



# Magnetocaloric effect study of ferromagnetic-charge ordered core-shell type manganite nanostructures



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## ABSTRACT

In the present study we have presented the magnetic and magnetocaloric properties of ferromagnetic ( $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ )-charge ordered ( $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ) core-shell nanostructures. We have also compared the magnetocaloric properties of  $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (PCMO) nanoparticles. Our study indicates that in case of the core-shell nanostructures, the magnetocaloric properties markedly modifies compared to its parent compound PCMO, additionally the low field magnetocaloric effect enhanced. More specifically, the large value of magnetocaloric entropy change ( $-\Delta S(T)$ ) was observed in wider temperature range in core-shell nanostructure which may be important from application point of view.

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## 1. Introduction

In the present global warming situation, the environment friendly energy saving cooling technology is one of the major important issue. To replace the harm full gasses, frequently used in gas compression cooling technology, the magnetic refrigeration technique is attracts a noticeable attention in current research. The magnetic refrigeration technique is based on the magnetocaloric effect. Magnetocaloric effect is the isothermal magnetic entropy changes or the adiabatic temperature changes of magnetic materials due to the application of the external magnetic field. From technological point of view, search of the materials, exhibiting large magnetocaloric effect in moderate magnetic field is most imperative quest to the researcher. Generally large magnetocaloric entropy changes associated with the large magnetic moment of the materials. Initially the materials namely Gadolinium (Gd) and Gd-based intermetallic compounds were extensively studied during previous few decades [1,2]. However, for selecting the materials as for magnetic refrigeration the operating range also important. Generally at the low temperature regime (cryogenic temperature range) and near to the room temperature, the materials which exhibits large magnetocaloric effect were get an utmost attention for using in technological perspectives [2–12]. For selecting the refrigerant materials, the important parameters are materials should be highly chemically stable, have low eddy current loss (high resistive) etc.. Moreover for commercial application, the cost of the materials should also plays the significant role. In this con-

text, along with the intermetallic magnetocaloric materials, rare earth based highly stable, comparatively cheaper manganite materials take an imperative role in study of magnetocaloric effect during previous two decades [10,11,13,14]. The doped perovskite manganite generally represented by  $\text{RE}_{1-x}\text{B}_x\text{MnO}_3$  (RE is trivalent and B is bivalent elements). There are many intriguing properties of doped perovskite manganites namely charge ordering, colossal magnetoresistance, large magnetocaloric effect etc.. In manganite families, the some of the very well studied materials are  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  and  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ . Depending upon the doping concentration 'x', these material shows many rich physical properties [15,16].

The large magnetocaloric effect in manganites generally observed at the vicinity of the disorder to order transition (more specifically near paramagnetic to ferromagnetic transition). However in some cases the magnetocaloric entropy changes also influence due to the magnetic precursor effect and appearance of the super paramagnetic behavior at the low temperature region [10,17]. Another advantage of the manganite materials is that, the ordering temperature (disorder to order) is usually higher which is also beneficial for technological perspectives. Regarding the issue of magnetocaloric effect in manganites,  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  is one of the most well studied materials [18,19]. In case of the Bulk compound, the paramagnetic to ferromagnetic ordering temperature,  $T_C$  is  $\sim 360$  K and maximum magnetic entropy changes appears at the vicinity of that ordering temperature. To reduce  $T_C$ , close to the room temperature, in case of the  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $x \sim 0.7$ ), partial substitution of the La-site by yttrium was recently reported [11]. On the other hand,  $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  is one of the well known charge ordered antiferromagnetic materials even in its nano forms [20,21]. Generally for the charge ordered

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antiferromagnetic systems, magnetic field induced destabilization of the charge ordering (antiferromagnetic ground state) inhibited the giant magnetoresistance. To reduce the required melting field, ferromagnetic  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  nanoparticles were doped with in the  $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  matrix (core-shell nanostructures), resulting in the giant enhancement of the magnetoresistance [21]. Regarding the magnetic and magnetocaloric effect, the reduction of the particle sizes in doped manganite systems played an important role. Previously it was reported that the significant enhancement of the magnetocaloric effect in doped manganite nanoparticles due to the fragile nature of the charge ordered antiferromagnetic phase with the reduction of the particle sizes [22,23]. On the other hand, the enhancement of refrigerant capacity for the oxygen deficiencies and due to the size reduction of ferromagnetic manganite compounds also reported recently [24,25]. Another remarkable point should be mentioned here, which is the modification of the magnetocaloric responses due to the interfacial magnetic coupling in low dimensional systems. Recently the observation of the giant magnetocaloric effect in epitaxial thin films was reported by Moya et al. where strain mediated magneto-structural coupling played the vital role [26].

