Research articles

Magnetocaloric effect at low temperature in robust charge ordered Sm$_{1-x}$Ca$_x$MnO$_3$ compounds

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ABSTRACT

We have presented the magnetic properties and magnetocaloric effect of Sm$_{1-x}$Ca$_x$MnO$_3$ compounds (x = 0.50, 0.55, 0.60 and 0.70) in this work. In association to the experimental verification regarding the formation of the ferromagnetic droplets in robust charge ordered materials through exchange bias and training effect measurements, utilization of the magnetocaloric effect for treating the same problem have been addressed here. Our present study indicates that magnetocaloric effect (isothermal magnetic entropy change) at low temperature regime gets drastically modified according to the influence of the stability of the charge ordering in the host matrix. Additionally, the modifications of the ground states was also addressed accordingly.

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1. Introduction

Magnetocaloric effect (MCE), which is a general phenomena of magnetic materials and defined as the isothermal magnetic entropy change (ΔS) or adiabatic temperature change (ΔT_{ad}) in the presence of an external magnetic field. In recent time, MCE study has become an utmost important from the technological perspectives for the development of the magnetic materials based cooling technology over the gas compression procedure. Moreover, from fundamental interest, MCE is also treated as a powerful tool to elucidate the nature of the magnetic ground state of a magnetic material and its modifications with the external magnetic field, pressure, dimensions *etc.* [1–3]. In the indirect method, the magnetocaloric parameters (ΔS and ΔT_{ad}) are generally deduced from the magnetic isotherm data or temperature and magnetic field dependence heat capacity data. From the heat capacity measurements, both parameters (ΔS and ΔT_{ad}) can be derived from the calculation of the total entropy (S) variation of the material with temperature (T). Total entropy of a magnetic material can be calculated from the heat capacity data by using the relation

$$S(0) = \int_0^T \frac{C(0)}{T} dT \qquad (1)$$

where, S(0) and C(0) represents the entropy and heat capacity in the absence of external magnetic field. Similarly total entropy variation in the presence of magnetic field (S(H) *vs.* T) can be calculated by the heat capacity data in the presence of magnetic field (C(H) *vs.* T). Whereas, from the magnetic isotherms (measured at different temperature) only magnetic entropy change, ΔS can be evaluated by using the Maxwell's thermodynamic relation which is given bellow

$$\Delta S = \int_0^H (\partial M/\partial T) dH \qquad (2)$$

From the fundamental aspects, magnetocaloric effect for numerous magnetic materials were extensively studied during previous two decades to explore the different kind of modification in the presence of magnetic field and temperature [1,4–7]. Regarding this context it should also be mentioned that numerical value of the magnetic entropy change is directly related with the bulk magnetization value of the compounds and the rate of its change with the temperature as given in Eq. (2).

During previous few years, the physical properties namely magnetic, magneto-transport, magnetocaloric effect *etc.* of doped perovskite manganite gets a notified attention from fundamental as well as technological perspectives [9–31]. Regarding the doped perovskite manganite, specially in case of charge ordered compounds at the low temperature below T = 100 K, the magnetization value generally increases (having small value) though the background is charge ordered antiferromagnetic [8,32,33]. To address such anomalous nature a few discrete studies have been reported earlier [8,32]. However, efforts to probe such general phenomena conclusively is quite rare.

Considering the above mentioned context the fundamental aim of the present study is to explore the magnetic and magnetocaloric responses for different charge ordered compounds at the low temperature. Our study confirms that the magnetic entropy change is directly correlated with the stability of the charge ordered state.

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Not only the magnetocaloric effect, bulk magnetization values also get influenced accordingly.

To emphasize this, as a demonstrative example, the study of MCE of robust charge ordered compound $Sm_{1-x}Ca_xMnO_3$ (x = 0.50, 0.55, 0.60, 0.70) are presented. According to the earlier reports on $Sm_{1-x}Ca_xMnO_3$, the charge ordering stability for x = 0.6 is most robust [34]. Recently Dasgupta et al. reported the exchange bias study of numerous compounds of $Sm_{1-x}Ca_xMnO_3$ and an attempt was taken to probe the magnetic ground state modification with doping concentration [8]. According to this study the formation of the ferromagnetic droplets and variation of droplet sizes and density in the low temperature region (T < 30 K) are mainly responsible for the anomalous exchange bias effect in these compounds. The detail exchange bias effect in these compounds indicate that with increasing of the stability, exchange bias increases up to doping concentration 'x' = 0.60 and for higher doping 'x' = 0.70, exchange bias is reduced.

