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Effect of potassium doping on physical properties of perovskites $La_{0.8}Cd_{0.2-x}K_xMnO_3$

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ABSTRACT

Polycrystalline perovskite manganites $La_{0.8}Cd_{0.2-x}K_xMnO_3$ ($x = 0.05$, 0.075 and 0.1) were prepared by sol–gel method. The crystal structure examined by X-ray powder diffraction indicates that the samples were single phase and crystallize in a rhombohedral ($R\bar{3}c$) structure with increasing the K content. Magnetization as a function of temperature, $M(T)$, shows that these compounds exhibit a paramagnetic (PM) to ferromagnetic (FM) phase transition with decreasing temperature. The Curie temperature (T_C) increases from 260 to 282 K as K-doping increases from 0.05 to 0.1.The resistivity measurements reveal that the samples exhibit a metallic to semiconductor transition and the electrical temperature transition T_P presents a similar trend of T_C, with increasing the K content. The magnetic entropy change $|\Delta S_M|$ has been deduced by two methods: a Maxwell relation, and the Landau theory. The maximum value of the magnetic entropy change obtained from the $M(H)$ plot data is $|\Delta S_M^{max}| \sim 3.25\,J\,kg^{-1}\,K^{-1}$ for applied magnetic field of 2 T. At this value of magnetic field the relative cooling power (RCP) is $62.59\,J\,kg^{-1}$. Close to T_C, large change in magnetic entropy has been observed in all samples. Our result on magnetocaloric properties suggests that $La_{0.8}Cd_{0.2-x}K_xMnO_3$ compounds are attractive as a possible refrigerant for near room temperature magnetic refrigeration.

1. Introduction

The interplay between structure, magnetic and transport properties in perovskite-type manganites $La_{1-x}A_xMnO_3$ (A: divalent alkali element such as Ca, Sr and Ba) becomes a hotspot in today's research [1–3]. These materials reveal many interesting effects such as magnetoresistance [4,5], magnetocaloric [6–8], and to the close correlation between structural, magnetic and electrical properties [9–11]. The parent compound, $LaMnO_3$, is an antiferromagnetic insulator (AFI) characterized by a super exchange coupling between Mn^{3+} sites facilitated by a single e_g electron which is subjected to strong correlation effects. Substitution on La^{3+}-site by a divalent or a monovalent ion results in a mixed valence states of Mn ($Mn^{3+}$and Mn^{4+}), where Mn^{4+} lacks e_g electron, and hence the itinerant hole associated with Mn^{4+} ion may hop to Mn^{3+}. The mixed valence state of Mn ions plays a major role in double exchange (DE) mechanism [12–15] which is responsible for the metallic character and ferromagnetic properties in these manganese oxides.

The aim of this work is to study the substitution of the divalent Cd^{2+} by monovalent K^+ ion on the properties of $La_{1-x}Cd_xMnO_3$ with $x = 0.2$. As the existence of phase purity of $La_{1-x}A_xMnO_3$ material for monovalent substitution (A is Na, K, Ag, etc.) is limited to $x = 0.20$ [16,17], we have studied the structural, magnetic, electrical and magnetocaloric properties of $La_{0.8}Cd_{0.2-x}K_xMnO_3$ compounds for $0.05 \leq x \leq 0.1$

2. Experimental

Polycrystalline $La_{0.8}Cd_{0.2-x}K_xMnO_3$ ($x = 0.05$, 0.075 and 0.1) samples were prepared using the sol–gel method from a stoichiometric mixture La_2O_3, $CdCO_3$, $Mn(NO_3)_2$ and K_2CO_3 .The constituent compounds were dissolved in dilute HNO_3 solution at 363 K. Suitable amounts of citric acid and ethylene glycol were added as coordinate agents to generate a complete homogenous transparent solution. With further heating at 373 K, a gel was developed. The gel was thermally treated at 873 K for 5 h to decompose the organic precursor. After grinding, the samples were calcined in air at 1273 K for 24 h.

Identification of the phase and structural analysis were carried out by X-ray diffraction technique with CuKα radiation ($\lambda = 1.54056$ Å). The data were analysed by Rietveld method using the FULLPROF program [18].

Magnetization (M) versus temperature (T) and magnetization versus magnetic field (H) curves were measured by using a Foner magnetometer equipped with a superconducting coil. The resistivity measurements as a function of temperature were carried out by using four-probe method without applying magnetic field. The samples were cut into square shape, with a typical dimension of 1 mm × 5 mm × 5 mm.

