



# Magnetocaloric effect in $\text{La}_{0.65}\text{Ca}_{0.35}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ ceramic perovskites

X. Bohigas<sup>a</sup>, E. del Barco<sup>b,\*</sup>, M. Sales<sup>b</sup>, J. Tejada<sup>b</sup>

<sup>a</sup>Departamento Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Diagonal 647, Barcelona, Spain

<sup>b</sup>Departamento Física Fonamental, Universitat de Barcelona, Diagonal 647-08028, Barcelona, Spain

## Abstract

In this paper, we comment on experiments we have carried out on ceramic perovskites of composition  $\text{La}_{0.65}\text{Ca}_{0.35}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ . From low- and high-field magnetic measurements recorded at different temperatures, we have discovered the existence of a large entropic change associated to the ferrimagnetic–paramagnetic transition. Our conclusion is that these materials are excellent candidates as working materials in refrigeration devices. © 1999 Published by Elsevier Science B.V. All rights reserved.

**Keywords:** Magnetocaloric effect; Perovskites; Entropy; Refrigeration

For many years there has been a great interest in using magnetic refrigeration at room temperature with the aim of suppressing the emission of polluting components (such as chloro fluoro-carbonates) which appear in conventional refrigeration systems.

The large entropy change inherent in the magnetic induction phenomena makes it suitable to use magnetic refrigeration as a refrigerant technique at high temperature [1].

The main problem in using magnetic refrigeration at temperatures above 20 K is to find the adequate material to produce a large entropy change when it goes through a magnetization–demagnetization process.

In the low-temperature range (between 1.5 and 20 K), the paramagnetic materials have been object of a deep study [2–4]. Their use in magnetic refrigeration is restricted to this region of temperatures. Above 40 K one can profit from the entropy change associated to the ferromagnetic–paramagnetic transition that the material undergoes when there is a variation of the applied magnetic field [5].

Recently, Pecharsky and Gschneider [6,7] have found a giant magnetocaloric effect in metallic alloys  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  in a range of temperatures going from 50 to 280 K. In this range we have also published results obtained with perovskite-structured materials [8,9].

From Maxwell's relation:

$$\left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial H}\right)_T, \quad (1)$$

one obtains the temperature change due to the variation of the magnetic applied field

$$dT = -\frac{T}{C_H} \left(\frac{\partial M}{\partial T}\right)_H dH. \quad (2)$$

Once integrated, this expression gives the change in temperature produced when a magnetic field with increasing intensity going from 0 to  $H_{\max}$  is applied.

$$\Delta T = \int_0^{H_{\max}} -\frac{T}{C_H} \left(\frac{\partial M}{\partial T}\right)_H dH. \quad (3)$$

On the other side, the entropic change produced by the variation of the magnetic field from 0 to  $H_{\max}$  is given by

\*Corresponding author. Fax: +34-93-402-11-59; e-mail: edb@hermes.ffn.ub.es.

the following expression:

$$\Delta S_H = \int_0^{H_{max}} \left( \frac{\partial M}{\partial T} \right)_H dH. \quad (4)$$

When the change of the applied field is done adiabatically, we have an entropic change in both, the magnetic and the non-magnetic subsystems. This is to say, if the process of changing the magnetic field is adiabatic, there will be a temperature variation

$$\Delta T = \frac{T}{C_H} \Delta S_H. \quad (5)$$

Therefore, to evaluate a magnetic material's refrigerant capacity we can look at both, entropic change and temperature variation.

All the magnetic measurements, dependence of magnetization on both the temperature and applied magnetic field, were performed by a quantum design SQUID magnetometer.  $\text{La}_2\text{O}_3$  (Fluka 99.98%),  $\text{TiO}_2$  (Aldrich 99.9%) were used as starting materials in addition to  $\text{CaCO}_3$  (Aldrich 99%) to synthesize compounds of general formula  $\text{La}_{0.65}\text{Ca}_{0.35}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$  with  $x = 0.6, 0.8$  and  $0.9$ .  $\text{La}_2\text{O}_3$  and  $\text{TiO}_2$  were dried overnight at  $900^\circ\text{C}$  prior to weighing. These chemicals were weighed, mixed in an agate mortar with acetone, dried and heated 2 h at  $950^\circ\text{C}$  to drive off  $\text{CO}_2$ . After grinding, samples were pressed into pellets. The pellets were fired at  $1100^\circ\text{C}$  for 12 h giving green products, which were reground, pressed and fired at  $1200^\circ\text{C}$  and  $1250^\circ\text{C}$  for 12 h.

