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Short communication

Magnetocaloric properties of $La_{0.666}Sr_{0.373}Mn_{0.943}Cu_{0.018}O_3$

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Abstract

Magnetocaloric properties of $La_{0.666}Sr_{0.373}Mn_{0.943}Cu_{0.018}O_3$ (LSMCO) perovskite (such as magnetic entropy change, full-width at half-maximum, relative cooling power and magnetic specific heat change) at applied magnetic field of 0.05 T were calculated using the phenomenological model. The results indicate the prospective application of LSMCO due to high magnetocaloric effect near the Curie temperature. Furthermore, the magnetocaloric properties of LSMCO sample are comparable with magnetocaloric properties of MnAs film, $La_{1-x}Cd_xMnO_3$ and $La_{1.25}Sr_{0.75}MnCoO_6$, and significantly larger than that of $Gd_{1-x}Ca_xBaCo_2O_{5.5}$ and $Ge_{0.95}Mn_{0.05}$. It is recommended that magnetocaloric effect of LSMCO can be used as a promising practical material of an apparatus based on the active magnetic regenerator cycle.

Keywords: *magnetocaloric effect, Cu-doped LSMO, magnetic entropy change*

I. Introduction

The modern refrigeration founded on the magnetocaloric effect (MCE) or electrocaloric effect is verified as a potential alternative technology to traditional refrigeration [1–14]. This is due to its high effectiveness, small size, energy saving and ecologically acceptable technology. The magnetic cooling refrigeration is based on the MCE applied to a variety of ferromagnetic materials named magnetocaloric materials. The characterization and application of the ferromagnetic materials become gradually more significant for the level of their reliability [15–17]. Especially, manganites with the formula $R_{1-x}T_xMnO_3$, where R is a rare earth atom (La, Pr, Nd, etc.) and T is an alkaline earth element (Sr, Ca, Ba, etc.), feature easy preparation, high chemical stability, small magnetic hysteresis, and high electrical resistivity that allows for a low eddy-current loss at high frequencies. Moreover, the perovskite manganites may have tunable Curie temperature (θ_C) and saturation magnetization through doping and can be potentially applied for magnetic refrigeration around room temperature [18]. In these manganites, the ratio of Mn^{3+}/Mn^{4+} is the most important factor to determine the metal to insulator and ferro to paramagnetic transitions in manganites [18]. Among the lanthanum-based manganites, the $La_{0.666}Sr_{0.373}Mn_{0.943}Cu_{0.018}O_3$ (LSMCO) has a prominent position as heating mediator for magnetic hyperthermia [19]. Consequently, from a practical point of view, it is important to study MCE of LSMCO in order to determine its employment.

In this paper, magnetocaloric properties of LSMCO were simulated. The phenomenological model for simulation of magnetization as function of temperature [20] was used to investigate magnetocaloric properties near phase transition, such as magnetic entropy change, specific heat change, temperature change, and relative cooling power.

II. Theoretical considerations

Temperature dependence of magnetization under constant applied field is shown in Fig. 1. It is well known that complete alignment of all electrons spins is possible only at low temperatures. An increase of temperature in the beginning causes a slow decrease of magnetization and then a drop until a critical temperature θ_C is reached (Fig. 1). Above θ_C, the specimen is no longer ferromagnetic and becomes paramagnetic. Such a cooperative process may be readily understood from thermodynamic reasoning, since the additional entropy associ-

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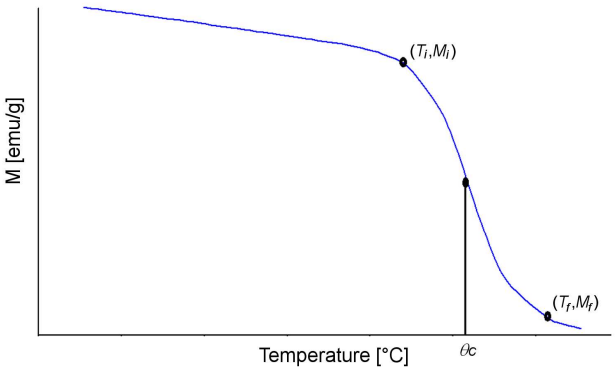