From this study it is very clear that the bulk (macroscopic) magnetization value influence the physical properties (exchange bias effect) of the compound. In context of MCE, it is also expected that since this property is correlated to the macroscopic value of the magnetization of the sample, it should also gets influenced with the stability of the charge ordering (as the formation of the ferromagnetic droplets density and size depends on stability of charge ordering). The experimental results suggest that the magnetic entropy change at low temperature region is smallest for more robust compound x = 0.60 (correlated with the smallest spread of bulk magnetization value with temperature).

2. Sample preparation, characterizations and measurements

Polycrystalline bulk $Sm_{1-x}Ca_xMnO_3$ (x = 0.50, 0.55, 0.60, 0.70) compounds were prepared by sol–gel route. For sample preparation, the starting elements were Sm_2O_3, $CaCO_3$ and MnO_2 having purity 99.99%. Pre-heated constituent elements were converted to their nitrates form by using HNO_3 and dissolved into millipore water (in case of MnO_2, suitable amount of oxalic acid was given). After proper dissolving, appropriate amount of citric acid was added and homogeneously mixed-up solution was slowly evaporated in a water bath (at 80–90 °C) until the gel was formed. After formation of gel, it was decomposed at slightly higher temperature (∼200 °C) and black porous powder was formed. The pelletized powder was annealed at 1300 °C for 36 h. to get crystalline compound.

Room temperature X-ray diffraction study was performed employing a Rigaku-TTRAX-III diffractometer which indicates the single phase nature of the all samples. Magnetic and magnetocaloric effect study were performed in a Super conducting Quantum Interference Device (SQUID) magnetometer (Quantum Design).

3. Results and discussion

3.1. X-ray diffraction and studies of magnetic properties

In addition to the single phase nature of the compounds, from the X-ray diffraction studies we have estimated the lattice parameters for all the compounds using the Rietveld refinement. The Rietveld refinement of the X-ray diffraction data were carried out considering the 'Pnma' space group symmetry. X-ray diffraction data for all the studied samples along with the Rietveld refinement patterns were shown in supplementary information part of Ref. [8]. The calculated lattice parameters are listed in Table 1.

Magnetization as a function of temperature at H = 1 kOe external magnetic field is shown in Fig. 1 for the $Sm_{1-x}Ca_xMnO_3$

Table 1
List of the lattice parameters of the $Sm_{1-x}Ca_xMnO_3$ (x = 0.50, 0.55, 0.60, 0.70) compounds.

Compound	a (Å)	b (Å)	c (Å)
$Sm_{0.50}Ca_{0.50}MnO_3$	5.364	7.561	5.420
$Sm_{0.45}Ca_{0.55}MnO_3$	5.356	7.547	5.403
$Sm_{0.40}Ca_{0.60}MnO_3$	5.349	7.532	5.387
$Sm_{0.30}Ca_{0.70}MnO_3$	5.364	7.609	5.513

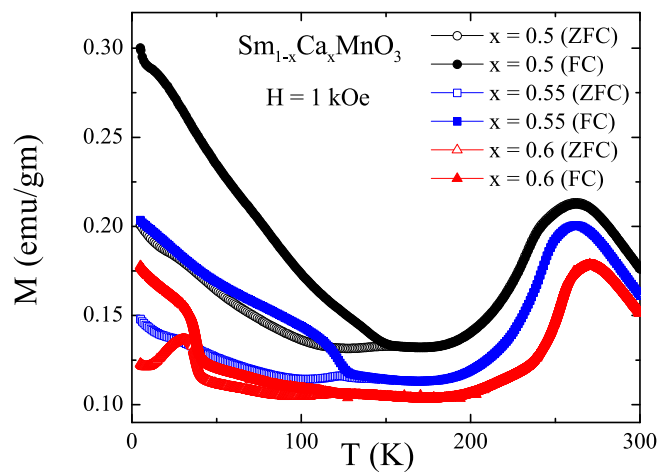**Fig. 1.** Magnetization (ZFC and FC) as a function of temperature in the presence of external magnetic field H = 1 kOe for $Sm_{1-x}Ca_xMnO_3$ (x = 0.50, 0.55, 0.60) compounds.

