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Effect of Co substitution on magnetocaloric effect in $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ $(0.15 \leq x \leq 0.3)$

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ABSTRACT

The series of cobaltite substituted manganese $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ has been studied and show the effect of cobaltite substitution. The magnetic and magnetocaloric properties of polycrystalline perovskite were investigated. From the measured magnetization data of the samples as a function of magnetic applied field, the associated magnetic entropy change close to their respective Curie temperature T_C and the relative cooling power (RCP) have been determined. The Curie temperature has been analyzed by two methods: a linear extrapolation of $M(T)$ to zero magnetization, and the thermodynamic model. It was found that the maximum change in magnetic entropy for $La_{0.67}Pb_{0.33}Mn_{0.7}Co_{0.3}O_3$ sample reached 3.22 J/kg K at $T_C = 260$ K for a magnetic field of 10 kOe and RCP = 63 J/kg. In view of these results the $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ compounds are strongly recommended to use as an active magnetic refrigerators.

1. Introduction

Isothermal entropy change of adiabatic temperature change caused by application/removal of magnetic field, called as magnetocaloric effect (MCE), can be exploited in magnetic refrigeration technique and offers considerable advantages over the conventional gas refrigeration, such as high-energy efficiency, environmental concern, and small volume [1].

The total entropy of a magnetic solid is the sum of the lattice, electronic, and magnetic entropies (S_L, S_E, and S_M, respectively). In most cases the lattice and electronic entropies are essentially independent of the magnetic field H, whereas the magnetic entropy depends strongly on H. An applied magnetic field will usually tend to align the magnetic spins and thus decrease the entropy of the spin system. Hence, if the applied field is changed by ΔH at a constant temperature T, the magnetic entropy is changed $\Delta S_M\ (T)_{\Delta H}$, while S_L and S_E remain constant. If the change of the magnetic field takes place adiabatically, the total entropy is conserved. In this case, the combined lattice and electronic entropies must change by $\Delta(S_L + S_E) = -\Delta S_M$ in order to fulfill the condition $\Delta S = 0$. For a long time, the pure gadolinium (Gd) was considered as the most prominent magnetic refrigerant for use in room temperature magnetic refrigerators because of its large magnetic entropy change around 294 K [2].

According to thermodynamics, MCE is large when the change of magnetization $(\delta M/\delta T)_H$ is large and heat capacity is smaller at the same temperature (M, T, and H are magnetization, temperature, and applied field, respectively). Since $(\delta M/\delta T)_H$ shows the highest value at the magnetic ordering temperature, a large MCE is expected to occur around this transition temperature. The spin–lattice interaction also contributes to MCE, and it is significant in systems in which the magnetic phase transition is coupled with the structural phase transition, such as $Gd_5(Si_xGe_{1-x})_4$ alloys [3,4] or accompanied by a discontinuous change in the lattice parameters, for example, in $MnFeP_{1-x}As_x$ alloys [5].

The overall aim of the present work is to substitute cobaltite (Co) for manganese (Mn) in $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ compounds to achieve large MCE at high temperatures since the substitution of Co for Mn have been found to decrease the Curie temperature of the parent compound $x = 0$ [6].

2. Experimental

Polycrystalline samples of composition $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ ($x = 0.15$, 0.2, 0.25 and 0.3) have been prepared by the sol–gel method. Details of the sample preparation and structure characterization are described in Ref. [7].

The magnetization (M) versus temperature (T) and magnetization versus magnetic field (H) curves were measured using a Foner magnetometer equipped with a super-conducting coil.

