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Magnetocaloric effect in nano- and polycrystalline manganites $La_{0.5}Ca_{0.5}MnO_3$

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ABSTRACT

Structure, magnetic and magnetocaloric properties of poly- and nanocrystalline $La_{0.5}Ca_{0.5}MnO_3$ manganites prepared by the citrate sol–gel method are studied in a broad temperature range. The Arrott plots show that the phase transition is of the second order. The cooling efficiency of 93–97 J/kg is found for the poly- and nanocrystalline samples. The relatively weaker magnetocaloric effect in nanocrystalline $La_{0.5}Ca_{0.5}MnO_3$ is spread over temperature range almost three times broader than for the polycrystalline one. Charge ordering effects decay in manganites with grain sizes below 150 nm.

1. Introduction

Magnetic refrigeration technology based on the magnetocaloric effect shows advantages over traditional gas compression technology [1,2] and may be considered as a promising alternative. Magnetic entropy change is known to achieve relatively high values at the para- to ferromagnetic transition. Theoretical predictions and experimental results for various classes of materials confirm that the magnetic entropy change is larger for the first than for the second order phase transition. The transition temperature of manganites may be varied mainly by a chemical composition. The magnitude of the magnetic entropy change is affected by the microstructure of the material. The technical parameter called the relative cooling power (RCP) depends also on the width of transition temperature interval [1,2] and determines potential applications. As the magnetocaloric properties of manganites are known only to a limited extend a search for new refrigerant materials and new preparation methods leading to the stronger magnetocaloric effect, is still desired. A present paper extends recent studies of manganites [3–6] and aims to investigate magnetocaloric effect in the nano- and polycrystalline $La_{0.5}Ca_{0.5}MnO_3$ manganites prepared by the citrate sol–gel method.

2. Samples

Nano- and polycrystalline $La_{0.5}Ca_{0.5}MnO_3$ were prepared by citrate sol–gel method. Stoichiometric amounts of high purity $CaCO_3$, La_2O_3 and MnO were dissolved in nitric acid. Citric acid (CA) and ethylene glycol (EG) were added to the solution of metal nitrates in the molar ratio metals: CA:EG = 1:5:5. The resultant solution was evaporated on a water bath at ca. 90 °C until a viscous gel-like product formed. The gels were decomposed by slow heating in air up to 400 °C. Nanocrystalline powder $La_{0.5}Ca_{0.5}MnO_3$ was obtained by calcination of the citrate precursor at 750 °C for 6 h. Nano-bulk samples were produced by sintering pelletized nano-powders at 750 °C for 2 h. Polycrystalline $La_{0.5}Ca_{0.5}MnO_3$ was prepared by sintering of the same precursor at 1300 °C in air for 24 h.

X-ray powder diffraction made in transmission geometry using Bruker GADDS/D8 X-ray system with Apex Smart CCD Detector and direct-drive rotating anode, shows that samples are single phase and orthorhombic (s.g. *Pnma*) at room temperature. Unit cell parameters equal to: $a = 0.54420(4)$ nm,

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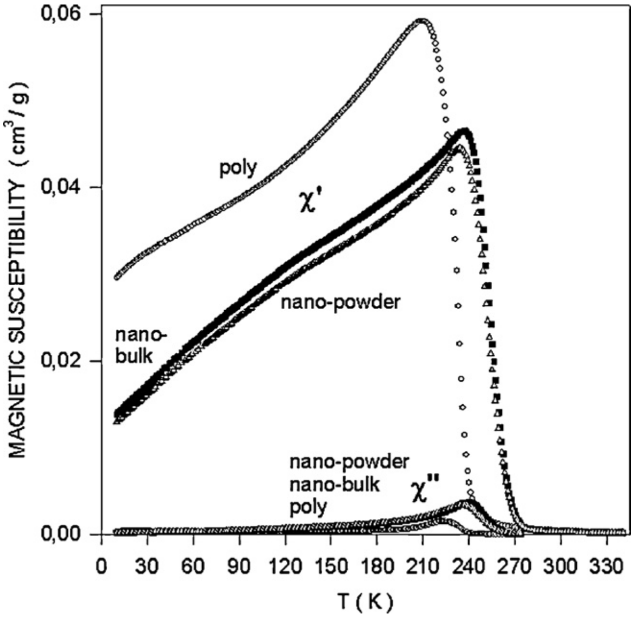

Fig. 1. Temperature variation of the in-phase and out-of-phase components of AC magnetic susceptibility for the polycrystalline (circles), nano-bulk (squares) and nano-powder (triangles) $La_{0.5}Ca_{0.5}MnO_3$ manganites.

