

# Magnetocaloric Effect in Nano- and Polycrystalline Manganites $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

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## Abstract

Structure, magnetic and magnetocaloric properties of poly- and nanocrystalline  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  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 to 97 J/kg is found for the poly- and nanocrystalline samples. The nanocrystalline  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  manganite may be applied for refrigeration in almost three times broader temperature range than the polycrystalline one.

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## 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  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  manganites prepared by the citrate sol-gel method.

## **Samples**

Nano- and polycrystalline  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  were prepared by citrate sol-gel method. Stoichiometric amounts of high purity  $\text{CaCO}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{MnO}$  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  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  was obtained by calcination of the citrate precursor at 750 °C for 6 h and polycrystalline  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  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,  $b = 0.75231(7)$  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.

## **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 K and 190 K.

## **Low field magnetic characterization**

The temperature variation of magnetic susceptibility (Fig. 1) confirm 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. 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 nanopowder 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.

### **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  $45 \text{ Gs cm}^3 / \text{g}$  being remarkably lower as compared to  $65 \text{ Gs cm}^3 / \text{g}$  for the polycrystalline one. Thus the magnetic moment at 2 T equals to 2.22 and  $1.55 \mu_B$  for the polycrystalline manganite at 199 K and nanocrystalline one at 138 K, respectively. These moments are smaller than the theoretical spin only value of  $3.5 \mu_B$ . 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 is found in the paramagnetic phase.

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

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

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- 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.

### Magnetocalori effect

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

$$DS(T,H) = \int_0^H (\partial M / \partial T) dH \quad (2)$$

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 35 K in polycrystalline manganite whereas the corresponding interval reaches about 130 K in nanocrystalline samples. On the other hand a magnitude of magnetocaloric effect decreases about fourfold when passing from poly- to nanocrystalline manganites. A magnitude of DS in a polycrystalline manganite is about 30 % larger as compared to that reported for a similar manganite  $(La_{0.6}Ca_{0.4})_{0.9}Mn_{1.1}O_3$  by Zubov et al. [12].

The minimum magnetic entropy change  $DS_{MIN}$  for the polycrystalline, nano bulk and nano powder  $La_{0.5}Ca_{0.5}MnO_3$  manganite 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. [12] for the  $(La_{0.6}Ca_{0.4})_{0.9}Mn_{1.1}O_3$  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  $DS_{\text{MIN}}$  and the width  $DT$  at half  $DS$  minimum as follows

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

At magnetic field of 2 T values of RCP fall in a range 93 to 97 J/kg for the three manganites studied. Such a RCP is somewhat larger as compared with that reported by Guo et al. [13] for  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  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  $DS_{\text{MIN}}$  value. The temperature intervals are much different being only 40 and more than 110 K for the poly- and nanocrystalline cases, respectively. This shows that at the same cooling efficiency the nanocrystalline  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  manganite may be applicable in the broader temperature range.

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### Figure captions

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)  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  manganites.

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)  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  manganites.

Fig. 3. Magnetization isotherms for the polycrystalline (A), nano bulk (B) and nano powder (C)  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  manganites registered up to 2 T.

Fig. 4. Arrot plots for the polycrystalline (A), nano bulk (B) and nano powder (C)  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  manganites.

Fig. 5. Thermodynamic parameter A derived from eq.  $AM+BM^3 = H$  as a function of temperature for the poly- and nanocrystalline  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  manganite.

Fig. 6. Magnetic entropy change around the Curie temperature for the polycrystalline (A), nano bulk (B) and nano powder (C)  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  manganite.

Fig. 7. Magnetic field dependence of minimum magnetic entropy change for the polycrystalline, nano bulk and nano powder  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  manganites.