Crystalline phase identification was carried out by powder X-ray diffraction with a Siemens-D500 diffractometer. Stoichiometry and homogeneity of selected samples were checked by electron probe microanalysis using a Cammera SX%1 EPMA. All samples were perovskite-type single phases.

The transition temperature has been determined from the temperature dependence of the magnetization. The transition temperature between the paramagnetic and ferromagnetic phases of the material has been taken to be that at which  $|\partial M/\partial T|$  has a minimum. We have checked that above Curie's Temperature ( $T_C$ ), all the studied samples follow a Curie-Weiss law in agreement with a paramagnetic behavior.

The entropic changes associated to magnetic phase changes at  $T_C$  have been calculated from the isotherm curves of magnetization versus applied field using the expression:

$$|\Delta S_B| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i, \quad (6)$$

where  $M_i$  and  $M_{i+1}$  are the experimental values of the magnetization at  $T_i$  and  $T_{i+1}$ , respectively, under an applied magnetic field of intensity  $H_i$ . This expression is a numerical approximation to the integral in Eq. (4).

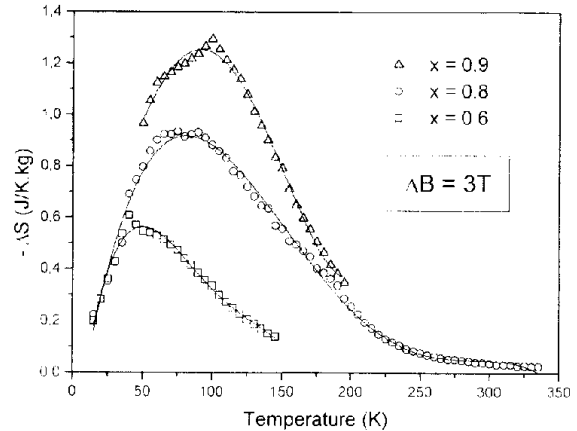


Fig. 1. The entropic change in the samples  $\text{La}_{0.65}\text{Ca}_{0.35}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$  with  $x = 0.6, 0.7, 0.9$  corresponding to a field variation of 3 T.

In Fig. 1 we plot the entropic changes, calculated using Eq. (6), produced when magnetizing three of the studied samples of compositions  $\text{La}_{0.65}\text{Ca}_{0.35}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$  with  $x = 0.6, 0.7, 0.9$  under a variation of applied field of 3 T.

In Fig. 2, we show the entropic change as a function of temperature corresponding to a sample of  $\text{La}_{0.65}\text{Ca}_{0.25}\text{MnO}_3$  for different increments of applied magnetic field. The temperatures at which the maxima in the entropic change are observed are in good agreement with the  $T_C$  obtained from the  $M(T)$  curves. This result was to be expected if we take into account Eq. (4), where we can see clearly that we will have the greatest entropic change at the point at which the variation of magnetization with temperature is the fastest, and this is so at a temperature close to the magnetic transition temperature.

In Fig. 2, we deduce that the largest the variation of the applied field is, the largest the entropic change we obtain, as it was expected from Eq. (4). For large increments of applied magnetic field it seems that the magnetic contribution to entropic change and applied magnetic field have a linear relation.

When changing the proportion of titanium and manganese ( $x$  in the general formula) we can see, from Figs. 1 and 2, that the temperature of the magnetic transition is modified. From Figs. 1 and 2 we also deduce that the magnetic contribution to the entropic change associated to variations of the applied magnetic field have a very strong dependence on the composition. In Fig. 3, we have plotted the obtained values of  $T_C$  from the minima in the derivative  $|\partial M/\partial T|$ , for each one of the studied samples. In Fig. 3, we can also see the highest value of the entropic change, produced by an increment of magnetic field of 3 T and calculated using Eq. (1), as a function of the composition of the studied materials.

