Large Magnetic Entropy Change in Perovskite-Type Manganese Oxides

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Magnetic entropy change larger than that of gadolinium has been observed in polycrystalline of $La_{1-x}Ca_xMnO_3$ ($x = 0.2$ and 0.33) perovskite-type manganese oxide. The large magnetic entropy change produced by the abrupt reduction of magnetization is attributed to the anomalous thermal expansion just at the Curie temperature. The considerable magnetic entropy change was also observed in $La_{0.75}Sr_{0.25-y}Ca_yMnO_3$ near room temperature. The phenomenon of large magnetic entropy change and the convenient adjustment of the Curie temperature make the perovskite-type manganese oxides useful for magnetic refrigerants in an extended high temperature range even at room temperature. [S0031-9007(97)02388-0]

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The solid state working substances for magnetic refrigeration have attracted attention, because they have a lot of advantages over the gas refrigerants [1]. Up to nowadays, the magnetocaloric effects have been extensively studied in two kinds of working substances for magnetic refrigeration: paramagnetic salts and ferromagnetic substances. The former have been conveniently used to obtain low temperature $T < 15$ K. The latter are useful for magnetic refrigeration at high temperature $T > 20$ K; in this temperature range, in order to remove the effect of the lattice entropy, the Ericsson cycle has been utilized [2–5]. In selecting magnetic refrigerants, attention was paid to the refrigerants which have large magnetic entropy change ($|\Delta S_M|$) under a magnetic field especially to those that can be used at room temperature [2].

According to the Curie-Weiss law for the ferromagnetic, large $|\Delta S_M(T,H)|$ is expected at Curie point T_c with large values of effective Bohr magneton number $p = g[J(J+1)]^{1/2}$, where g is the g factor and J is the total angular momentum quantum number [2]. In view of above, the previous studies mainly concentrated on intermetallic compounds and alloys of rare earths with high J, which allow an optimum choice of the Curie temperature for any desired range of operating temperature, such as MnAs, MnP, ~300 K [6], $R\mathrm{Al}_2$ (R represents Dy, Ho, Er), 20–80 K [7], $Y_2Fe_{12-x}Co_x$, 300–600 K [8]. The largest reported value of $|\Delta S_M|$ in the group of rare earths and their alloy was ~13.7 J/Kg K for Gd under a magnetic field of $H = 8$ T at T_c (~293 K), therefore Gd is thought to be the most adequate magnetic refrigerants used near room temperature [2].

Recently, large entropies have been observed in perovskite-type ferromagnetic oxides and in null field [9,10]. The intense interest in perovskite-type manganese oxides $R_{1-x}B_xMnO_3$ (where R is a rare earth ion and B is a divalent alkali) is prompted by the observation of colossal magnetoresistance [11–14]. Experimentally, anomalous thermal expansion has been observed in orthorhombic Nd-Sm-Sr-Mn-O [15], La-Ca-Mn-O [16,17], La-Y-Ca-Mn-O [18], and La-Sr-Mn-O [19] just at T_c, respectively; some of them exhibit discontinuous variation in the volume at the ferromagnetic transition, and the associated sharp change in magnetization. The simultaneous structural and magnetic transitions at T_c can strongly influence in the magnetic entropy change. From this viewpoint, we measured the magnetic entropy change of perovskite-type manganese oxides, and found that the compounds $La_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33) show larger magnetic entropy change than that of Gd.

Polycrystalline samples of $La_{1-x}Ca_xMnO_3$ ($x = 0.20$, 0.33, and 0.45) and $La_{0.75}Sr_{0.25-y}Ca_yMnO_3$ ($y = 0$, 0.10, and 0.125) were prepared by the sol-gel method in order to obtain high purity and homogeneous powders. X-ray powder diffraction showed that the sample is single phase without any other secondary or impurity phase.

The temperature dependence of magnetization for $La_{1-x}Ca_xMnO_3$ was measured using a vibrating sample magnetometer in a field of 0.7 T (Fig. 1). The Curie temperature T_c defined as the temperature of the maximum slope in dM/dT was found to be 230, 257, and 234 K for $x = 0.2$, 0.33, and 0.45, respectively.

From the thermodynamical theory, the magnetic entropy change $\Delta S_M(T,H)$ is given by [2]

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH\,.$$

Isothermal magnetization curves were measured in a field up to 1.5T, by using the equation, $\Delta S_M(T, 1.5\ \mathrm{T})$ is obtained, and Fig. 2(A) shows temperature dependence of $|\Delta S_M|$ for $La_{0.8}Ca_{0.2}MnO_3$. At the Curie temperature $T_c = 230$ K, $|\Delta S_M|$ attains 5.5 J/Kg · K. We also measured the magnetic entropy change of Gd [Fig. 2(A)] for comparison, and obtained $|\Delta S_M| \sim 4.2$ J/Kg · K at T_c; the value agrees with early reports [2]. $|\Delta S_M|$ for $La_{0.8}Ca_{0.2}MnO_3$ is larger than that of Gd.

