J Mater Sci (2008) 43:1734–1739
DOI 10.1007/s10853-007-2400-5

Magnetocaloric effect in $La_{1-x}Ca_xMnO_3$ for $x = 0.3$, 0.35, and 0.4

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Received: 15 February 2007 / Accepted: 5 July 2007 / Published online: 4 January 2008

Abstract We present systematic studies of the magnetocaloric properties of the polycrystalline $La_{1-x}Ca_xMnO_3$ system for $x = 0.3$, 0.35, and 0.4 near a second-order phase transition from a ferromagnetic to a paramagnetic state. The crystal structure of the studied manganites was shown to be in good agreement with previous reports. The value of the magnetocaloric effect has been determined from the measurement of magnetization as a function of temperature and external magnetic field. The maximum entropy change detected in $La_{0.7}Ca_{0.3}MnO_3$ at a field of 2 T reaches 8 J/kg K which exceeds that of gadolinium. In all studied samples, the paramagnetic–ferromagnetic transition is very narrow but no hysteresis is observed and the transitions are identified as second-order ones. The phase transition in $La_{0.7}Ca_{0.3}MnO_3$ appears to be almost of first-order.

Introduction

The properties of $La_{1-x}A_xMnO_3$ manganites, where A = Ca, Sr, Ba, Pb, have intrigued researchers for more than 50 years (see [1] for details and references), mainly because of the colossal magnetoresistivity discovered in this group of compounds. The parent compound ($x = 0$) is an antiferromagnetic insulator with the Neel temperature $T_N \approx 130$ K. When x exceeds $\approx 1/8$, the low-temperature phase becomes ferromagnetic and metallic. The Curie temperature, T_C, depends strongly on x and ionic size of A^{2+} ions, as well as on the ionic-size variance of A-site ions. It was shown [2] that the decrease of an average ionic size of A-site atoms toward that of La is accompanied by a simultaneous decrease of the transition temperature. However, even if the average ionic size is kept constant, T_C decreases as the variance in ionic size increases. It suggests a key role of the disorder in determining an average Curie temperature $\langle T_C \rangle$. Moreover, it also confirms the experimental finding that very often the value of $\langle T_C \rangle$ depends on the method of sample preparation.

In recent years, there has been an increasing interest in using manganites not only as a material having colossal magnetoresistivity but also as a material with interesting magnetocaloric properties, as suggested more than 10 years ago by Zhang et al. [3] who performed magnetocaloric measurements in $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.60}Ca_{0.33}Y_{0.07}MnO_3$. In the following years, many other manganites were examined from this point of view (see [4–6] for references). A large magnetocaloric effect makes manganites excellent candidates for working materials in magnetic refrigeration units especially because they are less costly than other materials, particularly those based on Gd.

One of the important criteria for a promising refrigerant is that the material should exhibit a large magnetic field-induced entropy change (see review papers [5–7]). The change in entropy is associated with the alignment of the spins in the magnetic material parallel to the applied magnetic field. Usually, the most important are changes in entropy taking place near the phase transition points, especially near first-order phase transitions which are accompanied by a substantial drop in magnetization. It is worth to note that the presence of short-range magnetic order above T_C depresses the magnetic entropy of the

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paramagnetic phase. Therefore, the entropy change near the field-induced paramagnetic-to-ferromagnetic phase transition is much smaller than that produced by a full order–disorder transition [8]. However, the presence of short-range magnetic order depends strongly on some extrinsic factors like crystal defects, internal stresses, etc., and thus the entropy changes would not be independent of the preparation method. Despite considerable progress in this area, materials with a strong magnetocaloric effect are still desired.

This article explores the strong dependence of both T_C and the changes in entropy near T_C on various extrinsic factors. These dependences suggest that the magnitude of the magnetocaloric effect depends on methods of sample preparation. In this article, studies of the magnetocaloric effect are presented for $La_{1-x}Ca_xMnO_3$ with $x = 0.3$, 0.35, and 0.4 prepared by a non-standard ceramic method.