3. Results and discussion

Fig. 1 shows the refinement of $La_{0.8}^{3+}Cd_{0.2-x}^{2+}K_x^{+}Mn_{0.8-x}^{3+}Mn_{0.2+x}^{4+}O_3^{2-}$ with $x = 0.05$. All the samples of $La_{0.8}Cd_{0.2-x}K_xMnO_3$

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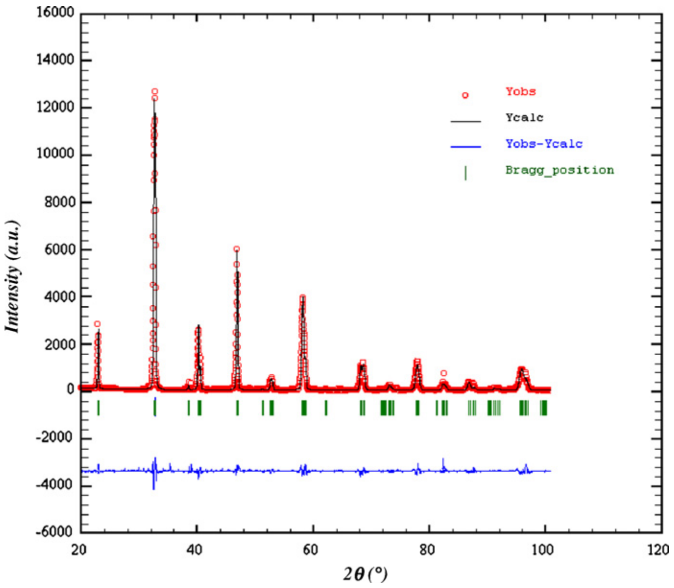

Fig. 1. Rietveld plot of XRD data for polycrystalline $La_{0.8}Cd_{0.2-x}K_xMnO_3$ ($x = 0.075$) pellet at 300 K. The circles are the observed profile; the solid line is the calculated one. Tick marks below the profile indicate the position of allowed Bragg reflections.

($x = 0.05$–0.1) are single phase without detectable secondary phase, within the sensitivity limits of the experiment (a few percent). The structural refinement of $La_{0.8}Cd_{0.2-x}K_xMnO_3$ samples was performed in the hexagonal setting of the $R\bar{3}c$ space group, in which the (La, Cd, K) atoms are 6a(0,0,1/4) position, Mn at 6b(0,0,0) and O at 18e(x,0,1/4). The quality of the refinement is evaluated through goodness of fit indicator χ^2. The structural parameters are obtained by refining the experimental data by Rietveld FULLPROF program and are listed in Table 1. One can see that the cell parameters increase with the potassium content. The increase in lattice parameters can be related to the big size of the K ion ($r_{K^+} = 1.55$ Å and $r_{Cd^{2+}} = 1.03$ Å) [19]. This is confirmed by the Rietveld refinement of Mn—O bond length calculated from the structural parameters, which also increase with x (Table 1). The refined Mn—O—Mn angles are slightly changed by increasing x.

The temperature dependence of magnetization $M(T)$ under an applied field of 0.05 T for the series $La_{0.8}Cd_{0.2-x}K_xMnO_3$ ($x = 0.05$–0.1) is shown in Fig. 2. All the samples show a steep paramagnetic–ferromagnetic (PM–FM) transition. The Curie temperature T_C, which is defined as the inflection point of M–T curve, is summarized in Table 2 for all the samples. T_C increases from 260 to 282 K as K-doping increases from 0.05 to 0.1. This increase in T_C can be interpreted in terms of increase in Mn^{4+} content from 25% to 30% compared to 20% Mn^{4+} content in $La_{0.8}Cd_{0.2}MnO_3$ samples. This increased Mn^{4+} content will favour Mn^{3+}—O^{2-}—Mn^{4+} double exchange reducing the super exchange interaction between Mn^{4+}—O^{2-}—Mn^{4+}.

Table 1
Results of Rietveld refinements for $La_{0.8}Cd_{0.2-x}K_xMnO_3$ compounds ($x = 0.05$, 0.075 and 0.1) at room temperature.

