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Magnetocaloric effect in potassium doped lanthanum manganite perovskites prepared by a pyrophoric method

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Abstract

The magnetocaloric effect (MCE) in fine grained perovskite manganites of the type $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($0 < x < 0.15$) prepared by a pyrophoric method has been investigated. Potassium addition in lanthanum manganite enhances the Curie temperature (T_C) of the system from 260.4 K ($x = 0.05$) to 309.7 K ($x = 0.15$). A large magnetic entropy change associated with the ferromagnetic–paramagnetic transition has been observed. The maximum entropy change $|\Delta S_M^{\text{Max}}|$ in an applied field of 1 T shows an enhancement by $\sim 10\%$ with increase in K content up to $x = 0.15$. $\text{La}_{0.85}\text{K}_{0.15}\text{MnO}_3$ exhibits the largest $|\Delta S_M^{\text{Max}}|$ value of $3.00 \text{ J kg}^{-1} \text{ K}^{-1}$ at 310 K amongst the compounds investigated. Moreover, the maximum magnetic entropy change exhibits a linear dependence with applied magnetic field. The estimated adiabatic temperature change at T_C and at 1 T field also increases with K doping, being a maximum of 2.1 K for the $\text{La}_{0.85}\text{K}_{0.15}\text{MnO}_3$ compound. The relative cooling power (RCP) of $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compounds is estimated to be about one-third of that of the prototype magnetic refrigerant material (pure Gd). However, $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compounds possess an MCE around room temperature, which is comparable to that of Gd. Further, tailoring of their T_C , higher chemical stability, lower eddy current heating and lower cost of synthesis are some of the attractive features of K doped lanthanum manganites that are advantageous for a magnetic refrigerant. The temperature dependence of the magnetic entropy change (ΔS_M) measured under various magnetic fields is explained fairly well using the Landau theory of phase transitions. Contributions of magnetoelastic and electron interaction are found to have a strong influence in the magnetocaloric effect of manganites.

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1. Introduction

Magnetic refrigeration based on the magnetocaloric effect (MCE) is a viable and competitive cooling technology in the near room temperature region and it has recently attracted much research interest due to its potential advantage of environmental friendliness over gas refrigeration [1, 2]. The magnetocaloric effect is intrinsic to magnetic solids and is induced via coupling of a magnetic sublattice with the magnetic field which alters the magnetic part of the total entropy due to a corresponding change of the magnetic field. The heavy rare-earth elements and their compounds, due to their high magnetic moments, are so far the best candidates for possessing an MCE [3, 4]. However, further investigation for new materials without rare-earth elements [5–8] having large MCE at a relatively small magnetic field has importance from the technological point of view. Doped lanthanum manganites, due to their colossal magnetoresistance, as well as the large change in temperature in adiabatic conditions under moderate external magnetic field, are also expected to be promising candidates in magnetic refrigeration technology [9–11]. While the pure LaMnO_3 is an antiferromagnetic insulator, the doping on the La-site gives rise to a mixed valence of Mn^{3+} ($t_{2g}^3 e_g^1$) and Mn^{4+} (t_{2g}^3), out of which the e_g electrons can be delocalized due to strong hybridization with oxygen 2p states and can therefore mediate the ferromagnetic interaction between localized t_{2g} spins. The effective interaction between the antiferromagnetic super exchange coupling and ferromagnetic double exchange gives rise to various magnetic structures and corresponding different properties with doping [12, 13]. The simultaneous magnetic transition and discontinuous volume variation at the Curie temperature (T_C) can strongly influence the magnetic entropy change [14, 15] and are found to be comparable with the changes observed in other solid magnetic refrigerants [5, 9, 16, 17]. The advantages of manganites are their higher chemical stability, lower eddy current heating due to higher resistivity, low cost, and tunable T_C [16, 18–21]. Therefore, a refrigeration unit composed of several manganites with different T_C can be spanned over a wide range of temperature (namely, 260–340 K).

The magnetic entropy changes in divalent alkaline-earth doped lanthanide manganites with various compositions have been reported widely [18–28]. However, detailed investigations on monovalent alkali-metal doped manganites are relatively few [9, 29, 30]. In the present communication, we report our recent results on the magnetocaloric effect in potassium doped lanthanum manganites of various compositions and having their T_C ranging between 260 and 309 K. A large magnetic entropy change around T_C under a moderate field of 1 T is obtained. The Landau theory for phase transitions, which takes into account the contribution of magnetoelastic and magneto-electronic couplings [26, 27], explains the magnetic entropy change observed in $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compounds very well.

2. Experimental details

Powder samples of $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.05, 0.10, 0.15$) were prepared through thermolysis of an aqueous, polymeric-bond precursor solution starting from water-soluble coordinated complexes of the composing metal ions. La_2O_3 and KNO_3 in appropriate molar ratios were dissolved into dilute nitric acid to obtain the stocks of respective metal nitrates. Separately, aqueous solutions of the $\text{Mn}(\text{CH}_3\text{COO})_2$ tetrahydrate (99% purity) (0.01 M) were prepared by dissolving stoichiometric amounts of the salt in distilled water. The nitrate stocks and the manganous acetate solution were mixed and heated to about 80 °C. Into the hot solution, calculated amount of poly-vinyl alcohol (PVA), tri-ethanol amine (TEA) and sucrose were added to obtain the final stock solution. An appropriate amount of this final solution was then heated over a hot plate (~200 °C) with continuous stirring and was eventually evaporated to

