Large magnetocaloric effect in $Sm_{0.52}Sr_{0.48}MnO_3$ in low magnetic field

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This letter reports on the magnetocaloric properties of $Sm_{0.52}Sr_{0.48}MnO_3$ single crystal. A magnetic field of only 1 T yields a change in the magnetic entropy by 5.9 J/(kg K) at T_C (=124 K), which is higher than those observed in several other perovskite manganites and rare earth alloys of comparable T_C. This change originates from a sharp magnetization jump, associated with a first-order metamagnetic transition. Such a large change in entropy at a low magnetic field makes this material useful for magnetic refrigeration. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2919732]

Magnetic refrigeration, based on the magnetocaloric effect (MCE), has attracted much research interest due to its potential advantage of environmental friendliness over gas refrigeration. Mostly, rare earth materials and their alloys show excellent magnetocaloric properties because of their large magnetic moment.[1–4] However, in recent years MCE has also been extensively studied in perovskite-type manganese oxides due to their low cost of preparation, higher chemical stability, high electrical resistivity that reduces the eddy current heating and, obviously, the large magnetic entropy change with applied magnetic field. Furthermore, the wide range of magnetic transition temperatures (100 K $< T_C <$ 375 K) of manganites would be useful for magnetic refrigeration at various temperatures.[1,5] Large MCE has been reported in several ferromagnetic (FM) manganites such as $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.62}Gd_{0.05}Ca_{0.33}MnO_3$, $La_{0.87}Sr_{0.13}MnO_3$, etc.[1,5–7] However, these materials show large MCE at intermediate or high magnetic field only. Therefore, the challenge remains to find out new materials that exhibit a large MCE at low magnetic field. The guideline for the choice of an appropriate material having large MCE is that it should have a sharp FM to paramagnetic (PM) phase transition. Manganites with large quenched disorder show metamagnetic transition and hence may be suitable candidates for MCE. It is already reported that $Sm_{1-x}Sr_xMnO_3$ shows a sharp first-order magnetic transition slightly below $x=0.5$.[8] In view of this, the magnetization and heat capacity of $Sm_{1-x}Sr_xMnO_3$ ($x=0.48$) single crystal have been measured as functions of temperature and magnetic field in order to estimate the MCE. Indeed, our results show that this system displays a large MCE at a low applied field.

Single crystals of $Sm_{0.52}Sr_{0.48}MnO_3$ were grown using a two-mirror optical floating zone furnace in oxygen atmosphere at a growth rate of 10 mm/h.[9,10] Both electron dispersive x-ray analysis and x-ray diffraction data show that the crystal is pure and stoichiometrically correct. The magnetization measurements were carried out on a parallelepiped crystal with dimensions of $2\times4\times0.5$ mm^3 using a superconducting quantum interference device magnetometer (magnetic property measurement system, Quantum Design) over a wide range of temperature (5–210 K) and magnetic field ($H=0-5$ T) using five-scan averaging. Magnetic field was applied only along the longest direction of the sample which is the (111) crystallographic direction. Heat capacity measurements were performed by semiadiabatic technique for $H=0$ and 1 T.

Figure 1 shows a set of isothermal magnetization (M) curves as a function of magnetic field for a few selected temperatures in the vicinity of Curie temperature (T_C =113 K at $H=0$). Isothermal magnetization measurements were done at a temperature interval of 1 K between 105 and 135 K. Above 135 K, measurements were done at a 5 K interval. Just above T_C, M exhibits a two-step behavior. This behavior indicates that both FM and PM phases coexist in the vicinity of T_C. With increasing T, the two-step behavior disappears and only the sharp metamagnetic transition survives. The S-shaped magnetization curve is the signature of a first-order metamagnetic transition. For further support, we have plotted H/M versus M^2 isotherms in the inset of Fig. 1. According to the Banerjee criterion, the slope of H/M versus M^2 plot should be negative for a first-order magnetic transition.[11] In the present case, the negative slope of H/M versus M^2 plot (excluding the initial part) is the indication of first-order metamagnetic transition.

