Research articles

Magnetic and magnetocaloric properties of polycrystalline $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ compound: Observation of large inverse magnetocaloric effect

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ABSTRACT

Magnetic and magnetocaloric effect of polycrystalline $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ compound have been studied extensively. Temperature dependent magnetization study reveals that the ferromagnetic transition takes place at T ~ 220 K and an antiferromagnetic transition appears at T ~ 150 K. Associated with the ferromagnetic and antiferromagnetic transition, large normal and inverse magnetocaloric effect of the polycrystalline $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ compound are observed. Magnetocaloric effect of that compound is addressed by considering the competing nature of ferromagnetic metallic and charge ordered antiferromagnetic insulating domains at the low temperature region.

1. Introduction

The electronic band width controlled physical properties of several magnetic materials are being studied extensively [1–12]. Upon the competing nature of the different magnetic ground state, the physical properties of these magnetic materials are greatly modified under the influence of external electric field as well as magnetic field [12]. Regarding this context, $Pr_{1-x}Ca_xMnO_3$ is considered as one of the most well studied reduced band width (W) system [12,13]. By the application of the external magnetic field, insulating charge and orbital ordered states are being transformed into the ferromagnetic metallic state [12, 13]. The critical magnetic field (H_c) for the melting of the charge ordered state is quite high (~270 kOe) for the compound having doping concentration of x ~ 0.5. However, it is somewhat reduced at [for] the doping concentration of x ~ 0.3 [12]. On the other hand, $Pr_{1-x}Sr_xMnO_3$ compounds having doping concentration of x = 0.35 and 0.45, are manifested as a wide band system where the ground state is stabilized by the ferromagnetic double exchange mechanism [12]. By keeping the hole doping concentration (i.e 'x') fixed, numerous appealing transport and magnetic properties were reported by substituting Ca-ions with Sr-ions in the $Pr_{1-x}Ca_xMnO_3$ compound [12,13]. It is important to study particularly the $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ system because of its bi-critical nature of phase separated state [13]. The physical properties of this compound are modified remarkably under the application of the magnetic field due to competing nature of

its ground state [13]. It is worth mentioning from the application point of view that the phase separation scenario in doped perovskite manganite plays a vital role in several aspects namely for colossal magnetoresistance effect, significantly large magnetocaloric effect etc.

Nowadays, a study of magnetocaloric effect (MCE) in a comparatively cheaper and chemically stable materials has become mandatory in the aspect of ongoing research for the replacement of harmful gas cooling technology by the environmental friendly magnetic refrigerant materials [14–17]. MCE is almost a generic property of the magnetic materials when it is exposed in an external magnetic field [18]. MCE is quantified by the numerical value of the isothermal magnetic entropy change or the adiabatic temperature change of magnetic materials with magnetic field. In the presence of the external magnetic field, re-orientation of the magnetic moment responsible for the large value of MCE required for the material to be used as a good refrigerant [18]. Two distinct types of temperature dependent magnetic entropy changes ($-\Delta S$) are observed based on the configuration changes in the magnetic moment. For the ferromagnetic materials, $-\Delta S(T)$ variation is positive with a maxima (known as normal magnetocaloric effect) at the vicinity of Curie temperature (T_C) [14,18]. However, for the antiferromagnetic materials, the variation of $-\Delta S(T)$ is somewhat different. On reduction of temperature to Tc under magnetic field, there is a sign of positive increase in the value of the magnetic entropy change ($-\Delta S$). A sharp change from positive increase to negative increase in $-\Delta S$ near Néel temperature (T_N) indicates its large inverse magnetocaloric effect

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(IMCE) [18]. Regarding such phenomena, it is important to mention that low temperature can be easily attained by adiabatically magnetizing of such IMCE materials. Materials, exhibiting inverse magnetocaloric effect, can also act as a heat sink for conventional magnetocaloric refrigeration before cooling (under adiabatic condition) [19,20]. Moreover, efficiency of conventional magnetocaloric materials can also be tuned by suitable mixing the IMCE materials in composite form [19]. Therefore, IMCE is also technologically very important in the field of magnetic refrigeration.