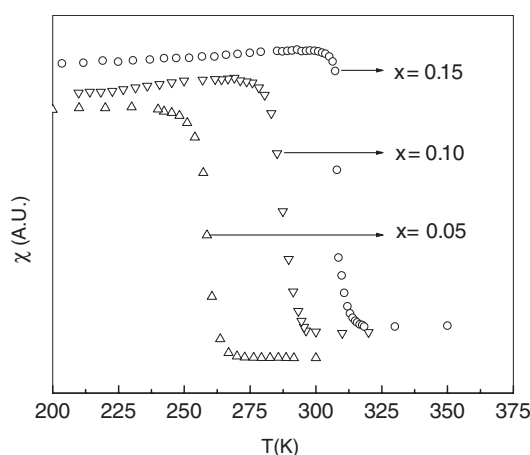


Figure 1. Temperature dependence of AC susceptibility for $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.05, 0.10$ and 0.15) compounds.

dryness. On complete evaporation, the precursor solution gave rise to a fluffy charred organic mass that had the desired metal ions embedded in its matrix. The carbon-rich mass was then crushed to constitute the precursor powders. Subsequent calcinations of the precursors at 800°C (8 h) resulted in carbon-free, nanosized powders with the desired compositions. Pellets prepared from these precursor powders were heat treated in air at 1000°C for 20 h and were subsequently furnace cooled to room temperature. Details of the x-ray diffraction characterization of the prepared samples are given in [31].

The AC susceptibility of all the samples was measured using a susceptometer operating at 111 Hz and a driving field of 0.10 G. The Curie temperature (T_C) was deduced from the minimum of the $\frac{\partial\chi}{\partial T}$ curves. Magnetization measurements were performed with an in-house fabricated vibrating sample magnetometer built over a Janis (model VT 100) gas flow liquid nitrogen cryostat, equipped with precision control of temperatures between 77 and 300 K. The isothermal magnetization at various magnetic fields (maximum 1 T) was measured for $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.05$ and 0.10) samples having T_C below 300 K. The measurements were taken around T_C with an interval of $1/3$ K. Sample temperature was controlled to within ± 0.1 K, with the help of a PID temperature controller (Lakeshore model 331). However, because of the lack of appropriate temperature control facility for $T > 300$ K, magnetization as a function of temperature between 300 and 340 K was measured for the $\text{La}_{0.85}\text{K}_{0.15}\text{MnO}_3$ ($T_C = 309.7$ K) sample under various fixed magnetic fields. The temperature between 300 and 340 K was raised very slowly over a period of 40 min by controlled heating using a hot air blower. All the experiments were conducted under computer control.

3. Results and discussion

Figure 1 shows the temperature dependence of the AC susceptibility of the $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compound with $x = 0.05, 0.10$ and 0.15 . The Curie temperature (T_C), defined as the temperature at which $d\chi/dT$ shows a minimum, increases from 260.4 to 309.7 K as the potassium content increases from 0.05 to 0.15. It may be noted that the ratio $\text{Mn}^{4+}/\text{Mn}^{3+}$ in the present K doped lanthanum manganites gradually increases (table 1) with increasing K content. The increase of Mn^{4+} fraction suggests an increase in the number of Mn^{3+} –

Table 1. Structural and some physical parameters of $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compounds, prepared by a pyrophoric method.

Sample x	Crystallite size (nm)	T_{MI} (K)	T_{C} (K)	$\text{Mn}^{4+}/\text{Mn}^{3+}$	Oxygen content
0.05	10	239.8	260.4	0.11	3.007
0.10	12	261.9	287.4	0.25	3.008
0.15	13	276.0	309.7	0.43	3.006

Mn^{4+} ion pairs, which causes enhancement of the double-exchange interaction and results in raising the Curie temperature (T_{C}) of the system. In the case of polycrystalline $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ samples, substitution of the smaller La^{3+} ion (ionic radius $\sim 1.016 \text{ \AA}$) by the larger K^{1+} ion (ionic radius $\sim 1.33 \text{ \AA}$) increases the average ionic radius of the La site, thereby introducing a crystallographic distortion and an increase in the Mn–O–Mn bond angle in the system [30]. In the framework of the theory of double-exchange interaction, a shorter Mn–O distance (larger Mn–O–Mn bond angle) leads to a stronger interaction and consequently higher T_{C} . Similar observations have also been reported by Itoh *et al* [32]. The temperature dependence of the electrical resistivity of $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compounds exhibits a metal–insulator transition (T_{MI}), details of which have been reported earlier [31]. It may be noted from table 1 that for the present compounds (grain size 10–13 nm), T_{C} and T_{MI} differ by >20 K. According to Zener [12], the metallicity in manganites occurs at the onset of ferromagnetism with T_{MI} coinciding with T_{C} . Detailed investigation on manganites having different grain size by Mahendiran *et al* [33] confirmed that the grain size plays a very significant role in determining their magnetic and electric behaviour and that T_{C} coincides with T_{MI} only when the sample has large grain size with a ferromagnetic state associated with long range order.