$b = 0.75231(7)$ nm, $c = 0.54733(4)$ nm and $a = 0.54440(6)$ nm, $b = 0.7525(1)$ nm, $c = 0.54628(6)$ nm, for poly- and nanocrystalline samples, respectively. A mean crystallite size of nanocrystalline manganite determined from broadening of diffraction peaks using Scherrer equation is 8.3 nm. Crystallites sizes of polycrystalline manganite are rather fine being about 100 nm.

3. Magnetic measurements

Magnetic characterization was made by measurements of the temperature dependence of magnetic susceptibility, with an AC field amplitude of 10 Oe, and of the magnetization with a DC magnetic field of 100 Oe in field cooled (FC) and zero field cooled (ZFC) conditions. Magnetization isotherms up to 2 T have been carried out between 138 and 190 K.

4. Low field magnetic characterization

The temperature variation of magnetic susceptibility (Fig. 1) confirms that both the poly- and nanocrystalline manganites are single phase. The in-phase component of magnetic susceptibility exhibits a maximum around 210 and 235 K for the poly- and nanocrystalline manganites, respectively. Such a maximum reveals the competing magnetic structures at low temperatures. No traces of charge ordering are seen both for the poly- and nanocrystalline samples studied, as discussed later. An abrupt drop in susceptibility occurs in relatively narrow temperature interval. The out-of-phase components have the corresponding maxima at 220 and 240 K, respectively. A magnitude of the out-of-phase component is roughly twice higher for the nanocrystalline than polycrystalline manganite. Such a ratio shows that energy dissipation is more intense in structurally disordered nanocrystalline manganites.

The registered temperature variation of field cooled (FC) and zero field cooled (ZFC) magnetization splits below the same irreversibility temperature $T_{IRR} = 225$ K for the poly- and nanocrystalline manganites (Fig. 2). A magnitude of FC and ZFC magnetization diminishes when passing from poly- to nano-powder manganite, which reveals the raising structural and magnetic disorder. A comparison of slopes in ZFC magnetization of poly- and nanocrystalline manganites below 200 K points to a remarkable contribution of competing ordering especially in the nanocrystalline manganites. The Curie temperatures determined from the highest slope dM/dT are equal to 233 and 245 K for the poly- and nanocrystalline samples, respectively. The Curie temperature of polycrystalline manganite falls in a lower limit of a range of previously reported values [7–10]. For nanocrystalline manganites the Curie temperature is somewhat lower as compared with that of 25 nm grains [8]. The abrupt drops in low field susceptibility and magnetization observed around the Curie temperature, suggest a possibly strong magnetocaloric effect in these materials.

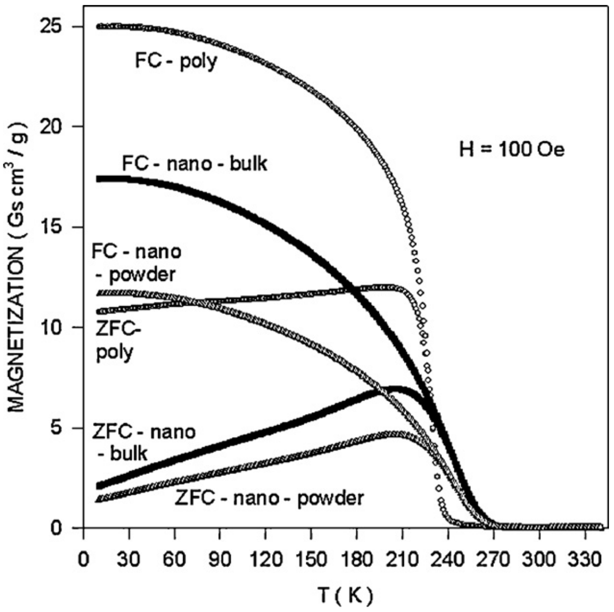

Fig. 2. Temperature variation of the zero field cooled (ZFC) and field cooled (FC) magnetization for the polycrystalline (circles), nano-bulk (squares) and nano-powder (triangles) $La_{0.5}Ca_{0.5}MnO_3$ manganites.