The motivation of the present study is to explore the interfacial effect in magnetocaloric responses of the ferromagnetic–charge ordered (antiferromagnetic) nanostructure compound. Additionally, the modification of the magnetocaloric effect in core-shell type nanostructures compared to its parent compound (PCMO nanoparticles).

Our study indicates that the magnetocaloric properties of the ferromagnetic–charge ordered core-shell type nanostructures (where core is well known half metallic ferromagnetic  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  (LSMO) nanoparticles and shell matrix is charge ordered antiferromagnetic  $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ) is markedly modified compared to PCMO nanoparticles. Additionally, the drastic modification of the magnetic nature of core-shell type nanostructures due to the influence of the ferromagnetic nature of LSMO nanoparticles is addressed. Moreover, though the absolute value of the magnetic entropy is not very high but comparatively larger magnetic entropy changes were observed within a broad temperature range in core-shell nanostructures which may be a future direction for the enhancement of the magnetocaloric effect in such core-shell compounds.

## 2. Experimental details, characterizations and measurements

To prepare the core-shell nanostructures, at first core material (LSMO nanoparticles) was prepared by sol gel route. After the successful formation of nanocrystalline LSMO powder, we have estimated the average particle size (which was found to  $\sim 20$  nm) it was mixed with the suitable amount of the gel of PCMO (prepared by the sol–gel route) at the last stage of the gel formation such that the approximate shell thickness will be  $\sim 10$  nm. For comparison, PCMO nanoparticles also prepared separately. The details of the sample preparation of core-shell and PCMO nanoparticles were given in Ref. [21].

The room temperature X-ray diffraction studies were carried out in Rigaku-TTRAX-III diffractometer. For further characterization the details Transmission Electron Microscopy (TEM) were performed using FEI, Tecnai G<sup>2</sup> F30 microscope operating at 300 kV. Magnetic measurements were done in Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design).

## 3. Results and discussion

The details about the characterizations of the core-shell and PCMO nanoparticles were reported in Ref. [21]. In this paper the

magnetocaloric properties of PCMO nanoparticles (average particle size  $\sim 47$  nm) and core-shell nanostructures are presented. Magnetocaloric entropy change ( $\Delta S$ ) is generally calculated from the heat capacity measurements data (in the absence and in the presence of external magnetic field) or from the magnetic isotherms. In our present study the magnetic entropy changes of the PCMO nanoparticles and core-shell nanostructures were evaluated from the magnetic isotherms data. For the sake of clarity some representative magnetic isotherms of PCMO nanoparticles and core-shell nanostructures are given in Fig. 1. Regarding this context it should be mentioned that to record each magnetic isotherm, at first the samples were cooled down to the specified temperature well above from the paramagnetic temperature region ( $T = 380$  K) in the absence of any external magnetic field to remove the previous magnetic history with in the sample if present. According to the earlier report on PCMO nanoparticles, charge ordering transition  $T_{CO} \sim 225$  K and antiferromagnetic ordering,  $T_N$  is  $\sim 150$  K [27]. In case of the PCMO nanoparticles, the sudden rise of the magnetization values indicate the destabilization of the charge ordered antiferromagnetic ground state at different magnetic field values depending upon the temperature. Whereas in core-shell compound such sudden increase of magnetization was not observed.

The magnetocaloric entropy changes ( $\Delta S$ ) of the compounds were calculated from the Maxwell's thermodynamic relation which is given below

$$\Delta S = \int_0^H (\partial M / \partial T) dH \quad (1)$$

The magnetocaloric entropy changes with respect to temperature at different constant magnetic field is given in Fig. 2. For com-