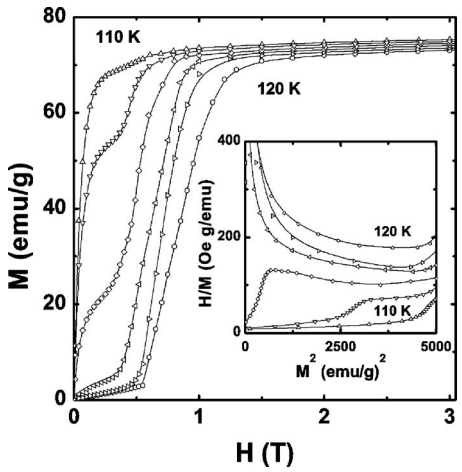

FIG. 1. Magnetization (M) of $Sm_{0.52}Sr_{0.48}MnO_3$ single crystal as a function of magnetic field (H) between 110 K (top) and 120 K (bottom) in 2 K interval. Inset: H/M vs M^2 plot of those isotherms.

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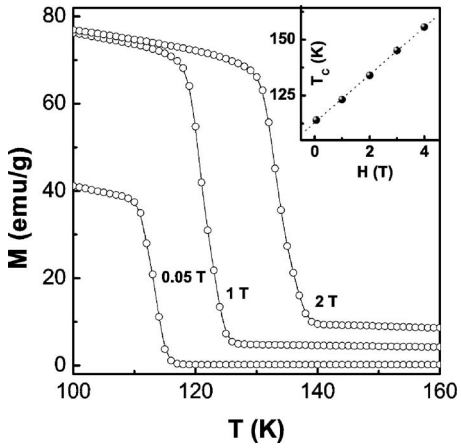

FIG. 2. Temperature dependence of magnetization (M) of $Sm_{0.52}Sr_{0.48}MnO_3$ single crystal for different magnetic fields. Inset: T_C vs H phase diagram.

Figure 2 displays the temperature dependence of magnetization of $Sm_{0.52}Sr_{0.48}MnO_3$ single crystal for different magnetic fields. In contrast to a gradual FM-PM transition, M shows a steplike jump at T_C for magnetic fields below 4 T. T_C linearly increases at the rate of 11.3 K/T. In this context, it is useful to compare the magnetization behavior of this sample with that of MnAs, a well known magnetic refrigerant.[4] In MnAs, the magnetic transition is sharp even up to a field of 5 T and T_C increases with H at the rate of 3.4 K/T. Therefore, the qualitative nature of MCE of the present sample is expected to be similar to that of MnAs. In order to calculate the MCE, one needs to study the magnetic entropy change under a magnetic field. Magnetic entropy change $\Delta S_M(T,H)$ can be calculated either by using the Maxwell relation $\Delta S_M(T,H)=\int_0^H(\partial M/\partial T)_H dH$ or by using the heat capacity (C_p) data[3]

$$\Delta S_M(T,H) = \int_0^T \frac{C_p(H) - C_p(0)}{T}\, dT.$$

Figure 3(a) presents $|\Delta S_M|$ as a function of temperature for a field change of 0–1 T. $|\Delta S_M|$ obtained from the heat capacity data exhibits a flat plateau with a height of ~5.9 J/kg K and a width of ~9 K. On the other hand, $|\Delta S_M|$ derived from the Maxwell relation shows a peak of ~9.3 J/kg K in the temperature region of two-step behavior in $M(H)$ curve (Fig. 1). Similar discrepancy is also observed in $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and the origin of the large peak in $|\Delta S_M|$ obtained from magnetization measurements has been attributed to the coexistence of FM and PM phases near T_C.[12] For a first-order magnetic transition, it is possible to calculate ΔS_M from the Maxwell relation if only the contribution from the metamagnetic transition is taken into account.[12] The peak value of $|\Delta S_M|$ in $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ drops from ~99 to ~22 J/kg K when only the contribution from the metamagnetic transition is considered. Following this prescription, we have recalculated $|\Delta S_M|$ and the result is shown in the same figure. As expected, the peak in $|\Delta S_M|$ disappears and the agreement between $|\Delta S_M|$ calculated from magnetic and heat capacity data becomes quite satisfactory. As both the methods yield the same result, there is no unaccounted systematic error. Liu *et al.* suggested that for a first-order phase transition the Clausius–Clapeyron equation is equivalent to the Maxwell relation.[12] To verify this, we use the Clausius–Clapeyron equation $[|\Delta S_M| = \Delta M/(dT_C/dH)]$ to estimate