Sample	x		
	0.05	0.075	0.1
a (Å)	5.541(3)	5.545(5)	5.547(2)
c (Å)	13.5302(6)	13.5355(3)	13.5401(7)
V (Å^3)	353.7593(3)	354.1084(7)	354.0437(4)
$\theta_{(Mn)-O-(Mn)}$ (°)	168.32(2)	168.46(5)	163.58(4)
$d_{(Mn)-O}$ (Å)	1.9481(2)	1.9495(3)	1.9527(2)
χ^2	2.15	2.53	1.89
$\langle r_A \rangle$ (Å)	1.204	1.217	1.230

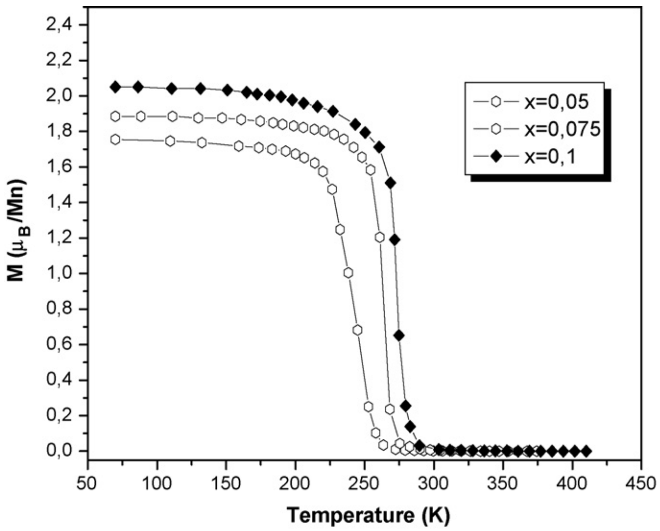

Fig. 2. Temperature dependence of magnetization for $La_{0.8}Cd_{0.2-x}K_xMnO_3$ samples measured as $H = 0.05$ T.

Table 2
Physical parameters of $La_{0.8}Cd_{0.2-x}K_xMnO_3$ ($0.05 \leq x \leq 0.1$) compounds.

x	0.05	0.075	0.1
T_C (K)	260	273	282
θ_P (K)	265	279	285
μ_{eff}^{th} (μ_B)	4.66	4.63	4.27
μ_{eff}^{exp} (μ_B)	3.9	3.73	4.05
RCP (J kg^{-1})	46.78	61	62.59
$\lvert\Delta S_M^{max}\rvert_{\Delta H=2T}$ (J kg^{-1} K^{-1})	2.6	2.81	3.25

In the paramagnetic region (above T_C) the inverse of magnetic susceptibility as a function of temperature for the above three samples, which is shown in Fig. 3

The data show that at high temperatures, all of our samples manifest Curie–Weiss dependence $1/\chi = (T - \theta_p)/C$. By fitting the linear paramagnetic region of the data, the Curie–Weiss parameters C and θ_p were obtained. The experimental effective paramagnetic moments, μ_{eff}^{exp}, were calculated from $C = (\mu_0/3k_B)\mu_{eff}^2$. The calculated effective paramagnetic moment should be: $\mu_{eff}^{cal} = \sqrt{(0.8 - x)\mu_{eff}^2(Mn^{3+}) + (0.2 + x)\mu_{eff}^2(Mn^{4+})}$. The temperature

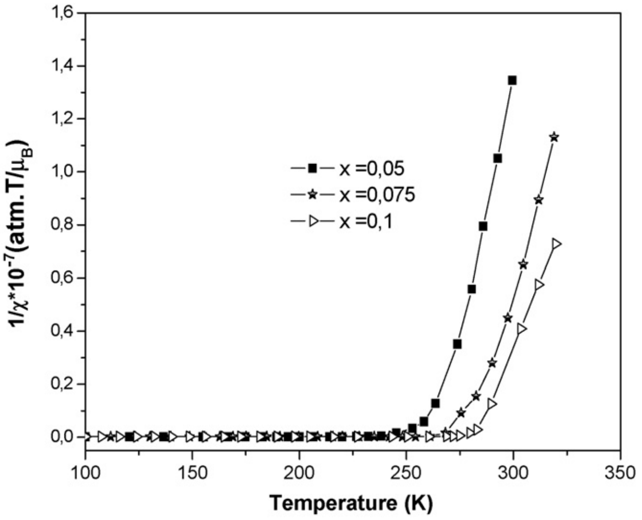

Fig. 3. The temperature dependence of the inverse of the magnetic susceptibility for $La_{0.8}Cd_{0.2-x}K_xMnO_3$ samples measured as $H = 0.05$ T.