In our present investigation, we have studied the magnetic and magnetocaloric effect of phase separated polycrystalline $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ compound. According to the reported phase diagram by Tomioka et al., the above mentioned compound lies at the phase boundary between charge ordered antiferromagnetic and ferromagnetic phase [13]. Moreover, there is a temperature dependent stability regime in the ferromagnetic and antiferromagnetic state [13]. Additionally, Biswas et al. reported the significant influence of the phase boundary in the magnetocaloric effect [21]. From this context, it is expected a rich magnetocaloric properties in the polycrystalline $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ compound. Our experimental result indicates that the compound goes to ferromagnetic state from paramagnetic state around 200 K (T_C) under cooling and thereafter, it goes to an antiferromagnetic ordering state around 150 K ($\sim T_N$). Near T_N, we have achieved significantly large IMCE which is not very common especially for manganite compound. More appealing context is that, in addition to the IMCE, this compound also exhibits considerably large conventional MCE near $T_C = 200$ K. The possible origin of the conventional MCE and IMCE were addressed by considering the bi-critical nature of the ground state of this compound [13].

2. Sample preparation and characterization

Polycrystalline $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ compound was prepared by the sol–gel route. High purity (99.9%) pre-heated Pr_6O_{11}, $CaCO_3$, $Sr(NO_3)_2$ and MnO_2 were used for the sample preparation. At first, the appropriate amount of the oxide and carbonate were converted to their nitrate forms by heating them separately with concentrated nitric acid. To dissolve the MnO_2, an extra amount of oxalic acid was added in the nitric acid solution. Finally, all the clear solutions of nitrate were mixed properly with a required amount of citric acid and evaporated slowly at 80–90 °C (using a water bath) until the gel was formed. After gel formation, it was decomposed at slightly higher temperature (~ 200 °C) and porous black powder was formed. The pelletized powder was annealed at 1300 °C for 36 h to get the polycrystalline $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ compound. Room temperature X-ray diffraction study was carried out by using Rigaku TTRAX-III diffractometer having Cu-K$_\alpha$ radiation ($\lambda = 1.54$ Å). Magnetic measurements were performed in a Physical Properties Measuring System (PPMS) of Cryogenic make.

3. Experimental results and discussion

Room temperature X-ray diffraction study indicates the single phase nature of this compound. To estimate the crystallographic parameters and unit cell dimension, experimental X-ray diffraction pattern was fitted with *Rietveld refinement* technique. The '*pbnm*' crystallographic symmetry was considered in the *Rietveld refinement* analysis [13]. The estimated lattice parameters are a = 5.4161 Å, b = 5.4181 Å and c = 7.6611 Å. X-ray diffraction data along with the profile fittings (red line) are shown in the Fig. 1.

Magnetization as a function of temperature was measured three different protocols which are Zero Field Cooled Warming (ZFCW), Field Cooled Cooling (FCC) and Field Cooled Warming (FCW). Before going to the experimental results regarding the magnetization, the measurement procedures in different protocols are described. In ZFCW, sample
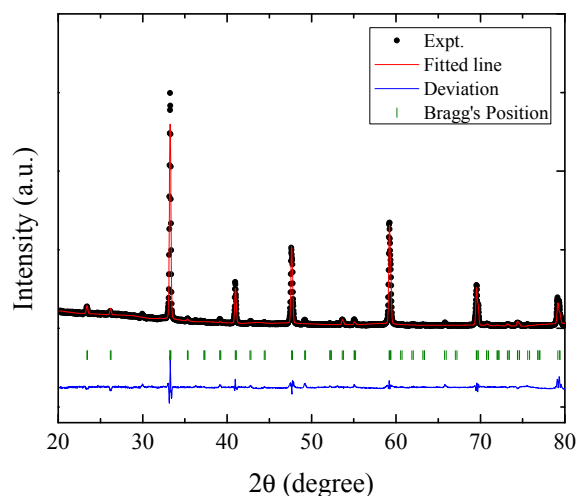

Fig. 1. Room temperature X-ray diffraction pattern (along with the profile fitting) of $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ compound.

