Magnetocaloric effect in $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$

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Abstract: The magnetocaloric effect is calculated for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ system near a phase transition from ferromagnetic to paramagnetic state as a function of temperature. It is suggested by the results that $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ material can be utilized as the working material in an active magnetic regenerative refrigerator with large temperature span, for its significant entropy change upon the application of a magnetic field and the easily tuned Curie temperature.

Keywords: ceramics; magnetic materials; phase transition; thermodynamic properties

1 Introduction

Recently, the materials showing pronounced magnetocaloric effect (MCE) and electrocaloric effect (ECE) can be used as alternatives to the conventional gas [1–13]. This newly refrigeration has the advantages of high efficiency of energy transformation, environmental protection, and low cost. In principle, magnetic refrigeration is based on the magnetocaloric effect, which is the temperature change of a magnetic material associated with an external magnetic field change in an adiabatic process. The same determination can be given for ECE by an electric field change.

There have been many investigations on perovskite manganites, $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (where R is a trivalent rare-earth ion and A is a divalent ion such as Ca, Sr, Ba, or Pb), due to their colossal magnetoresistance and large magnetic entropy change [14–17].

Some perovskite manganites exhibit discontinuous variation in volume at the ferromagnetic transition and

an associated sharp change in magnetization [18,19]. The simultaneous discontinuous volume variation and magnetic transition at T_C can strongly influence the magnetic entropy change. Furthermore, by adjusting the composition parameter x , the materials could exhibit very different Curie temperatures. Thus, it is possible to use them as the magnetic refrigerants working in quite a large temperature range. From this viewpoint, this paper reports the magnetocaloric properties of Ce-substituted perovskite manganites $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$. Characterization and application of the magnetic properties of ferromagnetic materials become increasingly important as magnetoelectronic devices for the level reliability [20,21].

A phenomenological model presented for simulation of magnetization dependence on temperature variation is used to predict magnetocaloric properties such as magnetic entropy change, heat capacity change, temperature change, and relative cooling power.

2 Phenomenological model

According to the phenomenological model [22], the dependence of magnetization on variation of

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temperature and Curie temperature T_C is represented by

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

where M_i and M_f are the initial and final values of magnetization at ferromagnetic–paramagnetic transition as shown in Fig. 1 respectively;

$A = \frac{2(B - S_C)}{M_i - M_f}$; B is the magnetization sensitivity

dM/dT at ferromagnetic state before transition; S_C

is the magnetization sensitivity dM/dT at Curie

temperature T_C ; and $C = \frac{M_i + M_f}{2} - BT_C$.

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

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

The foundation of large magnetic entropy change is attributed to high magnetic moment and rapid change of magnetization at T_C . A result of Eq. (2) is a maximum magnetic entropy change $\Delta S_{\max}$ (where $T = T_C$), which can be evaluated as in the following equation:

$$\Delta S_{\max} \approx H_{\max} S_C \quad (3)$$

Equation (3) is an important equation for taking into consideration the value of the magnetic entropy change to evaluate magnetic cooling efficiency with its full width at half maximum.

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

$$\delta T_{\text{FWHM}} = \frac{2}{A} \cosh^{-1} \left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}} \right) \quad (4)$$

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

This equation gives a full width at half maximum magnetic entropy change contributing for estimation of magnetic cooling efficiency as follows.

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} .

The product of $-\Delta S_{\max}$ and δT_{FWHM} is called relative cooling power (RCP) based on magnetic entropy change:

$$\begin{aligned} \text{RCP} &= -\Delta S_M(T, H_{\max}) \times \delta T_{\text{FWHM}} \\ &= \left(M_i - M_f - 2 \frac{B}{A} \right) H_{\max} \times \cosh^{-1} \left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}} \right) \end{aligned} \quad (5)$$

The magnetization-related change of the heat capacity is given by

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

According to this model [22], $\Delta C_{P,H}$ can be rewritten as

$$\begin{aligned} \Delta C_{P,H} &= \\ &= -TA^2(M_i - M_f) \operatorname{sech}^2(A(T_C - T)) \tanh(A(T_C - T)) H_{\max} \end{aligned} \quad (7)$$

From this phenomenological model, one can easily assess the values of δT_{FWHM} , $|\Delta S_M|_{\max}$, and RCP for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ under magnetic field variation.