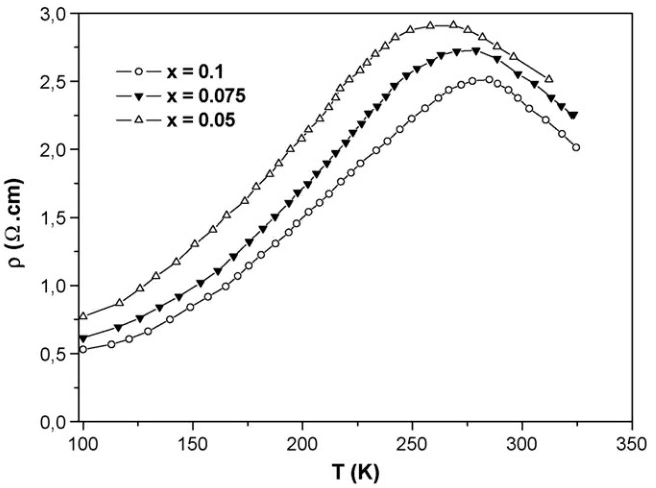

Fig. 4. Temperature dependence of the resistivity in zero magnetic applied field for $La_{0.8}Cd_{0.2-x}K_xMnO_3$ samples.

range of fit, θ_p, μ_{eff}^{exp} and μ_{eff}^{th} are listed in Table 2. When the contents of K and Cd are increased from 0.05 to 0.1, the Curie–Weiss temperatures also increase. The positive value of θ_p indicates the ferromagnetic interaction between spins.

The resistively evolution versus temperature in zero magnetic applied field for $La_{0.8}Cd_{0.2-x}K_xMnO_3$ samples is shown in Fig. 4. The $\rho(T)$ curves reveal that samples exhibit a metallic behaviour at low temperature and undergo a metal–semiconductor transition with increasing temperature at $T_P = 264, 275$ and 285 K, for $x = 0.05, 0.075$ and 0.1, respectively. On the other hand, the $\rho(T)$ curves expose that the increase of K-doping concentration decreases the resistivity and enhances the T_P temperature.

Fig. 5 displays the magnetic field dependence of magnetization for the $La_{0.8}Cd_{0.2-x}K_xMnO_3$ ($x = 0.05$) sample at various temperatures. It can clearly be seen that there is a drastic change of the magnetization around T_C, indicating a large isothermal magnetic entropy change.

Estimating the isothermal magnetic entropy change $\Delta S_M(T,H)$ from magnetization data is commonly done by the use of the following Maxwell relation:

$$\left(\frac{\partial M(H,T)}{\partial T}\right)_H = \left(\frac{\partial S_M(H,T)}{\partial H}\right)_T \tag{1}$$

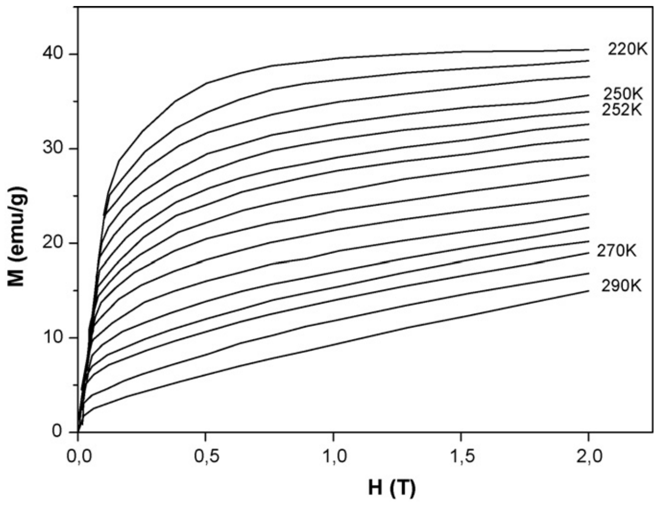

Fig. 5. Magnetization versus applied magnetic field H, measured at different temperatures, for the samples $La_{0.8}Cd_{0.2-x}K_xMnO_3$ ($x = 0.05$).