was first cooled down from the paramagnetic state (T = 300 K) to 5 K in the absence of any external magnetic field. Later on, Magnetization data as a function of temperature data were collected during the warming of the sample from T = 5 K to T = 300 K in the presence of H = 50 kOe external magnetic field. Temperature dependent magnetization during cooling (in the same external magnetic field) was marked as FCC. Whereas in the FCW protocols, magnetization data were collected during heating in presence of same external magnetic field (i.e H = 50 kOe). Experimentally recorded temperature dependent magnetization curves in three different protocols are shown in Fig. 2(a). A small bifurcation between ZFCW and FCW indicates negligible anisotropy in the polycrystalline compound. To elucidate the variation of the antiferromagnetic transition in the presence of different external magnetic field, the temperature dependent magnetization at different field is given in Fig. 2(b) during FCC and FCW protocols. Magnetic phase transition temperatures were determined from the maximum of the derivative of magnetization (with respect of temperature) as a function of temperature plots. The extracted transition temperatures during FCC and FCW were plotted in inset of Fig. 2(b) as a function of external magnetic field. As reported earlier by Tomioka et al. about the critical features of the $Pr_{1-x}(Ca_{1-y}Sr_y)_xMnO_3$ ($x = 0.45$, $0 \leq y \leq 1$) compound, there exist a phase boundary near y = 0.25 [13]. For $y \geq 0.25$, compounds exhibits pronounced ferromagnetic ground state [13]. However charge ordered ground state is appears for $y \leq 0.25$. Both T_C (for $y \geq 0.25$) and T_{CO} (for $y \leq 0.25$) are systematically decreases towards the charge ordered-ferromagnetic boundary (at y = 0.25) and finally coincide with each other ($T_C \approx T_{CO} \approx 200$ K) [13]. In our present study temperature dependent magnetization indicates the ferromagnetic ordering at $T_C \sim 210$ K. On further reduction of temperature, the compound goes to its antiferromagnetic state below 150 K (during FCW cycle). However during cooling cycle (FCC), the antiferromagnetic ground state appears below at 100 K. Regarding this context, it is worth to mention that the ferromagnetic to antiferromagnetic transition occurs very sharply in temperature scale (i.e large change in dM/dT). To elucidate the transition temperatures, derivative of magnetization (with respect to temperature) are plotted against temperature which is shown in inset of the Fig. 2(a). (FCW and FCC).

To explore further about the nature of the ground state, we have carried out the field dependent isothermal magnetization (M(H)) measurements at several fixed temperatures. Some selected isotherms at three different temperature regions (i.e 100 K to 150 K, 150 K to 200 K and 150 K to 250 K) are shown in Fig. 3(a)–(c). A linear dependency of the magnetization with field was observed in the paramagnetic region whereas, a non linear behavior of M(H) was observed
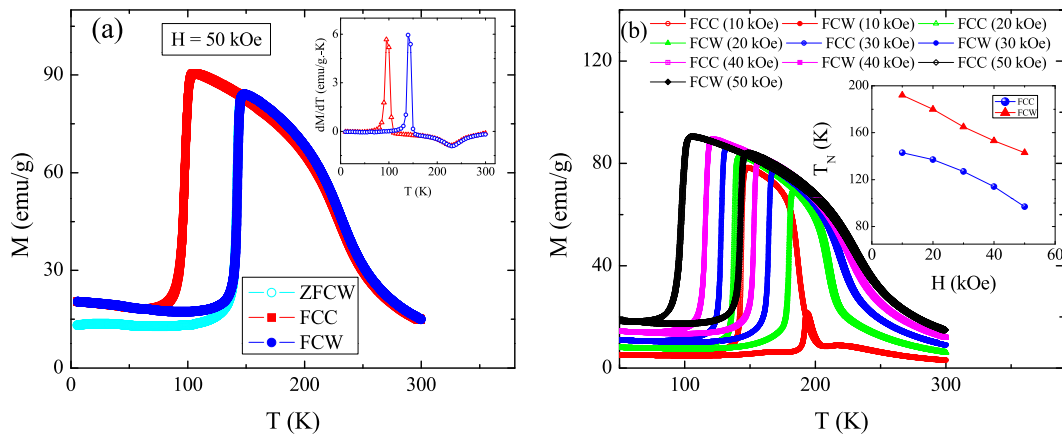
Fig. 2. (a) Magnetization as a function of temperature in the presence of H = 50 kOe external magnetic field in three different protocols. Inset indicates the temperature dependence of derivative of magnetization (FCC & FCW). (b) Magnetization as a function of temperature at different external magnetic field. Inset depicts the variation of the antiferromagnetic transition temperature with the external magnetic field.

close to the ferromagnetic region (Fig. 3(c)). The M(H) data for 170 K-200 K, illustrated an usual ferromagnetic nature of the compound. Interestingly below 170 K, magnetization increases almost linearly with the magnetic field up to a particular magnetic field (i.e critical field, H_C) and then magnetization jumps to a higher value depending upon the temperature (Fig. 3(b)). The critical field for the temperature T = 160 K and T = 140 K are $H_C \sim 30$ kOe and $H_C \sim 40$ kOe respectively. On further reduction of temperature, H_C is beyond our scope of the measurement limit (i.e 50 kOe).