3 Theoretical work

Numerical calculation was made with parameters as displayed in Table 1.

Figure 2 shows magnetization versus temperature in 0.1 T applied magnetic field for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$. The symbols represent experimental data from Ref. [23], while the dashed curves represent modeled data using model parameters given in Table 1. It is seen that for the given parameters the results of calculation are in good agreement with the experimental results. The magnetic entropy data as a function of temperature for

Table 1 Model parameters for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ in 0.1 T applied magnetic field

x	M_i (emu/g)	M_f (emu/g)	T_C (K)	B (emu/(g·K))	S_C (emu/(g·K))
0.2	48.37	1.17	225	−0.025	−2.80
0.3	39.10	1.39	232	−0.021	−2.80
0.4	32.86	1.39	236	−0.020	−2.09

Fig. 2 Magnetization versus temperature in 0.1 T applied magnetic field for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$. The dashed curves are modeled results and symbols represent experimental data from Ref. [23].

the samples at the external magnetic field variation of 0.1 T are plotted in Fig. 3. Obviously, $|\Delta S_M|$ reaches a maximum value of about 0.28 J/(kg·K) at T_C of 227 K upon 0.1 T applied field variation.

Fig. 3 Magnetic entropy change as a function of temperature for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ in 0.1 T applied magnetic field shift.

Furthermore, Fig. 4 shows predicted values for change of heat capacity versus temperature. The magnetic entropy change $|\Delta S_M|$ curves reveal the characteristics of the spin reorientation by the kinks in the ΔS_M curve. The maxima observed in the ΔS_M curves are associated to a spin reorientation that occurs continuously. The behavior of curves suggests how to extend the range of temperatures for use in MCE.

The values of maximum magnetic entropy change, full width at half maximum, and relative cooling power at 0.1 T magnetic field variation for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ are calculated by using Eqs. (3)–(5), respectively, and tabulated in Table 2.

ΔS_M reflects a fundamental importance on the understanding of the behavior of MCE, and ΔS_M can be approximately estimated using Eq. (2).

As shown in Fig. 3, $-\Delta S_M$ reaches a peak of about 0.28 J/(kg·K) at 225 K upon 0.1 T applied field variation. Moreover, the decreasing of Curie temperature is that which we are seeking by tuning the material composition, because an active magnetic regenerative refrigerator needs a series of magnetic refrigerants with different Curie temperatures working as active and passive materials to expand the working temperature from low temperature to high temperature. Also it should be noted that ΔS_M has a significant value below the peak temperature. This broad distribution could be ascribed to a spread of the ferromagnetic transition temperature in different ferromagnetic clusters caused by the inhomogeneity of structure and stoichiometry [24].

To explain a large magnetic entropy variation in perovskite manganites, the Zener double-exchange model has often been thought to be applicable [25,26]. The magnetic entropy change has been believed to

Fig. 4 Heat capacity change as a function of temperature for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ in 0.1 T applied magnetic field shift.

Table 2 Predicted values of applied magnetocaloric properties for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ and other compositions in low applied magnetic field changes

