Excellent magnetocaloric properties of $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($0.05 \leqslant x \leqslant 0.25$) single crystals

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This letter reports on the superior magnetocaloric properties of $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x=0.05$, 0.10, 0.20, and 0.25) single crystals. Upon 50 kOe applied field, the magnetic entropy changes (ΔS_M) reach values of ~10.5, 7.45, 6.97, and 6.86 J/kg K for $x=0.05$, 0.10, 0.20, and 0.25 compositions, respectively. The large magnetic entropy changes have been found to occur around 300 K, thus allowing magnetic refrigeration at room temperature. Due to the absence of grains in the single crystals, the ΔS_M distribution here is much more uniform than that of gadolinium and polycrystalline manganites, which is desirable for an Ericson-cycle magnetic refrigerator. The single crystals have the large magnetic entropy changes induced by low magnetic field change, which is beneficial for the household application of active magnetic refrigerant (AMR) materials. These results indicate that the present single crystals are excellent candidates as working materials for AMR. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1867564]

Magnetic refrigeration techniques based on magnetocaloric effect (MCE) have been demonstrated as a promising alternative to conventional gas compression refrigeration.[1] The MCE is understood as an isothermal magnetic entropy change or an adiabatic temperature change of a magnetic material upon the application of a magnetic field. It shows that the heating and cooling in the magnetic refrigeration process is proportional to the size of the magnetic moments and to the applied magnetic field. That is why research in the magnetic refrigeration has been being exclusively conducted on heavy rare-earth elements and their compounds.[2,3] With the highest magnetic moment, among the rare-earth metals, gadolinium was found to show the highest MCE and has been really demonstrated to provide success to the cooling between 270 and 310 K.[2] Nonetheless, the cost for a magnetic refrigerant using gadolinium is quite expensive ~$4000/kg and this actually limits the usage of it as an active magnetic refrigerant (AMR) in magnetic refrigerators. Recently, the authors[3] discovered an extraordinarily large MCE in $Gd_5(Si_2Ge_2)$—which undergoes a simultaneous first-order structural and magnetic-phase transition[4] that is believed to be responsive for the large MCE.[3] 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. Further efforts to seek for new materials, especially the materials without rare-earth elements,[5–7] and exhibiting large MCE in response to low applied field, are of significant importance. Among them, perovskite-type manganese oxide materials[7–10] having large MCEs are believed to be good candidates for magnetic refrigeration at various temperatures, since the magnetic properties of perovskite manganites, Curie temperature, and saturation magnetization, are strongly doping dependent.

In view of AMR requirements, note that besides the requirement for an AMR material that should have large magnetic entropy change (ΔS_M) induced by low magnetic field change, the ΔS_M distribution also plays an important role in achieving the magnetic cooling efficiency.[1,5] Unfortunately, the nonuniform ΔS_M distribution, which is not beneficial for an Ericson-cycle magnetic refrigerator, has been found on several AMR materials such as gadolinium[2] and polycrystalline perovskite manganites,[9,10] due to structural inhomogeneity.[11]

In this context, the study of MCE in such lanthanum manganite single crystals can be of great interest, because the absence of grains in these materials would be expected to show a uniform ΔS_M distribution—which is desirable for an Ericson-cycle magnetic refrigerator. Here, we report on the excellent magnetocaloric properties of $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x=0.05$, 0.10, 0.20, 0.25) single crystals, with which the requirements for an AMR material can be fulfilled.

Single crystals of $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x=0.05$, 0.10, 0.20, and 0.25) were prepared by the floating zone method using an infrared radiation convergence-type image furnace that consist of four mirrors and halogen lamps; details of the growth conditions can be found elsewhere.[12] The starting ceramic rods were obtained from the solid-state reaction of a stoichiometric mixture of La_2O_3, $CaCO_3$, $SrCO_3$, and $MnCO_3$. X-ray diffraction data and electron-probe microanalysis confirmed the quality of the crystal. The magnetic measurements were performed using either a Quantum Design MPMS-5 superconducting quantum interference device magnetometer or a PPMS-7 magnetometer.

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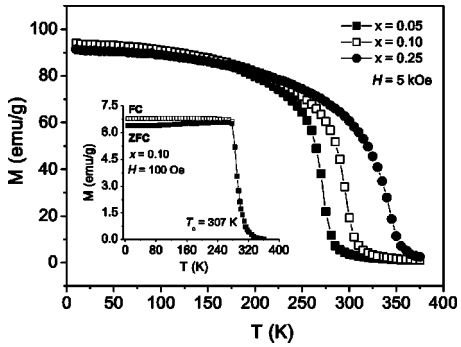

FIG. 1. Temperature-dependent magnetization taken both zero-field cooled and field cooled at $H=100$ Oe [in the inset, for $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x=0.10$) single crystal] and $H=5$ kOe for $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x=0.05$, 0.10, and 0.25) single crystals.