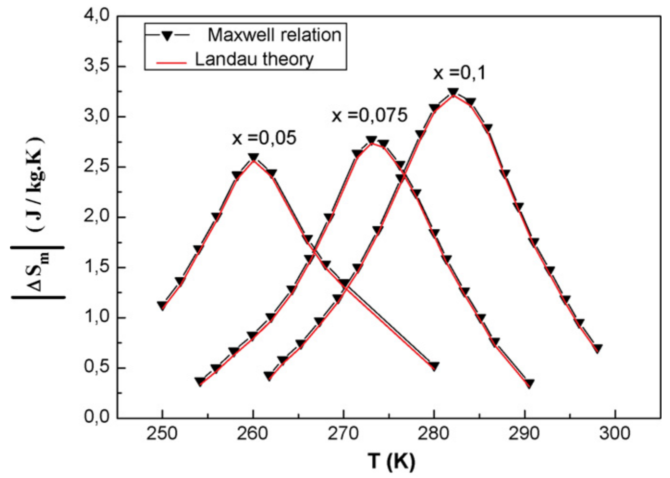

Fig. 6. Experimental and calculated curves of the magnetic entropy change ($|\Delta S_M|$) versus temperature upon a magnetic field change of 2 T for $La_{0.8}Cd_{0.2-x}K_xMnO_3$ samples.

which directly implies that

$$\Delta S_M(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \tag{2}$$

According to Eq. (2) the maximum magnetic entropy change is obtained at the Curie temperature where the ferromagnetic–paramagnetic phase transition takes place.

For magnetization measurements made at discrete field and temperature intervals, the magnetic entropy change (ΔS_M) can be approximated as:

$$\Delta S_M = \sum_i \frac{M_i - M_{i+1}}{T_i - T_{i+1}} \Delta H \tag{3}$$

where M_i and M_{i+1} are the magnetization values measured in a magnetic field H_i, at temperature T_i and T_{i+1}, respectively.

From the isothermal magnetization measurements, the magnetic entropy change associated with magnetic field change has been calculated using Eq. (3). In Fig. 6, we plot the magnetic entropy data as a function of temperature for the samples with $x = 0.05$, 0.075 and 0.1 at an applied magnetic field of 2 T.

The magnetic entropy change reaches the maximum value around T_C. The maximum isothermal entropy changes for the samples are listed in Table 2. Upon an application of a field 2 T for the samples, the largest value of $|\Delta S_M^{max}| \sim 3.25\,J\,kg^{-1}\,K^{-1}$ for the sample $x = 0.1$ is found at a temperature 282 K.

Moreover, the relative cooling power (RCP) is given by

$$RCP = -\Delta S_M^{max} \partial T_{fwhm}$$

where ∂T_{fwhm} is the full-width at the half maximum of the entropy change curve. RCP values estimated for the present set of $La_{0.8}Cd_{0.2-x}K_xMnO_3$ samples increase with K doping (Table 2).

This result is of practical importance, because it shows that the obtained manganites could be good working materials for magnetic refrigeration in household refrigerators or air conditioning. We believe that the larger magnetocaloric effect in the polycrystalline $La_{0.8}Cd_{0.2-x}K_xMnO_3$ samples is due to an abrupt jump in magnetization related to a magnetic phase transition near the T_C. The internal stress caused by the substitution of Cd^{2+} by a monovalent ion, viz., K^+ ion leads to a mixed Mn^{3+} and Mn^{4+} nominal valence .The double exchange interaction between Mn^{3+} and Mn^{4+} is usually considered to be responsible for the observed magnetic entropy change in perovskite manganites [20]. This interaction is strongest at the Mn^{3+}/Mn^{4+} ratio equal 8/2. With an increasing K

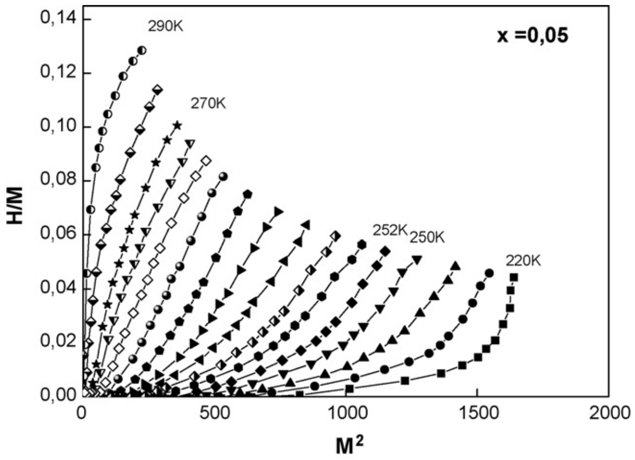

Fig. 7. A set of typical M^2 versus H/M curves obtained for $La_{0.8}Cd_{0.2-x}K_xMnO_3$ (with $x = 0.05$) sample.