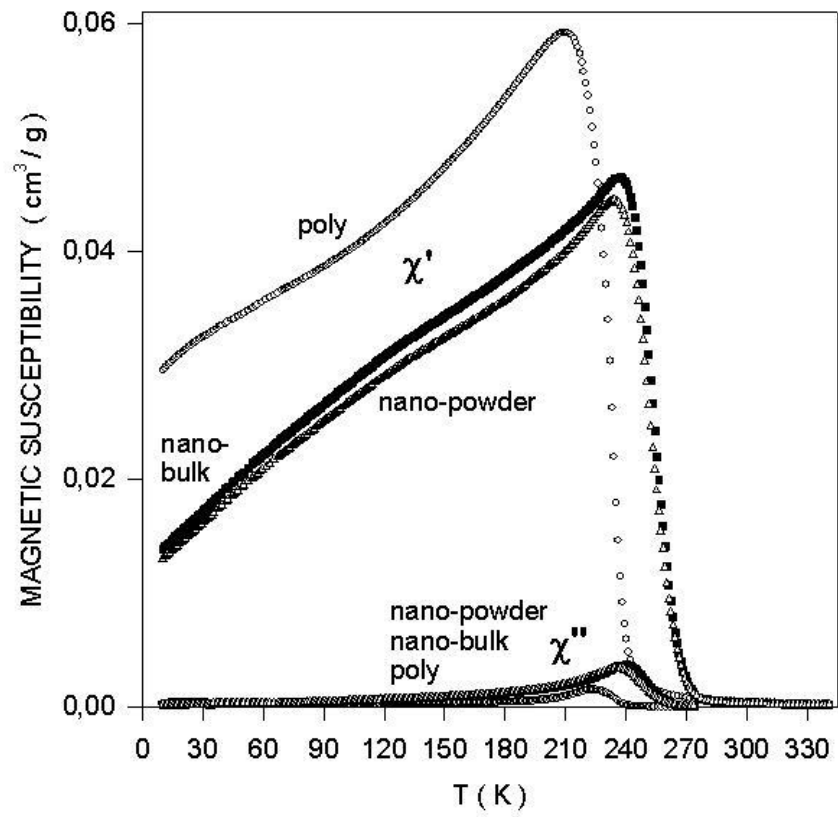


Fig 1

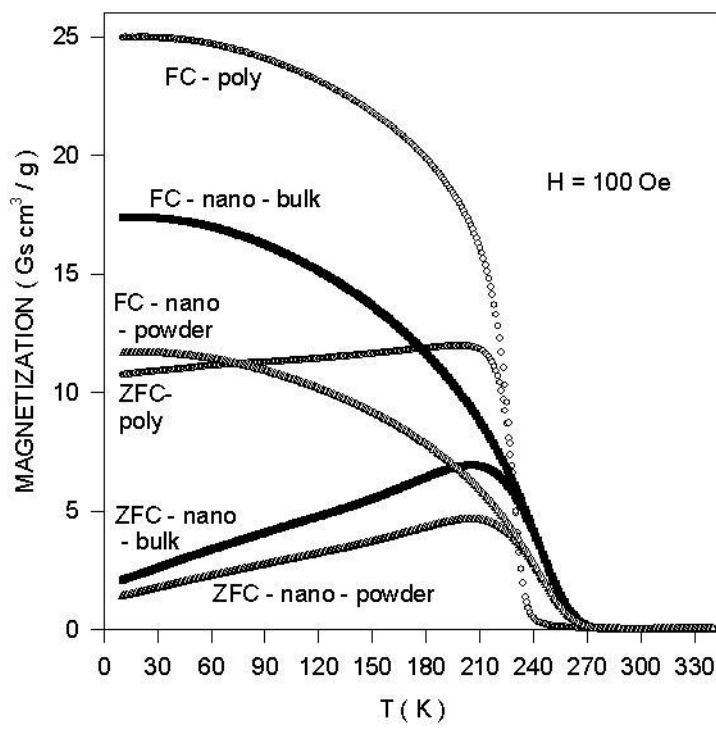