5. Magnetization isotherms

The magnetization isotherms demonstrate a gradual change in shape when passing from ferro- to paramagnetic phase. In the ferromagnetic phase an abrupt magnetization increase between zero and 0.15 T is followed by a slow approach to saturation (Fig. 3). At 2 T magnetization of nanocrystalline manganites achieves only 45 Gs cm^3/g being remarkably lower as compared to 65 Gs cm^3/g for the polycrystalline one. The extrapolation to zero magnetic field results in the mean magnetic moment equal to 2.06 and 1.37 μ_B for the polycrystalline manganite at 199 K and nanocrystalline one at 138 K, respectively. These magnetic moments correspond to 59% and 39% of the ferromagnetic phase, respectively. These moments are smaller than the theoretical spin only value of 3.5 μ_B. Such a large difference is obviously due to the structural and chemical disorder within the surface layer of nanocrystallites. On the other hand, the approximately linear dependence of magnetization with magnetic field is found in the paramagnetic phase.

In vicinity of Curie temperature magnetization of a ferromagnet obeys an equation:

$$AM + BM^3 = H \qquad (1)$$

where the A and B are the temperature dependent parameters. The magnetization isotherms were transformed into the so-called Arrott plots of M^2 vs. H/M for a broad temperature intervals (Fig. 4). The positive slope observed for all the curves reveals that the ferro-

