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Large magnetocaloric effect in perovskite manganites: changes of the magnetic entropy above 300 K

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We present results of the investigation of the large magnetic entropy change, ΔS_M, above 300 K, in a series of $La_{0.65}Sr_{0.35}MnO_3$, $La_{0.6}Sr_{0.2}Ca_{0.2}MnO_3$, $La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$, $La_{0.7}Ba_{0.3}MnO_3$ and $La_{0.7}Ba_{0.24}Ca_{0.06}MnO_3$ perovskite manganites. Of the compositions studied, $La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$ exhibits the highest value of $\Delta S_M^{\max}$ equal to 2.26 J/(kg·K) at the Curie temperature T_C = 354 K when the magnetic field is changed from 0 to 10 kOe. The adiabatic temperature change ΔT_{ad} of this sample is ~1.1 K and ~4.95 K in the fields of 10 kOe and 50 kOe, respectively. Due to a strong magnetocaloric effect produced in those materials above the Curie temperature of 300 K, they seem to be attractive for the above room-temperature magnetic-refrigeration applications.

Key words: *entropy; magnetocaloric effect; magnetic refrigeration; perovskite; double exchange*

1. Introduction

A magnetocaloric effect (MCE), consisting in the change of magnetic entropy closely related to the change of temperature of a magnetic material when it passes through a magnetization–demagnetization process, was primarily discovered by Warburg [1]. The MCE, being intrinsic to all magnetic materials, results from the coupling of the magnetic sublattice with the magnetic field, which changes the magnetic part of the entropy of solid [2, 3]. There are two crucial requirements for a magnetic material to possess a large MCE. One is a large enough spontaneous magnetization (such as in the case of a heavy rare-earth metal, Gd, for example) and the other is a sharp drop in magnetization with increasing temperature, associated with ferromagnetic–paramagnetic transitions at the Curie temperature (as was found in perovskite manganites).

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In recent years, Pecharsky and Gschneidner [4] discovered a giant magnetic entropy change associated with a first-order phase transition in $Gd_5Si_2Ge_2$ alloy. This compound exhibits the MCE about twice as large as that exhibited by gadolinium, the best known magnetic refrigerant material for near room temperature applications. However, efforts to search a proper material that exhibits a large magnetic entropy change in a wide temperature region required for application are still extremely promoted. Thereby, recently rare-earth perovskite manganites of the general formula $La_{1-x}M_xMnO_3$ (M = Ca, Sr, Ba, etc.) having a substantial magnetic-entropy change associated with the ferromagnetic–paramagnetic transition at the Curie temperature have generated considerable interest of many scientists because of a practical aspect of the research [5–11].

In the present work, we report on the magnetocaloric effect in perovskite manganites such as $La_{0.65}Sr_{0.35}MnO_3$, $La_{0.6}Sr_{0.2}Ca_{0.2}MnO_3$, $La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$, $La_{0.7}Ba_{0.3}MnO_3$ and $La_{0.7}Ba_{0.24}Ca_{0.06}MnO_3$. A considerable magnetic entropy change associated with ferromagnetic–paramagnetic transition is interpreted in terms of the Zener double -exchange model.

2. Experimental details

$La_{0.65}Sr_{0.35}MnO_3$ (LSMO), $La_{0.6}Sr_{0.2}Ca_{0.2}MnO_3$ (LSCMO), $La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$ (LSBMO), $La_{0.7}Ba_{0.3}MnO_3$ (LBMO) and $La_{0.7}Ba_{0.24}Ca_{0.06}MnO_3$ (LBCMO) samples were prepared by the conventional solid-state reaction technique from a stoichiometric mixture of La_2O_3, $SrCO_3$, $CaCO_3$, $BaCO_3$ and MnO_2 at a pre-sintering temperature of 1250 °C for 16 hrs. They were sintered at 1350 °C for 18 h after regrinding and pressing into pellets. X-ray diffraction confirmed the single-phase rhombohedral perovskite structure in all the samples. The magnetic measurements were carried out with a vibrating sample magnetometer (VSM) in the fields up to 10 kOe.