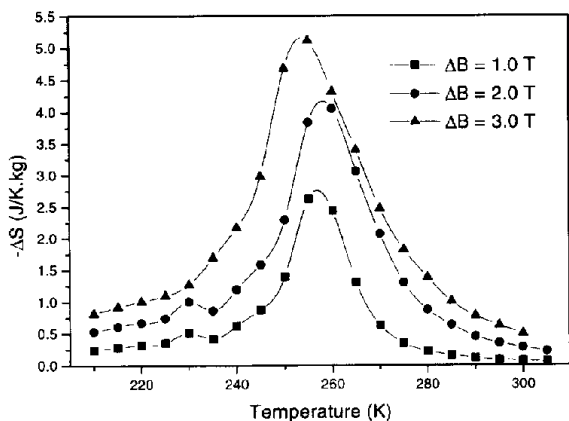


Fig. 2. Entropic change of the sample  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$  for different applied magnetic fields (1, 2 and 3 T).

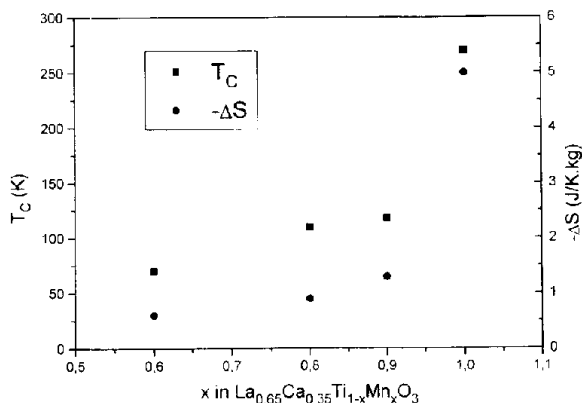


Fig. 3. Curie temperature (■) and maxima of entropic change (●) obtained with the studied series of materials,  $\text{La}_{0.65}\text{Ca}_{0.35}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ , as a function of composition.

The high value of the magnetic component in the entropic change, as well as the width of the corresponding peaks, make these materials suitable to be included as active materials in refrigerant systems that describe Ericsson or Brayton cycles.

The refrigerant technique based on magnetocaloric effect needs materials which show an entropic change big enough in a wide range of temperatures. This property is difficult to obtain with only one material, but it is possible if we take an ensemble of materials that have the transition at different temperatures, such as the materials with perovskite-type structure with formula  $\text{La}_{0.65}\text{Ca}_{0.35}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ .

In conclusion, we have presented experimental data of  $T_C$  and of the magnetic component of the entropic change associated to variations of applied magnetic field of perovskites with formula  $\text{La}_{0.65}\text{Ca}_{0.35}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ . The results obtained show a strong dependence on the composition of the material. The magnetocaloric effect of these materials is large and tunable, suggesting that they are excellent candidates as working materials in refrigerant devices.

The authors thank ENHER (ENDESA Group) and CARBUROS METÁLICOS for their financial support. E. del Barco and M. Sales acknowledge the support from the Universitat de Barcelona and Ministerio de Educación y Cultura, respectively.

## References

- [1] G.V. Brown, *J. Appl. Phys.* 47 (1976) 3673.
- [2] J.A. Barday, D. Moze, L. Paterson, *J. Appl. Phys.* 50 (1979) 50870.
- [3] R.D. Shull, R.D. McMichael, J.J. Ritter, *Nanostruct. Mater.* 2 (1993) 205.
- [4] H. Kimura, T. Numazawa, M. Sato, T. Ikoya, T. Fukuda, *J. Appl. Phys.* 77 (1995) 432.
- [5] R.D. Shull, *IEEE Trans. Magn.* 29 (1993) 2614.
- [6] V.K. Pecharsky, K.A. Gschneider, *J. Magn. Magn. Mater.* 167 (1997) L179.
- [7] V.K. Pecharsky, K.A. Gschneider, *Phys. Rev. Lett.* 78 (1997) 4494.
- [8] X.X. Zhang, J. Tejada, Y. Xin, G.F. Sun, K.W. Wong, X. Bohigas, *Appl. Phys. Lett.* 69 (1996) 3596.
- [9] X. Bohigas, J. Tejada, E. del Barco, X.X. Zhang, M. Sales, *Appl. Phys. Lett.* 73 (1998) 390.