Tunable magnetocaloric effect in ceramic perovskites

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A large entropy variation (magnetocaloric effect) has been discovered in ceramic perovskites with the formulas $La_{0.65}Ca_{0.35}Ti_{1-x}Mn_xO_{3-z}$ and $La_{0.5+x+y}Li_{0.5-3y}Ti_{1-3x}Mn_{3x}O_{3-z}$. Both Curie temperature and entropy change were studied from 4.2 to 400 K for different stoichiometric compositions and applied magnetic fields. Our conclusion is that these materials are excellent candidates for working materials in magnetic refrigeration and liquefaction devices in a wide temperature range. © *1998 American Institute of Physics.* [S0003-6951(98)03129-5]

The removal of a magnetic field from a material results in a reduction in magnetic spin alignment representing an increase in the material's spin entropy. This is the method used to obtain mK temperatures in magnetic adiabatic cooling with paramagnetic salts.[1] Although the experimental method and the physics involved have been well known since the beginning of this century, no real advancements have been made in high temperature applications until very recently. The discovery of new ordered magnetic intermetallic compounds and magnetic nanocomposites both presenting extremely large adiabatic temperatures changes, together with a better quantitative understanding of the magnetic regenerative cycle, suggests that magnetic refrigerators could then be substantially reduced in size and made more efficient.

In recent years, there has been increasing interest in the search for new materials with enhanced magnetocaloric properties. At first, the most investigated materials for low temperature applications, between 1.5 and 20 K, were paramagnetic salts, for example $Gd_3Ga_5O_{12}$ and $Dy_3Al_5O_{12}$.[2-4] More recently, Shull and co-workers[5,6] announced magnetic nanocomposites. Shull's idea was to use the alignment of the magnetic moment of magnetic nanoparticles which should be superparamagnetic at the working temperature. These researchers demonstrated that some of these composites display a magnetocaloric effect exceeding that of paramagnetic salts. Also using nanomaterials, but as liquids, we prepared several different iron based ferrofluids which show a large magnetocaloric effect.[7] Recently Pecharsky and Gschneidner[8,9] reported a giant magnetocaloric effect in the $Gd_5(Si_xGe_{1-x})_4$ pseudobinary alloys for the temperature range between 50 and 280 K. This work may have enormous importance for both physics and technology. In the same direction as Pecharsky and Gschneidner, we have also published data for magnetic perovskites proposing these materials for high temperature magnetocaloric effect applications.[10] In this letter we describe the results obtained for a series of magnetic perovskites which are good candidates for refrigeration at both subroom temperature (250–300 K) and the liquefaction temperature of cryogenic gases (4.2 K and 60–80 K).

According to classical thermodynamics, the infinitesimal change in temperature observed when a magnetic field is applied adiabatically is expressed as

$$dT = -\frac{T}{C_B}\left(\frac{\partial M}{\partial T}\right)_B dB. \tag{1}$$

Then, integrating over the magnetic field, one obtains the temperature change involved when a final magnetic field, B_{max}, is applied:

$$\Delta T = \int_0^{B_{max}} -\frac{T}{C_B}\left(\frac{\partial M}{\partial T}\right)_B dB. \tag{2}$$

When isothermal magnetization processes are carried out, the total magnetic entropy change ΔS_B of the magnetic system due to the application of a magnetic field is

$$\Delta S_B(T,B) = \int_0^{B_{max}}\left(\frac{\partial M}{\partial T}\right)_B dB, \tag{3}$$

where B_{max} is the final applied magnetic field.

This change in entropy is associated with the alignment of the spins in the system parallel to the magnetic field. When the magnetic field is applied adiabatically the lattice entropy increases, therefore, by the same amount.

It seems clear, therefore, that the best magnetocaloric materials should: (a) have a sharp magnetic transition, (b) have high magnetic moment per unit volume, and (c) be easy to produce, having high chemical stability.

Our materials can best be described as perovskitelike crystals, and have the compositions

$$La_{0.65}Ca_{0.35}Ti_{1-x}Mn_xO_{3-z}$$

and

$$La_{0.5+x+y}Li_{0.5-3y}Ti_{1-3x}Mn_{3x}O_{3-z}.$$
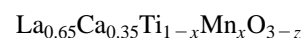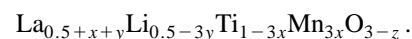
By tuning both the composition parameter, x or y, and the oxygen stoichiometry, z, these materials show ferromagnetic spin structure with very different ordering temperatures and intensities of saturation magnetization. The samples were
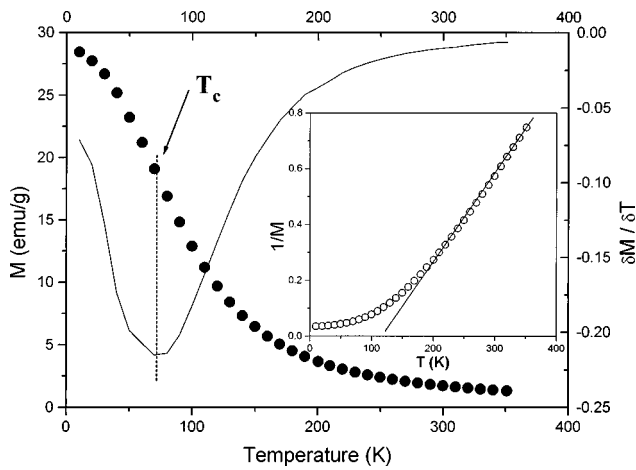
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FIG. 1. Temperature dependence of the magnetic moment for the sample with the composition $La_{0.65}Ca_{0.35}Ti_{0.4}Mn_{0.6}O_3$ when the applied field is 3 T. The Curie temperature, T_C, is deduced from the $\partial M/\partial T$ curve. In the inset we show the inverse magnetization vs temperature for the same sample. Above T_C the magnetization shows a linear dependence following the Curie–Weiss law.

