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Journal of Magnetism and Magnetic Materials 272–276 (2004) 2385–2386
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Magnetocaloric effect on the $Pr_{0.43}Gd_{0.25}Ca_{0.32}MnO_3$ manganite

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Abstract

We investigated the influence of the Gd doping element to the magnetocaloric effect in the $Pr_{0.68-x}Gd_xCa_{0.32}MnO_3$ manganite ($x = 0.25$). Isothermal magnetization measurements up to 40 kOe from $7 < T < 300$ K were performed and the data were used to calculate the magnetic entropy change. The results show a low magnetocaloric effect when compared to the compound with $x = 0$.

PACS: 75.30.Sg; 75.47.Lx

Keywords: Magnetocaloric effect; Manganites

In the last years, we observe a renewed and increasing interest devoted to the study of magnetocaloric properties of materials, this is due to the possibility of technological application of magnetic materials to be the substitute of non-green chemicals (CFC, HCFC) used for refrigeration at room temperature [1]. Even at lower temperatures, the magnetic refrigeration still have drawn attention, mainly to be applied to gas liquefaction as natural gas, hydrogen and helium. Therefore, it is important to characterize new promising magnetic materials for magnetic refrigeration in a large temperature span.

In this article we present a study of magnetocaloric properties of the $Pr_{0.68-x}Gd_xCa_{0.32}MnO_3$ manganite. The aim of this study was to investigate the effect of the doping element Gd in the compound and compare the magnetocaloric thermodynamical property, namely the magnetic entropy change ΔS_{mag} to the $Pr_{0.68}Ca_{0.32}MnO_3$ system which presents a huge effect at low temperatures. The magnetocaloric effect (MCE) is an intrinsic property of all magnetic materials. It is induced by the coupling of the magnetic sublattice with the magnetic field, thus changing the total entropy of the system in response of a magnetic field change [2].

The sample was prepared by ceramic route from the stoichiometric mixture Pr_2O_3 (99.9%) + Gd_2O_3 (99.99%) + $CaCO_3$ (99%) + $MnCO_3$ (99.9%). The sample passed through five thermal treatments, being milled and pressed after each one. In the last one, the sample was fired at 1300°C for 20 h, followed by a fast quench in air. We have performed magnetization experiments in a commercial magnetometer, from 5 up to 300 K. In Fig. 1, the zero field cooled (ZFC) and field cooled (FC) curves obtained in a magnetic field of 50 Oe are shown. The critical temperature (T_c) was calculated from the minimum in derivative of the magnetization curve with respect to the temperature. For this system, the calculated T_c is 108 K.

Isothermal magnetization experiments were carried up to 40 kOe in small field steps (2.5 kOe). Each isothermal curve is separated from the other by 1.5 K, from 4 up to 20 K, and by 5 K up to room temperature.

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doi:10.1016/j.jmmm.2003.12.1129

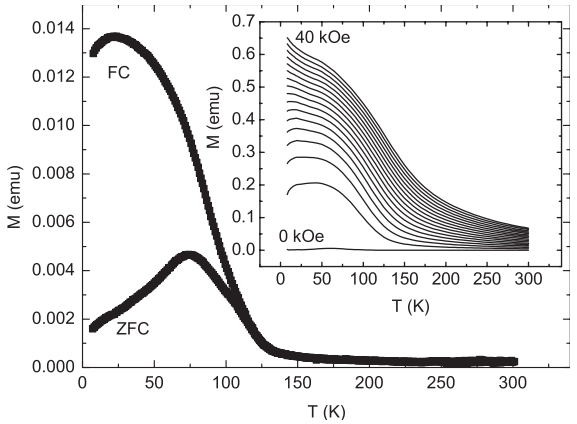

Fig. 1. Zero field cooled (ZFC) and field cooled (FC) magnetization curves measured with $H = 50$ Oe and $m = 12.5$ mg. Inset: isofield curves, from 0 up to 40 kOe (upper curve) in steps of 2.5 kOe.

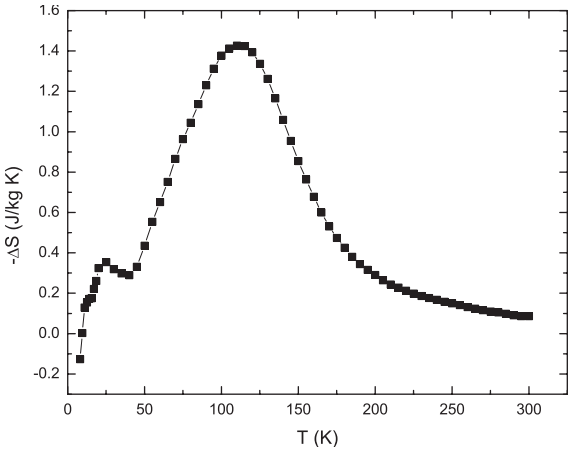

Fig. 2. Magnetic entropy change for a magnetic field change of 40 kOe.

After obtaining each isothermal magnetization curve, the magnetic field is set to 10 kOe and it is zeroed by a degauss procedure, where the magnetic field is oscillated through zero. The set of isothermal curves is transposed to isofield curves, shown in the inset of Fig. 1, in order to calculate the magnetocaloric property ΔS_{mag}. Based on Maxwell thermodynamical relations, we calculate ΔS_{mag} performing the following integration:

$$\Delta S_{mag}(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H. \quad (1)$$

Actually ΔS_{mag} is calculated using a numerical method approximation which is valid for small field and temperature steps. The calculated ΔS_{mag} is shown in Fig. 2. We clearly observe two maxima, at 25 K with $-0.35\ \mathrm{J\,kg^{-1}\,K^{-1}}$ and at 108 K with $-1.43\ \mathrm{J\,kg^{-1}\,K^{-1}}$. This second peak occurs at the paramagnetic transition as expected. These values are considerably lower than those found in the $x = 0$ compound [3]. In the latter, the huge value of ΔS_{mag} occurs around 11 K and well below T_c.

We conclude that the doping element Gd, in the concentration $x = 0.25$ does not contribute to increase the magnetocaloric effect in $(Pr, Ca)MnO_3$ manganites. The low value of magnetic entropy change peak at lower temperature and at the transition temperature are under investigation. These results can be ascribed to the different contribution of the charge ordering in the Gd-doped compound.

The authors acknowledge CNPq, CAPES and FAPERJ (Brasil), FCT and ICCTI (Portugal) for financial support.

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