Experiment

The polycrystalline samples of composition $La_{1-x}Ca_xMnO_3$ ($x = 0.3$, 0.35, 0.4, and 0.5) were prepared by the ceramic method. The lanthanum oxide [La_2O_3] of 99.99% purity, manganese oxide [Mn_2O_3] of 99% purity, and analytically pure calcium carbonate [$CaCO_3$] were used as starting materials. These materials were weighed directly after drying conducted at a temperature of 200 °C. The mixtures were manually wet mixed for 15 min in an agate mortar with an addition of acetone and then dried and again ground to a powder form. The powders obtained by this method were pressed under the pressure of 150 MPa into pellets. The pellets were then subjected to sintering in small aluminum oxide crucibles at 1,100 °C in a chamber furnace under air atmosphere. In the next technological cycle, the fine powder was sintered in ceramic crucibles and the obtained sinters were again ground to the powder form. These operations were repeated during subsequent technological cycles, with the sintering temperature increased for each cycle. The parameters of the sintering process are given in Table 1. Before final sintering was conducted at 1,350 °C, the fine powders were pressed under the pressure of 200 MPa into pellets with a diameter of 10 mm. After completion of the final sintering, the samples were slowly cooled down together with the furnace.

Table 1 Sintering parameters

Cycle	Temperature (°C)	Sintering time (h)
I	1,100	20
II	1,150	20
III	1,250	20
IV	1,300	20
V	1,350	20

Table 2 Crystallographic data for $La_{1-x}Ca_xMnO_3$ compounds

Manganite	*a* (nm)	*b* (nm)	*c* (nm)
$La_{0.7}Ca_{0.3}MnO_3$	0.549	0.545	0.773
$La_{0.65}Ca_{0.35}MnO_3$	0.546	0.545	0.773
$La_{0.6}Ca_{0.4}MnO_3$	0.544	0.545	0.773

After final sintering of the samples, their density was calculated based on the measurements of mass and dimensions. For the compositions under investigation, the values of density were similar and reached about 5 g/cm^3.

Powder X-ray diffraction indicated a single-phase compound. The determined lattice parameters are gathered in Table 2. These parameters are in good agreement with previous reports [9, 10] confirming a composition close to the nominal value.

Magnetic measurements were performed using a Quantum Design MPMS-5 superconducting quantum interference (SQUID) device magnetometer.

Results and discussion

For isothermal processes, the total magnetic entropy change ΔS_H of the magnetic system due to the application of a magnetic field H is [5, 6]:

$$\Delta S_H(T,H) = \int_0^H \left({}^{\partial M}\!/_{\partial T} \right)_H \mathrm{d}H \tag{1}$$

In order to evaluate ΔS_H (T,H) one usually resorts to a numerical approximation to the integral in (1) of the form

$$|\Delta S_H(T,H)| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i, \tag{2}$$

where M_i is the experimental value of the magnetization at the temperature T_i.

Figures 1–3 present the temperature dependences of magnetization, $M(T)$, for studied polycrystals measured in low field (1.6 kA/m) for field cooling (FC) and zero field cooling (ZFC) regimes. The characteristic feature of the presented data is the bifurcation between ZFC and FC dependences.

Several mechanisms are suggested in literature to be responsible for this type of bifurcation in magnetic materials:

1. The movement of magnetic domain walls [11, 12]. This mechanism exists in any kind of magnetic materials possessing domain structure, and differences

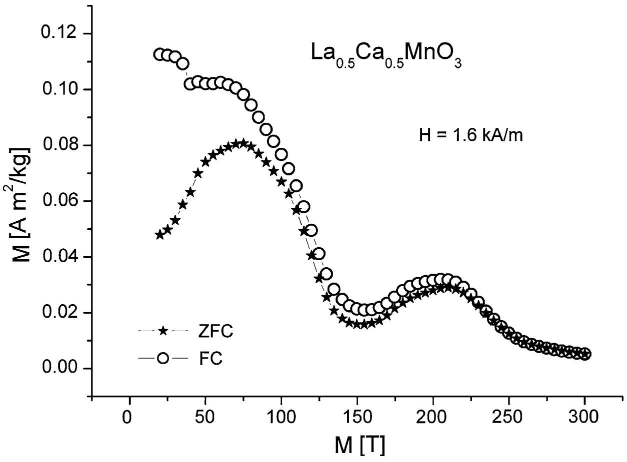

Fig. 1 Temperature dependence of magnetization for $La_{0.5}Ca_{0.5}MnO_3$ polycrystals measured in low field (1.6 kA/m) for field cooling (FC) and zero field cooling (ZFC) regimes