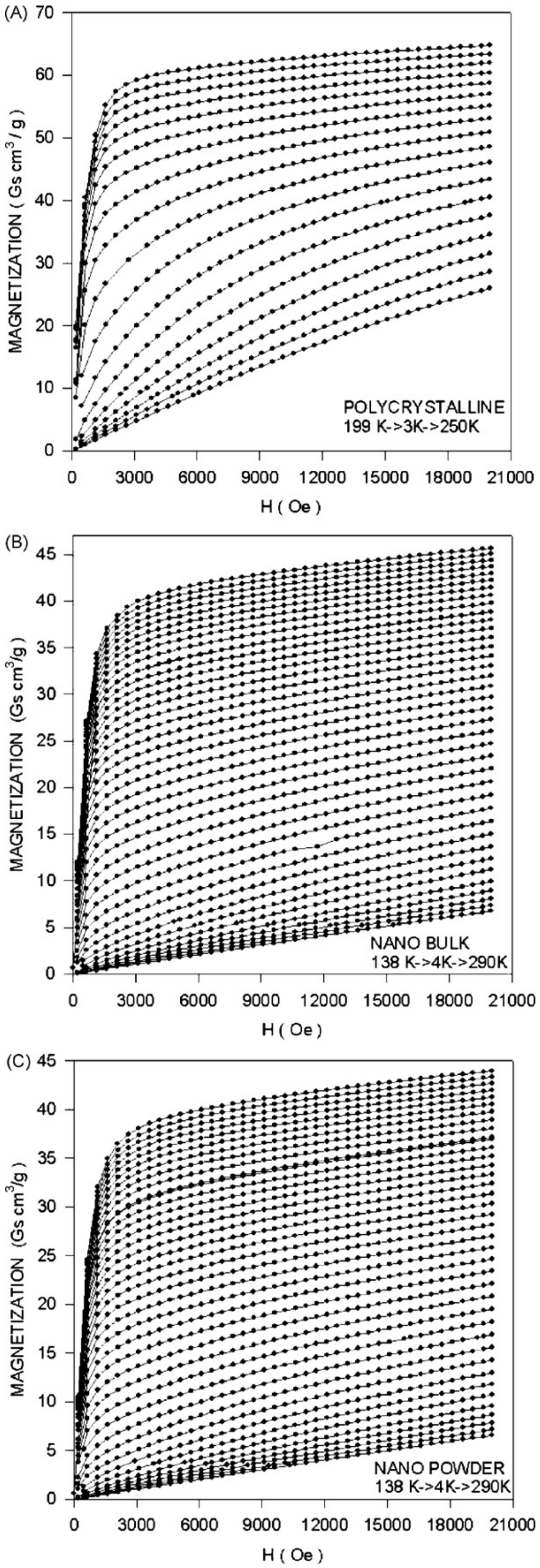

Fig. 3. Magnetization isotherms for the polycrystalline (A), nano-bulk (B) and nano-powder (C) $La_{0.5}Ca_{0.5}MnO_3$ manganites registered up to 2 T.

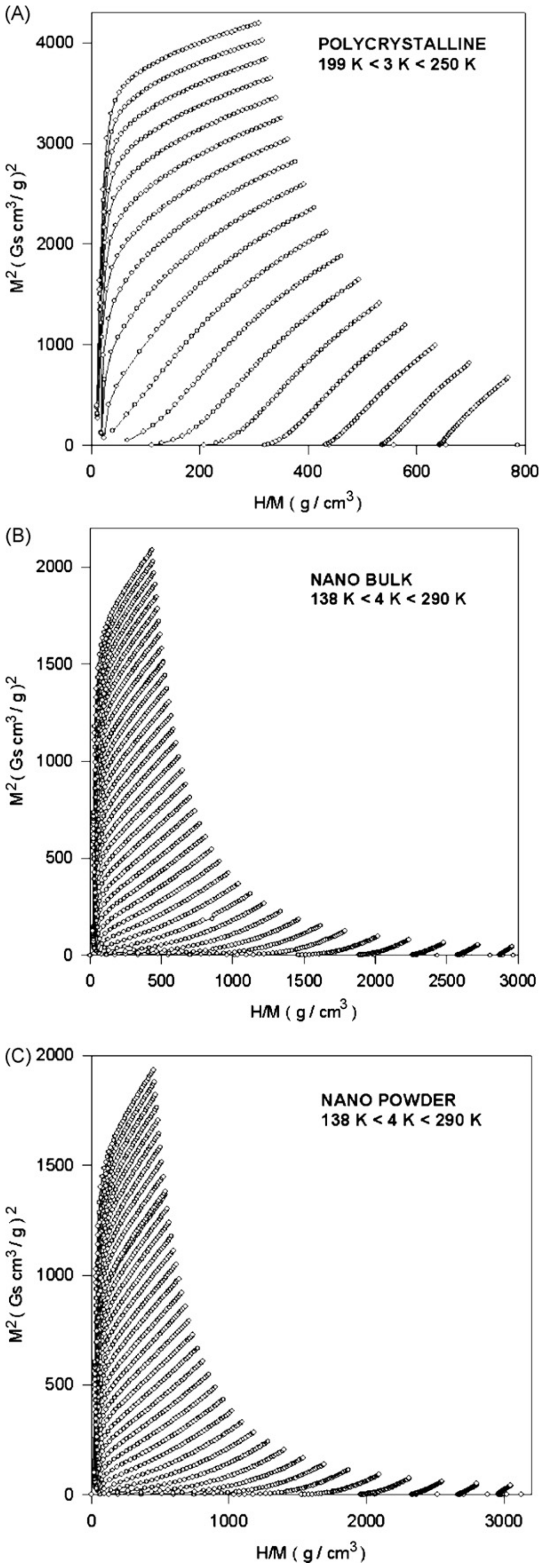

Fig. 4. Arrott plots for the polycrystalline (A), nano-bulk (B) and nano-powder (C) $La_{0.5}Ca_{0.5}MnO_3$ manganites.