Figure 1. Temperature dependence of magnetization under constant applied field (T_i and T_f indicate the onset and finalization of the phase transition)

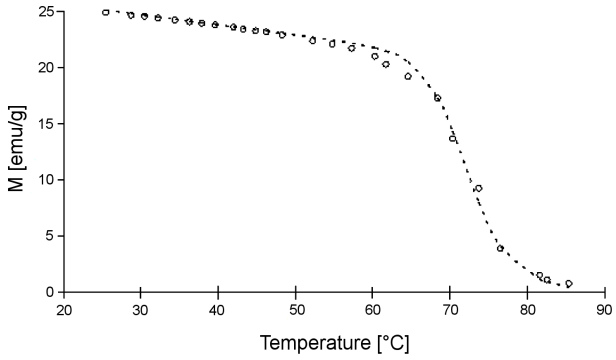

Figure 2. Magnetization versus temperature for LSMCO in applied field of 0.05 T (the dashed curve is modelled result and symbols represent experimental data [19])

ated with disorder of electron spins makes disordered (paramagnetic) state thermodynamically more stable at high temperatures.

In the previous paper [20] the phenomenological model, describing magnetization (M) as function of temperature (T) and the Curie temperature (θ_C), was developed. The model can also be used for calculation of a magnetic entropy change (ΔS_M) of a magnetic system under adiabatic magnetic field variation, as well as a maximum magnetic entropy change ΔS_{max} (for $T = \theta_C$) [20]:

$$\Delta S_{max} = H_{max}\left(-A\left(\frac{M_i - M_f}{2}\right) + B\right) \qquad (1)$$

In addition to the magnetic entropy change, relative cooling power (RCP) and magnetic specific heat change ($\Delta C_{P,H}$) are important, as they can also be used to evaluate magnetocaloric effect near the Curie temperature and prospective application of a material in an apparatus based on the active magnetic regenerator cycle. A relative cooling power (RCP) is described by the following equation [20]:

$$RCP = -\Delta S_{max} \times \delta T_{FWHM} \qquad (2)$$

where δT_{FWHM} is a full-width at half-maximum of magnetic entropy change curve and is given by [20]:

$$\delta T_{FWHM} = \frac{2}{A}\cosh^{-1}\left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}}\right) \qquad (3)$$

Finally, the magnetization-related change of the specific heat ($\Delta C_{P,H}$) can also be calculated form the phenomenological model [20] and is given by:

$$\Delta C_{P,H} = -TA^2(M_i - M_f)\,\mathrm{sech}^2(\Delta T)\tanh(\Delta T)H_{max} \qquad (4)$$

where $\Delta T = A(\theta_C - T)$.

III. Results and discussion

Figure 2 shows magnetization of LSMCO as function of temperature in 0.05 T magnetic field, where the symbols represent experimental data [19]. The dashed curve characterizes the modelled data using model parameters given in Table 1. It can be seen that the results of calculations are in a good agreement with the experimental results. Figures 3 and 4 show modelled results for changes of both magnetic entropy $|\Delta S_M|$ and specific heat ΔC_p as functions of temperature, respectively. The maxima observed in the $|\Delta S_M|$ curve may be related to a spin reorientation that occurs continuously [21]. This spin reorientation occurs due to the combined effects of spin-orbit coupling and momentum scattering in manganites [22]. In addition, ΔS_M of manganites relies on a strong spin lattice coupling in the magnetic ordering process which would lead to an additional magnetic entropy change near θ_C [6]. The values of $|\Delta S|_{max}$, δT_{FWHM}, and RCP for LSMCO under 0.05 T magnetic field variation were calculated by using equations 1, 2 and 3, respectively, and are given in Table 2.