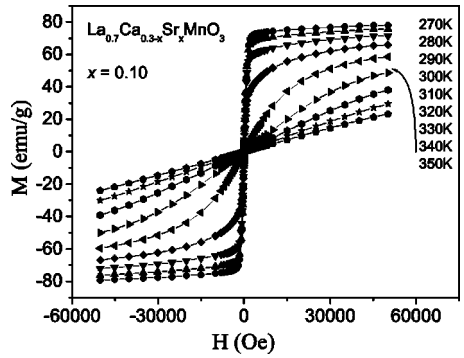

FIG. 2. Magnetic field dependence of magnetization measured at various temperatures around T_C for $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x=0.10$) single crystal.

Figure 1 shows temperature dependences of the magnetization of $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x=0.05$, 0.10, and 0.25) single crystals measured in the fields of 100 Oe and 5 kOe. The Curie temperature (T_C), defined by the maximum in the "absolute value" of dM/dT, has been determined from the M-T curve. The Curie temperatures of the samples are summarized in Table I. As shown in Fig. 1, when increasing the applied magnetic field, the T_C of the $x=0.10$ sample increases from ~307 K for $H=100$ Oe (the inset of Fig. 1) to ~308 K for $H=5$ kOe. This is attributed to enhancement in the ferromagnetic interactions with higher applied fields. As shown clearly in Ref. 5, the AMR material of $MnAs_{0.9}Sb_{0.1}$ indicated smooth temperature variation of the magnetization under high fields whereas the shape of the M-T curve for MnAs was almost unchanged. As a result, MnAs exhibited the larger MCE. As it is noted from Fig. 1, upon $H=5$ kOe the shape of the M-T curve remains almost unchanged while the T_C is shifted to a higher temperature. Therefore, the lanthanum manganite single crystals in the present study will be expected to show large MCEs near their Curie temperature.

In order to confirm this, the isothermal magnetization of all the samples were measured with a field step of 500 Oe in a range of 0–50 kOe and a temperature interval of 5 K in a range of temperatures around T_C. To ensure the readability of the figure, only some of isotherms are presented in Fig. 2, for a representative sample of $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x=0.10$). It can be seen clearly from Fig. 2 that there is a drastic change of the magnetization around the T_C, indicating a large magnetic entropy change. This coincides with the rapid reduction of magnetization at the T_C (Fig. 1). Another feature to be noted is that a large proportion of changes of the magnetization occurs in a relative low-field range (<20 kOe), which is beneficial for the household application of MCE materials.[1]

In order to evaluate the MCE of the present materials, we calculated changes of the magnetic entropy (ΔS_M) caused by the application of external magnetic fields from the isothermal curves of magnetization versus the applied field by using the following expression[10]

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

where M_i and M_{i+1} are the magnetization values measured at temperatures T_i and T_{i+1} in a field H, respectively.

Figure 3 shows the magnetic entropy change as a function of temperature for the samples with $x=0.05$, 0.10, and 0.25 at $\Delta H=50$ kOe. Upon 50 kOe applied field, among the samples investigated the highest value of ΔS_M ~10.5 J/kg K of the $x=0.05$ sample is found at a temperature of ~275 K. This value is obviously larger than that of gadolinium[2] ($\Delta S_M \sim 10.2$ J/kg K at $\Delta H=50$ kOe) and several other manganese oxides.[7–10] The large magnetic entropy changes for the $x=0.10$, 0.20, and 0.25 samples have been found to occur at and above 300 K (see Table I) and which allow water to be used as a heat transfer fluid in the room-temperature magnetic refrigeration regime. This result is of practical importance, because it shows that the present manganite single crystals could be good working materials for magnetic refrigeration in household refrigerators or air conditioning. It is worth noting that, due to the absence of grains in the present manganite single crystals, the $\Delta S_M(T)$ distri-

TABLE I. Maximum entropy change, $|\Delta S_M^{\max}|$, occurring at the Curie temperature, T_C, at $H=50$ kOe, and values of the saturation magnetization, M_s, for several magnetic refrigerant materials.

Material	M_s (emu/g)	T_C (K)	$\lvert\Delta S_M^{\max}\rvert$ (J/kg K)	Reference No.
$La_{0.7}Ca_{0.25}Sr_{0.05}MnO_3$	99.26	275	10.50	Present
$La_{0.7}Ca_{0.20}Sr_{0.10}MnO_3$	95.05	308	7.45	Present
$La_{0.7}Ca_{0.10}Sr_{0.20}MnO_3$	94.11	340	6.97	Present
$La_{0.7}Ca_{0.05}Sr_{0.25}MnO_3$	93.07	341	6.86	Present
$La_{0.87}Sr_{0.13}MnO_3$	···	196	5.80	9
$La_{0.84}Sr_{0.16}MnO_3$	···	243	5.75	9
Gd	···	294	10.20	2
$Gd_5Si_2Ge_2$	···	276	18.40	3
$MnFeP_{0.45}As_{0.55}$	···	310	18.00	6

