

Nguyen Hoang Luong^{1,*}, Nguyen Thi Mai Phuong^{1,2}, Phung Thu Hien¹,
Hoang Nam Nhat¹, Luc Huy Hoang², Nguyen Chau¹, Nguyen Hoang Hai¹

¹ Center for Materials Science, College of Science, Vietnam National University, Hanoi, 334 Nguyen Trai, Hanoi, Vietnam

² Hanoi University of Education, 136 Xuan Thuy, Hanoi, Vietnam

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Abstract. Study of the effect of Nd substitution for La on magnetocaloric effect (MCE) of polycrystalline perovskites $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) is presented. Large MCE is observed in all samples. The presence of Nd affects to both maximum magnetic entropy change, $|\Delta S_m|_{\max}$, and Curie temperature, T_C . $|\Delta S_m|_{\max}$ slightly reduces with low content and increases with high content of Nd and gets maximum value of 4.83 J/kg.K for $x = 0.8$. T_C of the samples determined from the thermomagnetic curves somewhat increases from 346 K for $x = 0.0$ to 350 K for $x = 0.2$, then decreases to 235 K for $x = 1.0$. The sample with $x = 0.4$ exhibiting the largest value of 74 J/kg for the relative cooling power among the studied samples has $T_C = 325$ K, i.e. higher than room temperature. Our studied samples are promising materials for magnetic refrigerants in the room-temperature region.

Keywords: Magnetocaloric effect, perovskites, manganites.

1. Introduction

The magnetocaloric effect (MCE) is detected as the heating or the cooling of magnetic materials due to a varying magnetic field. Magnetic refrigeration provides an alternative method for cooling [1,2]. The material used to provide the MCE is called a magnetic refrigerant. The MCE has been used for many years to obtain low temperatures (of the order of milikelvins) through adiabatic demagnetization of paramagnetic salts [3]. At present the magnetic refrigeration around room temperature is of particular interest because of potential impact on energy savings as well as environmental concerns (the desire to eliminate the chlorofluorocarbons present in high-temperature gas-cycle systems).

MCE is represented by a adiabatic temperature change, ΔT_{ad} , or isothermal magnetic entropy change, ΔS_m , which are correlated with magnetization, M , magnetic field change, ΔH , heat capacity, C , and absolute temperature, T , by the following equations:

* Corresponding author. Tel: 84-4-8589496
E-mail: luongnh@vnu.edu.vn

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

$$\Delta T_{ad}(T, \Delta H) = - \int_0^{H_{\max}} \frac{T}{C(T, H)_H} \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH \quad (2)$$

obtained from Maxwell fundamental relation. In Eqs. (1) and (2) H_{\max} is the final applied magnetic field. Eqs. (1) and (2) have a fundamental importance on the understanding of the behaviour of the MCE in solids and serve as a guide for the search of new materials with a large MCE [2].

The high cooling efficiency of magnetic refrigerators is only realised in high magnetic fields of about 50 kOe or higher. Therefore, research for new magnetic materials displaying large MCE, which can be operated in low fields of about 20 kOe that can be generated by permanent magnets, is very important. In this direction, in last years we have studied perovskite-type manganites.

The perovskite-type manganites $\text{Ln}_{1-x}\text{A}'_x\text{MnO}_3$ (Ln = rare-earth element, A' = alkaline element) are attracting considerable interest because they reveal interesting phenomena such as magnetoresistance, MCE, charge ordering, spin-glass behaviour, and magnetostriction effect. Particularly, the compound $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ has received much attention due to its interesting magnetic and magnetotransport properties and its promise for future technological applications (see, for instance, [4]).

Chau et al. [5] have studied structure, magnetic and magnetocaloric properties of perovskite $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ with small amount of Cu substituted for Mn. They have found that these materials exhibit maximum magnetic entropy change around Curie temperature, T_C , of about 350 K. $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is ferromagnetic with value for T_C of about 210 K, i.e. far below room temperature [6].

The purpose of this work is study of the structure and properties of $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) perovskites with the expectation that they could establish MCE at room-temperature region.