(x = 0.50, 0.55, 0.60) compounds. The magnetization was measured under both zero-field-cooled (ZFC) and field-cooled (FC) protocols. In case of the ZFC measurements, the samples were first cooled down to T = 5 K from the room temperature (T = 300 K) in the absence of any external magnetic field. After stabilization of the temperature at T = 5 K, the magnetic field H = 1 kOe was applied and magnetization data was recorded during warming cycle (from 5 K to 300 K, sweeping rate 5 K/ min.). Whereas in FC protocol, the sample was cooled down from 300 K to 5 K in the presence of 1 kOe external magnetic field and magnetization data was recorded during warming from 5 K to 300 K. The irreversibility of magnetization in FC and ZFC protocols were found for all the samples. This irreversibility indicates some spin freezing nature of the samples as reported earlier for such compounds [8]. Regarding the numerical values of magnetizations (weight normalized) it should be mentioned that the magnetization value decreases with the concentration of 'x' (from 'x' = 0.50 to 0.60). Moreover, with the increase of doping concentration 'x' the bifurcation point (ZFC and FC) also shifted towards the lower temperature region. Additionally at the high temperature region, compounds exhibit as usual charge ordering signature which manifested as a peak in the temperature dependence of the magnetization.

Now to concentrate on the filed dependence of magnetic properties for the compounds, magnetization as a function of external magnetic field at different temperatures were recorded. Very interestingly, in the low temperature region (5–30 K) the magnetization decreases with increasing temperature for the all studied compounds. However in the high temperature region (T ⩾ 100 K) the magnetization increases with the temperature increment. The magnetization as a function of magnetic field for all compounds is given in Fig. 2 for two different temperature regions separately. Regarding this context another important point should also be mentioned about the spread of magnetization (with increasing temperature), especially in the low temperature region (given in
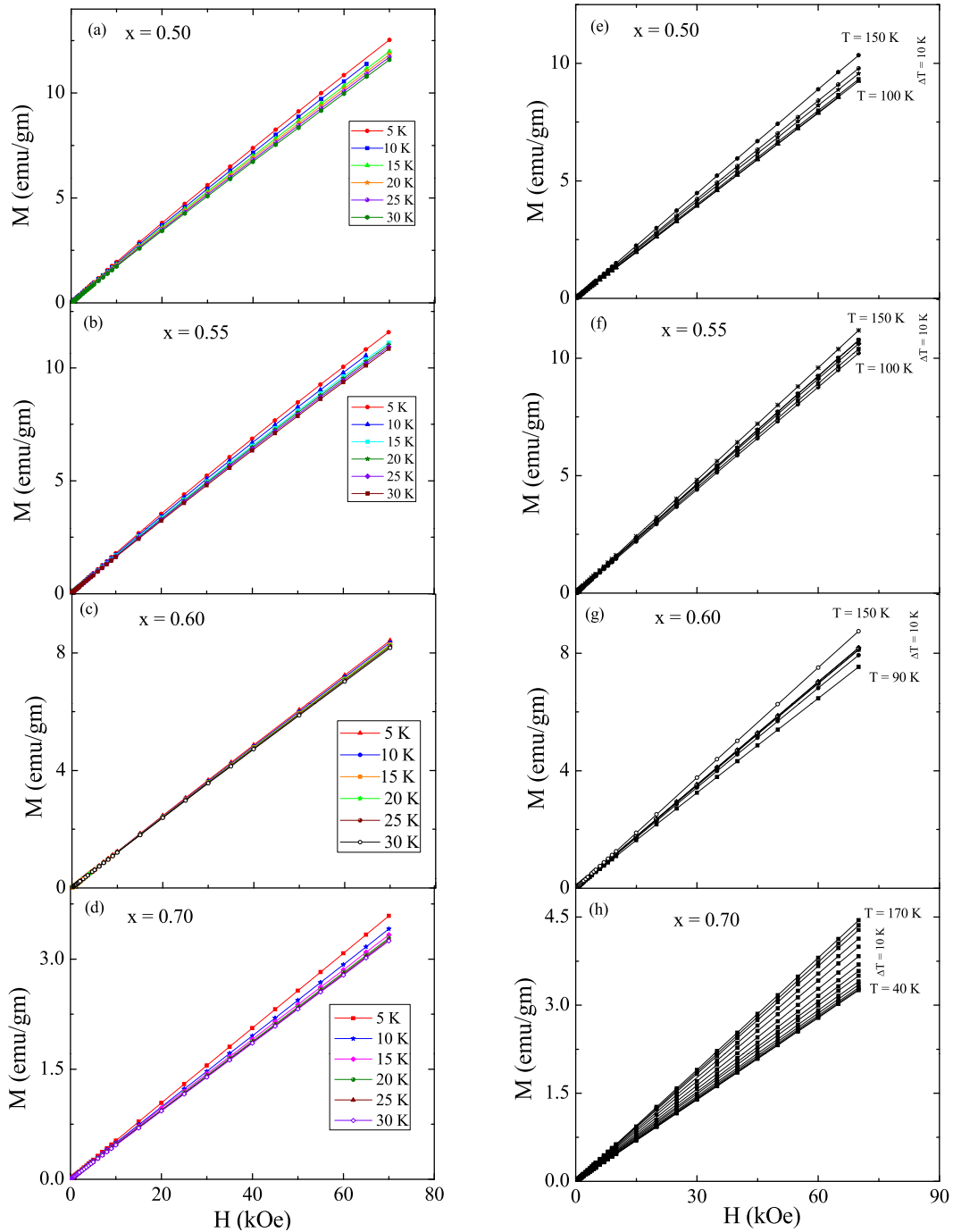
Fig. 2. Some selected curves of magnetization as a function of external magnetic field at different temperature for $Sm_{1-x}Ca_xMnO_3$ (x = 0.50, 0.55, 0.60, 0.70) compounds.