Figures 2(a) and (b) show the measured isothermal magnetization for $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.05$ and 0.10) for various magnetic fields up to 1 T and at various temperatures around their respective Curie temperatures. Figure 2(c) shows the isofield magnetization data for the $\text{La}_{0.85}\text{K}_{0.15}\text{MnO}_3$ compound ($T_{\text{C}} = 309.7$ K) measured between 300 and 340 K. For magnetization measured at discrete field and temperature intervals (for samples with $x = 0.05$ and 0.10), the magnetic entropy change ΔS_{M} can be approximated by using the numerical formula [34]

$$-\Delta S_{\text{M}} = \sum_i \frac{1}{T_{i+1} - T_i} (M_i - M_{i+1}) \Delta H_i \quad (1)$$

where M_i and M_{i+1} are the magnetization values obtained at temperatures T_i and T_{i+1} in a field H_i , respectively. Similarly, from the temperature dependence of magnetization measured under different magnetic fields for the $\text{La}_{0.85}\text{K}_{0.15}\text{MnO}_3$ compound, the magnetic entropy change (ΔS_{M}) is calculated from

$$-\Delta S_{\text{M}} = \sum_i \left[\left(\frac{\partial M}{\partial T} \right)_{H_i} + \left(\frac{\partial M}{\partial T} \right)_{H_{i+1}} \right] \times \frac{1}{2} \times \Delta H_i \quad (2)$$

where $\left(\frac{\partial M}{\partial T} \right)_{H_i}$ is the experimental value obtained from the isofield M – T curve under the magnetic field H_i . Figures 3(a) and (b) show ΔS_{M} as a function of temperature under different magnetic fields for samples with $x = 0.05$ and 0.10 , calculated using equation (1). Figure 3(c) shows the ΔS_{M} versus T curve for the $\text{La}_{0.85}\text{K}_{0.15}\text{MnO}_3$ sample obtained from equation (2). As expected, the maximum magnetic entropy change $\Delta S_{\text{M}}^{\text{max}}$ for all the samples obtained (table 2) is close to their respective Curie temperatures (T_{C}), where the variation of magnetization with temperature is the fastest.

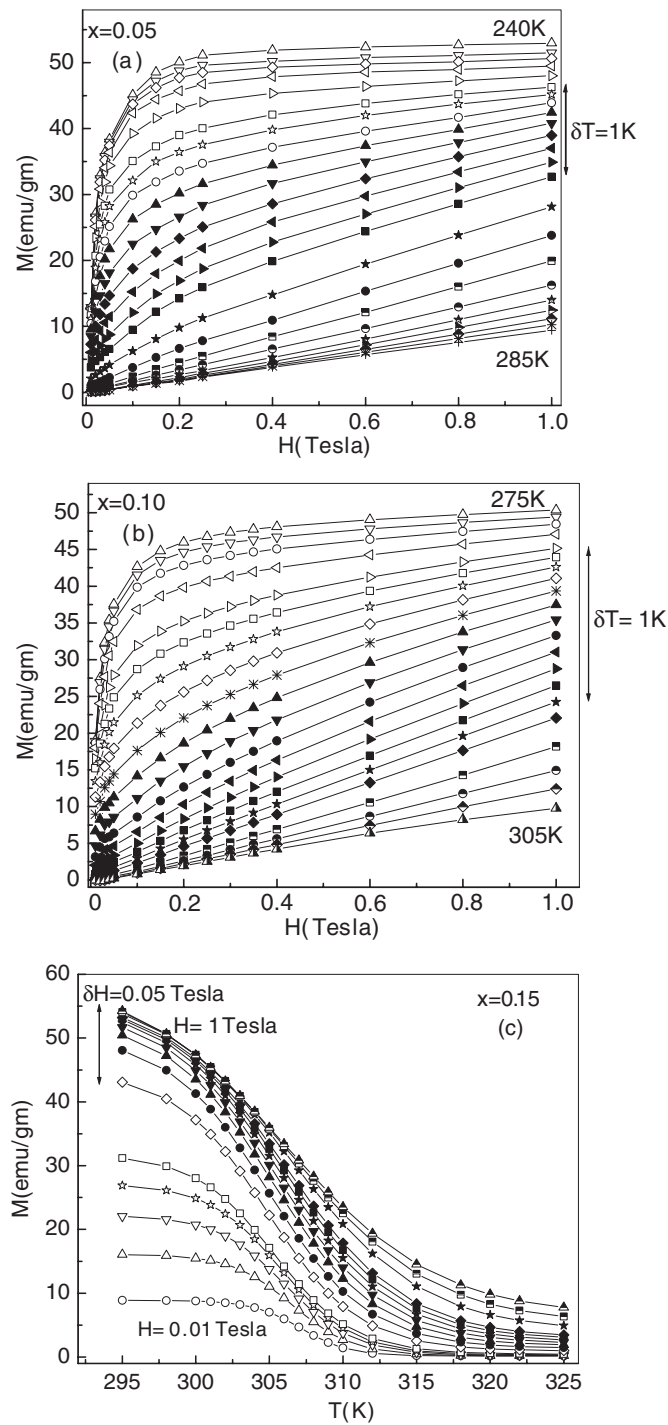


Figure 2. (a) The isothermal magnetization curves measured at different temperatures for $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.05$ and 0.10). (b) The temperature dependence of magnetization measured at different magnetic fields for the $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.15$) sample.