The origin of the larger $|\Delta S_M|$ in the present, perovskite-type manganese oxides as compared with

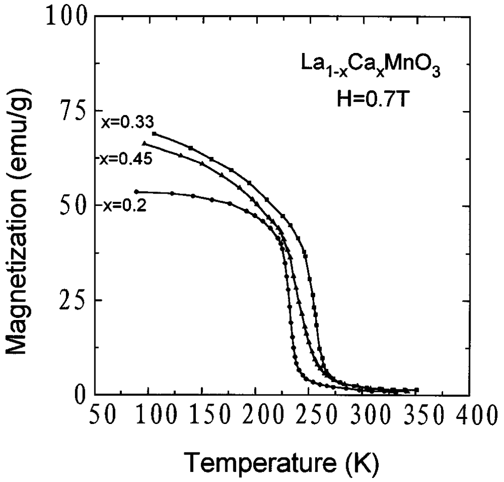

FIG. 1. Temperature dependence of magnetization (measured in a magnetic field $H = 0.7$ T) in polycrystalline $La_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33, and 0.45). The magnetization change was sharper at T_c for $x = 0.2$ and 0.33 than that of $x = 0.45$.

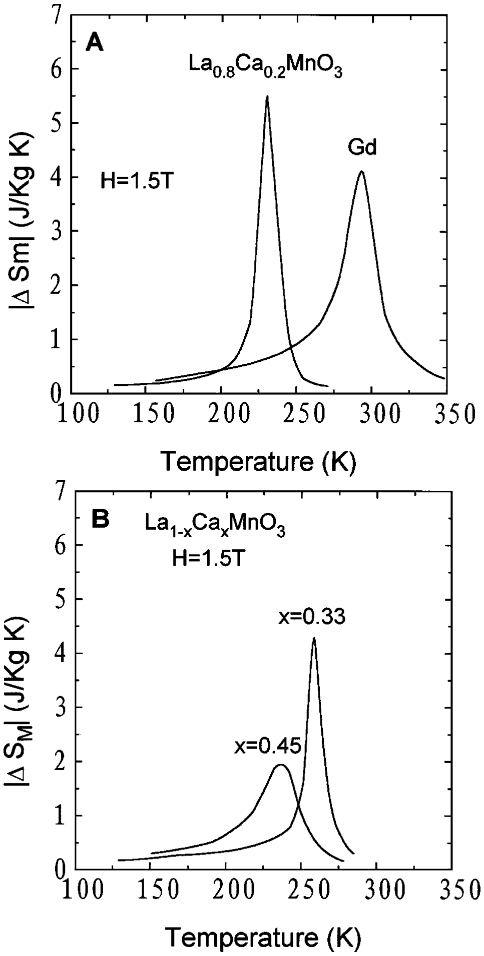

FIG. 2. Magnetic entropy change of (A) $La_{1-x}Ca_xMnO_3$ ($x = 0.2$) and Gd (B) $La_{1-x}Ca_xMnO_3$ ($x = 0.33$ and 0.45) at a magnetic field $H = 1.5$ T as a function of temperature. The temperatures of the maximum magnetic entropy change are just at their Curie temperatures. Magnetic entropy change for $x = 0.2$ and 0.33 is larger than that of Gd.

Gd should be attributed to the considerable variation of magnetization near T_c. The observation of the structural phase transition driven by an external magnetic field indicates that there is considerable coupling between magnetism and the lattice in manganese perovskites [20]. Because of the coupling mechanism, the lattice structural change in the Mn-O bond distances and Mn-O-Mn bond angles with temperature which exhibit variation in the volume can cause an additional change in magnetism; the abrupt change in magnetization must therefore be associated with the discontinuity of the size of the volume change at T_c, which results in a large $|\Delta S_M|$ in $La_{0.8}Ca_{0.2}MnO_3$.

Figure 2(B) shows the temperature dependence of $|\Delta S_M|$ for $x = 0.33$ and 0.45. $|\Delta S_M(T, 1.5\ \mathrm{T})|$ is 4.3 and 2 J/Kg · K at T_c, respectively. Compared with $x = 0.2$ and 0.33, $|\Delta S_M(T, 1.5\ \mathrm{T})|$ for $x = 0.45$ is smaller and the peak of $|\Delta S_M| \sim T$ curve is broader, which should correspond to a less sharp change in magnetization at T_c and the possibility of parasitic ferromagnetism above T_c, as can be seen in Fig. 1. This different feature may be explained by the different crystal structure with the different composition *x*, which can cause different change in the lattice parameters *a*, *b*, and *c* and bond angles with the variation of temperature [16], which further influence ΔS_M at T_c.