Magnetization of samples was measured in an isothermal regime under an applied magnetic field varying from 0 to 10 kOe. In the vicinity of Curie temper-

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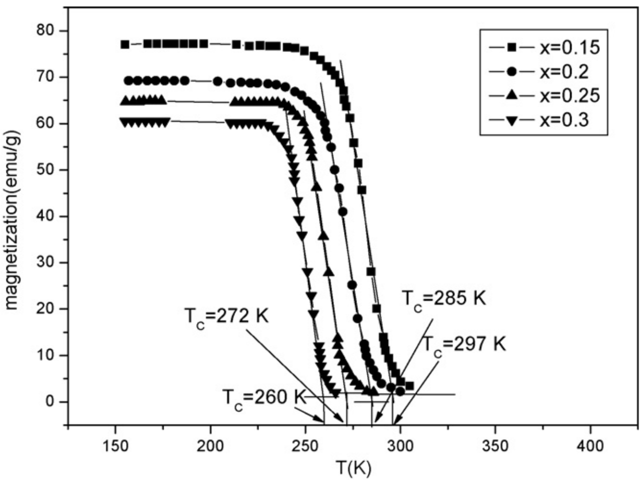

Fig. 1. Temperature dependence of magnetization for $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ ($x = 0.15$, 0.2, 0.25 and 0.3) samples at a magnetic field of 500 Oe.

ature, isothermal $M(H)$ curves were obtained by steps of 5 and 2 K. The temperature steps were smaller near T_C and larger further away.

3. Results and discussion

3.1. X-ray analysis

X-ray diffraction (XRD) studies for $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ ($0.15 \leq x \leq 0.3$) manganites perovskite in our pervious investigation [7] indicate that all the samples are single phase without detectable secondary phase within the sensitivity limits of the experiment (a few percent). The diffraction peaks are indexed with respect to the rhombohedral perovskite-type structure with a space group of $R\bar{3}c$. All details of the applied methodology and results of the refinements were recently summarized earlier in context with our structure investigation $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ system [7].

3.2. Magnetization investigation

In order to analyse the effect of Co substitution on the Curie temperature, two methods to determine T_C have been used:

(i) The first one is a linear extrapolation of $M(T)$ to zero magnetization. The Curie temperature T_C of the samples, defined as the temperature corresponding to the inflection point of the $M(T)$ curve. Fig. 1 shows the temperature dependence of magnetization for the $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ ($0.15 \leq x \leq 0.3$) samples in low field 500 Oe, and T_C data extracted by extrapolation are shown in it. The obtained values of Curie temperature T_C are 297, 285, 272 and 260 K, respectively, for $x = 0.15$, 0.2, 0.25 and 0.3.

(ii) The second one is based on the thermodynamic model: Amaral et al. [8,9] discussed the magnetic properties of manganites in terms of the Landau theory of phase transitions. Here, the magnetic energy MH has been included in the expression of Gibb's

