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Research Article

Magnetocaloric effect in $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites

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Abstract: The magnetocaloric effect (MCE) achieved for $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites has been investigated. The maximum value of magnetic entropy change of $La_{0.7}Sr_{0.3}MnO_3$ composites is found to decrease slightly with the further increasing of Ta_2O_5 concentration. It is shown that $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites exhibit much more uniform magnetic entropy change than that of gadolinium. Moreover, the results indicate that the temperature range between 100 K and 400 K can be covered using the $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites. Therefore, MCE makes the composites promising for room-temperature magnetic cooling applications.

Keywords: magnetic materials; simulation and modeling

1 Introduction

The new refrigeration based on magnetocaloric effect (MCE) or electrocaloric effect has been demonstrated as a promising alternative technology to classical refrigeration (air conditioning, refrigeration, liquefaction of gases, etc.), and has a great potential to compete successfully with compression and relaxation of the gases for refrigeration [1–15]. The magnetic cooling technology is based on the use of MCE applied to various metallic materials and new alloys named magnetocaloric materials. The characterization and application of magnetic properties of the ferromagnetic materials become increasingly important as magnetoelectronic devices for the level reliability [16,17].

Recently, perovskite manganites, $R_{1-x}A_xMnO_3$ (where R is a trivalent rare-earth ion, and A is a divalent ion such as Ca, Sr, Ba and Pb), have attracted the widest interest in aspects of experimental and theoretical researches due to their colossal magnetoresistance and large magnetic entropy change [18–20]. In this paper, the magnetocaloric properties of $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites sintered at different temperatures have been investigated. It used phenomenological model to predict magnetocaloric properties of the composites, such as magnetic entropy change, heat capacity change, and relative cooling power.

2 Theoretical considerations

According to the phenomenological model in Ref. [21], the dependence of magnetization on the variation of temperature and Curie temperature T_C is presented by

$$M = \left(\frac{M_i - M_f}{2}\right)\tanh[A(T_C - T)] + BT + C \quad (1)$$

where M_i is an initial value of magnetization at

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ferromagnetic–paramagnetic transition and M_f is a final value of magnetization at ferromagnetic–paramagnetic transition as shown in Fig. 1; $A=\dfrac{2(B-S_C)}{M_i-M_f}$; B is the magnetization sensitivity $\dfrac{dM}{dT}$ at ferromagnetic state before transition; S_C is the magnetization sensitivity $\dfrac{dM}{dT}$ at Curie temperature T_C; and $C=\left(\dfrac{M_i+M_f}{2}\right)-BT_C$.

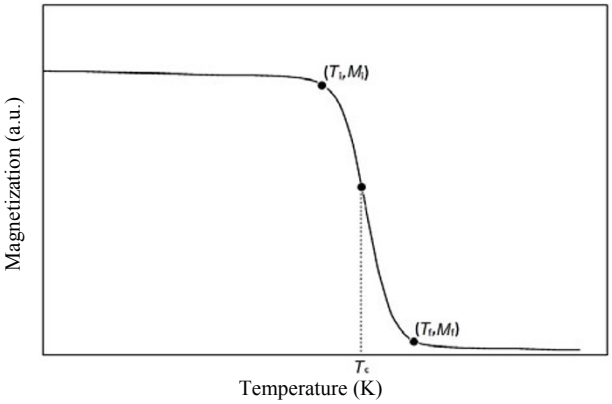

Fig. 1 Temperature dependence of magnetization in constant applied magnetic field.

The magnetic entropy change of a magnetic system under adiabatic magnetic field variation from 0 to final value H_{max} is available by

$$\Delta S_M=\left\{-A\left(\frac{M_i-M_f}{2}\right)\mathrm{sech}^2[A(T_C-T)]+B\right\}H_{max} \quad (2)$$

The result of Eq. (2) is the maximum magnetic entropy change, and ΔS_{max} (where $T=T_C$) can be evaluated as the following equation:

$$\Delta S_{max}=H_{max}\left[-A\left(\frac{M_i-M_f}{2}\right)+B\right] \quad (3)$$

The determination of full-width at half-maximum δT_{FWHM} can be carried out as follows:

$$\delta T_{FWHM}=\frac{2}{A}\mathrm{sech}\left[\sqrt{\frac{2A(M_i-M_f)}{A(M_i-M_f)+2B}}\right] \quad (4)$$