From the temperature and field dependent magnetization measurements, it is clear that the ground state is quite unstable near the antiferromagnetic transition (i.e 100 K–150 K). In this temperature regime, a small external magnetic field can influence the ground state drastically. However at sufficiently lower temperature, the field requirement for destabilization the ground state may be much higher than 50 kOe.

We have studied also the magnetocaloric effect in the temperature region 100 K to 250 K. As MCE is quantified by the modification of magnetic randomness due to the application of the magnetic field, it is expected that the large MCE can be observed in this compound near T_N. Magnetocaloric entropy change ($-\Delta S$) was calculated by using Maxwell's thermodynamic relation $\Delta S = \int_0^H \frac{\partial M}{\partial T} dH$ from the isothermal magnetic measurements at different temperatures. Temperature dependent magnetocaloric entropy changes ($-\Delta S(T)$) at different external magnetic fields are shown in Fig. 4. Our experimental observation suggests that the conventional (MCE) as well as inverse (IMCE) type of magnetocaloric effects are present in this compound. At T ~ 200 K, the conventional magnetocaloric effect is possibly governed by the existence of the ferromagnetic nature of the compound. However, at T ~ 150 K, since the magnetic ground state transforms to the

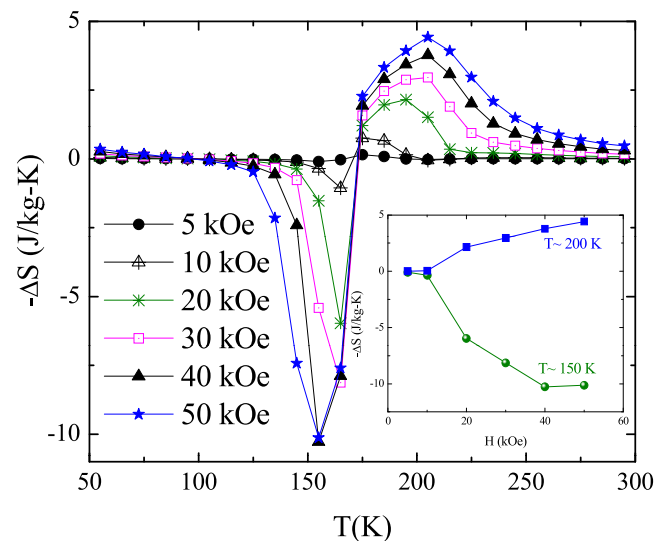**Fig. 4.** Temperature dependence of the magnetocaloric entropy change at different external magnetic field of $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ compound. Inset: maximum value of the magnetic entropy change with respect to external magnetic field at two different temperature regions (near T = 200 K and T = 150 K).