Figure 4 shows the dependence of ΔC_p on the temperature under 0.05 T magnetic field variations for the sample calculated from equation 4. Since $\mathrm{d}M/\mathrm{d}T < 0$ and therefore $\Delta S_M < 0$, this leads to the total entropy decrease upon magnetization. Furthermore, at $T < \theta_C$, $\Delta C_p < 0$, and at $T > \theta_C$, $\Delta C_p > 0$ [23]. The ΔC_p undergoes a sudden change from positive to negative around θ_C with a positive value above θ_C and a negative value below θ_C and rapidly decreases with decreasing temperature. The positive or negative values of ΔC_p closely above or below θ_C may strongly alter the total specific heat.

The maximum and minimum values of specific heat change for LSMCO are determined from Fig. 4 and also summarized in Table 2. With applied magnetic field variation of 0.05 T, the peak value of $|\Delta S_M|$ is

Table 1. Model parameters for LSMCO in a field of 0.05 T (B is magnetization sensitivity ($\mathrm{d}M/\mathrm{d}T$) at ferromagnetic state before transition, S_C is magnetization sensitivity ($\mathrm{d}M/\mathrm{d}T$) at the Curie temperature)

M_i [emu/g]	M_f [emu/g]	θ_C [°C]	B [emu/g·K]	S_C [emu/g·K]
20.93	1.57	72	-0.09	-1.92

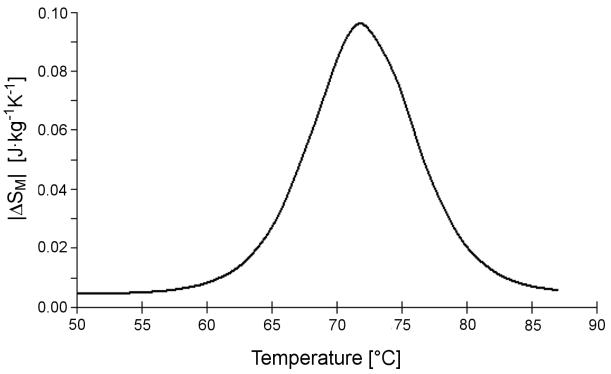

Figure 3. Magnetic entropy change as function of temperature for LSMCO in a field of 0.05 T

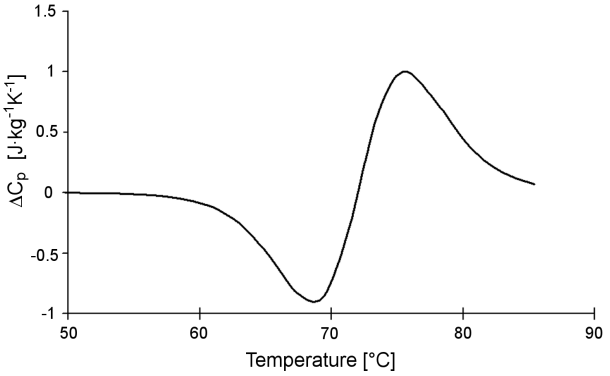

Figure 4. Specific heat change as function of temperature for LSMCO in a field of 0.05 T

0.096 J/(kg·K) and δT_{FWHM} = 9.7 K. The calculations show that at 0.05 T magnetic field change, RCP = 0.931 J/kg.

In addition, the refrigerant capacity (RC) was computed, as it is considered to be the most important factor for assessing the efficiency of a magnetic refrigerant material. RC was calculated from [24]:

$$RC = \int_{\theta_C - \frac{\delta T_{FWHM}}{2}}^{\theta_C + \frac{\delta T_{FWHM}}{2}} \Delta S \, \mathrm{d}T \qquad (5)$$

The calculation shows that at 0.05 T magnetic field change, RC = 0.744 J/kg.

Table 2 shows comparisons between LSMCO sample and other compositions in low applied magnetic field change. The magnetocaloric properties of LSMCO sample are comparable with some magnetocaloric properties of $La_{1-x}Cd_xMnO_3$, $La_{1.25}Sr_{0.75}MnCoO_6$ and MnAs and they ar significantly larger than that of $Ge_{0.95}Mn_{0.05}$ and $Gd_{1-x}Ca_xBaCo_2O_{5.5}$, as shown in Table 2 [25–29].