In terms of the thermodynamic theory, the entropy change caused by the variation of the magnetic field from 0 to H_{max} is given by

$$\Delta S_M = \int_0^{H_{max}} \left(\frac{\partial S}{\partial H}\right)_T dH \tag{1}$$

On the other hand, by using Maxwell's thermodynamic relationship

$$\left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial H}\right)_T \tag{2}$$

Equation (1) can be re-written in the following form:

$$\Delta S_M = \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right)_H dH \tag{3}$$

Furthermore, according to [7] we have for an isobaric process at constant H

$$\left(\frac{\partial S}{\partial T}\right)_H = \frac{C_{P,H}}{T} \tag{4}$$

where $C_{P,H}$ is the heat capacity at a constant pressure and constant magnetic field. Considering a reversible adiabatic process ($dS_M = 0$) and combining Eqs. (2) and (4), we arrive at

$$dT = -\frac{T}{C_{P,H}}\left(\frac{\partial M}{\partial T}\right)_H dH \tag{5}$$

The adiabatic temperature change can now be obtained by integrating Eq. (5) over the magnetic field

$$\Delta T_{ad} = -\int_{H_1}^{H_F} \frac{T}{C_{P,H}}\left(\frac{\partial M}{\partial T}\right)_H dH \tag{6}$$

where H_1 is the initial magnetic field and H_F is the final magnetic field.

For simplification, numerical evaluation of the change of magnetic entropy was carried out based on Eq. (3), which is estimated from the isothermal magnetization measurements. In the case of magnetization measurements at small discrete field and temperature intervals, ΔS_M can be approximated using Eq. (3) by

$$\left|\Delta S_M\right| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i}\Delta H_i \tag{7}$$

where M_i and M_{i+1} are the magnetization magnitudes measured in the field H at the temperature T_i and T_{i+1}, respectively. Thereby, the changes of magnetic entropy associated with the variations of the field applied can be calculated from Eq. (7).

3. Results and discussion

Figure 1 shows the temperature dependencies of magnetization for two selected samples (LSBMO and LSCMO), for which the Curie temperatures were 354 K and 337 K, respectively. The Curie temperature T_C, defined as the temperature at which the curve $\partial M/\partial T$–T reaches a minimum, has been determined from the M–T curves. The values of T_C of all the samples studied are summarized in the table. In Figure 2, the dependencies of magnetization of LSBMO on magnetic field are presented as a representative example. They show a substantial variation of magnetization around the Curie temperature. As will be discussed later in detail, a considerable magnetic entropy variation associated with the ferromagnetic–paramagnetic transition temperature (T_C) can be observed.

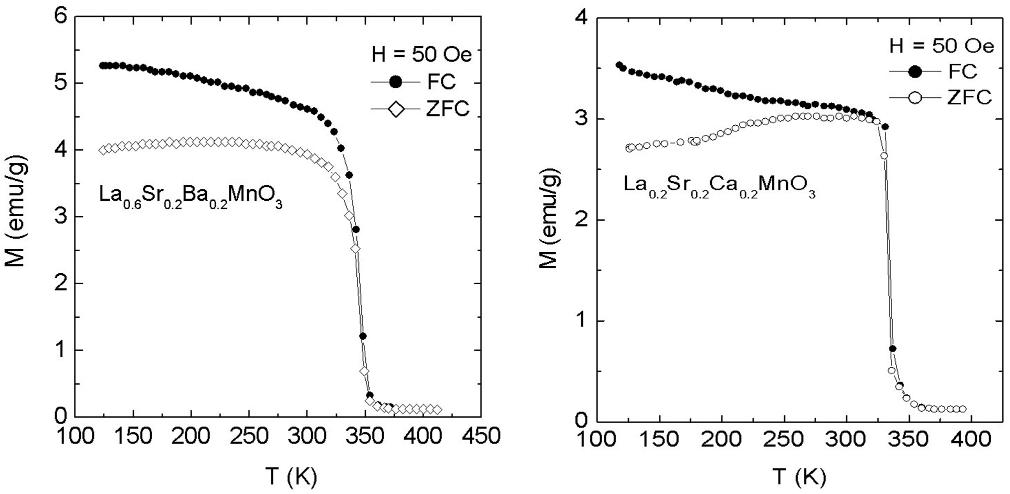

Fig. 1. Temperature dependencies of magnetization measured for both zero-field-cooled (ZFC) and field-cooled (FC) $La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$ and $La_{0.6}Sr_{0.2}Ca_{0.2}MnO_3$ samples in the field of 50 Oe