Fig. 2(a)–(d)), is lowest for the x = 0.60 compound. However, the increasing tendency of magnetization in high temperature region (given in Fig. 2(e)–(h)) may be ascribed as the dominating charge ordered antiferromagnetic counterparts of the compounds.

As describe in the introduction, the qualitative nature of the magnetocaloric entropy change of a magnetic material can be easily visualize from the nature of the field dependence of magnetization data. For this present study two important things can be outlined. First, normal magnetocaloric effect expected for all compounds at the low temperature region and inverse magnetocaloric effect should be observed at high temperature region. Secondly, the magnetic entropy change ($-\Delta S$) should be smallest for the x = 0.60

compound at the low temperature region as rate of change of magnetization is smallest for this compound.

3.2. Magnetocaloric effect study

We have calculated the magnetocaloric effect of $Sm_{1-x}Ca_xMnO_3$ (x = 0.50, 0.55, 0.60, 0.70) compounds from T ~ 5 K to T ~ 170 K range from the magnetic isotherms. Magnetic entropy change (ΔS) has been evaluated by using the Maxwell's thermodynamic relation given in Eq. (2). The magnetic entropy change ($-\Delta S$) as a function of temperature for 70 kOe external magnetic field is shown in Fig. 3. From the magnetic entropy change ($-\Delta S$) as a
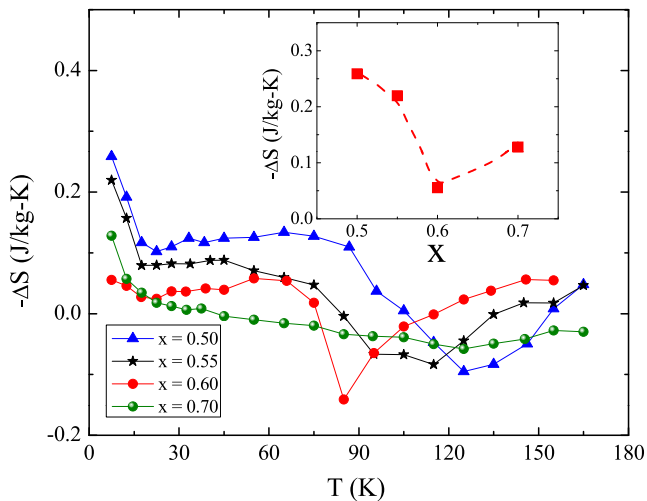
Fig. 3. Magnetic entropy change as a function of temperature at H = 70 kOe external magnetic field for $Sm_{1-x}Ca_xMnO_3$ (x = 0.50, 0.55, 0.60, 0.70) compounds. Inset indicate the variation of magnetic entropy changes (at T = 7.5 K) with doping concentration 'x'.
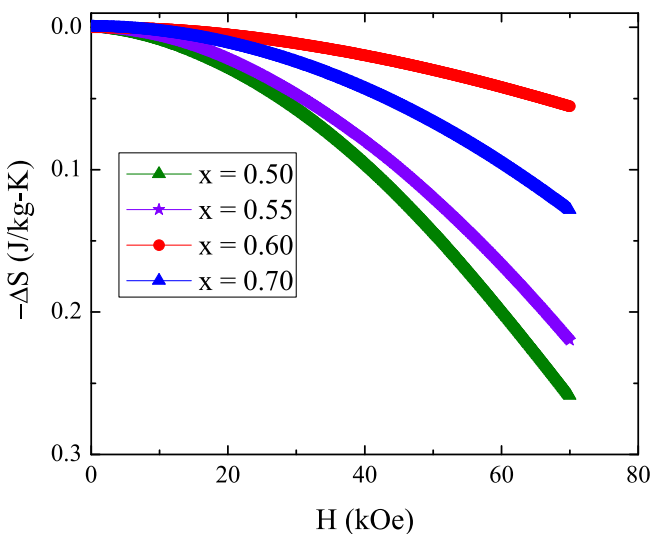