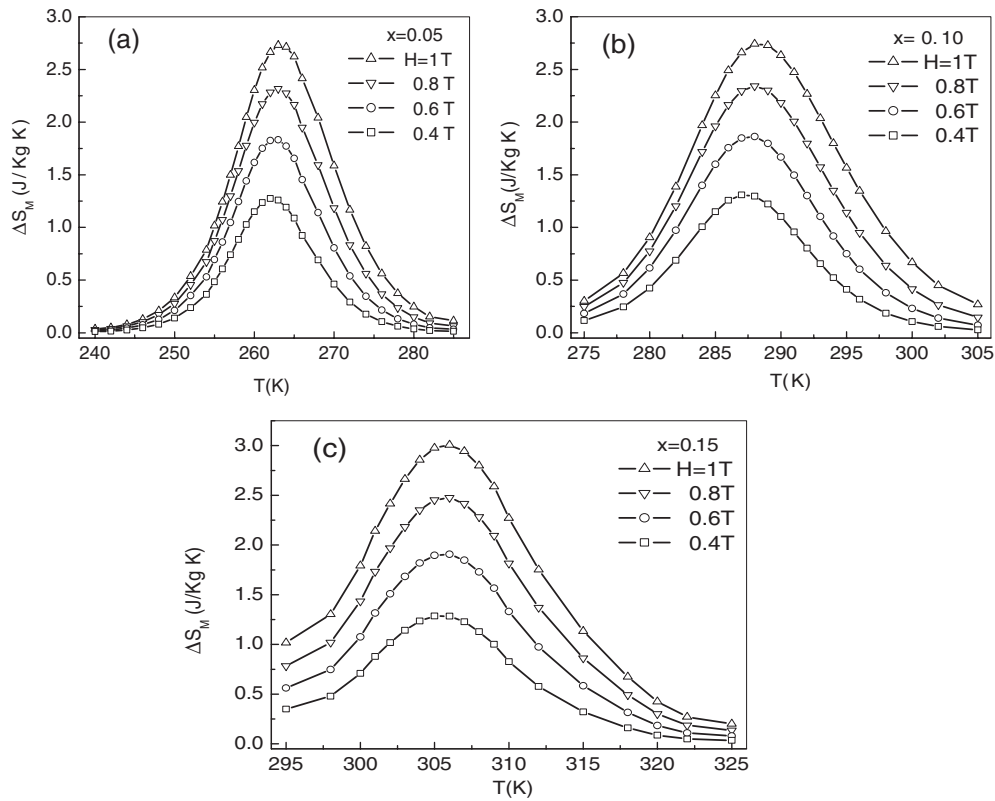


Figure 3. (a)–(c) Magnetic entropy change (ΔS_M) as a function of temperature in various magnetic fields for $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.05, 0.10$ and 0.15) compounds. The lines are guides to the eyes.

Table 2. Summary of the magnetocaloric properties obtained for the $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compounds with a field change of 1 T. Present results on $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compounds have been compared with some of the divalent and monovalent doped lanthanum manganites as well as with Gd.

Sample	T_C (K)	ΔS_M^{\max} ($\text{J kg}^{-1} \text{K}^{-1}$)	H (T)	RCP (mJ cm^{-3})	$\Delta T_{\text{ad}}^{\max}$ (K)	$ \Delta Q_M(T_C \pm 10 \text{ K}) _{1T}$ (J kg^{-1})	Ref.
$\text{La}_{0.95}\text{K}_{0.05}\text{MnO}_3$	260.4	2.73	1	282	1.68	35.0	Present work
$\text{La}_{0.90}\text{K}_{0.10}\text{MnO}_3$	287.4	2.74	1	286	1.79	38.0	Present work
$\text{La}_{0.85}\text{K}_{0.15}\text{MnO}_3$	309.7	3.00	1	303	2.08	38.6	Present work
$\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$	275	3.40	2	—	—	59.5 ^a (2 T)	[24]
$\text{La}_{0.60}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$	230	1.50	3	—	—	10.5 ^a	[18]
$\text{La}_{0.67}\text{Ca}_{0.275}\text{Sr}_{0.055}\text{MnO}_3$	285	2.80	1.2	307	1.0	24.9 ^a (0.7 T)	[23]
$\text{La}_{0.893}\text{K}_{0.070}\text{MnO}_3$	230	1.19	1.5	—	—	58.4	[30]
$\text{La}_{0.796}\text{K}_{0.196}\text{MnO}_3$	344	2.19	1.5	—	—	83.9	[30]
$\text{La}_{0.80}\text{Ag}_{0.20}\text{MnO}_3$	278	3.40	1	—	—	30.9 ^a	[9]
Gd	292	3.25	1	940	4.2	122 ($T_C \pm 25 \text{ K}$)	[39]

^a Estimated from reported data.

The large magnetic entropy change in perovskite manganites is usually attributed to the large variation of magnetization near T_C . The substitution of divalent/monovalent dopant in LaMnO_3 leads to a mixed valence state of the Mn ion, and double-exchange interaction is

supposed to occur between $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$, which is responsible for large magnetic entropy change at the Curie temperature [12, 35]. Again, the spin–lattice coupling in the magnetic ordering process also affects the magnetic entropy change [5, 36]. Due to this coupling, the change in magnetism in manganites arises due to the change in Mn–O bond distance and Mn–O–Mn bond angles with temperature inducing a volume variation favouring spin ordering [14, 32].