In general, the magnetic entropy change in perovskite manganites, such as LSMCO sample, has been related to the considerable variation of magnetization near θ_C. There are two contributions to the total entropy of the system [30,31]: i) magnetic entropy that is related to the order of magnetic moments, and ii) lattice entropy that is related to the temperature. 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 is removed, the material returns to ambient temperature. The adiabatic process (elimination of the applied field) 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, significant lattice change accompanying magnetic transition in perovskite manganites has been observed [32,33]. The lattice structural change in the <Mn–O> bond distance as well as <Mn–O–Mn> bond angle would, in turn, favour the spin ordering. Thereby, a more abrupt reduction of magnetization near θ_C occurs and results in a significant magnetic-entropy change [34,35]. In this way, a conclusion might be drawn that a strong spin-lattice coupling in the magnetic transition process would lead to the additional magnetic entropy change near θ_C, and consequently, favours the MCE.

IV. Conclusions

Magnetocaloric properties of LSMCO perovskite (such as magnetic entropy change, full-width at half-maximum, relative cooling power and magnetic specific heat change) at applied magnetic field of 0.05 T were calculated using the phenomenological model. It was shown that magnetocaloric effects of LSMCO sample are comparable with magnetocaloric properties of MnAs film, $La_{1-x}Cd_xMnO_3$ and $La_{1.25}Sr_{0.75}MnCoO_6$, whereas significantly larger than that of $Gd_{1-x}Ca_xBaCo_2O_{5.5}$ and $Ge_{0.95}Mn_{0.05}$.

Table 2. The predicted values of applied magnetocaloric properties for LSMCO and other compositions in low applied magnetic field changes

Composition [reference]	H [T]	$-\Delta S_{max}$ [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)]
LSMCO [this work]	0.05	0.096	9.7	0.931	1	−0.86
$La_{1-x}Cd_xMnO_3$ [26]	0.05	0.011	29.65–44.03	0.326–0.484	0.087–0.105	−0.076–−0.094
$Ge_{0.95}Mn_{0.05}$ film [27]	0.1	$(0.4–3.6)\cdot10^{-6}$	12.69–17.75	$(0.63–0.451)\cdot10^{-5}$	$(0.077–1.1)\cdot10^{-4}$	$(-0.073–-1)\cdot10^{-4}$
$Gd_{1-x}Ca_xBaCo_2O_{5.5}$ [28]	0.1	$(1.65–2.2)\cdot10^{-6}$	9.77–13.85	$(1.61–3.04)\cdot10^{-5}$	$(6.14–6.34)\cdot10^{-5}$	$(-6.94–-6.13)\cdot10^{-5}$
$La_{1.25}Sr_{0.75}MnCoO_6$ [29]	0.5	0.0175	26–124	0.45–2.18	0.04–0.19	−0.03–−0.17
(001)-oriented MnAs film [30]	0.03	0.01–0.02	55.47–75.50	0.07–1.22	0.07–0.083	−0.06–−0.07

The results indicate the prospective application for LSMCO to obtain magnetocaloric effect near θ_C. It is recommended that LSMCO can be used as a promising practical material of an apparatus based on the active magnetic regenerator cycle. The results also confirmed that the phenomenological model is useful for prediction of MCE for magnetic materials.