Fig 2



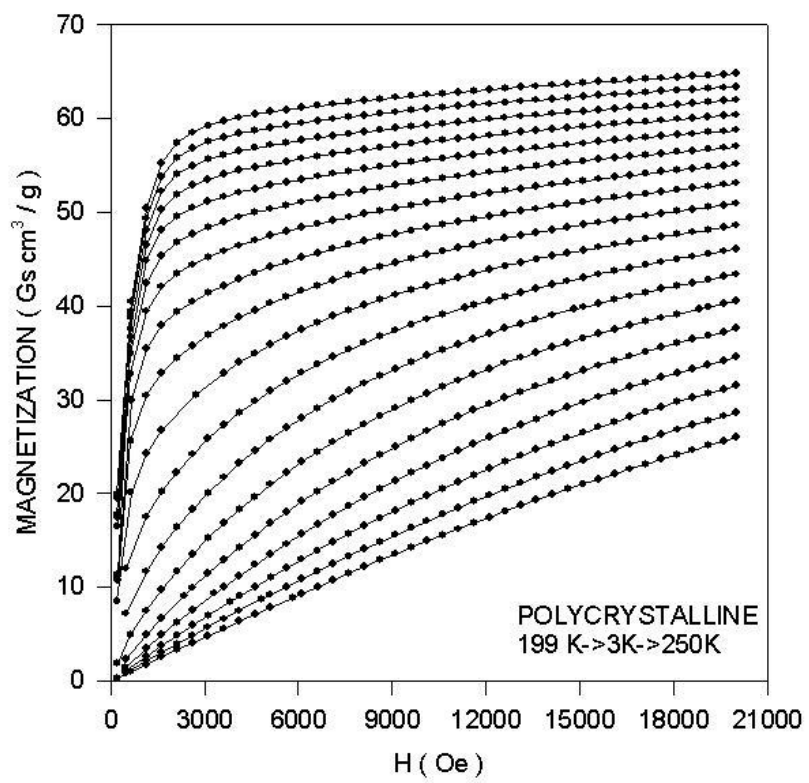


Fig 3A

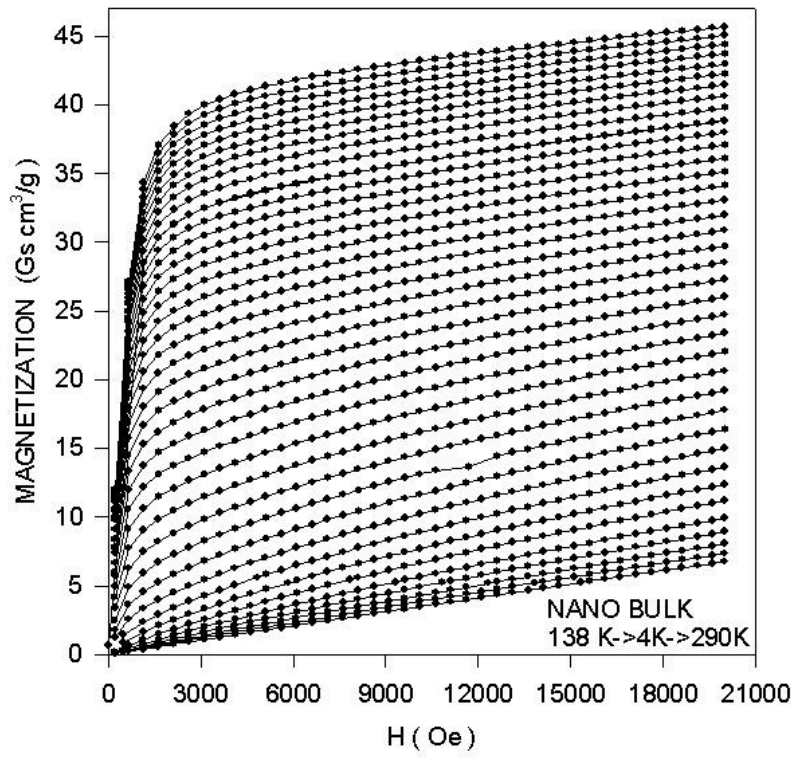