Composition	ΔH (T)	$-\Delta S_{\text{max}}$ (J/(kg·K))	δT_{FWHM} (K)	RCP (J/kg)	$\Delta C_{P,H(\text{max})}$ (J/(kg·K))	$\Delta C_{P,H(\text{min})}$ (J/(kg·K))	Ref.
$\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$	0.1	0.28	15.10	4.23	5.70	−5.48	This work
$\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$	0.1	0.28	12.03	3.37	7.30	−7.14	This work
$\text{La}_{0.6}\text{Ce}_{0.4}\text{MnO}_3$	0.1	0.21	13.50	2.82	4.96	−4.74	This work
$\text{Ge}_{0.95}\text{Mn}_{0.05}$ films	0.1	4E−7–3.6E−6	12.69–17.75	6.3E−6–0.451E−5	7.7E−6–1.1E−4	−1E−4–−7.3E−6	[28]
$\text{La}_{1-x}\text{Cd}_x\text{MnO}_3$	0.05	0.011	29.65–44.03	0.326–0.484	0.087–0.105	−0.094–−0.076	[29]
$\text{Gd}_{1-x}\text{Ca}_x\text{BaCo}_2\text{O}_{5.5}$	0.1	1.65E−6–2.2E−6	9.77–13.85	1.61E−5–3.04E−5	6.14E−5–6.34E−5	−6.94E−5–−6.13E−5	[30]

relate closely to the mechanism of double-exchange interaction between Mn^{3+} and Mn^{4+} ions arising from the change in the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio, under the doping process [27].

In addition, it is proposed that the large magnetic entropy change in perovskite manganites could originate from the spin lattice coupling in the magnetic ordering process [27]. Because of the strong coupling between spin and lattice, a significant change in the lattice accompanying the magnetic transition in perovskite manganites has been observed.

Table 2 shows comparisons between $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ and other compositions in low applied magnetic field change (ΔH). The magnetocaloric properties of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ are significantly larger, and comparable with magnetocaloric properties of $\text{Ge}_{0.95}\text{Mn}_{0.05}$, $\text{La}_{1-x}\text{Cd}_x\text{MnO}_3$, and $\text{Gd}_{1-x}\text{Ca}_x\text{BaCo}_2\text{O}_{5.5}$ as shown in Table 2 [28–30].

4 Conclusions

The results show that $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ based manganite materials are promising candidate of magnetic refrigerant working in wide temperature range due to the magnetic entropy change upon an application of a low and modest magnetic field, well defined temperature, easily tuned Curie temperature making any temperature span be covered, magnetic softness and isotropic, and good chemical stability.

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References

[1] Hamad MA. Lanthanum concentration effect of

magnetocaloric properties in $\text{La}_x\text{MnO}_{3-\delta}$. *J Supercond Nov Magn* 2015, **28**: 173–178.

- [2] Hamad MA. Magnetocaloric effect in $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3/\text{Pd}$ composites prepared by chemical plating. *Journal of Applied Physical Science International* 2015, **3**: 92–98.
- [3] Hamad MA. Detecting giant electrocaloric properties of ferroelectric SbSI at room temperature. *J Adv Dielect* 2013, **4**: 1350008.
- [4] Hamad MA. Magnetocaloric effect in $\text{Sr}_2\text{FeMoO}_6/\text{Ag}$ composites. *Processing and Application of Ceramics* 2015, **9**: 11–15.
- [5] Hamad MA. Magnetocaloric effect in (001)-oriented MnAs thin film. *J Supercond Nov Magn* 2014, **27**: 263–267.
- [6] Hamad MA. Calculations of the low-field magnetocaloric effect in $\text{Fe}_4\text{MnSi}_3\text{B}_x$. *J Supercond Nov Magn* 2015, **28**: 2223–2227.
- [7] Hamad MA. Monte Carlo calculations of magnetic heat capacity of $\text{La}_{0.7}\text{Sr}_{0.3-x}\text{MnO}_{3-d}$. *J Supercond Nov Magn* 2015, DOI: 10.1007/s10948-015-3041-6.
- [8] Hamad MA. Effects of addition of rare earth on magnetocaloric effect in $\text{Fe}_{82}\text{Nb}_2\text{B}_{14}$. *J Supercond Nov Magn* 2015, DOI: 10.1007/s10948-015-3140-4.
- [9] Hamad MA. Magnetocaloric effect in $\text{La}_{0.65-x}\text{Eu}_x\text{Sr}_{0.35}\text{MnO}_3$. *Phase Transit* 2014, **87**: 460–467.
- [10] Hamad MA. Simulation of magnetocaloric effect in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ceramics fabricated by fast sintering process. *J Supercond Nov Magn* 2014, **27**: 269–272.
- [11] Hamad MA. Giant isothermal entropy change In (111)-oriented PMN–PT thin film. *J Adv Dielect* 2014, **4**: 1450026
- [12] Hamad MA. Theoretical investigations on electrocaloric properties of (111)-oriented $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ single crystal. *J Adv Ceram* 2013, **2**: 308–312.
- [13] Hamad MA. Magnetocaloric effect in $\text{La}_{1.25}\text{Sr}_{0.75}\text{MnCoO}_6$. *J Therm Anal Calorim* 2014, **115**: 523–526.
- [14] Debnath JC, Zeng R, Kim JH, et al. Improvement of refrigerant capacity of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ material with a few percent Co doping. *J Magn Magn Mater* 2011, **323**: 138–143.
- [15] Hamad MA. Magnetocaloric properties of $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$. *J Therm Anal Calorim* 2013, **113**: 609–613.
- [16] Tang W, Lu W, Luo X, et al. Particle size effects on $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$: Size-induced changes of magnetic phase transition order and magnetocaloric study. *J Magn Magn Mater* 2010, **322**: 2360–2368.