An approximate estimation of adiabatic temperature change ΔT_{ad} of these samples has been performed from the measured ΔS_{M} using the expression

$$\Delta T_{\text{ad}} = -\Delta S_{\text{M}} \frac{T}{C_{P,H}}. \quad (3)$$

The specific heat $C_{P,H}$ in equation (3) is taken as the sum of the lattice and magnetic contributions ($C_{P,H} = C_{\text{D}} + C_{\text{M}}$). The Debye specific heat C_{D} is calculated from

$$C_{\text{D}} = 9KN \left(\frac{T}{\theta_{\text{D}}} \right)^3 \int_0^{\frac{\theta_{\text{D}}}{T}} \frac{e^x x^4}{(e^x - 1)^2} dx \quad (4)$$

where K is the Boltzmann constant, N is the number of atoms per unit mass, and θ_{D} is the Debye temperature. The magnetic contribution to the specific heat capacity (C_{M}) is given by the temperature derivative of the internal energy ($\frac{\partial U_{\text{M}}}{\partial T}$), and is expressed as

$$C_{\text{H}} = -H_{\text{ext}} \frac{\partial M}{\partial T} - \frac{1}{2} N_{\text{int}} \frac{\partial M^2}{\partial T}. \quad (5)$$

In equation (5), $N_{\text{int}} = \frac{3KT_{\text{C}}}{N_{\text{S}}g^2\mu_{\text{B}}J(J+1)}$ is the mean field constant, N_{S} is the number of spins per unit mass, g is the Landé factor and J is the total angular momentum. The estimated adiabatic temperature change ΔT_{ad} for the present set of K doped lanthanum manganites is shown in figures 4(a)–(c). It may be observed that ΔT_{ad} almost maintains the nature of ΔS_{M} and lies between 1.68 and 2.0 K at 1 T. ΔT_{ad} obtained for $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compounds compares favourably with those reported for divalent doped lanthanum manganites (table 2).

Figure 5(a) shows the temperature dependence of $\Delta S_{\text{M}}/\Delta S_{\text{M}}^{\text{max}}$ for a typical sample ($x = 0.05$) in a magnetic field of 1 T. A temperature range of ~ 10 K is obtained in which ΔS_{M} exceeds 75% of $\Delta S_{\text{M}}^{\text{max}}$. As the adiabatic temperature change ΔT_{ad} is assumed to be mainly affected by the magnetic entropy change [17], this wide temperature span with large magnetic entropy change in $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compounds results in its wide temperature span with large adiabatic temperature change ΔT_{ad} [37]. The temperature span corresponding to 75% of $\Delta S_{\text{M}}^{\text{max}}$ for other compositions ($x = 0.10$ and 0.15) obtained is ~ 9 K. For an ideal Ericsson refrigeration cycle [38], such a wide temperature range associated with large magnetic entropy change should be useful. In the present series of K doped manganites, $\Delta S_{\text{M}}^{\text{max}}$ increases from $2.73 \text{ J kg}^{-1} \text{ K}^{-1}$ for $x = 0.05$ to $3.00 \text{ J kg}^{-1} \text{ K}^{-1}$ for $x = 0.15$ at 1 T near their respective T_{C} . Zhong *et al* [30] reported for polycrystalline $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ samples $\Delta S_{\text{M}}^{\text{max}}$ values between $1.19 \text{ J kg}^{-1} \text{ K}^{-1}$ for $x = 0.07$ and $2.19 \text{ J kg}^{-1} \text{ K}^{-1}$ for $x = 0.196$ at 1.5 T. Table 2 gives a comparison of the magnetocaloric properties of the present $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compounds with pure Gd and also with some alkaline-earth doped lanthanum manganites reported earlier. It may be noted that while $\Delta S_{\text{M}}^{\text{max}}$ of our $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ compounds is slightly lower than that of pure Gd, $\Delta S_{\text{M}}^{\text{max}}$ values of the present set of K doped samples are better than those of alkaline-earth lanthanum manganites. For all our samples, the maximum magnetic entropy change $\Delta S_{\text{M}}^{\text{max}}$ exhibits a linear rise ($\Delta S_{\text{M}}^{\text{max}} = p + qH$) with increasing magnetic field (figure 5(b)) which is indicative of a much larger magnetic entropy change to be expected at higher magnetic fields. Strong dependence of the field-dependent part (q) on dopant (K) concentration (figure 5(c)) possibly signifies the influence of the associated structural change on the magnetocaloric (MCE) properties of the system.