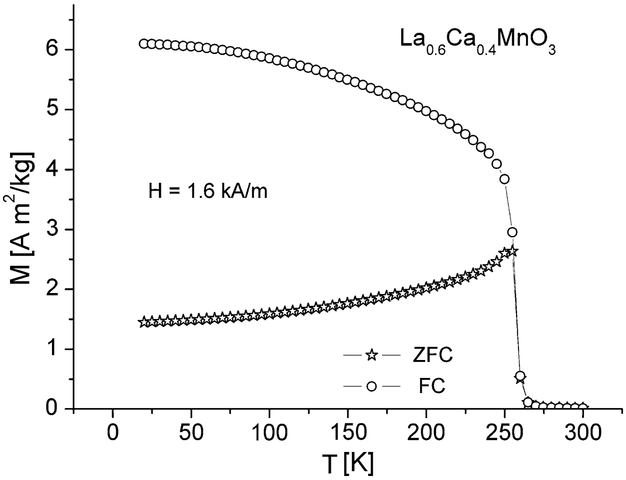

Fig. 2 Temperature dependence of magnetization for $La_{0.6}Ca_{0.4}MnO_3$ polycrystals measured in low field (1.6 kA/m) for FC and ZFC regimes

between ZFC and FC dependences depend on the domain wall pinning centers.

2. Magnetic anisotropy which aligns the spins in a preferred direction. During the ZFC process, the spins are locked in random direction for a polycrystalline specimen. In contrast in the FC case presence of magnetic field during the cooling changes distribution of spin directions [13].
3. Phase separation. Under some conditions, manganite specimen may separate itself into hole-rich ferromagnetic clusters and hole-poor matrix dominated usually by the antiferromagnetic interactions due to superexchange. The properties of such system may be described in terms of a spin-glass like behavior including ZFC and FC bifurcation [14].

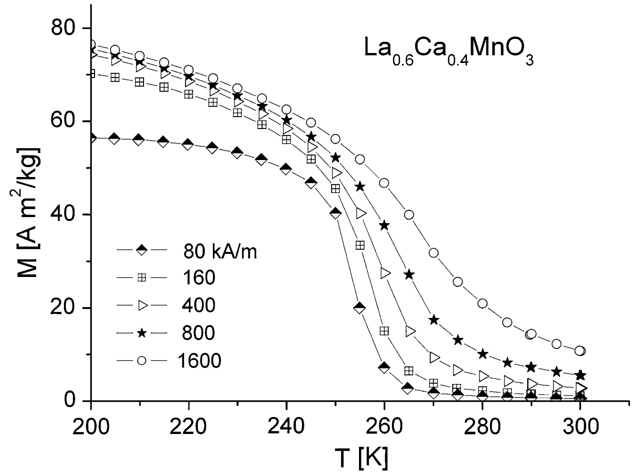

Fig. 3 Temperature dependence of magnetization for $La_{0.6}Ca_{0.4}MnO_3$ polycrystals measured at various fixed values of the external magnetic field

It has to be mentioned that the proposed mechanisms may coexist, although one mechanism may sometimes dominate.

In the case of $La_{0.5}Ca_{0.5}MnO_3$ polycrystal (see Fig. 1) the FC data differ strongly from the ZFC data for $T < 220$ K. This indicates the coexistence of antiferromagnetic and ferromagnetic clusters, which is confirmed by neutron diffraction measurements [15]. The studied manganite represents a boundary between a low-temperature ferromagnetic ground state (for $x < 0.5$) and a low-temperature antiferromagnetic ground state ($x > 0.5$). At half-doping (for $x \approx 0.5$) below $T_N \approx 150$ K metallic ferromagnetism is unstable against charge ordering of Mn^{3+} and Mn^{4+} ions, and an insulating antiferromagnetic ground state is realized. At T_N a first-order magnetic-phase transition occurs simultaneously with a metal–insulator transition. At T_C the manganite undergoes second-order phase transition from the ferromagnetic to the paramagnetic state. This transition is very broad suggesting a smearing of the transition due to lattice defects. The M versus T data of this sample resemble those reported by Xiao et al. [16]. In particular, T_N in both cases is the same while T_C in [16] is lower than that in our sample (Fig. 1). This confirms that a first-order transition is of an intrinsic character independent of the method of sample preparation and that T_C may be shifted due to extrinsic effects. Because of a smearing of the paramagnetic to the ferromagnetic transition the magnetocaloric effect is expected to be small and was not studied in this article.