The magnetic cooling efficiency is estimated by considering the magnitude of magnetic entropy change ΔS_M, and its full-width at half-maximum δT_{FWHM} [22]. The product of $-\Delta S_{max}$ and δT_{FWHM} is called relative cooling power (RCP) based on magnetic entropy change.

$$\mathrm{RCP}=-\Delta S_M(T,H_{max})\times\delta T_{FWHM}$$
$$=\left(M_i-M_f-2\frac{B}{A}\right)H_{max}\times\mathrm{sech}\left[\sqrt{\frac{2A(M_i-M_f)}{A(M_i-M_f)+2B}}\right] \quad (5)$$

The magnetization-related change of the specific heat is given by Ref. [22]:

$$\Delta C_{p,H}=T\frac{\delta\Delta S_M}{\delta T} \quad (6)$$

According this model [21], $\Delta C_{p,H}$ can be rewritten as

$$\Delta C_{p,H}=-TA^2(M_i-M_f)\mathrm{sech}^2[A(T_C-T)]\times\tanh[A(T_C-T)]H_{max} \quad (7)$$

From this phenomenological model, it can simply evaluate δT_{FWHM}, $|\Delta S|_{max}$ and RCP for $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites under magnetic field variation.

3 Results and discussion

Figure 2 shows the magnetization of the precursor $La_{0.7}Sr_{0.3}MnO_3$ powders mixed with Ta_2O_5 (weight fraction of 0%, 4%, 10% and 15%, respectively) versus temperature in 0.5 T magnetic field. The symbols represent the experimental data from Ref. [23], while the dashed curves represent the modeled data using model parameters given in Table 1. These parameters are determined from the experimental data. Figures 3 and 4 show the predicted values for changes of magnetic entropy and heat capacity as functions of temperature, respectively. ΔS_M is expanded for different concentrations of Ta_2O_5. Since Fig. 3 indicates that the temperature range between 100 K and 400 K can be covered using the $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites, the composites is beneficial for manipulating magnetocaloric refrigeration that occurs in various temperatures. Furthermore, the ΔS_M distribution of $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ is much more uniform than that of gadolinium [24]. This feature is desirable for an Ericson-cycle magnetic refrigerator [25]. In addition, perovskite-like structured materials are easier to fabricate and possess higher chemical stability as well as higher resistivity. The high resistivity is beneficial to lowering the eddy current heating. Thus, due to these features,

$La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites can be considered as active magnetic refrigerant for near room-temperature magnetic refrigeration.

The values of maximum magnetic entropy change, full-width at half-maximum, and relative cooling power at different Ta_2O_5 contents in 0.5 T magnetic field, are calculated by using Eqs. (3)–(5) respectively, and tabulated in Table 2. Furthermore, the maximum and minimum values of specific heat change for each sample are determined from Fig. 4.

Table 1 Model parameters for $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites in 0.5 T applied magnetic field

Ta_2O_5 (wt%)	M_i (emu/g)	M_f (emu/g)	T_C (K)	B (emu/(g·K))	S_C (emu/(g·K))
0	72.9	3.2	309	–0.05	–0.59
4	61.9	1.9	317	–0.05	–0.59
10	53.1	1.9	323	–0.05	–0.59
15	35.1	2.4	318	–0.05	–0.40

Table 2 The predicted values of magnetocaloric properties for $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites in 0.5 T applied magnetic field

Ta_2O_5 (wt%)	$-\Delta S_{max}$ (J/(kg·K))	δT_{FWHM} (K)	RCP (J/kg)	$\Delta C_{p,H(max)}$ (J/(kg·K))	$-\Delta C_{p,H(min)}$ (J/(kg·K))
0	0.295	122.43	36.12	1.14	–0.86
4	0.293	105.39	30.88	1.33	–1.05
10	0.295	89.94	26.51	1.56	–1.28
15	0.200	92.18	18.42	1.01	–0.83

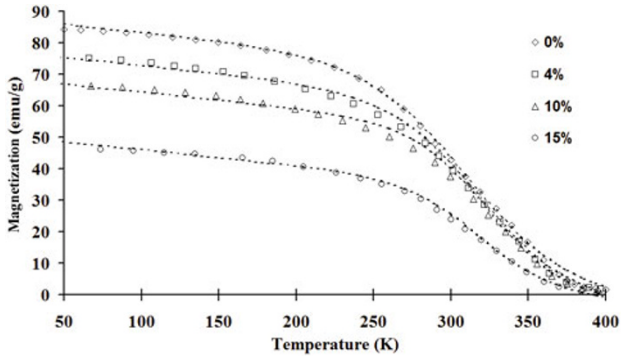

Fig. 2 Magnetization in 0.5 T magnetic field for the $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites versus temperature. The dashed curves are modeled results and symbols represent the experimental data from Ref. [23].