prepared by the ceramic route. La_2O_3 (Fluka 99.98%), Mn_2O_3 (Aldrich >99%), TiO_2 (Aldrich 99.9%), Li_2CO_3 (Aldrich 99%), and $CaCO_3$ (Aldrich 99%) were used as starting materials to synthesize compounds with the general formula $La_{0.5+x+y}Li_{0.5-3x}Ti_{1-3y}Mn_{3y}O_3$ with $0.33 > y > 0.2$ and $x < 0.16$, and $La_{0.65}Ca_{0.35}Ti_{1-x}Mn_xO_3$ with $x=0.6, 0.8$, and 0.9. La_2O_3 and TiO_2 were dried overnight at 900 °C prior to weighing. These chemicals were weighted, mixed in an agate mortar with acetone, dried and heated for 2 h at 950 °C to eliminate CO_2. After grinding, the samples were pressed into pellets. The pellets were fired at 1100 °C for 12 h, giving green products, which were reground, repelleted, and fired at 1200 and 1250 °C for 12 h. A further treatment was carried out on the samples in the system $La_{0.5+x+y}Li_{0.5-3x}Ti_{1-3y}Mn_{3y}O_3$ with $y > 0.27$ at 1400 °C for 4 h, followed by quenching with liquid nitrogen.

Crystalline phase identification was carried out by powder x-ray diffraction with a Siemens-D500 diffractometer. The stoichiometry and homogeneity of the selected samples was checked by electron probe microanalysis using a Cam-
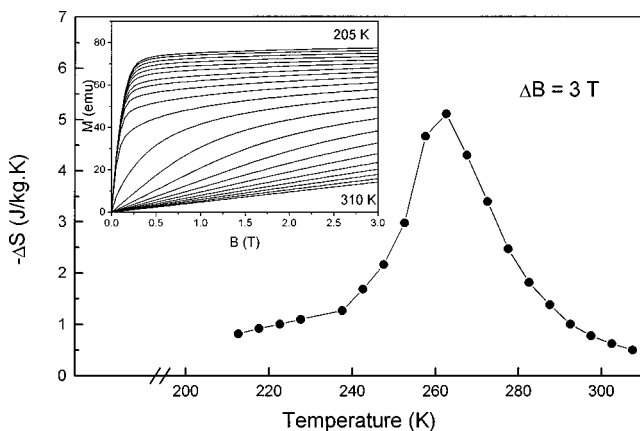
eca SX51 EPMA. All samples were perovskite-type single phases. Magnetic characterization was performed using a SQUID magnetometer.

Low field magnetization data as a function of temperature were obtained to determine the transition temperature, T_C, of the samples. The T_C is defined as the temperature at which $|\partial M/\partial T|$ shows a minimum. We also verified that for all samples the magnetization data above T_C obey the Curie–Weiss law in agreement with their paramagnetic behavior. In Fig. 1 we show these data for the samples with the composition $La_{0.65}Li_{0.35}Ti_{0.4}Mn_{0.6}O_3$.

The calculations of the entropy change, ΔS_B, associated with the second order magnetic phase transition at the T_C were performed using isothermal magnetic measurements. In the case of magnetization measurements at small discrete field and temperature intervals, ΔS_B, can be approximated from Eq. (3) by

$$|\Delta S_B| = \sum \frac{1}{T_{i+1}-T_i} \ (M_i - M_{i+1})_B \ \Delta B_i, \qquad (4)$$

where M_i and M_{i+1} are the magnetization values measured in a field B at temperatures T_i and T_{i+1}, respectively. In Fig. 2 we show isothermal magnetization measurements at differ-

FIG. 3. Entropy change for samples of $La_{0.65}Ca_{0.35}Ti_{1-x}Mn_xO_3$ with different degrees of substitution (x), when the magnetic field is 3 T.