Table. Curie temperature T_C and the maximum magnetic entropy change $\left|\Delta S_M^{\max}\right|$ for different compositions

Composition	T_C (K)	$\left\|\Delta S_M^{\max}\right\|$ (J/(kg·K)	ΔH (T)	Reference
$La_{0.6}Ca_{0.4}MnO_3$	263	5.0	3	[7]
$La_{0.65}Ca_{0.35}Mn_{0.9}Ti_{0.1}O_3$	103	1.3	3	[7]
$La_{0.975}Li_{0.025}Mn_{0.9}Ti_{0.1}O_3$	90	2.0	3	[7]
$La_{0.65}Sr_{0.35}MnO_3$	305	2.12	1	present work
$La_{0.6}Sr_{0.2}Ca_{0.2}MnO_3$	337	1.96	1	present work
$La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$	354	2.26	1	present work
$La_{0.7}Ba_{0.3}MnO_3$	336	1.60	1	present work
$La_{0.7}Ca_{0.06}Ba_{0.24}MnO_3$	320	1.72	1	present work
$La_{0.65}Nd_{0.05}Ca_{0.3}MnO_3$	250	1.68	1	[9]
$La_{0.65}Nd_{0.05}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$	220	0.96	1	[9]
$La_{0.65}Nd_{0.05}Ca_{0.3}Mn_{0.9}Fe_{0.1}O_3$	130	0.42	1	[9]
Gd	294	4.2	1.5	[4]
$Gd_5(Si_2Ge_2)$	276	14	2	[4]

Using Eq. (7), the changes of magnetic entropy under the influence of the field of 10 kOe have been calculated for all the samples and plotted as a function of temperature (Fig. 3). We summarized the changes of the maximum magnetic entropy $\left|\Delta S_M^{\max}\right|$ for all the samples in the table. Among the compositions investigated, LSBMO exhibits the highest value of $\left|\Delta S_M^{\max}\right|$ (2.26 J/(kg·K) at $T_C = 354$ K (Fig. 3).

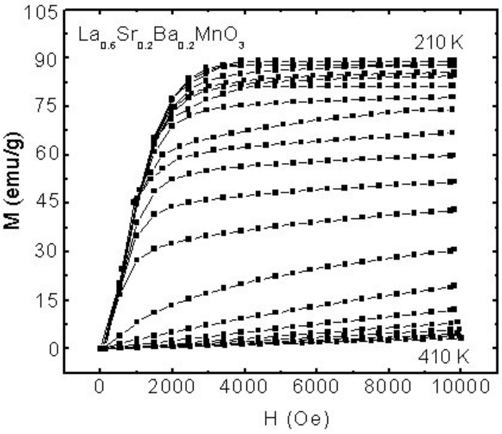

Fig. 2. Magnetic field dependencies of the magnetization for $La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$ at various temperatures ranging from 210 K to 410 K (ΔT = 10 K)

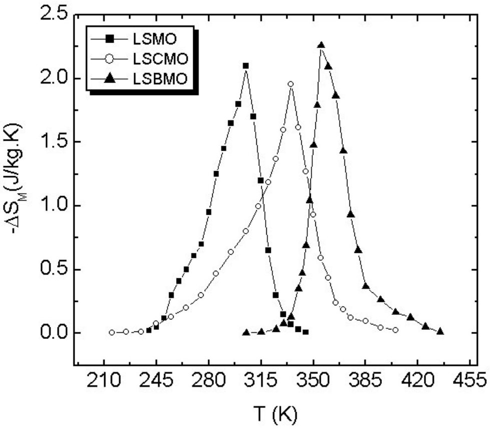

Fig. 3. Magnetic entropy changes induced by the field of 10 kOe as a function of temperature for the samples of $La_{0.65}Sr_{0.35}MnO_3$ (LSMO), $La_{0.6}Sr_{0.2}Ca_{0.2}MnO_3$ (LSCMO), and $La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$ (LSBMO)