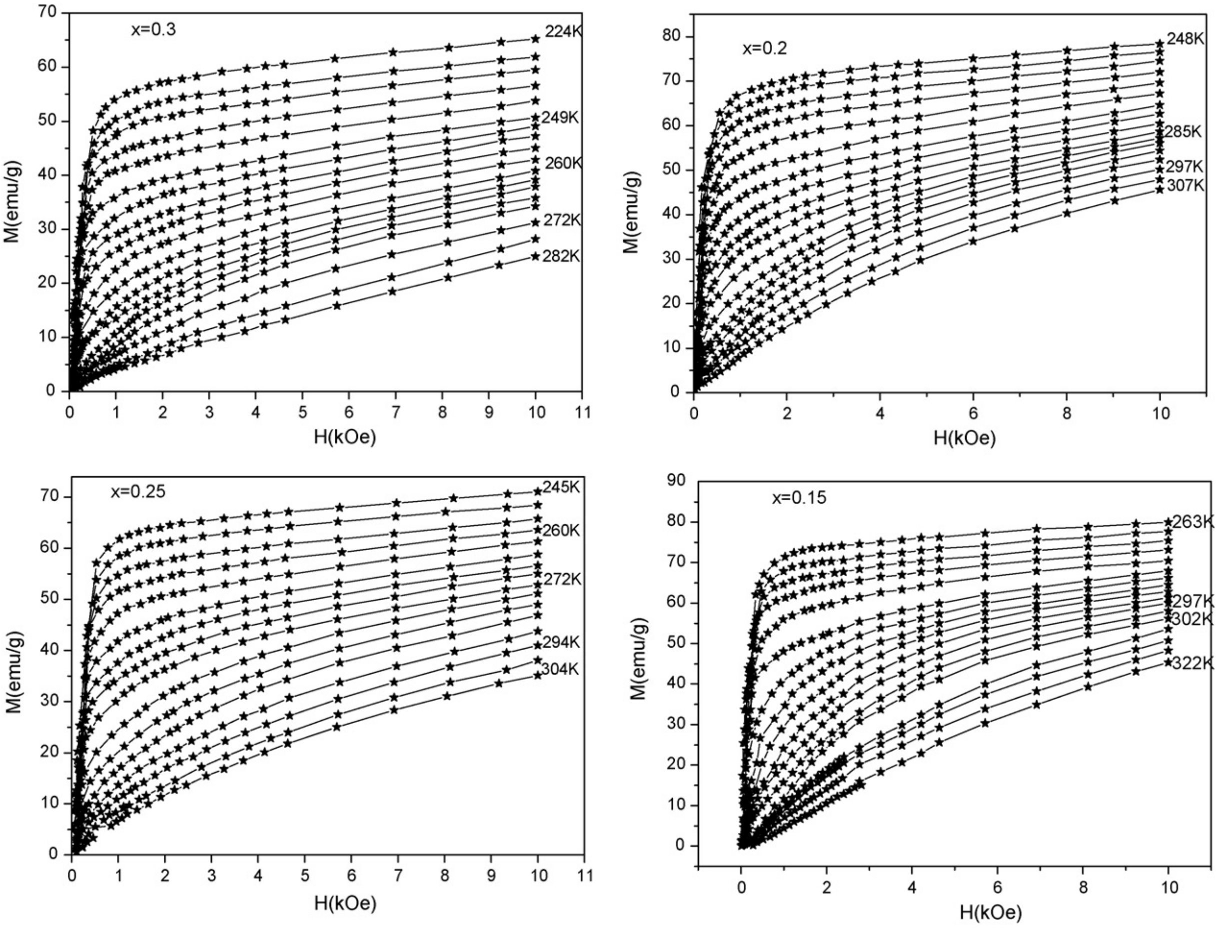

Fig. 2. The field dependence of the magnetization for $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ ($x = 0.15$, 0.2, 0.25 and 0.3) samples measured at different temperatures around T_C.

free energy as given by:

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

where the coefficients A and B are temperature-dependent parameters containing the elastic and magnetoelastic terms of free energy [10].

By assuming equilibrium condition of Gibb's free energy: $(\delta G/\delta M) = 0$, the magnetic equation of state is obtained as:

$$AM + BM^3 = H$$

Thus, by plotting the experimental data in the form, $A + BM^2 = H/M$, the temperature dependence of parameters A and B can be extracted.

The evolution of magnetization vs. the applied magnetic field (from 0 to 10 kOe) obtained at various temperatures for the $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ samples are shown in Fig. 2. Theses curves reveal a strong variation of magnetization around the Curie temperature (T_C). It indicates that there is a possible large magnetic entropy change associated with the ferromagnetic–paramagnetic transition temperature, occurred at T_C. We derive the Arrott plots (H/M vs. M^2) from $M(H)$ and the results plotted are shown in Fig. 3. According to Banerjee's criterion [11], a negative or a positive sign of the slope of the H/M vs. M^2 curves corresponds to the first- or the second-order magnetic phase transition, respectively. As shown in Fig. 3, the second-order magnetic phase transition behavior occurs because of the positive slope in the high-field regions for all the samples. The temperature dependence of parameter A can be extracted by the fit to the linear section of the transformed curves (Fig. 4). The Curie temperature T_C is given by $A = A'(T - T_C)$, where A is negative for $T < T_C$, equal to 0 for $T = T_C$ and positive for $T > T_C$. The values of T_C obtained for the samples $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ ($x = 0.15$, 0.2, 0.25 and 0.3) are respectively 299, 286, 273 and 261 K. The values of T_C determined by the two methods mentioned above are nearly the same. This indicates that the Curie temperatures of