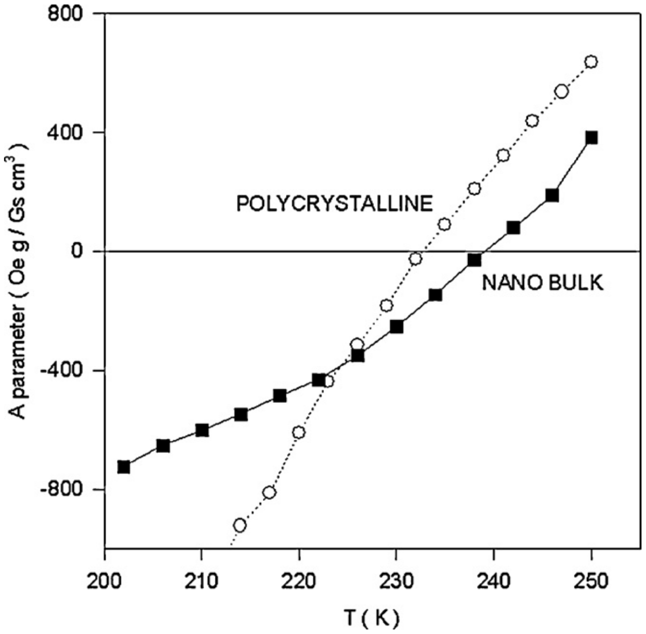

Fig. 5. Thermodynamic parameter A derived from Eq. $AM + BM^3 = H$ as a function of temperature for the poly- and nanocrystalline $La_{0.5}Ca_{0.5}MnO_3$ manganite.

to paramagnetic transition is of the second order both for the poly- and nanocrystalline manganites studied [11]. The straight high field fraction of isotherms of Arrott plots were numerically fitted to Eq. (1) in order to derive the temperature variation of the A parameter, which is plotted in Fig. 5. The Curie temperatures of poly- and nanocrystalline manganites indicated by the sign change of A parameter are only a few degrees lower as compared with values determined from low field magnetization measurements.

6. Magnetocaloric effect

The magnetic entropy change DS was numerically calculated from magnetization isotherms according to the formula:

$$\mathrm{DS}(T, H) = \int_0^H (\partial M/\partial T)_H dH \qquad (2)$$

The poly- and nanocrystalline manganites exhibit remarkably different behavior of DS. The magnetic entropy change DS calculated for magnetic fields of 0.5, 1, 1.5 and 2 T achieves a minimum located close to the Curie temperatures (Fig. 6). The magnetocaloric effect occurs in a relatively narrow interval of 40 K in polycrystalline manganite whereas the corresponding interval reaches about 115 K in nanocrystalline samples. On the other hand a magnitude of magnetocaloric effect decreases about fourfold from −2.7 down to −0.75 J/kg K when passing from poly- to nanocrystalline manganites. A reduction in DS magnitude accompanied by a broadening of DS peak is a characteristic feature observed for manganites when grain sizes diminish. Such an evolution occurs since the increasing surface to volume ratio enhances structural and magnetic disorder and broadens the ferro- to paramagnetic transition. Recently it was reported for various classes of Ca and Sr containing manganites [3,5,12], including also nanocrystalline manganites, e.g. $La_{0.125}Ca_{0.875}MnO_3$, $Pr_{0.65}(Ca_{0.7}Sr_{0.3})_{0.35}MnO_3$ and $Pr_{0.65}(Ca_{0.6}Sr_{0.4})_{0.35}MnO_3$ with grain sizes below 100 nm [13–15].

The present results can be directly compared to the polycrystalline $La_{0.5}Ca_{0.5}MnO_3$ manganite prepared by the solid-state reaction [16], which probably contains coarser grains of micrometer size. The magnetocaloric effect at Curie temperature of 230 K