2. Experimental

The perovskites manganites $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) were prepared by using conventional powder solid-state reaction technique. After have been homogeneously mixed and completely ground, the samples were pre-sintered at 900°C for 15 h. The heated samples were cooled to room temperature, reground to fine particles, and sintered at 1200°C for 15 h.

The structure of samples was examined by using a Bruker D5005 X-ray diffractometer. The microstructure was studied in a scanning electron microscope (SEM) 5410 LV Jeol. Magnetic measurements were performed with a vibrating sample magnetometer (VSM) Digital Measurement Systems DMS 880 in magnetic fields up to 13.5 kOe.

3. Results and discussion

For all samples, the SEM images show that the crystallites are homogeneous with average size of 1 - 2 μm . Fig. 1 shows the SEM image for $(\text{La}_{0.4}\text{Nd}_{0.6})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ as an example. The X-ray

diffraction patterns of the samples are presented in Fig. 2. These patterns reveal that all the studied samples are of single phase with hexagonal structure with R-3c space group.

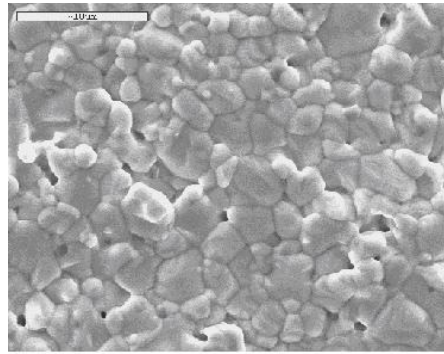


Fig. 1. SEM image of the sample $(\text{La}_{0.4}\text{Nd}_{0.6})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$.

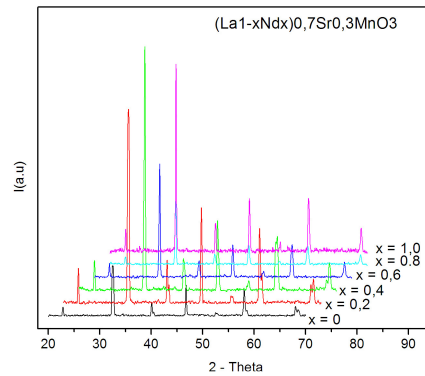


Fig. 2. X-ray diffraction patterns of the $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ perovskites.

Field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves for all samples were measured in the magnetic field of 20 Oe. Results are presented in Fig. 3. From Fig. 3 we can see that the FC and ZFC magnetization curves are separated from each other at below irreversibility temperature, T_i , and there is a cusp in ZFC curves at a so-called freezing or spin-glass-like transition temperature, T_f . These phenomena are specific features of spin-glass- or cluster-glass-like state. The ferromagnetic-paramagnetic transition temperature, T_C , determined from these measurements (see Table 1) decreases with increasing Nd content and this dependence is similar to that for system $(\text{La-Nd-Ca})\text{MnO}_3$ [7] and $(\text{La-Nd-Ba})\text{MnO}_3$ [8]. The value of T_C somewhat increases from 346 K for $x = 0.0$ to 350 K for $x = 0.2$, then decreases to 235 K for $x = 1.0$. The general decrease of T_C can be due to the decrease of $\langle r_A \rangle$ and the decrease of $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio. While La^{3+} ions are substituted for Nd^{3+} ions in the sample, the ratio $\text{Mn}^{4+}/\text{Mn}^{3+}$ keeps unchanged. So the decrease of T_C with increasing x can be explained by the reduction of the double exchange interaction due to the decrease of $\langle r_A \rangle$.

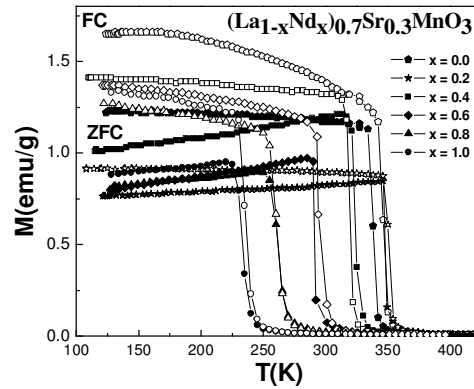


Fig. 3. FC and ZFC thermomagnetic curves of the $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ samples in a magnetic field of 20 Oe.