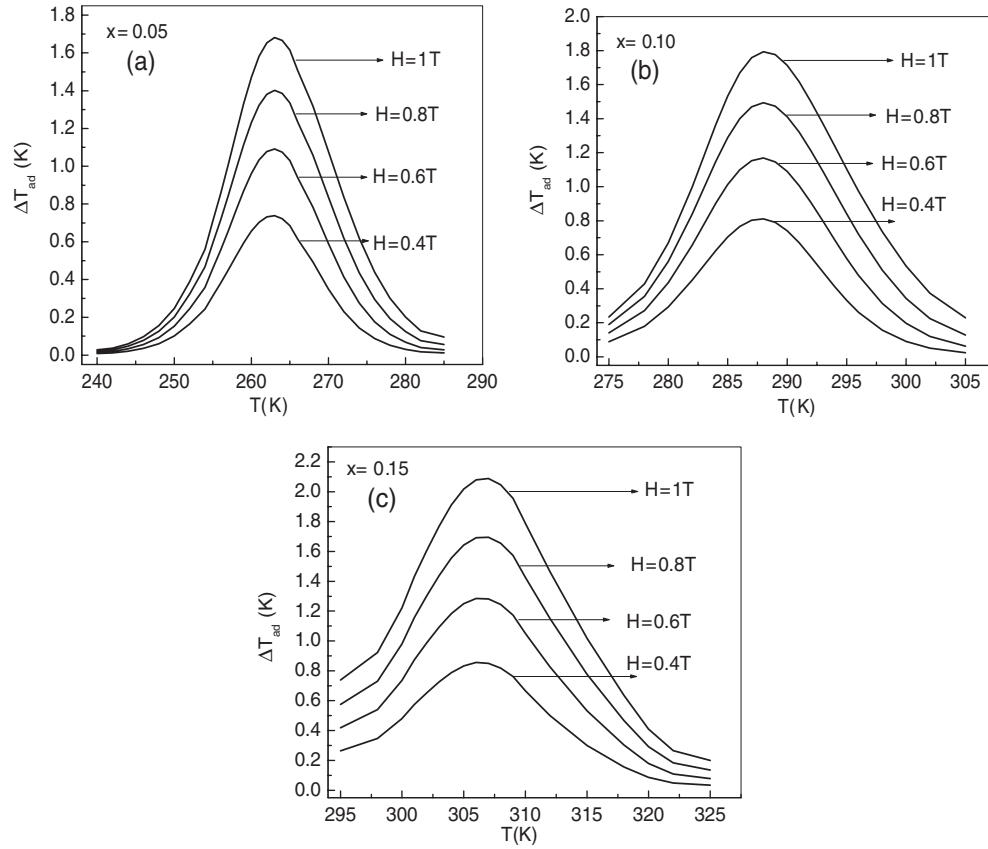


Figure 4. (a)–(c) Adiabatic temperature change (ΔT_{ad}) estimated for $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.05, 0.10$ and 0.15) compounds under different magnetic fields.

The relative cooling power (RCP) based on the magnetic entropy change (ΔS_M) is defined as

$$\text{RCP}(S) = -\Delta S_M^{\max} \delta T_{\text{fwhm}} \quad (6)$$

where δT_{fwhm} denotes the full width temperature span of ΔS_M versus T curve at its half maximum. The RCP estimated (table 2) for the present set of $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ samples increases with K content (figure 5(c)) and is approximately one-third of that of pure Gd [39]. This means that in order to achieve an equivalent cooling capacity the refrigerant unit employing LKMO will need nearly three times the volume of a refrigerant unit consisting of pure Gd. Similar RCP values have also been reported by Dinissen *et al* [23] for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Sr}_x\text{MnO}_3$ ($0 < x < 0.33$) manganites. The heat originated only from magnetic entropy change around ± 10 K of T_C is estimated using

$$|\Delta Q_M(T_C \pm 10 \text{ K}, H = 1 \text{ T})| = \int_{T_C - 10 \text{ K}}^{T_C + 10 \text{ K}} |\Delta S_M(T, H = 1 \text{ T})| dT. \quad (7)$$

The value obtained at 1 T, around ± 10 K of T_C , increases with increasing K content (table 2) and typically is $\sim 31\%$ of that of pure Gd (122.0 J kg^{-1} at $T_C \pm 25 \text{ K}$). However, it may be mentioned that compared to Gd or Gd based compounds, manganites are inexpensive, easier to fabricate, possess tunable T_C , are chemically stable and have respectable ΔS_M in a relatively

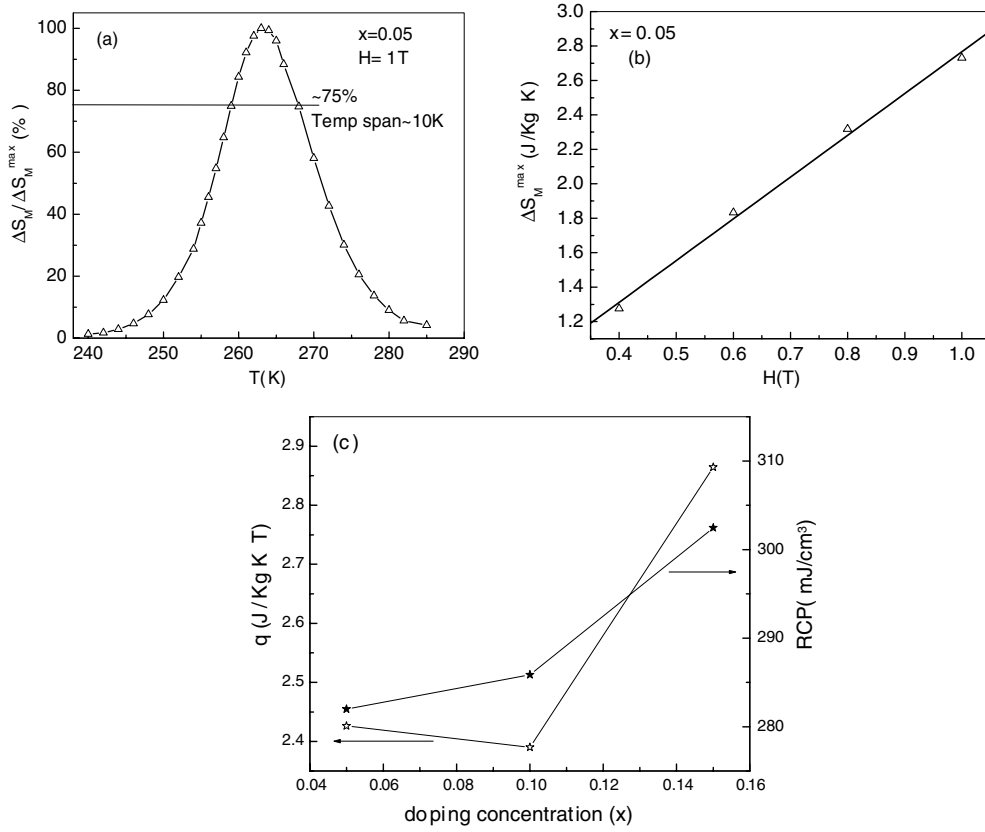


Figure 5. (a) Typical plot showing $\frac{\Delta S_M^{\max}}{\Delta S_M}$ versus T and (b) field dependence of ΔS_M^{\max} for the $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.05$) sample. (c) Relative cooling power (RCP) and the coefficient q as a function of K concentration.

low field range (1 T) and, therefore, could be considered as a potential solid refrigerant in magnetic refrigeration technology for consumer applications.