FIG. 2. Magnetic entropy change at different temperatures when the applied magnetic field is 3 T for the sample with the composition $La_{0.6}Ca_{0.4}MnO_3$. The entropy change was calculated from isothermal magnetization curves vs applied magnetic field, which are shown in the inset.
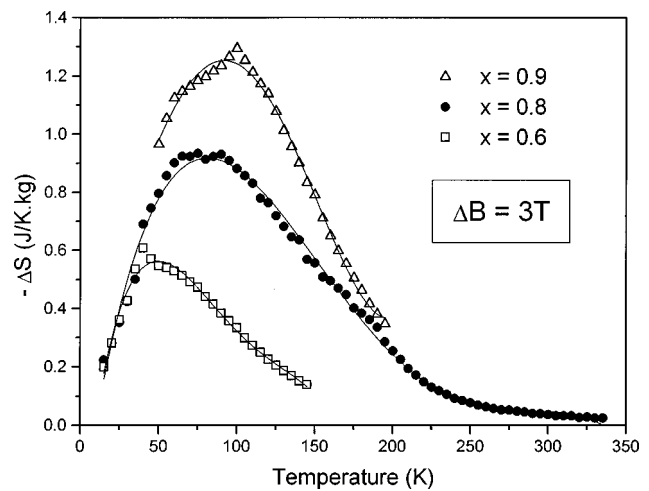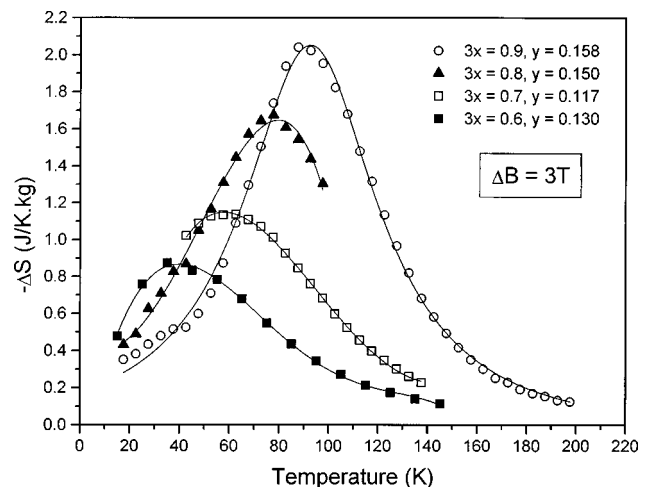

FIG. 4. Entropy change for samples of $La_{0.5+x+y}Li_{0.5-3y}Ti_{1-3x}Mn_{3x}O_3$ with different degrees of substitution (x), when the magnetic field is 3 T.

TABLE I. Values of the saturation magnetization, M_s, Curie temperature T_C, and entropy change, $\Delta S_{B,\max}$, for the different samples studied.

Sample	M_s (emu/g)	T_C (K)	$-\Delta S_{B,\max}$ (J/kg K) ($\Delta B = 3$ T)
$La_{0.65}Ca_{0.35}Ti_{0.4}Mn_{0.6}O_3$	30	42	0.6
$La_{0.65}Ca_{0.35}Ti_{0.2}Mn_{0.8}O_3$	60	87	0.9
$La_{0.65}Ca_{0.35}Ti_{0.1}Mn_{0.9}O_3$	70	103	1.3
$La_{0.6}Ca_{0.4}MnO_3$	100	263	5.0
$La_{0.83}Li_{0.1}Ti_{0.4}Mn_{0.6}O_3$	30	35	0.9
$La_{0.85}Li_{0.15}Ti_{0.3}Mn_{0.7}O_3$	43	60	1.1
$La_{0.917}Li_{0.05}Ti_{0.2}Mn_{0.8}O_8$	60	77	1.7
$La_{0.958}Li_{0.025}Ti_{0.1}Mn_{0.9}O_3$	64	90	2.0

ent temperatures and in Fig. 3 we plot the corresponding entropy variation, calculated using Eq. (4), for different temperatures and when the applied field is 30 kOe. In Figs. 3 and 4 we plot the entropy data for two sets of samples in which we have introduced Li and Ca in different proportions. In Table I we summarize all the data.

From the obtained data, summarized in Table I, it is clear that the Curie temperature of these materials expand over the entire temperature range from very low temperatures to near 300 K, and that some of them show a large enough magnetocaloric effect to be used as magnetic refrigerants. In all the samples the maximum entropy change is observed at T_C. The width of the peak of the entropy depends on the applied magnetic field, and at high fields it has the behavior desirable for an Ericsson-cycle magnetic refrigerator. The reduction in the variation of the entropy observed in those materials having low Curie temperature may be compensated with the linear decrease of the specific heat with temperature. The temperature variation in these materials may, therefore, be even larger than for those transiting at near room temperature. The variation of the entropy change for the two sets of samples as a function of the substitution degree of Li and Ca is due to the variation of the saturation magnetization with substitution. Our materials fulfill quite well the requirements of magnetic refrigerants for the active magnetic regenerator materials suggested by Barclay.[11]

In conclusion, we have shown data for the magnetocaloric effect in ceramic perovskitelike crystals as a function of the applied field, temperature, and composition. These data clearly indicate that the magnetocaloric effect in these materials is high and tunable. These materials are, therefore, good candidates to work as magnetic refrigerants in a wide temperature interval.

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