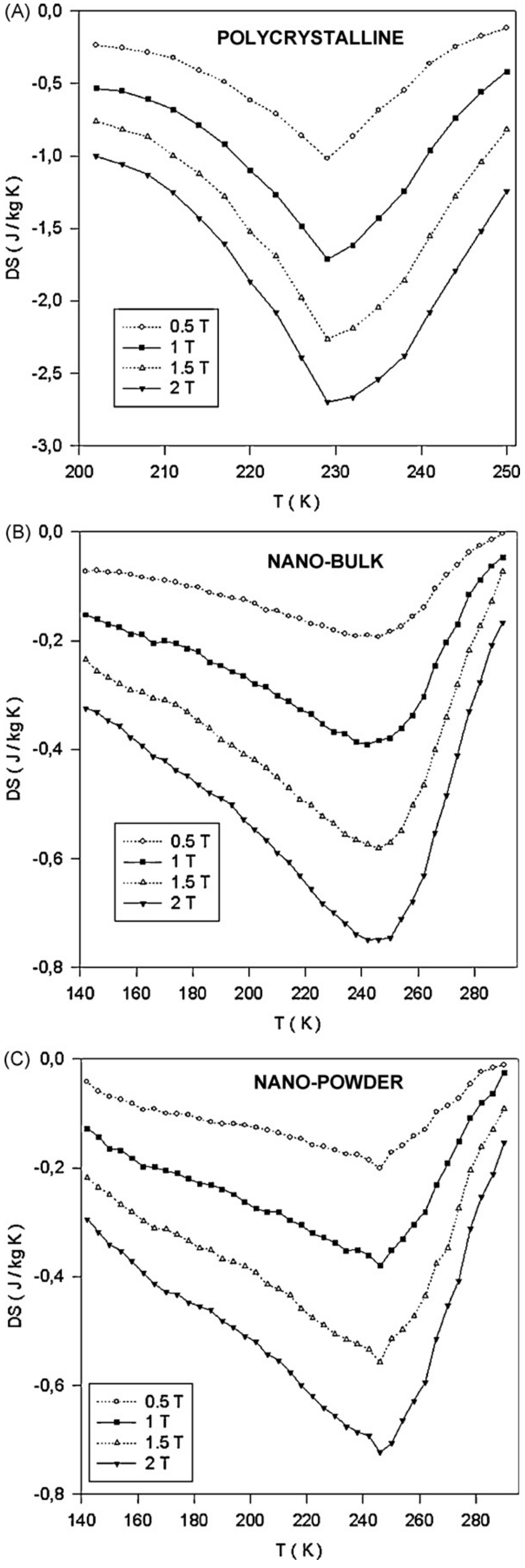

Fig. 6. Magnetic entropy change around the Curie temperature for the polycrystalline (A), nano-bulk (B) and nano-powder (C) $La_{0.5}Ca_{0.5}MnO_3$ manganite.

achieves only 1.2 J/kg K and a peak half width is about 50 K at magnetic field of 2 T. One may also see that a magnitude of DS in a polycrystalline manganite is about 30% larger as compared to that reported for a similar calcium manganite $(La_{.6}Ca_{.4})_{.9}Mn_{1.1}O_3$ by Zubov et al. [17].

It is worth to notice the contrasting difference between the poly- and nanocrystalline manganites studied and that reported by Krishnamoorthi et al. [16]. Namely, the coarse grain manganite exhibits additional inverse magnetocaloric effect at charge ordering temperature T_{CO} about 165 K [16], which is absent both in the poly- and nanocrystalline manganites studied.

The issue of charge ordering is of high importance for $La_{0.5}Ca_{0.5}MnO_3$ manganite since the 50/50 La/Ca ratio is known to facilitate a formation of charge ordered state, which coexists and competes with ferromagnetic ordering [7,8,18,19]. This competition leads to gradual suppression of ferromagnetic order observed below the charge ordering temperature $T_{CO} = 210$ K in samples with micrometer sized grains. Moreover, at low temperatures the magnetic structure is changing to the antiferromagnetic one, as revealed by the susceptibility maximum located at Neel temperature T_N located between 135 and 160 K depending on a sample [8,18]. No traces of such features around 210 K and 150 K can be found both in the smooth field cooled and zero field cooled magnetization curves of Fig. 2.

The present investigation supplies an additional proves for an absence of charge ordering in the fine grain poly- and nanocrystalline $La_{0.5}Ca_{0.5}MnO_3$ manganites studied. For the coarse grained polycrystalline $La_{0.5}Ca_{0.5}MnO_3$ manganites a magnitude of magnetization isotherms diminishes when a temperature is reduced below $T_{CO} = 210$ K. This tendency is in agreement a changeover to antiferromagnetic ordering accompanying the charge ordering, as shown e.g. in Fig. 2A in [16]. The entirely opposite tendency is demonstrated by magnetization isotherms of poly- (100 nm grain size) and nanocrystalline (8.3 nm grain size) $La_{0.5}Ca_{0.5}MnO_3$ manganites studied (Fig. 3), where magnetization magnitude diminishes monotonically with raising temperature. Thus, the present study corroborates that the threshold grain size for charge ordering decay in $La_{0.5}Ca_{0.5}MnO_3$ manganite is about 150 nm, as indicated in [18].