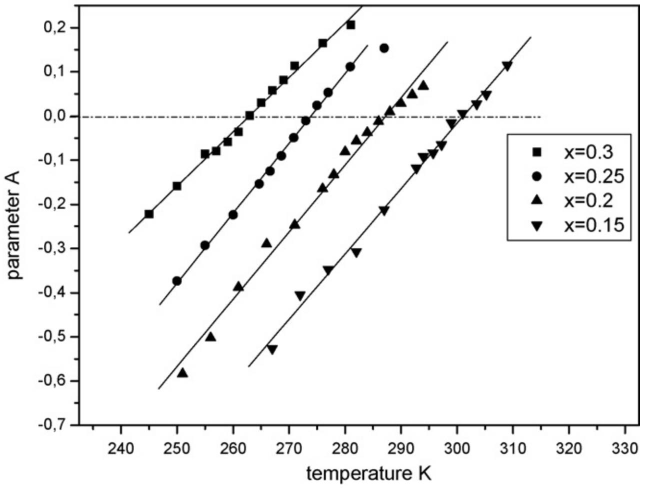

Fig. 4. Parameter (A) as a function of temperature.

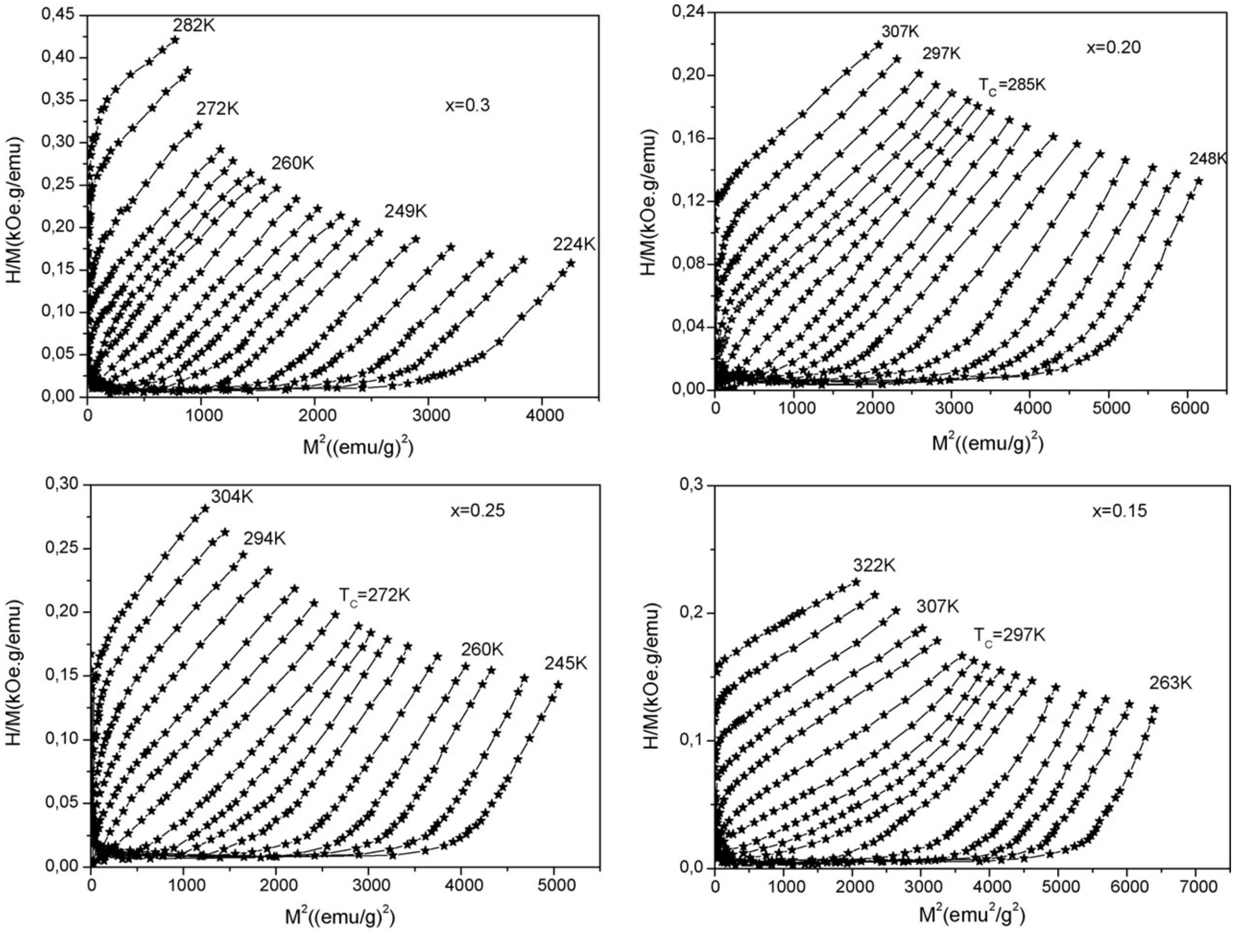

Fig. 3. H/M vs. M^2 isotherms for the samples $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ ($x = 0.15$, 0.2, 0.25 and 0.3). The temperatures of the isotherms are indicated.

Table 1
The Curie temperature and magnetocaloric parameters of the $La_{0.67}Pb_{0.33}Mn_{0.7}Co_{0.3}O_3$ and some important magnetic refrigerant candidate materials.

Sample	T_C (K)	H (kOe)	$\lvert\Delta S_M^{max}\rvert$ (J/kg K)	$\lvert Q_M (T_C \pm 10\,K, H = 10\,kOe)\rvert$ (J/kg)	RCP (J/kg)	Refs.
Gd	292	10	3.25	122 ($T_C \pm 25$ K)	–	[22]
$La_{0.67}Pb_{0.33}Mn_{0.85}Co_{0.15}O_3$	297	10	2.73	36.15	39	This work
$La_{0.67}Pb_{0.33}Mn_{0.8}Co_{0.2}O_3$	285	10	2.90	35.5	42	This work
$La_{0.67}Pb_{0.33}Mn_{0.75}Co_{0.25}O_3$	272	10	3.00	42.75	54	This work
$La_{0.67}Pb_{0.33}Mn_{0.7}Co_{0.3}O_3$	260	10	3.22	45.87	63	This work
$La_{0.7}Sr_{0.3}Mn_{0.9}Cu_{0.1}O_3$	347	10	3.24	–	–	[23]
$La_{0.7}Sr_{0.3}Mn_{0.95}Cu_{0.05}O_3$	345	10	3.05	–	–	[23]
$La_{0.80}Ag_{0.20}MnO_3$	278	10	3.40	30.9	–	[24]
$La_{2/3}Ba_{1/3}MnO_3$	337	10	2.70	–	–	[25]
$La_{0.835}Na_{0.165}MnO_3$	342	10	2.11	–	63	[26]

this series of compounds span the room temperature range, which is important for magnetic refrigeration at room temperature. That conclusion allows us to choose the temperature range in the vicinity of T_C determined by the first method for isothermal $M(H)$ data measurement for all samples.

3.3. Magnetocaloric effect

The magnetic entropy, which is associated with the MCE, can be calculated from the isothermal magnetization curves under the influence of a magnetic field. According to the classical thermodynamical theory, the magnetic entropy change ΔS_M produced by the variation of a magnetic field from 0 to H_{max} is given by: [12]

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^{H_{max}} \left(\frac{\delta S}{\delta H}\right)_T dH \tag{1}$$

From the Maxwell's thermodynamic relationship:

$$\left(\frac{\delta S}{\delta H}\right)_T = \left(\frac{\delta M}{\delta T}\right)_H \tag{2}$$

One can obtain the following expression:

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^{H_{max}} \left(\frac{\delta M}{\delta T}\right)_H dH \tag{3}$$

where H_{max} is the maximum external field [13].

According to Eq. (3) the maximum magnetic entropy change is obtained at the Curie temperature where the ferromagnetic–paramagnetic phase transition takes place.