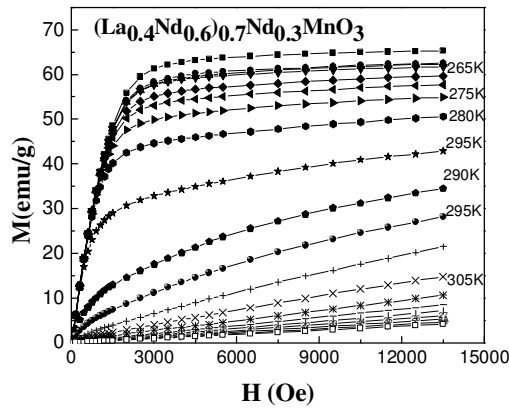


Fig. 4. The isothermal magnetization curves for the sample $(\text{La}_{0.4}\text{Nd}_{0.6})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$.

The $M(H)$ isotherms have been measured for all investigated samples at various temperatures in a narrow temperature interval around the respective T_C , in magnetic field up to 13.5 kOe. Fig. 4 shows a set of isothermal $M(H)$ curves of perovskite $(\text{La}_{0.4}\text{Nd}_{0.6})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ as an example. The temperature dependence of $|\Delta S_m|$ has been determined from the $M(H)$ isotherms correspondingly. Fig. 5 presents the dependence of $|\Delta S_m|$ on temperature for all the samples investigated. From this figure one can see that all the samples exhibit large MCE, at moderately low magnetic field change. Values of $|\Delta S_m|_{\max}$ for all the samples are shown in Table 1. $|\Delta S_m|_{\max}$ reaches highest value of 4.83 J/kg.K for the composition $x = 0.8$. Sample with $x = 0.6$ possesses $|\Delta S_m|_{\max}$ of 3.56 J/kg.K and T_C of 293 K.

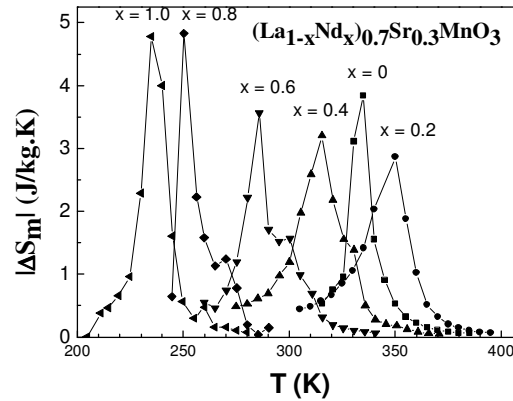


Fig. 5. The magnetic entropy change as a function of temperature of the $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ samples.

For magnetic materials, the relative cooling power (RCP) represents a good way for comparing them and is defined as

$$\text{RCP} = |\Delta S_m|_{\text{max}} \cdot \delta T_{\text{FWHM}}, \quad (3)$$

where δT_{FWHM} means the full-width at half-maximum of the magnetic entropy change versus temperature [9]. The RCP values for all studied samples are listed in Table 1. A promising materials for magnetic refrigeration application should have high RCP and the value for T_C close to room temperature. Our studied materials satisfy these requirements.

Table 1. Curie temperature, T_C , magnetization measured at 13.5 kOe, $M_{13.5}$, maximum magnetic entropy change, $|\Delta S_m|_{\text{max}}$, and relative cooling power (RCP) value for $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Sr}_{0.3}\text{MnO}_3$.

x	T_C (K)	$M_{13.5}$ (emu/g)	$ \Delta S_m _{\text{max}}$ (J/kg.K)	RCP (J/kg)
0.0	346	58.6	3.84	42
0.2	350	61.8	2.86	71
0.4	325	61.7	3.20	74
0.6	293	65.3	3.56	43
0.8	263	71.7	4.83	43
1.0	235	75.1	4.78	62

4. Conclusion

The results show that $(\text{La}_{1-x}\text{Nd}_x)_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ materials are promising candidates for magnetic refrigerants working in the room-temperature region under a moderate applied magnetic field.

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