The transition from the paramagnetic phase to the ferromagnetic one is considerably sharper in $La_{0.6}Ca_{0.4}MnO_3$ polycrystals (Fig. 2). In this case, the observed difference between the FC data and the ZFC data arises because of the presence of a magnetic domain structure. This domain

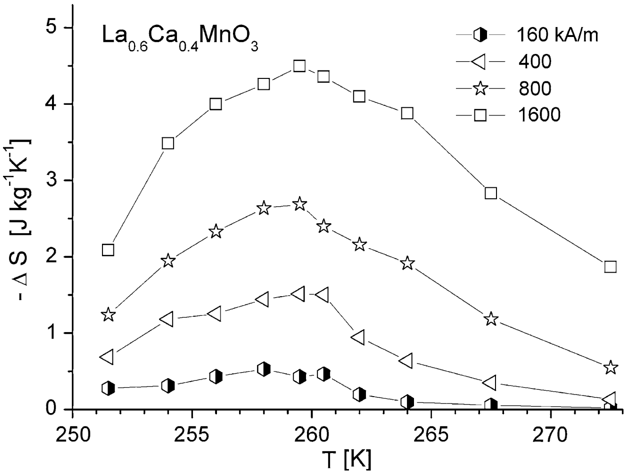

Fig. 4 Change of the magnetic entropy of $La_{0.6}Ca_{0.4}MnO_3$ polycrystals as a function of temperature at fixed values of the external magnetic field

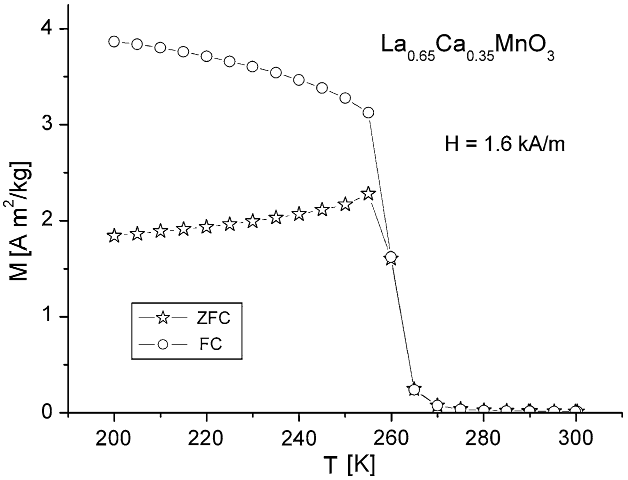

Fig. 5 Temperature dependence of magnetization for $La_{0.65}Ca_{0.35}MnO_3$ polycrystals measured in low field (1.6 kA/m) for ZFC and FC regimes

structure arises very near T_C as can be seen from the analysis of the divergence between FC and ZFC data. Figure 3 presents the high-temperature part of the $M(T)$ dependence measured in various magnetic fields. Using these data the entropy changes were calculated using (2) (Fig. 4). A remarkable feature of Fig. 4 is that the maximum entropy change is observed at the temperatures close to the Curie temperature. This may be explained using the fact that

$$\Delta S = \int \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H$$

and observing that $\mathrm{d}M/\mathrm{d}T$ has a delta-like character if the distribution of local T_C temperatures is sharply peaked. The results reported are similar to those obtained by Bohigas et al. [17].

The sharpness of the paramagnetic-to-ferromagnetic transition increases with decrease of Ca doping. It is seen in Fig. 5 that this transition is very sharp in $La_{0.65}Ca_{0.35}MnO_3$ polycrystals. The characteristic maximum of $M(T)$ observed in a low field (1.6 kA/m) is due to the critical behavior of the magnetic parameters which determine the domain wall structure. The Curie temperature determined from the sharp transition was found to be 260 K. Although the sharpness of the transition indicates a first-order character the M versus H dependences (Fig. 6) show no anomalies characteristic of this type of transition (e.g., changes in the slopes similar to a metamagnetic transition as suggested by Banerjee [18]). At the same time, the Arrott plot M^2 versus H/M (Fig. 7) exhibits unusual character suggesting that for this system the mean-field theory is not valid. Such behavior may indicate the coupling of the magnetic subsystem to other modes. It is interesting to note that for another compound with almost the same level of doping, $La_{0.67}Ca_{0.33}MnO_3$, the paramagnetic–ferromagnetic transition was shown to be of first order (see [19] and discussion therein). According to [19] the thermally driven first-order transitions may be rounded by quenched disorder. This mechanism, related to the method of sample preparation, may be responsible for the second-order transition observed in our sample. Such samples show a large magnitude of magnetocaloric effect reaching 6.5 J/(kg K) for 4,000 kA/m (Fig. 8).