In general, the magnetic entropy change ΔS_M is often evaluated by two different numerical calculations. The first approximation method is to directly use the measurement of the M–T curve under different applied magnetic fields. In the case of small discrete field $\Delta H_{i,}$ the magnetic entropy change defined in Eq. (1) can be approximated by:

$$\Delta S_M\left(\frac{T_1+T_2}{2}\right) = \left(\frac{1}{T_2-T_1}\right)\left[\int_0^{H_{max}} M(T_2,H)\,\mu_0 dH - \int_0^{H_{max}} M(T_1,H)\mu_0 dH\right] \tag{4}$$

Another method is to use isothermal magnetization measurements. In order to evaluate the magnetic entropy change ΔS_M one needs to make a numerical approximation to the integral in Eq. (3). The usual method is to use isothermal magnetization measurements at small discrete field intervals, $|\Delta S_M|$ can be approximated as:

$$|\Delta S_M| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1}-T_i}\Delta H_i \tag{5}$$

where M_i and M_{i+1} are the experimental values of the magnetization at T_i and T_{i+1}, respectively, under an applied magnetic field H_i. Using Eq. (4), by measuring the M–H curve at various temperatures, one can calculate the magnetic entropy change associated with the magnetic field variation. In this paper, we adopt the first method to evaluate the magnetic entropy change.

Based on expression (4) the magnetic–entropy changes as a function of temperature for the $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ ($0.15 \le x \le 0.3$) samples at the external magnetic fields of 10 kOe were calculated and plotted in Fig. 5. The broad peaks of $\left|\Delta S_M^{max}\right|$ of the samples also reveal the second-order character of the transition. Large magnetic entropy changes ($|\Delta S_M^{max}|$) are reported for all the samples and they are summarized in Table 1. Among the investigated samples, $La_{0.67}Pb_{0.33}Mn_{0.7}Co_{0.3}O_3$ exhibits a highest value of 3.22 J/(kg K) for $|\Delta S_M^{max}|$ at the Curie temperature T_C of 260 K. These results indicate that the present investigated samples are very good substances for magnetic refrigeration applications. To explain a large magnetic entropy variation in perovskite manganites, the Zener double-exchange model has often been thought to be applicable [14]. The magnetic entropy change has been believed to relate closely to the mechanism of double-exchange interaction between Mn^{3+} and Mn^{4+} ions arising from the change in the Mn^{3+}/Mn^{4+} ratio, under the doping process [15–17]. In addition, Guo et al. [17] proposed that the large magnetic entropy change in perovskite manganites could originate from the spin–lattice coupling in the magnetic ordering process. Because of the strong coupling between spin and lattice, a significant change in the lattice accompanying the magnetic transition in perovskite manganites has been observed [18,19]. The lattice structural change in the ⟨Mn–O⟩ bond length as well as ⟨Mn–O–Mn⟩ bond angle would in turn favor the spin ordering. As a result, a more abrupt variation of magnetization near T_C occurs, which leads to a large magnetic entropy change as the large

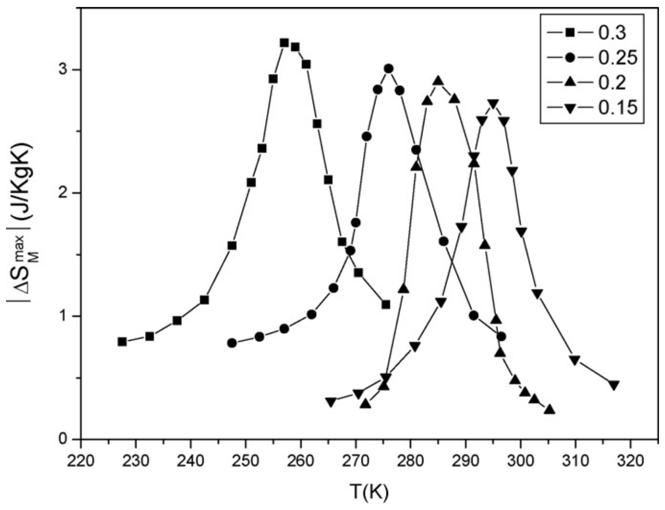

Fig. 5. Magnetic entropy change as a function of temperature of the samples $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$.