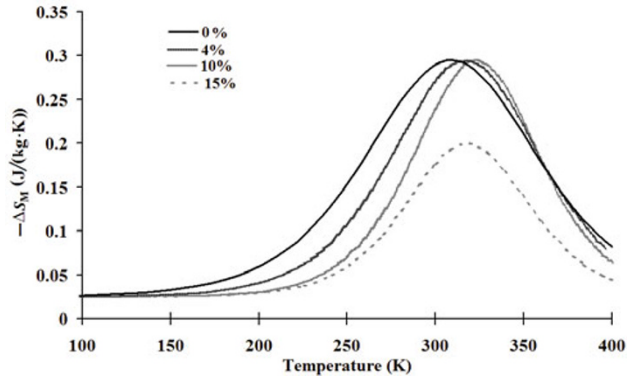

Fig. 3 Magnetic entropy change as function of temperature for $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites in 0.5 T magnetic field.

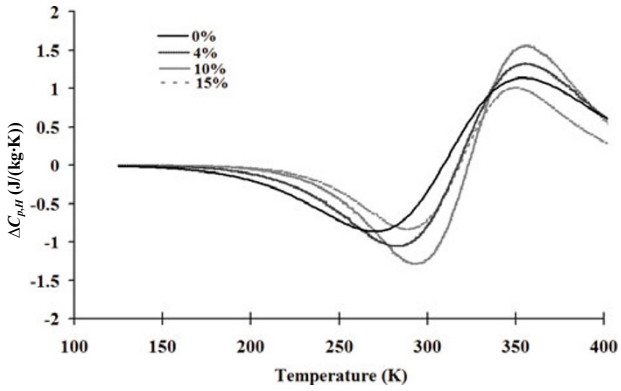

Fig. 4 Heat capacity change as function of temperature for $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites in 0.5 T magnetic field.

In general, the magnetic entropy change in perovskite manganites has been believed to be related to the considerable variation of magnetization near T_C [26]. The spin–lattice coupling in the magnetic ordering process could play a significant role in additional magnetic entropy change [27].

Magnetic refrigeration works because there are two contributions to the total entropy of the system: a magnetic entropy that is related to the order of magnetic moments, and a lattice entropy that is related to the temperature. It is convenient to start with a material with disordered magnetic moments, which is typically found with the lowest field magnitude and ambient temperature within the refrigeration cycle.

Applying a magnetic field adiabatically causes the spins in the material to align. Recalling that no heat is exchanged in an adiabatic process, the decrease in magnetic entropy must be compensated by an increase in the lattice entropy, which implies that the material must heat up. Once the moments are aligned and excess heat has been removed, the material returns to ambient temperature. The adiabatic removal of the applied field then leads to an increase in magnetic entropy, which is compensated by a decrease in the lattice entropy, and thus the temperature of the material decreases below ambient.

Due to the strong coupling between spin and lattice, the significant lattice change accompanying magnetic transition in perovskite manganites has been observed [28,29]. The lattice structural change in the Mn–O bond distance as well as Mn–O–Mn bond angle would, in turn, favor the spin ordering. Thereby, a more abrupt reduction of magnetization near T_C occurs and results in a significant magnetic entropy change [30–32]. In this way, a conclusion might be drawn that a strong spin–lattice coupling in the magnetic transition process would lead to additional magnetic entropy change near T_C, and consequently, favors the MCE.

4 Conclusions

The calculations show that the $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites provide temperature span and obtain a considerable ΔS_M against temperature variation. ΔS_M distribution is uniform, which is desirable for Ericsson-cycle magnetic refrigerator, magnetic softness and isotropic and low priced. In addition, these samples are convenient to prepare and exhibit higher chemical stability as well as higher resistivity that is favorable for lowering eddy current heating.

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