content, the fraction of Mn^{4+} increases, which leads to a reduction of the Mn^{3+}/Mn^{4+} ratio. However, the strong spin-lattice coupling arising from a reasonable variation in Mn—O bond distances and Mn—O—Mn bond angles at T_C may also contribute to the enhancement of magnetic change [17] observed.

An attempt to the theoretical modeling of the magnetocaloric effect was done by Amaral et al. [21,22] based on Landau theory of phase transition. The effect of the magnetoelastic coupling and electron condensation energy on the magnetic entropy change in manganites has been studied. Here, the magnetic energy MH has been included in the expression of Gibb's free energy as given by

$$G(T,H) = G_0 + \frac{1}{2}A(T)M^2 + \frac{1}{4}B(T)M^4 - MH \tag{4}$$

where the coefficients A and B are temperature-dependent parameters containing the elastic and magnetoelastic terms of free energy [23]. From the condition of equilibrium at T_C, the magnetic equation of state is obtained as

$$\frac{H}{M} = A(T) + B(T)M^2 \tag{5}$$

The nature of the magnetic transition in the present set of K doped samples is checked using the Banerjee criterion [24]. For all the samples, a second order phase transition has been confirmed with the positive slope of H/M versus M^2 curve (Fig. 7).

The magnetic entropy change obtained from Gibb's free energy using Eq. (4) is

$$-S_M(T,H) = \left(\frac{\partial G}{\partial T}\right)_H = \frac{1}{2}\frac{\partial A}{\partial T}M^2 + \frac{1}{4}\frac{\partial B}{\partial T}M^4 \tag{6}$$

where the values of the coefficients (A and B) and their dependence on temperature can be obtained from experimental isothermal magnetization measurements from polynomial fitting of H/M vs. M^2 Arrott plots. A set of typical H/M versus M^2 curves for $La_{0.8}Cd_{0.2-x}K_xMnO_3$ ($x = 0.05$) sample is shown in Fig. 7.

Thermal variation of the parameter A is found to be linear for all the samples, whereas the temperature dependence of the parameter B is highly nonlinear. This nature of the parameter B takes a crucial role in determining $|\Delta S_M|$ as suggested by Amaral et al. [21,22]. Using the parameters A and B extracted from the data, the temperature dependence of the magnetic entropy change ($|\Delta S_M|$) is calculated from Eq. (6) at an applied magnetic field of 2 T and are shown as solid lines in Fig. 6. A clear correspondence between the measured $|\Delta S_M|$ and those estimated using Eq. (6) is evident from Fig. 6 (the experimental errors is smaller than one-thousandth). This indicates the influence of both magnetoelastic coupling and electron interaction on the magnetocaloric properties.

4. Conclusion

In this work, we have investigated the physical properties of perovskite $La_{0.8}Cd_{0.2-x}K_xMnO_3$ ($x = 0.05$, 0.075 and 0.1) compounds. We have found that all samples crystallize in the rhombohedral system. All our synthesized samples exhibit a semiconducting-paramagnetic state at high temperatures and metallic-ferromagnetic one at low temperatures. The Curie temperature T_C and the electrical transition temperature increase with increasing K content.

The maximum value of the magnetic entropy change obtained from the $M(H)$ plot data is for the $La_{0.8}Cd_{0.2-x}K_xMnO_3$ ($x = 0.1$) sample reaches $3.25\,J\,kg^{-1}\,K^{-1}$ in a magnetic field of 2 T.

At this value of magnetic field the relative cooling power (RCP) is $62.59\,J\,kg^{-1}$. This investigation suggests the polycrystalline $La_{0.8}Cd_{0.1}K_{0.1}MnO_3$ is a good candidate as a working material for active magnetic refrigerant. Analysis of the measured $|\Delta S_M|$ data for $La_{0.8}Cd_{0.2-x}K_xMnO_3$ samples using Landau theory confirms the importance of magnetoelastic coupling and electron interaction in magnetocaloric properties of manganites.

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