Fig 3B

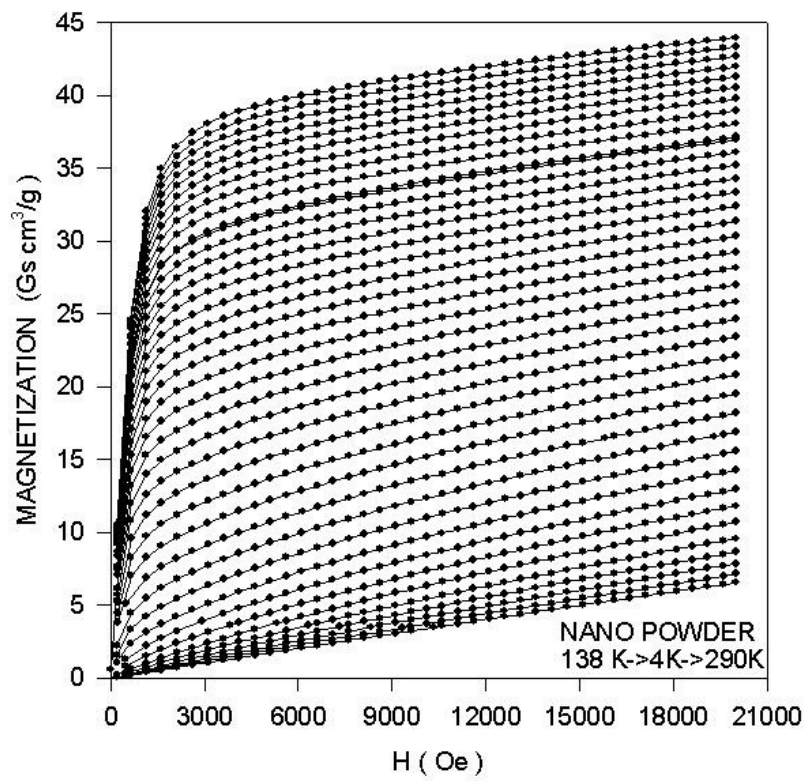


Fig 3C

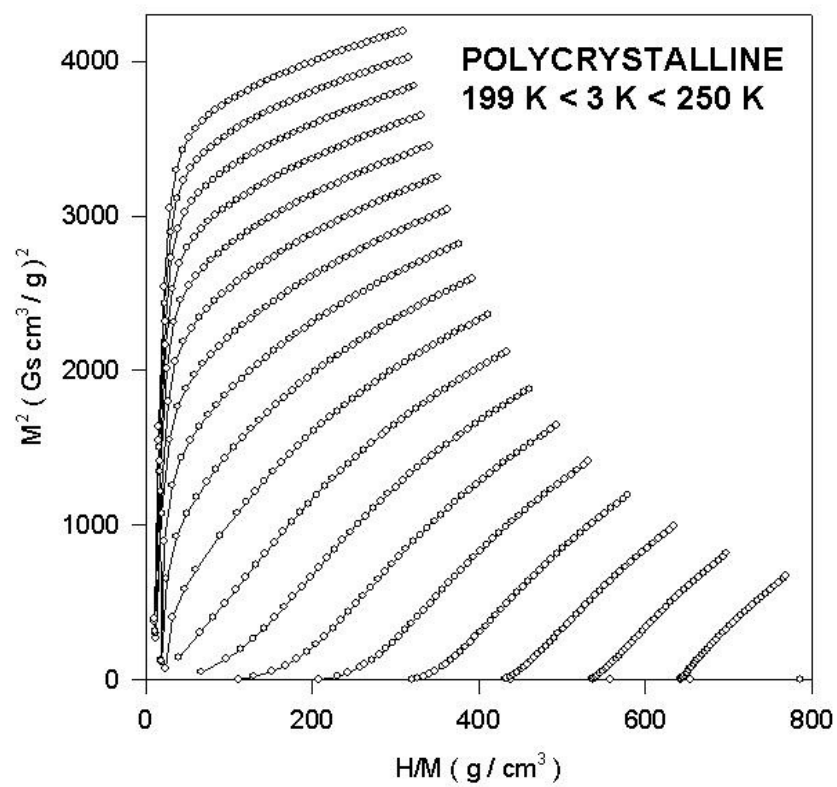