A similar situation was observed for $La_{0.7}Ca_{0.3}MnO_3$. The paramagnetic–ferromagnetic transition (Fig. 9) is extremely sharp indicating its first-order phase character. In addition, the Arrott plot M^2 versus H/M has a characteristic shape (Fig. 10) typical of material with first-order paramagnetic–

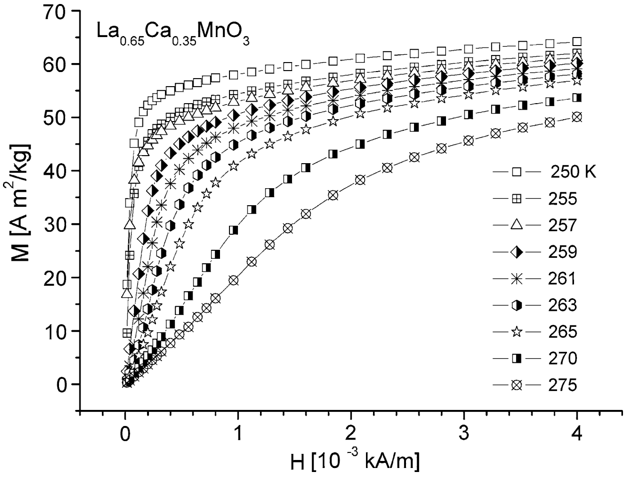

Fig. 6 Magnetic field dependence of magnetization at various temperatures for $La_{0.65}Ca_{0.35}MnO_3$ polycrystals

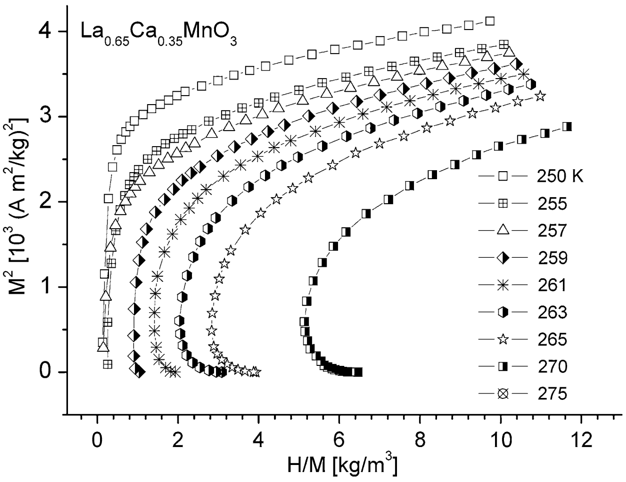

Fig. 7 Arrott plots for $La_{0.65}Ca_{0.35}MnO_3$ polycrystals at temperatures near T_C

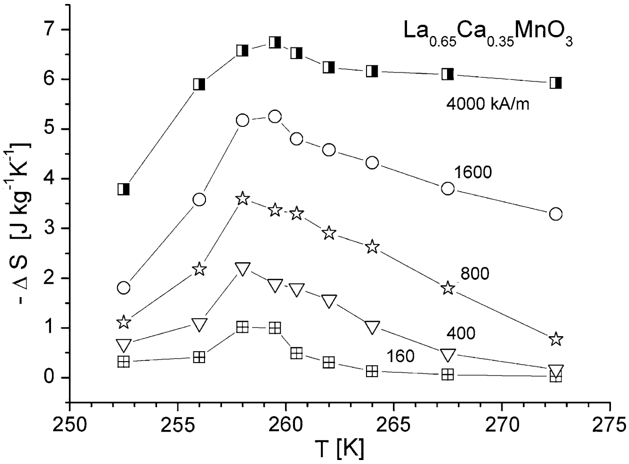

Fig. 8 Change of the magnetic entropy of $La_{0.65}Ca_{0.35}MnO_3$ polycrystals as a function of temperature at fixed values of the external magnetic field

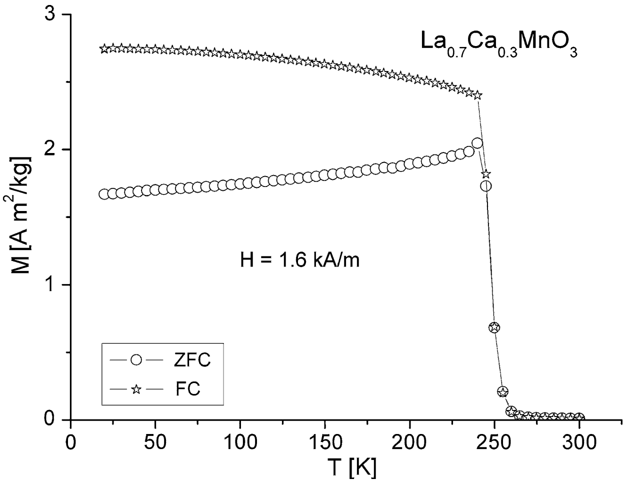

Fig. 9 Temperature dependence of magnetization for $La_{0.7}Ca_{0.3}MnO_3$ polycrystals measured in low field (1.6 kA/m) for FC and ZFC regimes