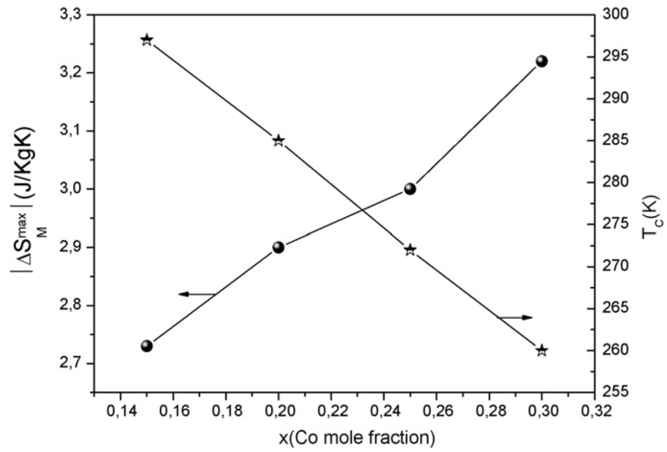

Fig. 6. The dependences of the Curie temperature (T_C) and the magnetic entropy change on the Co-doped concentration (x) for $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ (x = 0.15, 0.2, 0.25 and 0.3) compounds.

MCE [20,21]. For comparison, the data of several magnetic materials, which could be used as active refrigerants, are summarized in Table 1.

In Fig. 6, the maximum magnetic entropy change $|\Delta S_M^{max}|$ and the Curie temperature T_C were plotted as functions of Co concentration. Based on the experimental results, one can see that the increase in the x could be attributed to the decrease of the T_C, while the slight increase in $|\Delta S_M^{max}|$ for the Cobaltite addition could originate from the decrease of spin–lattice interaction.

Generally, the important index for selecting magnetic refrigerants is based on the cooling power per unit volume, namely, the relative cooling power (RCP) [22]. The RCP has been defined as:$\mathrm{RCP}(S) = \left|\Delta S_M^{max}\right| \times \delta T_{FWHM}$where $|\Delta S_M^{max}|$ is the maximum magnetic entropy change and δT_{FWHM} is the full width at half maximum of the magnetic entropy change curve, has also been calculated for our samples. RCP value estimated for the present set of $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ increases with Co content (Table 1). The heat originated only from magnetic entropy change around ±10 K of T_C, can also be estimated as: $\left|Q_M(T_C \pm 10\,\mathrm{K},\ H = 10\,\mathrm{kOe})\right| = \int_{T_C-10\,\mathrm{K}}^{T_C+10\,\mathrm{K}} \Delta S_M(T,\ H = 10\,\mathrm{kOe})dT$. Q_M obtained at 10 kOe around ±10 K of T_C decreases with Co content (Table 1) and is typically found to be ≈37% that of Gd (122.0 J/kg at $T_C \pm 25$ K).

4. Conclusion

We present hear, the results of an investigation of the magnetocaloric effect in $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ materials. A large magnetic entropy at the Curie temperature has been observed even though the spin–lattice coupling has been reduced in present system. The Curie temperature T_C decreases from 297 K (x = 0.15) to 260 K (x = 0.3). This decrease is accompanied by an increase of the magnetic entropy change. $La_{0.67}Pb_{0.33}Mn_{0.7}Co_{0.3}O_3$ exhibits the highest value of 3.22 J/(K kg) for $|\Delta S_M^{max}|$ at the Curie temperature of 260 K, upon 10 kOe applied field variation. The refrigerant capacity (Q_M) as well as the relative cooling power (RCP) of these compounds increases with Co-doping. These perovskite manganites are easy to fabricate and exhibit higher chemical stability as well as higher resistivity which are favorable for the lowering of eddy current heating. Besides, it is possible to adjust the Curie temperature T_C of perovskite manganites by either A- or B-site doping, and consequently, a large magnetic entropy change can be tuned from low temperature to near or above room temperature, which is beneficial for operating magnetic refrigeration at various temperature range. Our results suggest that the polycrystalline $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$ have some appropriate properties for a good candidate as a working material for active magnetic refrigerant.

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