antiferromagnetic state sharply from its ferromagnetic state, a significant large inverse magnetocaloric effect is observed. The maximum entropy changes with external magnetic fields are shown in the inset of Fig. 4. Quantitatively, the value of IMCE is achieved as high as 10.2 J/
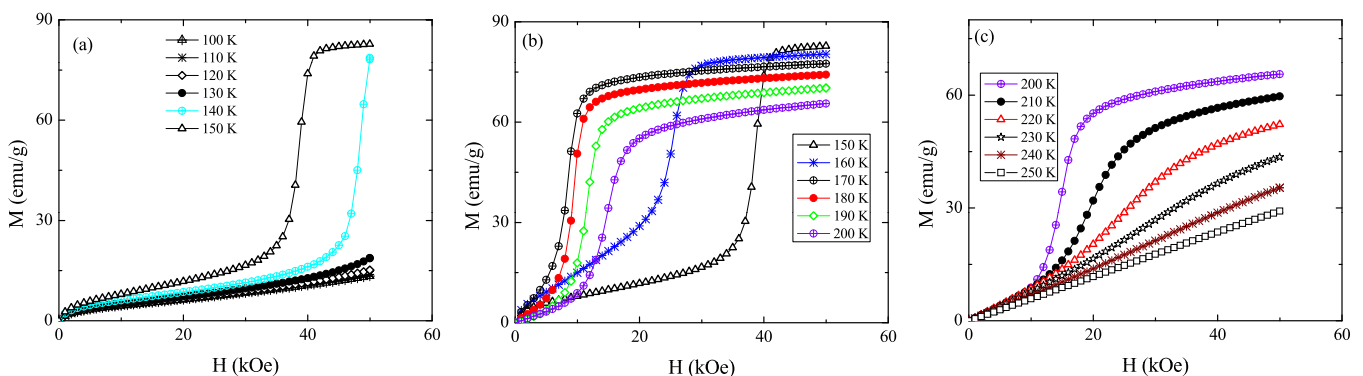

Fig. 3. (a)–(c) Magnetization as a function of external magnetic field at different temperature.

Table 1
Magnetocaloric entropy change of several compounds.

Compound	Temperature (K)	Magnetic field (kOe)	Magnetic entropy Change $|\Delta S|$ (J/kg-K)	Refs.
$Pr_{0.65}(Ca_{0.7}Sr_{0.3})_{0.35}MnO_3$	220	50	6.0	[22]
$Pr_{0.65}(Ca_{0.7}Sr_{0.3})_{0.35}MnO_3$	220	50	3.5	[22]
$La_{0.125}Ca_{0.875}MnO_3$	110	70	1.4	[23]
$La_{0.67}Sr_{0.33}MnO_3$	369	15	1.74	[24]
$La_{0.67}Ca_{0.33}MnO_{3-\delta}$	265	10	5	[25]
$La_{0.45}Sr_{0.55}MnO_3$	200	50	5.5	[26]
$La_{0.35}Pr_{0.275}Ca_{0.375}MnO_3$	215	50	6.2	[27]
$Nd_{0.5}Sr_{0.5}MnO_3$	155	10	2.8	[5]
$La_{0.87}Sr_{0.13}MnO_3$	195	10	2.0	[28]
$Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$	205	40	3.8	This work
$Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$	155	40	10.2	This work

kg-K for 40 kOe external magnetic field.

To compare the magnetocaloric response of the present studied material, a comprehensive table is made (Table 1) where the magnetocaloric entropy changes ($|\Delta S|$) of several materials are given. The material having coexistence of both type of magnetocaloric effect (i.e conventional and inverse) has incredibly importance from the application point of view [19–21]. According to our experimental observation, this low cost, stable, polycrystalline $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ compound can be considered as a promising candidate in the field of magnetic refrigerant due to its high magnetocaloric effect. To explore the fundamental origin of the large magnetocaloric effect of this compound, the following discussion is made. According to the magnetic and magneto-transport study reported by Tomioka et al. for $Pr_{1-x}(Ca_{1-y}Sr_y)_xMnO_3$ ($x = 0.45$, $0 \leq y \leq 1$), the increasing competition between the charge ordered state and ferromagnetic phases was found for $y = 0.25$ compound [13]. Such competing nature of the different magnetic phases increases the fluctuation of the respective components. The application of the external magnetic field reduces the spin fluctuation rapidly close to the vicinity of the phase transition temperature and corroborates the large magnetocaloric effect.

4. Conclusion

To summarize, magnetic and magnetocaloric effect have been studied extensively for the polycrystalline $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ compound. The magnetic properties indicate that the paramagnetic to ferromagnetic transition appears at $T_C \sim 210$ K and the ferromagnetic to antiferromagnetic ground state observes at $T_N = 150$ K. The transition of ferromagnetic to antiferromagnetic state (higher magnetization to lower magnetization) is very sharp. The influence of such transition is greatly reflected in magnetocaloric effect. The possible origin of the conventional MCE and IMCE were analyzed in light of the bi-critical nature of their ground state. Conventional and inverse magnetocaloric effects were found associated with T_C and T_N respectively. For the significantly large inverse magnetocaloric effect near T_N, this material may be suitable for the magnetic refrigeration.

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