Fig 4A

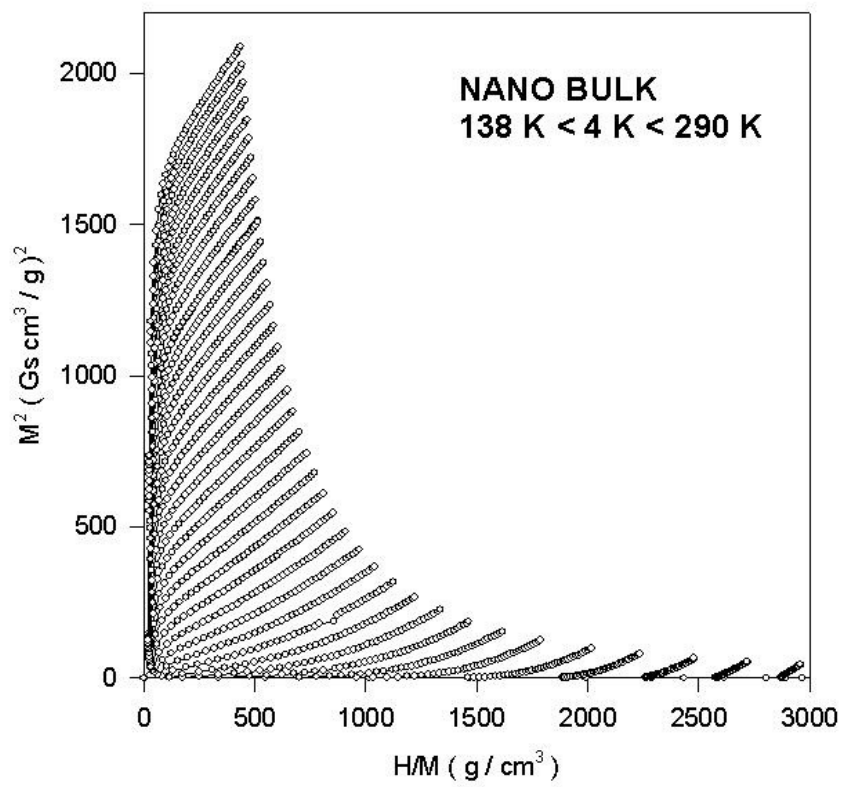


Fig 4B

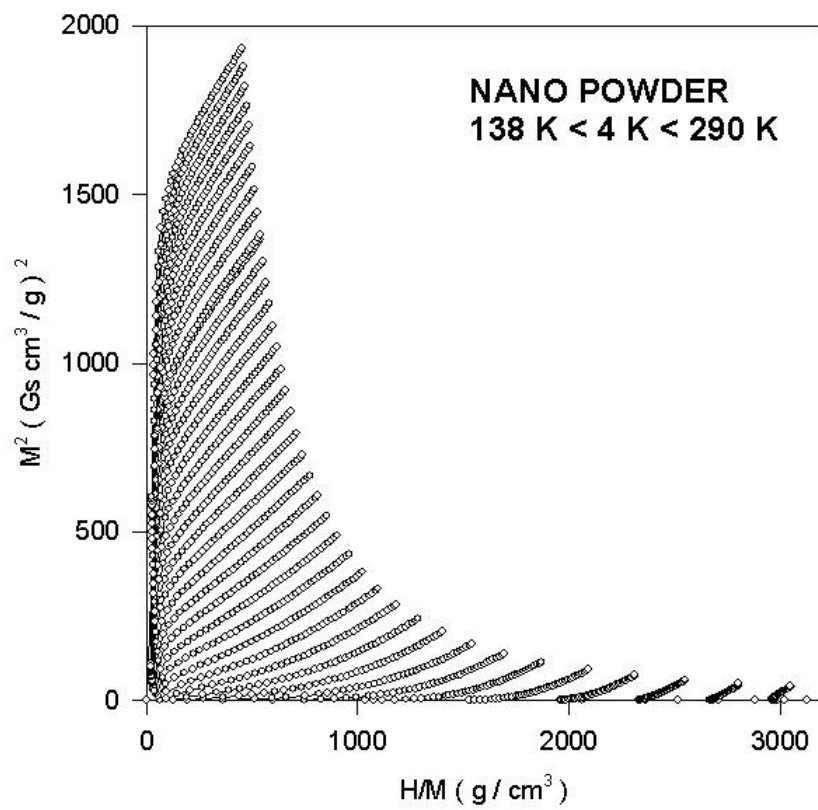