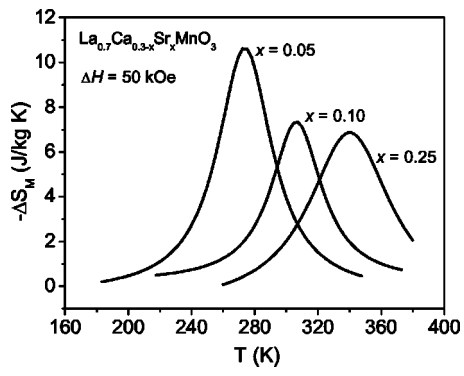

FIG. 3. The magnetic entropy change ($-\Delta S_M$) as a function of temperature in an applied field of 50 kOe for $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x=0.05$, 0.10, and 0.25) single crystals.

bution here is much more uniform than that of gadolinium[2] and polycrystalline manganites.[9,10] This is desirable for an Ericson-cycle magnetic refrigerator.[1] Another remarkable feature is that the present samples exhibited a relatively small magnetic hysteresis with coercivity of ~30 Oe near their T_C, which is beneficial to the magnetic cooling efficiency. In addition, compared with gadolinium[2] and its compounds,[3] perovskitelike structured materials are easier to fabricate and possessing a higher chemical stability as well as a higher resistivity. The high resistivity is beneficial to lowering the eddy current heating. All these excellent magnetocaloric features make the present manganite single crystals a competitive material for active magnetic-refrigeration applications.

In general, the large magnetic entropy change in perovskite manganites originates mainly from the considerable variation of magnetization near T_C. In addition, the spin-lattice coupling in the magnetic ordering process also plays an important role.[7–10] Due to strong coupling between spin and lattice, significant lattice change accompanying magnetic transitions in perovskite manganites has been observed.[7] The lattice structural change in the $\langle Mn-O \rangle$ bond distance as well as the $\langle Mn-O-Mn \rangle$ 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. 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, enhances the MCE.

In the present study, the large magnetic entropy changes in the manganite single crystals likely originate from the abrupt reduction of magnetization—which is associated with a ferromagnetic-to-paramagnetic phase transition near the Curie temperature. The additional entropy change can probably be attributed to the fact that the magnetic transition greatly enhances the effect of the applied magnetic field.[5] That is probably the reason why a sharp magnetic phase transition retains almost unchanged even under high fields. The larger magnetic entropy change of $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x=0.05$) single crystal compared to gadolinium is a direct consequence of the fact that the change in magnetization in this sample at its ordering temperature T_C is much sharper than that of Gd, despite the magnetic moment of Gd is much larger at low temperatures.[6] On the other hand, with further substituting Ca by Sr, the *M-T* curve became smoother (see Fig. 1) together with the decrease of the order of saturation magnetization (M_s) as measured at a low temperature of 10 K and magnetic fields up to 30 kOe (see Fig. 4 and Table I). This is likely due to the difference in the volume thermal expansion at T_C which is influenced by the average mean A-site radius.[13] It is the weakening of the coupling between magnetism and lattice occurring near T_C in the $LaCaMnO_3$ system due to strontium substitution that resulted in a drop of the MCE.[14] In terms of our experimental results, it is reasonable to conclude that there are two key requirements for a magnetic material to possess a large MCE. One is a large enough spontaneous magnetization, belonging to a class of heavy rare-earth metals[2] and, the other is a sharp drop in magnetization which is associated with the ferromagnetic-paramagnetic transition at the Curie temperature, as was found in perovskite manganites.[7–10] The larger the spontaneous magnetization and, the sharper the change in magnetization with respect to temperature at the ordering temperature, the larger the magnetic entropy change is obtained. In such rare-earth materials, the magnetic moment fully develops only at low temperatures, and therefore the magnetic entropy change near room temperature is only a fraction of the potential value. Whereas, the spin-lattice coupling in 3*d* transition-metal oxides may strongly occur in the magnetic ordering process and thereby results in a rapid change of magnetization in the magnetic ordering phase transition.[7] Even if the magnetic moment of manganese is only about half that of heavy rare-earth elements, further enhancement of the MCE associated with magnetic moment alignments may be achieved through the induction of magnetic ordering phase transition, which will result in much higher efficiency of the magnetic refrigerator.[6]

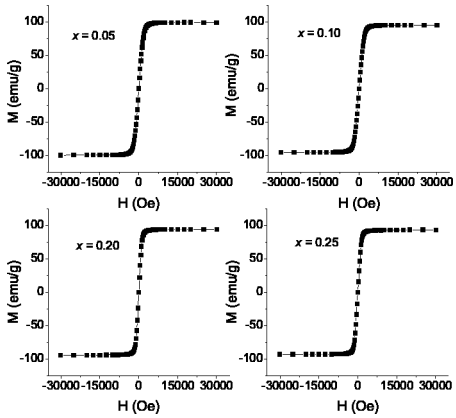

FIG. 4. The *M-H* loops of the $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ samples measured at $T=10$ K.

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