An early attempt on the theoretical modelling of the magnetocaloric effect based on Weiss molecular mean field theory for ferromagnetic interaction in lanthanum manganites was reported by Dinesen *et al* [23]. Later, Szewczyk *et al* [20] derived an expression for the magnetic entropy of the system, as well as the entropy change under the influence of a magnetic field, in the molecular field approximation. However, the discrepancies between the theoretical and experimental values for LSMO compounds were reported to be significant. Recently, Amaral *et al* [26, 27] discussed the magnetic properties of manganites in terms of the Landau theory of phase transitions and argued in favour of the magnetoelastic coupling and electron condensation energy on the magnitude and the temperature dependence of magnetic entropy change observed in manganites. Accordingly, the Gibbs free energy is expressed as

$$G(T, M) = G_0 + \frac{1}{2}AM^2 + \frac{1}{4}BM^4 - MH \quad (8)$$

where the coefficients A and B are temperature-dependent parameters. The elastic and magnetoelastic terms of free energy are included in the coefficient B [40]. From the condition

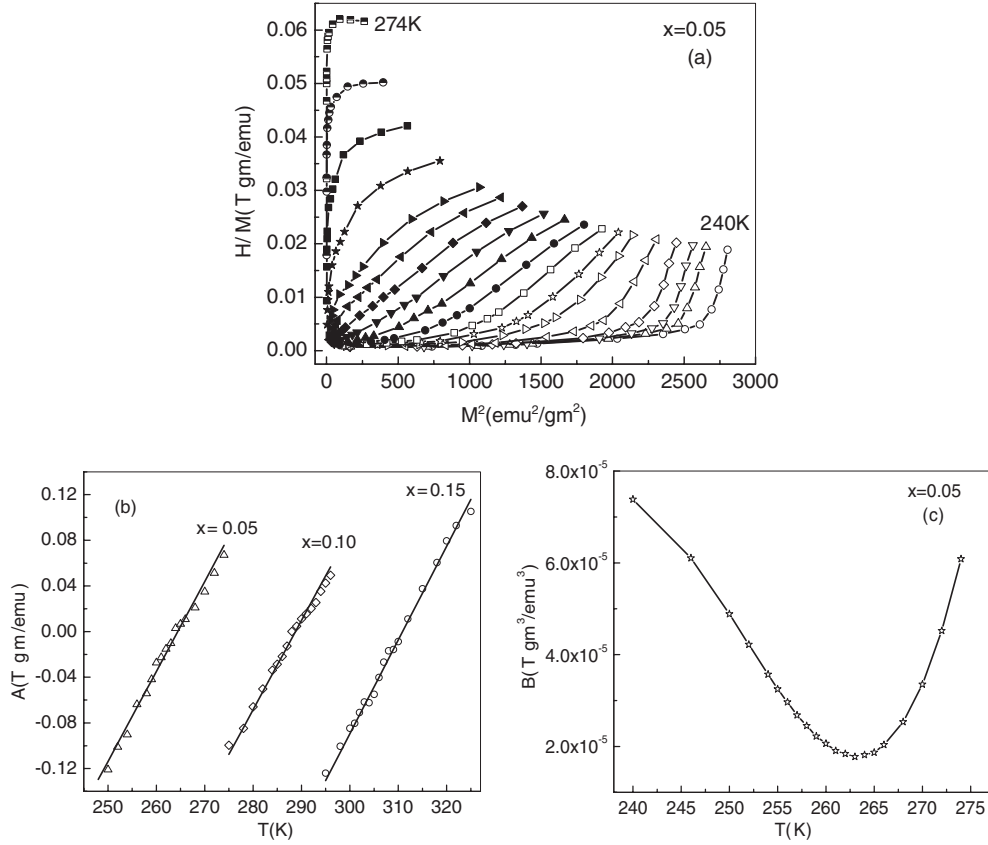


Figure 6. (a) M^2 versus H/M (Arrott) plot for the $x = 0.05$ sample. (b) Parameter A as a function of temperature and (c) temperature dependence of parameter B .

of equilibrium, $\frac{\partial G}{\partial M} = 0$, the magnetic equation of state is obtained as

$$\frac{H}{M} = A + BM^2. \quad (9)$$

The nature of the magnetic transition in the present set of K doped samples may be checked using the Banerjee criterion [41]. According to this criterion, the slope of H/M versus M^2 curves denotes whether the observed magnetic transition is of the first order (negative slope) or second order (positive slope). H/M versus M^2 curves obtained for all the $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ samples clearly indicate positive slope in their complete M^2 range and this confirms the transition to be of the second order. A set of typical H/M versus M^2 curves for the $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.05$) sample is shown in figure 6(a).