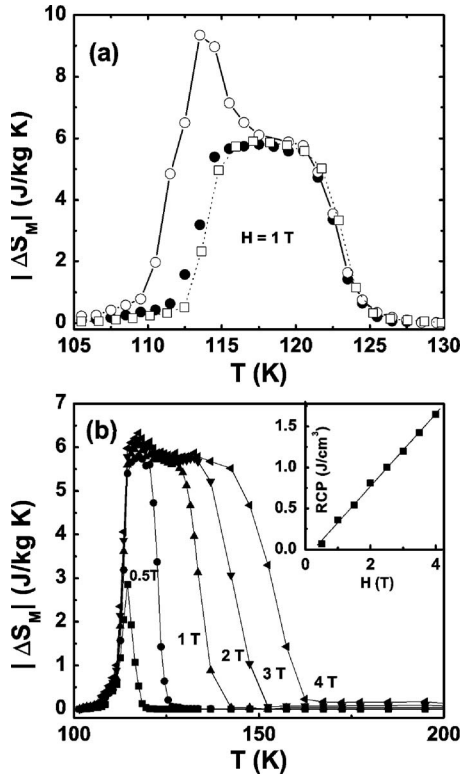

FIG. 3. (a) Temperature dependence of magnetic entropy change $|\Delta S_M|$ of $Sm_{0.52}Sr_{0.48}MnO_3$ single crystal at $H=1$ T calculated from the magnetic data using the Maxwell relation (open circles) and the heat capacity (open square). The peak value drops from ~9.8 to ~5.8 J/kg K if only the contribution from metamagnetic transition is considered (closed circle). (b) Temperature dependence of $|\Delta S_M|$ for different H calculated from the magnetic data by noting the contribution from the metamagnetic transition only. Inset: RCP as a function of magnetic field.

$|\Delta S_M|$ at T_C for $H=1$ T; $\Delta M = M_{FM} - M_{PM} = 67$ emu/g is calculated from the magnetization jump in $M(H)$.[13] The calculation yields $|\Delta S_M| = 5.92$ J/kg K at $H=1$ T. Thus, the values of $|\Delta S_M|$ obtained by using the Maxwell relation, the Clausius–Clapeyron equation and the heat capacity data are in good agreement. Figure 3(b) shows the thermal distribution of $|\Delta S_M|$ for different H, calculated using the Maxwell relation by only taking into account the contribution from the metamagnetic transition. The maximum entropy change ($|\Delta S_M^{max}|$), increases with field and attains a value of 5.8 J/kg K at $H=1$ T. Such a large magnetic entropy change is mainly due to the sharp change in magnetization near T_C, which might have been enhanced because of the strong spin-lattice coupling.[7,14] For $H>1$ T, the height of $|\Delta S_M|$ is insensitive to magnetic field change, whereas the peak width increases with field. This kind of plateaulike behavior of $|\Delta S_M|$ is a typical characteristic of the first-order phase transition.[15] Some small spikes are observed in $|\Delta S_M|$ versus T curves, which are probably artifacts of the procedure of the calculation and are also observed in MnAs.[4] Apart from large $|\Delta S_M^{max}|$, the relative cooling power (RCP) and the adiabatic temperature change (ΔT_{ad}) are also important parameters to determine the efficiency of magnetic cooling. RCP is defined as $|\Delta S_M^{max}|\delta T_{FWHM}$, where δT_{FWHM} is the full width at half maximum of $|\Delta S_M|$ versus T curve.[1,16] The RCP values of $Sm_{0.52}Sr_{0.48}MnO_3$ for different H are shown in the inset of Fig. 3(b). The value of RCP is 346 mJ/cm^3 for $H=1$ T, which is large compared to other manganites in the low-field regime and is about 37% of that of pure Gd.[2,5] ΔT_{ad} at a