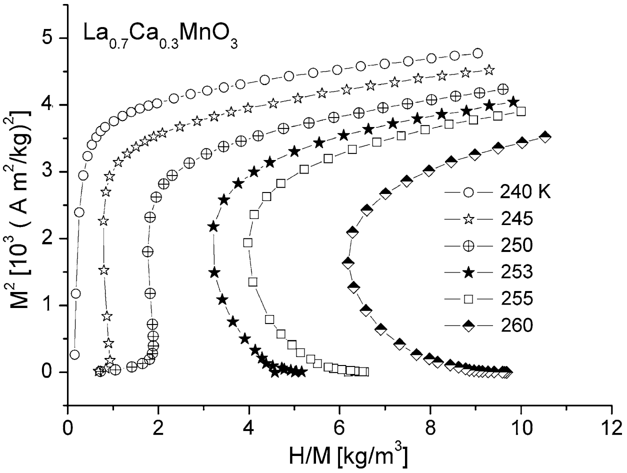

Fig. 10 Arrott plots for $La_{0.7}Ca_{0.3}MnO_3$ polycrystals at temperatures near T_C

ferromagnetic transition. In addition, experimental results presented in the literature [20–22] suggest that $La_{0.7}Ca_{0.3}MnO_3$ shows a first-order paramagnetic–ferromagnetic transition. Nevertheless, one should take into account that T_C reported in the literature is considerably lower ($T_C = 222$–227 K) than T_C of our sample ($\approx$250 K). This effect may arise due to disorder and the first-order transitions may be rounded by disorder. Since no temperature hysteresis is observed, we think that our $La_{0.7}Ca_{0.3}MnO_3$ manganite is characterized by a second-order transition close to a first-order one. In this system, magnetocaloric effect is very high and reaches 8 J/(kg K) for $\Delta H = 1{,}600$ kA/m (Fig. 11). It is the highest value ever observed for doped $LaMnO_3$ manganites (see Table 1 in [6]), larger than that observed in gadolinium. This result does not mean that manganites are more suitable for magnetic refrigerators. Generally, the efficiency of a magnetocaloric refrigerator depends on several parameters, not only on ΔS_M. It is because this type of refrigerators acts as a heat storage medium and participates also in the cycle like a regenerator. Among various parameters determining its effectiveness there is heat conductivity which in manganites is not very high [23].

In conclusion, we have shown that manganites prepared by the developed ceramic method are suitable candidates as magnetic refrigerants. Although for all studied samples the paramagnetic–ferromagnetic transition is very narrow no hysteresis was observed near T_C and the transitions were identified as second-order one. The magnetic entropy change in $La_{0.7}Ca_{0.3}MnO_3$ was shown to be larger than that exhibited by gadolinium.

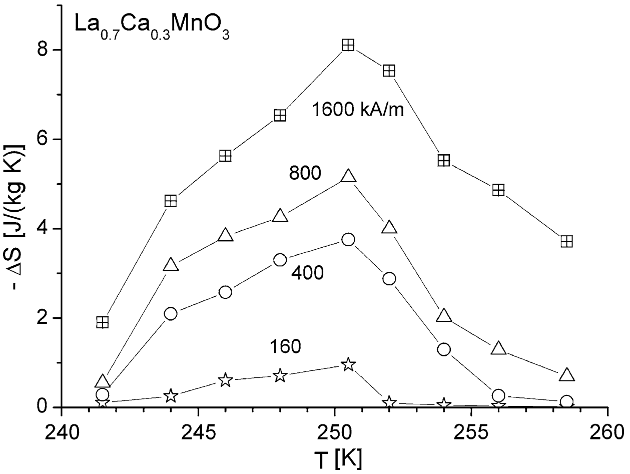

Fig. 11 Change of the magnetic entropy of $La_{0.7}Ca_{0.3}MnO_3$ polycrystals as a function of temperature at fixed values of the external magnetic field

Acknowledgement This work was partly supported by the Ministry of Science and Higher Education of Poland Project PBZ-KBN-115/T08/2004. The authors thank W. Adamczuk for assistance during the experiment.

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