Fig. 4. Magnetic entropy change as a function of external magnetic field at T = 7.5 K for $Sm_{1-x}Ca_xMnO_3$ (x = 0.50, 0.55, 0.60, 0.70) compounds.

function of temperature (as given in Fig. 3) indicates the inverse magnetocaloric effect at the high temperature region as expected from the M(H) data as plotted in Fig. 2(e)–(h). However, from the low temperature region value of $-\Delta S$ is positive for all the studied compounds (specially at T ⩽ 30 K). Regarding this fact, it should also be mentioned that the quantitative value of $-\Delta S$ is different according to the doping concentration 'x'. The variation of $-\Delta S$ at T = 7.5 K with doping concentration 'x' is given in inset of the Fig. 3 which indicates that the smallest magnetocaloric entropy change appears for x = 0.60 compound. Such smallest change of magnetic entropy may be interpreted as the small change appears in the M(H) data (with temperature) given in Fig. 2(c) compared to other samples. This behavior of magnetic isotherms and smallest change in magnetocaloric entropy also infer the stability of charge ordering.

Not only at the high magnetic field, such nature also present even lower values of the magnetic field. The field dependence magnetic entropy change (ΔS) at T = 7.5 K is given in Fig. 4 for all the studied compounds. Interestingly the variation of $\Delta S(H)$ indicates

that the entropy change is smallest for the x = 0.60 compound even at low field region. From the magnetic isotherms and variation of magnetic entropy change (with temperature and magnetic field) it can be argued that stability of charge ordering influence these physical properties of the compounds. Particularly for x = 0.60 compound as the stability of charge ordering is more, the rate of change of magnetization with temperature (at low temperature region) is quite small (given in Fig. 2(c)) which inhibits smallest change of magnetic entropy as given in Figs. 3 and 4.

Regarding the numerical values of the magnetic entropy change, it should important to mention that the experimentally observed values are very small for the $Sm_{1-x}Ca_xMnO_3$ (x = 0.50, 0.55, 0.60, 0.70) compounds. As mentioned earlier, magnetocaloric effect is the measure of the suppression of the magnetic randomness via the application of the external magnetic field. Generally large magnetocaloric effect can be expected for the systems where high magnetic randomness is present. Previously it was reported that the large relative cooling power as well as large magnetocaloric effect can be achieved due to the suppression of the magnetic randomness in geometrically frustrated magnetic materials and even in the nanoparticles of the charge ordered compounds [3,7,9]. Whereas, the materials having stable long range magnetic ordering exhibit small magnetic entropy change even for the larger applied magnetic field value. In case of the $Sm_{1-x}Ca_xMnO_3$ (x = 0.50, 0.55, 0.60, 0.70) compounds, the charge ordered antiferromagnetic ground state (having long range ordering) is quite stable and result in the smaller value of the magnetic entropy change of the compounds.

4. Conclusions

To summarize, magnetic and magnetocaloric effect study have been performed for $Sm_{1-x}Ca_xMnO_3$ (x = 0.50, 0.55, 0.60, 0.70) compounds. The variation of the magnetic entropy change at low temperature for different compounds were analyzed considering the bulk magnetization values and change of it with the temperature for the compounds. Additionally the systematic dependence with the doping concentration and magnetization was presented. Hence it may be ascribe that the MCE properties also depends on the stability of charge ordering for robust charge ordered materials and it may be used as a tool from fundamental aspects.

Acknowledgements

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