In order to complete the analysis, in terms of Eq. (6), we also estimated the adiabatic temperature change ΔT_{ad} for the LSBMO sample. The estimated value of ΔT_{ad} is ~ 1.1 K in the field of 10 kOe and ~ 4.95 K in the field of 50 kOe. These results indicate that the samples investigated are promising materials for magnetic refrigerators. To explain in detail such a large change of magnetic entropy in perovskite manganites, the Zener double-exchange model has been taken into account [12]. According to this model, the changes of magnetic entropy caused by the presence of the external magnetic field relate closely to the mechanism of double-exchange interaction between Mn^{3+} and Mn^{4+} ions and vary substantially with the change in the Mn^{4+}/Mn^{3+} ratio due to various doping processes [8–10].

In the cases where increase of the Mn^{4+}/Mn^{3+} ratio leads to an enhancement in the double-exchange interaction between $Mn^{3+}$and Mn^{4+} ions, a substantial magnetic entropy variation is observed. For our samples, the partial replacement of La with Sr or (Ba, Ca) favoured the double-exchange interaction arising from the increase of the Mn^{4+}/Mn^{3+} ratio, and that, in turn, led to a significant change of magnetic entropy. Additionally, Guo et al. [13] proposed that the considerable change of magnetic entropy in perovskite manganites could originate from the spin-lattice coupling in the magnetic ordering process. Because of the strong coupling between spin and lattice, significant changes of the lattice accompanying magnetic transition in perovskite manganites has been observed [14]. The lattice structural change in the $\langle \mathrm{Mn-O} \rangle$ bond distance as well as in the $\langle \mathrm{Mn-O-Mn} \rangle$ bond angle would, in turn, favour the spin ordering. Therefore, a more abrupt variation of magnetization occurring near T_C and resulting in a substantial change of the magnetic entropy, i.e. in the strong MC effect, could be attributed to this effect. For comparison, the data of several magnetic materials, which could be used as active refrigerants, were summarized in the table. Though the values of $\left|\Delta S_M^{\max}\right|$ for manganites are smaller than those for the most conspicuous magneto-caloric material $Gd_5(Si_2Ge_2)$, the perovskite manganites are easy to fabricate and exhibit a higher chemical stability as well as a higher resistivity, which is favourable for lowering of eddy current heating. Furthermore, T_C of ceramic materials can be easily adjusted by tuning the doping concentration. As a result of this procedure, a considerable magnetic entropy change can be observed in different temperature ranges from low temperature to near or above room temperature, which is beneficial for magnetic refrigerators operating in a desired variety of temperatures.

4. Conclusions

Changes of maximum magnetic entropy in $La_{0.65}Sr_{0.35}MnO_3$, $La_{0.6}Sr_{0.2}Ca_{0.2}MnO_3$, $La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$, $La_{0.7}Ba_{0.3}MnO_3$ and $La_{0.7}Ba_{0.24}Ca_{0.06}MnO_3$ perovskite manganites occurring at their Curie temperatures of above 300 K were observed. Among the compositions investigated, $La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$ reveals the highest value of 2.26 J/(kg·K) for $\left|\Delta S_M^{\max}\right|$ at $T_C = 354$ K, under the 10 kOe field applied. The estimated ΔT_{ad} value for this sample is ~1.1 K and ~4.95 K in the fields of 10 kOe and 50 kOe, respectively. The increase of the Mn^{4+}/Mn^{3+} ratio leads to an enhancement in the double-exchange interaction between $Mn^{3+}$and Mn^{4+} ions, and hence it results in a substantial magnetic entropy variation. The significant magnetocaloric effect was observed in the presently investigated materials above the Curie temperature of 300 K, indicating that these materials can be very appropriate for above room temperaturemagnetic refrigeration applications.

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