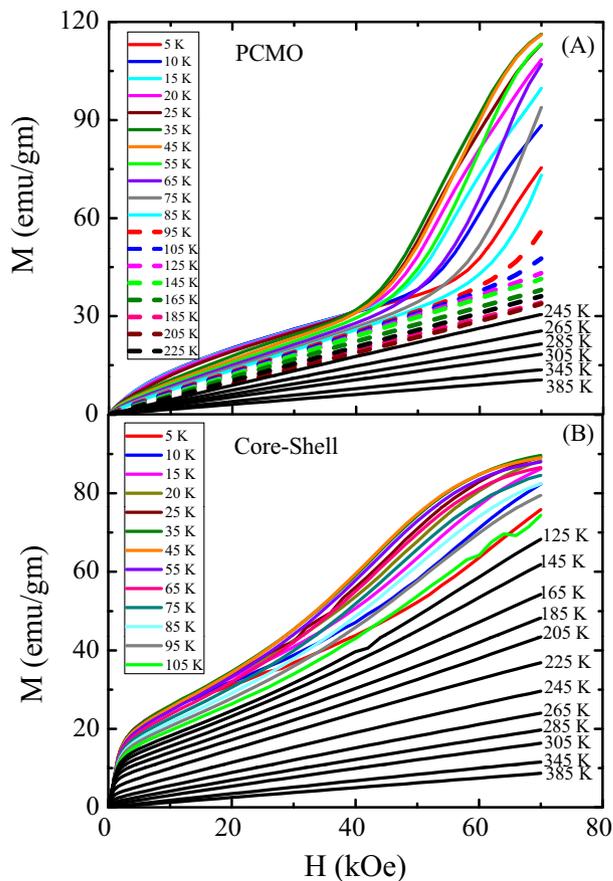
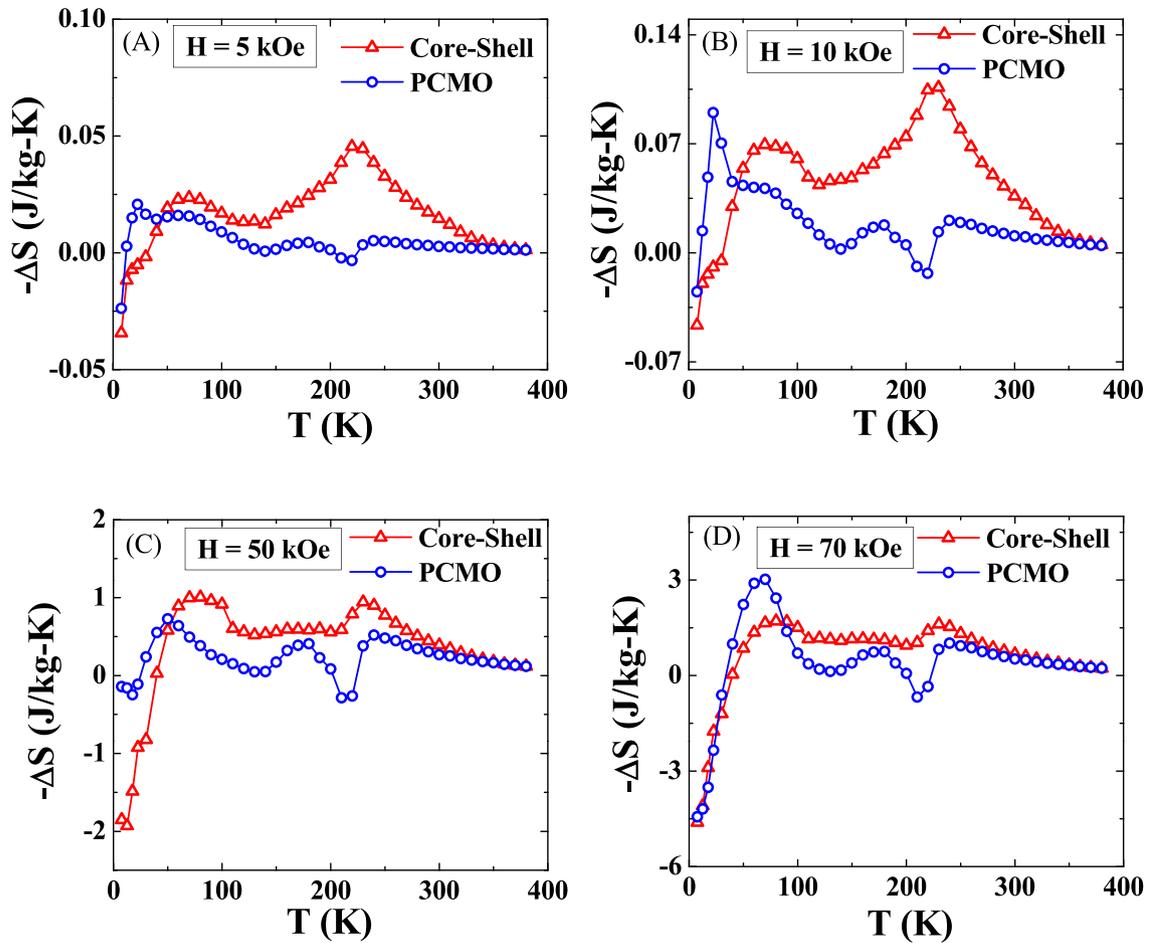


Fig. 1. Magnetization as a function of external magnetic field at several fixed temperatures for (A) PCMO nanoparticles and (B) core-shell nanostructures.