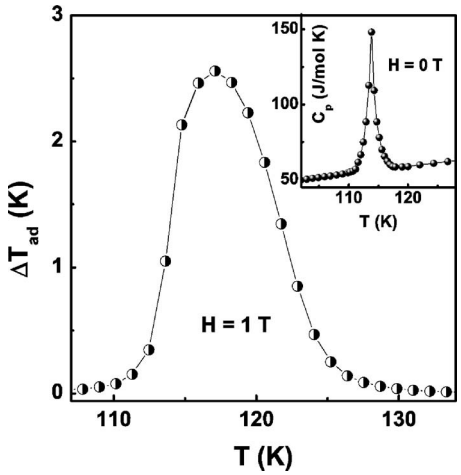

FIG. 4. Temperature dependence of the adiabatic temperature change (ΔT_{ad}) of $Sm_{0.52}Sr_{0.48}MnO_3$ single crystal for $H=1$ T. Inset: zero-field heat capacity (C_p) as a function of temperature.

given field H is calculated from the heat capacity data by noting the isentropic difference between the entropy curves $S(0,T)$ and $S(H,T)$.[3,17] Figure 4 shows the temperature dependence of ΔT_{ad} for $H=1$ T. The maximum value of ΔT_{ad} at $H=1$ T is 2.56 K, which is large compared to that for several other manganites and is about 61% of pure Gd.[2,5]

To assess the applicability of $Sm_{0.52}Sr_{0.48}MnO_3$ as a magnetic refrigerant $|\Delta S_M^{max}|$, determined in the present study, is compared in Table I with that reported in literature for several other magnetic refrigerants with T_C in the range of 100–200 K. As is evident from the table, $Sm_{0.52}Sr_{0.48}MnO_3$ shows quite large $|\Delta S_M^{max}|$ among the listed manganites and rare earth alloys in the low-field region. Moreover, the respectable values of RCP and ΔT_{ad} in a relatively low-field range (~1 T) are important for achieving high magnetic cooling efficiency. We believe that all these excellent magnetocaloric properties make $Sm_{0.52}Sr_{0.48}MnO_3$ single crystal an important low-temperature magnetocaloric material.

TABLE I. Maximum entropy change $|\Delta S_M^{max}|$ occurring at the Curie temperature T_C at low magnetic field H for several magnetic refrigerants.

Composition	$H(T)$	T_C (K)	$\lvert\Delta S_M^{max}\rvert$ (J/kg K)	Reference
$La_{0.87}Sr_{0.13}MnO_3$	1.50	196.5	2.90	7
$La_{0.7}Cd_{0.3}MnO_3$	1.35	150	2.88	18
$La_{0.9}Pb_{0.1}MnO_3$	1.50	160	0.53	19
$La_{0.8}Ca_{0.2}MnO_3$	1.00	176	2.75	6
$La_{0.65}Ca_{0.35}Ti_{0.1}Mn_{0.9}O_3$	3.00	103	1.30	14
$Pr_{0.9}Pb_{0.1}MnO_3$	1.35	150	3.91	20
$Nd_{0.25}Pr_{0.25}Sr_{0.5}MnO_3$	1.35	170	1.65	21
$La_{1.6}Ca_{1.4}Mn_2O_7$	1.50	168	3.80	22
$DyCo_2$	1.00	142	5.80	1
GdCoAl	2.00	100	4.88	23
$TbAl_2$	2.00	105	7.50	24
$LaFe_{11.375}Al_{1.625}$	1.00	145	3.90	25
$Sm_{0.52}Sr_{0.48}MnO_3$[a]	1.00	124	5.90	This work

[a]Value is calculated by considering the phase coexistence effect.

To summarize, $Sm_{0.52}Sr_{0.48}MnO_3$ single crystal exhibits large MCE, mainly due to the field-induced metamagnetic transition. A large magnetic entropy change (ΔS_M^{max} = 5.9 J/kg K) has been observed at a relatively low magnetic field (1 T). Besides the large values of ΔS_M^{max}, RCP, and ΔT_{ad}, high chemical stability, high electrical resistivity, and low cost of production indicate a great potential of $Sm_{0.52}Sr_{0.48}MnO_3$ as a magnetic refrigerant.

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