Jirak et al. [8] have ascribed an absence of charge ordering in nanocrystalline manganites to the grain surface disorder. This is justified by the surface to volume ratio enhanced with diminishing grain size, which in turn modifies the atomic coordination as well as interatomic exchange interactions within the surface layer. Thus, the disordered spin glass phase develops in the surface layer in contrast to the long range ferromagnetic phase in grain cores. Therefore, the charge ordering in the grain cores is truncated by the grain surface layer hindering a coherence from grain to grain. However, it seems that additional factors, like fluctuation in local chemical stoichiometry, oxygen deficiency and tendency to phase separation, may play a role too.

The minimum magnetic entropy change DS_{MIN} for the polycrystalline, nano-bulk and nano-powder $La_{0.5}Ca_{0.5}MnO_3$ manganites plotted in Fig. 7 as a function of magnetic field shows the remarkable difference between the poly- and nanocrystalline manganites studied. The minimum magnetic entropy change DS_{MIN} with magnetic field strength for the polycrystalline manganite is slower than the linear one and agrees with observation reported by Zubov et al. [17] for the $(La_{.6}Ca_{.4})_{.9}Mn_{1.1}O_3$ manganite. This is in contrast with the strictly proportional relation found for the nanocrystalline manganite in a broad field interval up to 2 T.

The effective cooling efficiency is expressed by the entropy change minimum DS_{MIN} and the width DT at half DS minimum as follows:

$$RCP = DS_{MIN} \times DT \quad (3)$$

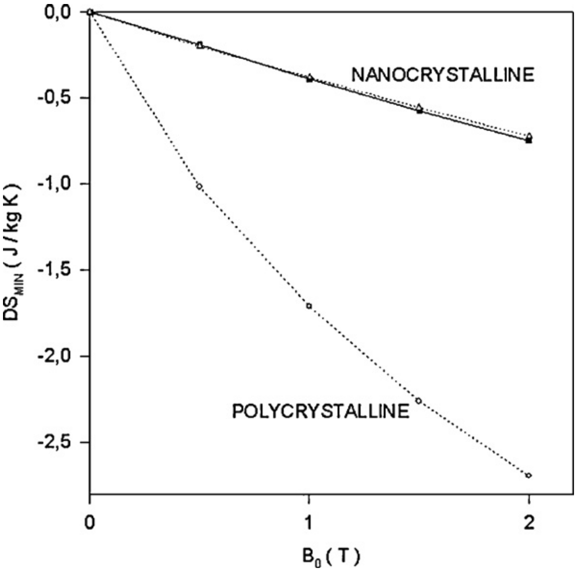

Fig. 7. Magnetic field dependence of minimum magnetic entropy change for the polycrystalline, nano-bulk and nano-powder $La_{0.5}Ca_{0.5}MnO_3$ manganites.

At magnetic field of 2 T values of RCP fall in a range 93–97 J/kg for the three manganites studied. Such a RCP value considerably exceeds 60 J/kg at 2 T field, which may be estimated from for the coarse grain $La_{0.5}Ca_{0.5}MnO_3$ manganite [16]. The measured RCP is somewhat larger as compared with that reported by Guo et al. [20] for $La_{.55}Ca_{.45}MnO_3$ manganite. The RCP values are almost equal for the poly- and nanocrystalline manganites studied. The temperature interval, where the materials may be applied or refrigeration, is usually evaluated at a half of DS_{MIN} value. The temperature intervals are much different being only 40 K and more than 110 K for the poly- and nanocrystalline cases, respectively. The relatively low magnitude of magnetocaloric effect in nanocrystalline $La_{0.5}Ca_{0.5}MnO_3$ manganite hinders direct practical applications. However, the investigated evolution of magnetocaloric effect with grain sizes and chemical composition allows to tailor a series of materials with high enough magnetic entropy change and varying Curie temperatures, which may be applied in multistep cooling devices.

Acknowledgements

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