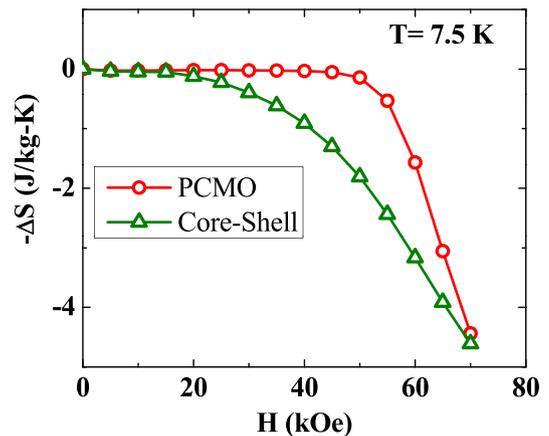


**Fig. 2.** Comparison of magnetocaloric entropy changes as a function of temperature at different external magnetic field for PCMO nanoparticles and core-shell nanostructures.

parison, the magnetocaloric entropy changes of the core-shell nanostructures with PCMO nanoparticles were shown in different panels of the Fig. 2. Our results indicate that the magnetic ground state of PCMO nanoparticles is markedly modifies with in the core-shell nanostructures. The nature of the temperature dependent magnetocaloric entropy changes signifying that the antiferromagnetic ground state of PCMO nanoparticles modifies and predominant ferromagnetic nature of  $-\Delta S(T)$  was observed.

To discuss the magnetocaloric properties it is worth mentioning that magnetocaloric effect can be used as a powerful tool to identify the nature of the magnetic ground state. In our present study, in case of PCMO nanoparticles, the variation of magnetic entropy changes ( $-\Delta S(T)$ ) clearly indicate the charge ordering and antiferromagnetic ordering with lowering the temperature. Moreover, the signature of spin reorientation transition below  $T = 50$  K, also present in the magnetocaloric effect for both the samples. On the other hand in core-shell type nanostructures, the magnetocaloric entropy changes enhances especially at the lower magnetic field values which is very important for the application point of view (especially at  $H = 5$  and  $10$  kOe).

Another important issue regarding this context is the large inverse magnetocaloric effect of the PCMO nanoparticles and core-shell compound was found at the low temperature region (at higher values of magnetic field) which is shown in Fig. 3. The large magnetocaloric effect of  $\text{Pr}_{0.68}\text{Ca}_{0.32}\text{MnO}_3$  compound was reported earlier also [28]. In our present manuscript we have compared the magnetocaloric entropy changes as a function of magnetic field. Our results indicate that in charge ordered PCMO



**Fig. 3.** Comparison of magnetocaloric entropy changes as a function of external magnetic field at  $T = 7.5$  K for PCMO nanoparticles and core-shell nanostructures.

nanoparticles, the magnetic entropy changes rapidly after the melting of the charge ordering ( $H > 50$  kOe). In contrast to that in core-shell nanostructures, the magnetic entropy changes from the lower magnetic field region.

In PCMO nanoparticles, the ground state is charge ordered antiferromagnetic (long range ordered state), the magnetic large magnetic randomness appears when the ground state is destabilize by the external magnetic field which inhibits the large magnetic

entropy changes at the low temperature for higher values of the external magnetic field. However in the core-shell nanostructures, the ferromagnetic environments created by the LSMO nanoparticles, partially destabilize the magnetic ground state of the PCMO nanoparticles and resulting the increases of magnetic randomness even at the lower values of the external magnetic field which is clearly shown in Fig. 3. The interfacial magnetic coupling in this phase separated compound may also plays the crucial role for the comparatively large inverse magnetocaloric effect at low magnetic field a reported earlier [26].

#### 4. Conclusions

In our present paper we have highlighted the enhancement of low field magnetocaloric effect in ferromagnetic-charge ordered core shell nanostructures where core is ferromagnetic  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  nanoparticles and shell matrix is charge ordered antiferromagnetic  $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ . Additionally the ground state of the charge ordered  $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  was drastically modified in core-shell nanostructures, inhibits the gradual changes of magnetic entropy at the low temperature with external magnetic field compared to  $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  nanoparticles.

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