Fig 4C

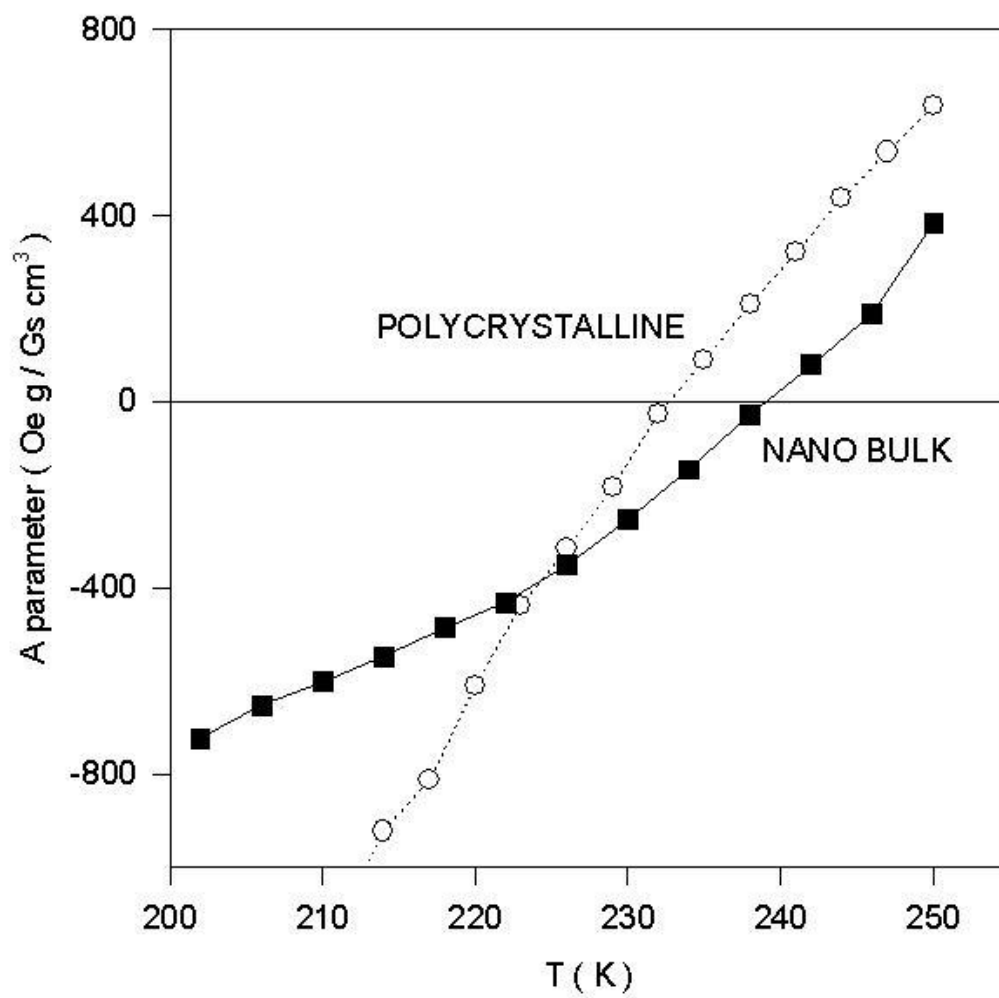


Fig 5