References

1. S. El Kossi, J. Dhahri, E.K. Hlil, "Structural, magnetic and theoretical investigations on the magnetocaloric properties of $La_{0.7}Sr_{0.25}K_{0.05}MnO_3$ perovskite", *RSC Adv.*, **6** (2016) 63497–63507.
2. N.S. Bingham, A.K. Suszka, C.A.F. Vaz, H. Kim, L.J. Heyderman, "Interfacial room temperature magnetism and enhanced magnetocaloric effect in strained $La_{0.66}Ca_{0.34}MnO_3/BaTiO_3$ heterostructures", *Phys. Rev. B*, **96** [2] (2017) 024419.
3. A.M. Tishin, Y.I. Spichkin, *The Magnetocaloric Effect and its Applications*, 1st Ed., Institute of Physics, Bristol, 2003.
4. L. Li, K. Nishimura, H. Yamane, "Giant reversible magnetocaloric effect in antiferromagnetic $GdCo_2B_2$ compound", *Appl. Phys. Lett.*, **94** (2009) 102509.
5. X. Bohigas, J. Tajada, E. del Barco, X.X. Zhang, M. Sales, "Tunable magnetocaloric effect in ceramic perovskites", *Appl. Phys. Lett.*, **73** [3] (1998) 390–392.
6. Y. Sun, X. Xu, Y. Zhang, "Large magnetic entropy change in the colossal magnetoresistance material $La_{2/3}Ca_{1/3}MnO_3$", *J. Magn. Magn. Mater.*, **219** (2000) 183–185.
7. X.X. Zhang, J. Tejada, Y. Xin, G.F. Sun, K.W. Wong, X. Bohigas, "Magnetocaloric effect in $La_{0.67}Ca_{0.33}MnO\delta$ and $La_{0.60}Y_{0.07}Ca_{0.33}MnO_\delta$ bulk materials", *Appl. Phys. Lett.*, **69** (1996) 3596–3598.
8. M.H. Phan, S.B. Tian, S.C. Yu, A.N. Ulyanov, "Magnetic and magnetocaloric properties of $La_{0.7}Ca_{0.3-x}Ba_xMnO_3$ compounds", *J. Magn. Magn. Mater.*, **256** (2003) 306–310.
9. M.A. Hamad, "Magnetocaloric effect in Sr_2FeMoO_6/Ag composites", *Process. Appl. Ceram.*, **9** (2015) 11–15.
10. M.A. Hamad, "Simulated magnetocaloric properties of $MnCr_2O_4$ spinel", *Process. Appl. Ceram.*, **10** (2016) 33–36.
11. M. Foldeaki, R. Chahine, T.K. Bose, "Magnetic measurements: A powerful tool in magnetic refrigerator design", *J. Appl. Phys.*, **77** (1995) 3528–3537.
12. Y. Xu, U. Memmert, U. Hartmann, "Thermomagnetic properties of ferromagnetic perovskite manganites", *J. Magn. Magn. Mater.*, **242-245** (2002) 698–700.
13. G. Akcay, S.P. Alpay, J.V. Mantese, G.A. Rossetti Jr., "Magnitude of the intrinsic electrocaloric effect in ferroelectric perovskite thin films at high electric fields", *Appl. Phys. Lett.*, **90** (2007) 252909.
14. B. Neese, B. Chu, S. Lu, Y. Wang, E. Furman, Q.M. Zhang, "Large electrocaloric effect in ferroelectric polymers near room temperature", *Science*, **321** (2008) 821–823.
15. M.A. Hamad, "Ni-Co-Mo-Ti maraging steel hysteretic loops calculations", *Arab. J. Sci. Eng.*, **39** (2014) 569–574.
16. M.A. Hamad, "Prediction of energy loss of $Ni_{0.58}Zn_{0.42}Fe_2O_4$ nanocrystalline and Fe_3O_4 nanowire arrays", *Jpn. J. Appl. Phys.*, **49** (2010) 085004.
17. M.A. Hamad, "Calculations on nanocrystalline $CoFe_2O_4$ prepared by polymeric precursor method", *J. Supercond. Nov. Magn.*, **26** (2013) 669–673.
18. M.H. Phan, S.C. Yu, "Review of the magnetocaloric effect in manganite materials", *J. Magn. Magn. Mater.*, **308** (2007) 325–340