The magnetic transition in $La_{1-x}Ca_xMnO_3$ accompanied by significant lattice changes has been observed by high-resolution synchrotron x-ray powder diffraction [16]. The phenomenon was also conformed in our samples by internal friction (Q^{-1}) measurements with vibrating reed techniques, which are very sensitive to the lattice changes. The occurrence of both a Q^{-1} peak accompanied by the softening of Young's modulus for $x = 0.33$ sample is located at T_c (Fig. 3). Because the measurements were carried with a polycrystalline sample sintered at 1300 °C for 8 h, the softening of Young's modulus near phase transition should be much less conspicuous than that of a single crystal.

The Curie temperature of $La_{1-x}Ca_xMnO_3$ investigated above is below room temperature, to further explore the magnetic entropy change of the perovskite-type manganese oxides with T_c near room temperature, we prepared the materials of $La_{0.75}Sr_{0.25-y}Ca_yMnO_3$, due to the Curie temperature ($T_c = 348$ K) higher than room temperature in $La_{0.75}Sr_{0.25}MnO_3$, the replacement of Sr by Ca leads the decrease of T_c. For $y = 0.10$ and 0.125, T_c is 327 and 283 K, and considerable magnetic entropy change $|\Delta S_M(T, 1.5\ \mathrm{T})| = 2.8$ and 1.5 J/Kg · K are obtained at T_c near room temperature, respectively (Fig. 4). The phenomenon indicates the perovskite-type manganese oxides may have the potential for applications

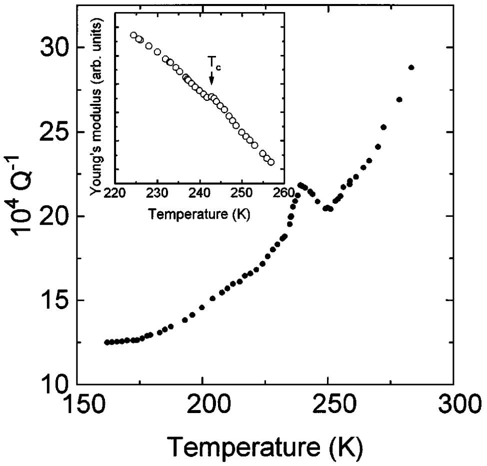

FIG. 3. Temperature dependence of internal friction (Q^{-1}) and Young's modules for $La_{1-x}Ca_xMnO_3$ ($x = 0.33$); both a peak of Q^{-1} and (inset) the softening of Young's modules are located at T_c.

as working materials for magnetic refrigeration near room temperature.

The comparatively large $|\Delta S_M|$ in Ca-doped $LaMnO_3$ is induced by a sharp volume change just at T_c, this mechanism is different from that of Gd. The $R_{1-x}B_xMnO_3$ perovskite-type manganese oxides display variation of Curie temperature with the doping. The observation of decreasing the average ionic radius of A site causes a decrease in T_c and provides certain guidelines for convenient adjustment of the Curie temperature [21,22]. Using a complex magnetic refrigerant composed of several kinds of perovskite-type manganese oxides which have different T_c can get large temperature span and obtain a constant ΔS_M against temperature variation; these materials are suitable for the ideal Ericsson cycle [7]. On the other hand, the perovskite-type manganese oxides exhibit considerably small magnetic hysteresis with coercivity of about 50 Oe near T_c [23], which would be beneficial for the magnetic cooling efficiency. In this Letter we report the first observation to our knowledge of a material with magnetic entropy change larger than Gd in perovskite compounds. Compared with rare earths and their alloys, the perovskite-type manganese oxides exhibit higher chemical stability and higher electrical resistivity that favors a lower value of eddy current heating and lower cost, and would be more suitable candidates for magnetic refrigerants at high temperature, especially the potential for application near room temperature.

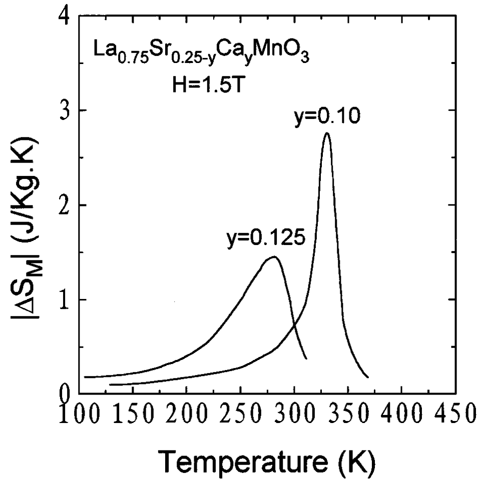

FIG. 4. Magnetic entropy change of $La_{0.75}Sr_{0.25-y}Ca_yMnO_3$ ($y = 0.10$and 0.125) at a magnetic field $H = 1.5$ T as a function of temperature. The maximum magnetic entropy change was located at their Curie temperatures (near room temperature), respectively.

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