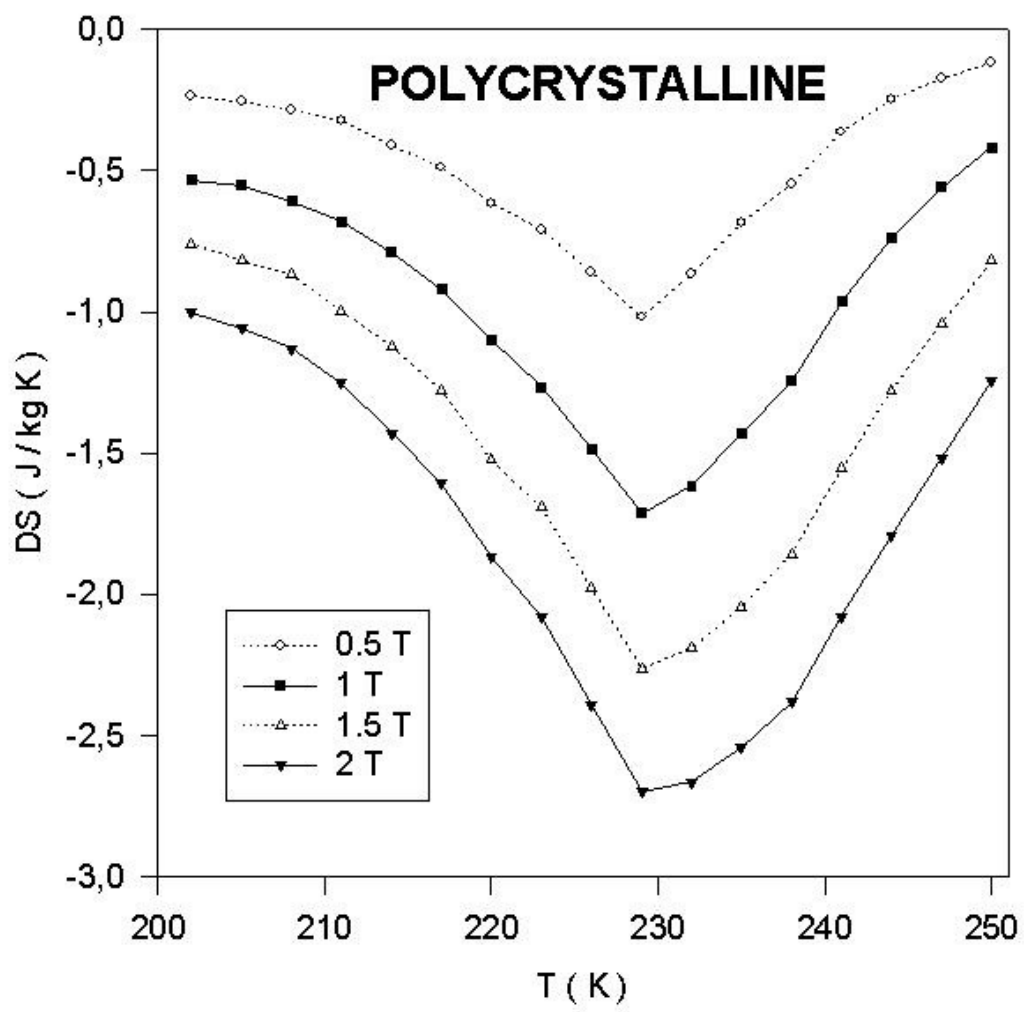


Fig 6A



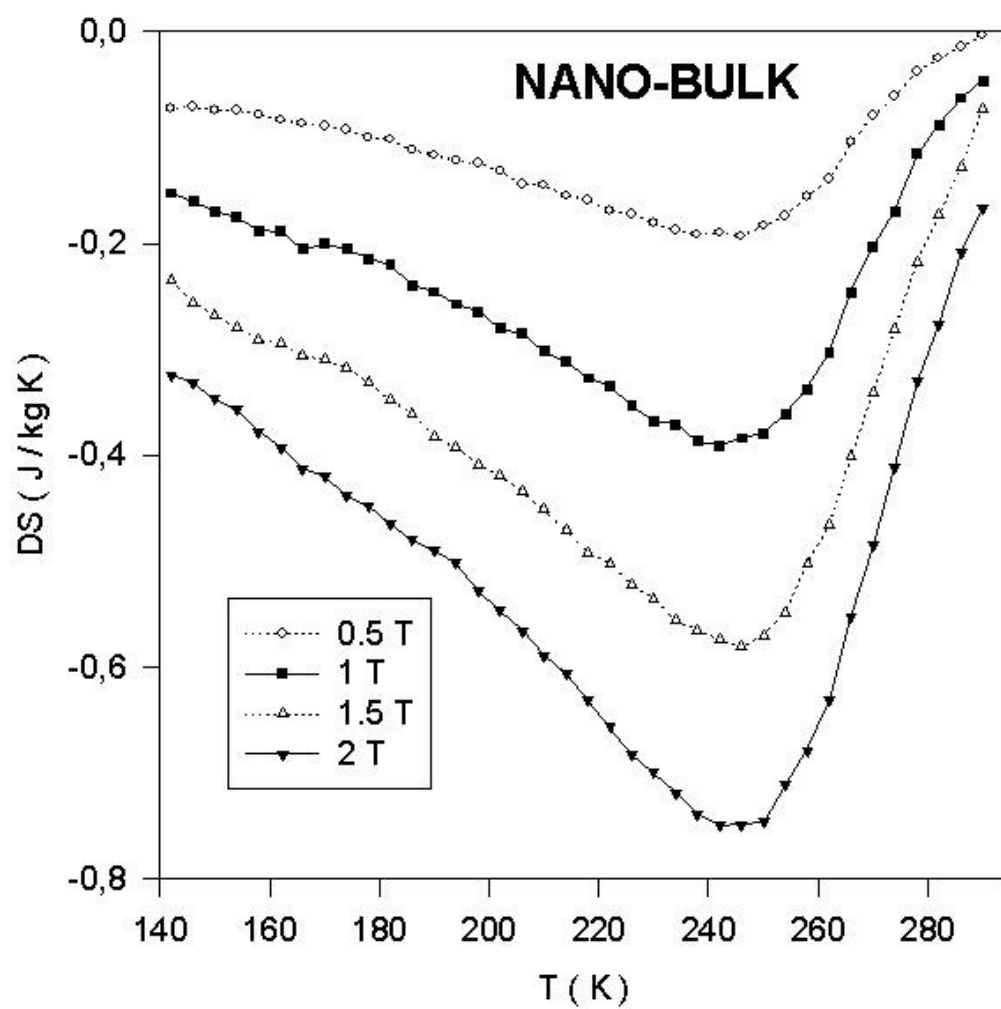


Fig 6B