- [17] Hamad MA. Magnetocaloric effect in nanopowders of $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$. *J Supercond Nov Magn* 2014, **27**: 223–227.
- [18] Radaelli PG, Cox DE, Marezio M, *et al.* Simultaneous structural, magnetic, and electronic transitions in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x=0.25$ and 0.50 . *Phys Rev Lett* 1995, **75**: 4488.
- [19] Ibarra MR, Algarable PA, Marquina C, *et al.* Large magnetovolume effect in yttrium doped La–Ca–Mn–O perovskite. *Phys Rev Lett* 1995, **75**: 3541.
- [20] Hamad MA. Prediction of energy loss of $\text{Ni}_{0.58}\text{Zn}_{0.42}\text{Fe}_2\text{O}_4$ nanocrystalline and Fe_3O_4 nanowire arrays. *Jpn J Appl Phys* 2010, **49**: 085004.
- [21] Hamad MA. Calculations on nanocrystalline CoFe_2O_4 prepared by polymeric precursor method. *J Supercond Nov Magn* 2013, **26**: 669–673.
- [22] Hamad MA. Magnetocaloric effect in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{Ta}_2\text{O}_5$ composites. *J Adv Ceram* 2013, **2**: 213–217.
- [23] Gebhardt JR, Roy S, Ali N. Colossal magnetoresistance in Ce doped manganese oxides. *J Appl Phys* 1999, **85**: 5390.
- [24] Phan M-H, Tian S-B, Yu S-C, *et al.* Magnetic and magnetocaloric properties of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Ba}_x\text{MnO}_3$ compounds. *J Magn Magn Mater* 2003, **256**: 306–310.
- [25] Zener C. Interaction between the d shells in the transition metals. *Phys Rev* 1951, **81**: 440–444.
- [26] Zener C. Interaction between the d -shells in the transition metals. II. Ferromagnetic compounds of manganese with perovskite structure. *Phys Rev* 1951, **82**: 403–405.
- [27] Guo ZB, Du YM, Zhu JS, *et al.* Large magnetic entropy change in perovskite-type manganese oxides. *Phys Rev Lett* 1997, **78**: 1142.
- [28] Hamad MA. Magneto-caloric effect in $\text{Ge}_{0.95}\text{Mn}_{0.05}$ films. *J Supercond Nov Magn* 2013, **26**: 449–453.
- [29] Hamad MA. Magnetocaloric effect in $\text{La}_{1-x}\text{Cd}_x\text{MnO}_3$. *J Supercond Nov Magn* 2013, **26**: 3459–3462.
- [30] Hamad MA. Magnetocaloric effect in polycrystalline $\text{Gd}_{1-x}\text{Ca}_x\text{BaCo}_2\text{O}_{5.5}$. *Mater Lett* 2012, **82**: 181–183.