19. M. Horiki, T. Nakagawa, S. Seino, T.A. Yamamoto, "Heating ability of La–Sr–Mn–Cu perovskite spheres under an alternating current magnetic field for magnetic hyperthermia mediators", *J. Magn. Magn. Mater.*, **329** (2013) 49–52.
20. M.A. Hamad, "Prediction of thermomagnetic properties of $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Sr_{0.33}MnO_3$", *Phase Transitions*, **85** (2012) 106–112.
21. J.C. Debnath, R. Zeng, J.H. Kim, P. Shampa, D.P. Chen, S.X. Dou, "Effect of frozen spin on the magnetocaloric property of $La_{0.7}Ca_{0.3}CoO_3$ polycrystalline and single crystal samples", *J. Alloys Compd.*, **510** [1] (2012) 125–133.
22. R.D. Averitt, A.I. Lobad, C. Kwon, S.A. Trugman, V.K. Thorsmølle, A.J. Taylor, "Ultrafast conductivity dynamics in colossal magnetoresistance manganites", *Phys. Rev. Lett.*, **87** [1] (2001) 017401.
23. N. Dhahri, M. Abassi, J. Dhahri, E.K. Hlil, "Magnetocaloric effect in perovskite manganite $La_{0.67-x}Eu_xSr_{0.33}MnO_3$", *J. Supercond. Nov. Magn.*, **28** [9] (2015) 2795–2799.
24. M.A. Hamad, "Magnetocaloric effect in nanopowders of $Pr_{0.67}Ca_{0.33}Fe_xMn_{1-x}O_3$", *J. Supercond. Nov. Magn.*, **27** (2014) 223–227.
25. M.A. Hamad, "Magnetocaloric effect in $La_{1-x}Cd_xMnO_3$", *J. Supercond. Nov. Magn.*, **26** (2013) 3459–3462.
26. M.A. Hamad, "Magnetocaloric effect in $Ge_{0.95}Mn_{0.05}$ films", *J. Superconduct. Novel Magn.*, **26** (2013) 449–453.
27. M.A. Hamad, "Magnetocaloric effect in polycrystalline $Gd_{1-x}Ca_xBaCo_2O_{5.5}$", *Mater. Lett.*, **82** (2012) 181–183.
28. M.A. Hamad, "Magnetocaloric effect in $La_{1.25}Sr_{0.75}MnCoO_6$", *J. Therm. Anal. Calorim.*, **115** (2014) 523-526.
29. M.A. Hamad, "Magnetocaloric effect in (001)-oriented MnAs thin film", *J. Supercond. Nov. Magn.*, **27** (2014) 263–267.
30. V. Franco, J.S. Blázquez, B. Ingale, A. Conde, "The magnetocaloric effect and magnetic refrigeration near room temperature: materials and models", *Ann. Rev. Mater. Res.*, **42** (2012) 305–342.
31. V.K. Pecharsky, K.A. Gschneidner Jr., Y. Mudryk, D. Paudyal, "Making the most of the magnetic and lattice entropy changes", *J. Magn. Magn. Mater.*, **321** (2009) 3541–3547.
32. P.G. Radaelli, D.E. Cox, M. Marezio, S.-W. Cheong, P.E. Schiffer, A.P. Ramirez, "Simultaneous structural, magnetic, and electronic transitions in $La_{1-x}Ca_xMnO_3$ with x = 0.25 and 0.50", *Phys. Rev. Lett.*, **75** (1995) 4488–4491.
33. K.H. Kim, J.Y. Gu, H.S. Choi, G.W. Park, T.W. Noh, "Frequency shifts of the internal phonon modes in $La_{0.7}Ca_{0.3}MnO_3$", *Phys. Rev. Lett.*, **77** (1996) 1877–1880.
34. T. Tang, K.M. Gu, Q.Q. Cao, D.H. Wang, S.Y. Zhang, Y.W. Du, "Magnetocaloric properties of Ag-substituted perovskite-type manganites", *J. Magn. Magn. Mater.*, **222** (2000) 110–114.
35. Y. Sun, W. Tong, Y.H. Zhang, "Large magnetic entropy change above 300 K in $La_{0.67}Sr_{0.33}Mn_{0.9}Cr_{0.1}O_3$", *J. Magn. Magn. Mater.*, **232** (2001) 205–208.