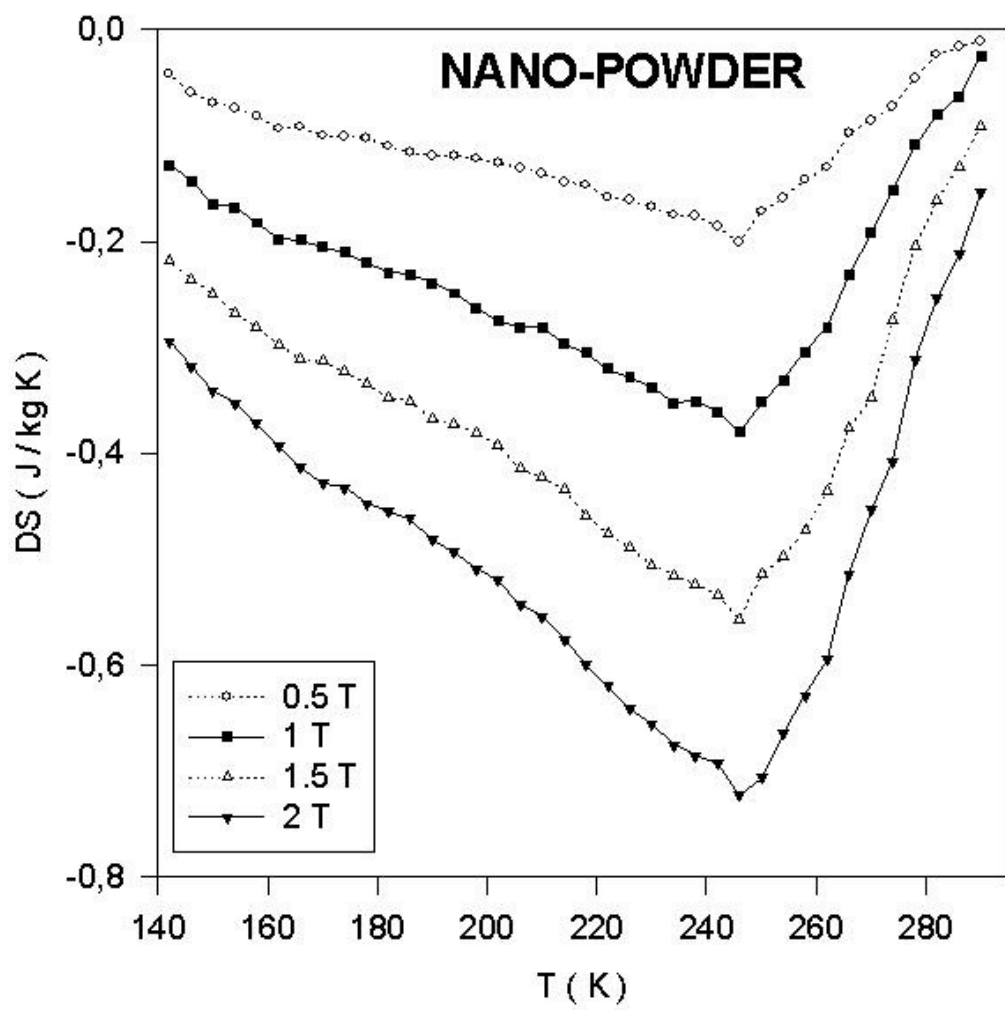


Fig 6C

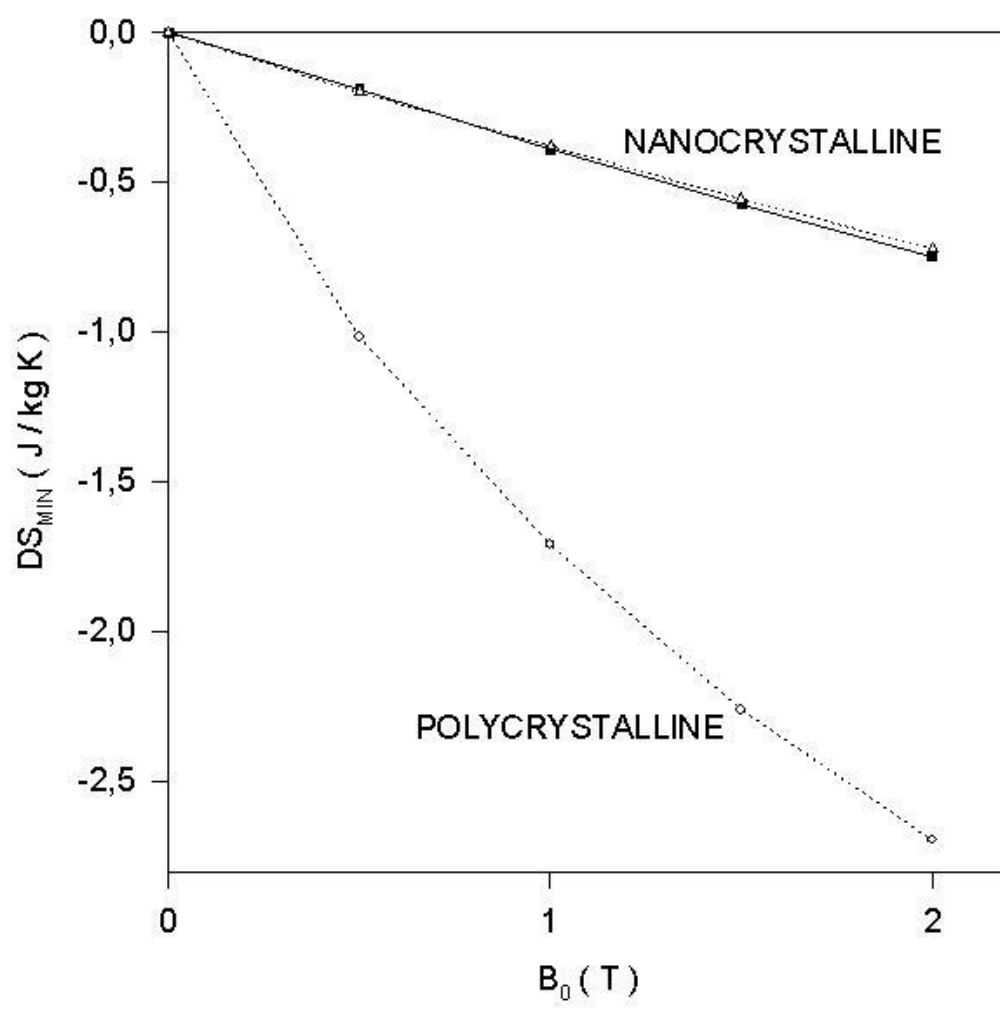


Fig 7