By differentiation of the magnetic part of Gibb's free energy with respect to temperature the magnetic entropy change is obtained:

$$S_M(T, H) = -\frac{1}{2} \frac{\partial A}{\partial T} M^2 - \frac{1}{4} \frac{\partial B}{\partial T} M^4. \quad (10)$$

Amaral *et al* [27] found, for La manganites, the parameter B to be strongly dependent on temperature, and consequently, magnetoelastic coupling and electron interactions contribute directly to ΔS_M , and its temperature dependence defines the shape of ΔS_M versus T curves. In order to apply the above formulation, the temperature dependence of the parameters A and B is

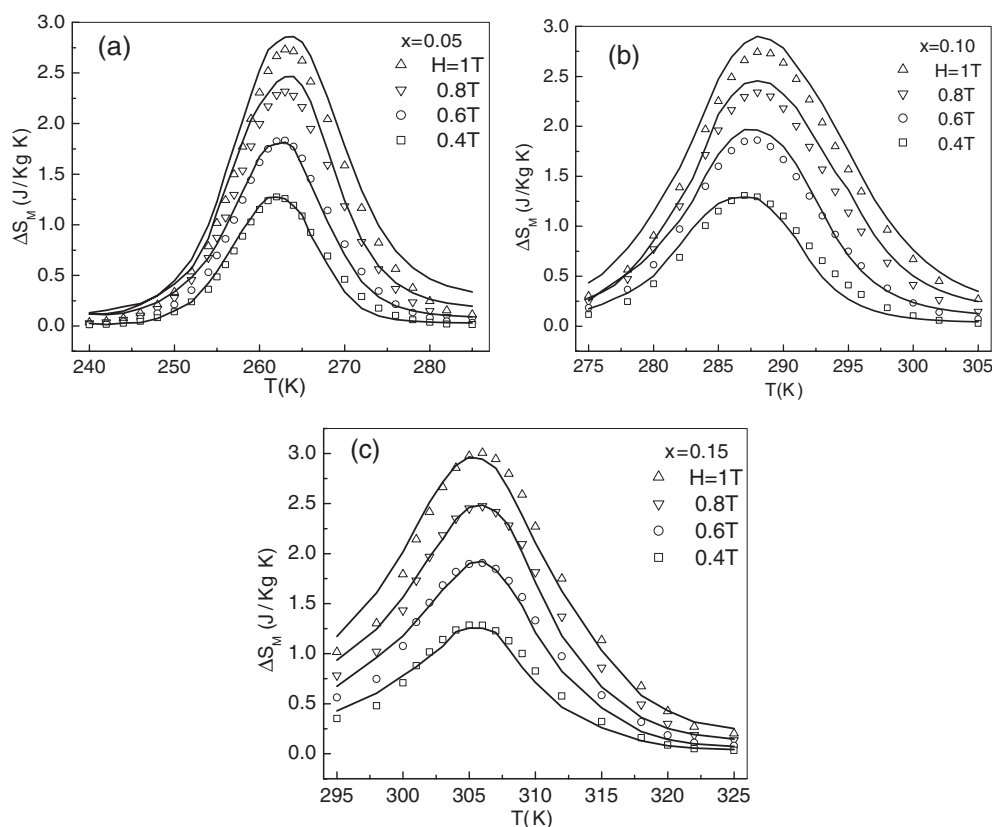


Figure 7. (a)–(c) Magnetic entropy change (ΔS_M) for $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.05, 0.10$ and 0.15) samples. Points are the measured values and the solid lines represent ΔS_M calculated from Landau theory.

obtained from the linear region of the Arrott plot of H/M versus M^2 (figure 6(a)). The thermal variation of the parameter A is found to be linear for all the samples (figure 6(b)). Amaral *et al* [26, 27] strongly emphasized the importance of the temperature dependence of the parameter B , which for a typical K doped lanthanum manganite ($x = 0.05$) is shown in figure 6(c). Using the parameters A and B extracted from the data, the temperature dependence of the change in magnetic entropy (ΔS_M) is calculated for various applied fields. The solid lines in figures 7(a)–(c) are the calculated values of ΔS_M , and points represent the experimental data. It may be seen that the agreement between the theoretical and measured data is very satisfactory, considering the fact that the present model does not take into account the influence of the Jahn–Teller effect and exchange interactions on the magnetic properties of manganites. Nevertheless, the analysis clearly demonstrates the importance of magnetoelastic coupling and electron interaction in understanding the magnetocaloric properties of lanthanum manganites [27].

4. Conclusions

In conclusion, we have studied the magnetocaloric effect on a set of fine-grained K doped perovskite manganites of the type $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($0.05 < x < 0.15$), prepared by a pyrophoric method. The Curie temperatures (T_C) of the studied compounds depend strongly

on the K content in the system and vary between 260.4 K (for $x = 0.05$) and 309.7 K (for $x = 0.15$). Results show that K doped lanthanum manganites present a large magnetic entropy change (ΔS_M) under a moderate magnetic field around the ferromagnetic ordering temperature (T_C). The magnitude of the change in magnetic entropy obtained in a magnetic field of 1 T in the present system is better than that reported for Gd and for many divalent and monovalent perovskite manganites. The relative cooling power (RCP) of LKMO compounds is estimated to be about one-third of that for Gd. However, the studied K doped lanthanum compounds are inexpensive, easy to synthesize, and chemically stable. Moreover, as their Curie temperatures can be tailored between 260 and 310 K by adjusting the dopant (K) concentration, the monovalent (K) doped lanthanum manganites could be possible candidates for a multi-component magnetic refrigerator over a wide temperature range. Analysis of the measured ΔS_M data for LKMO compounds shows excellent agreement with those calculated using Landau theory and confirms the importance of magnetoelastic coupling and electron interaction in magnetocaloric properties of manganites.

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