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Magnetocaloric effect above room temperature in the K-doped $La_{0.8}Na_{0.2-x}K_xMnO_3$ manganites

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ABSTRACT

Structural, magnetic and magnetocaloric properties of $La_{0.8}Na_{0.2-x}K_xMnO_3$ $(0 \le x \le 0.2)$ powder samples have been investigated by X-ray diffraction (XRD) and magnetic measurements. Our samples have been synthesized using the solid state reaction method at high temperature. Rietveld refinements of the X-ray diffraction patterns show that all our samples are single phase and crystallize in the distorted rhombohedral system with $R\bar{3}c$ space group. Magnetization measurements versus temperature in a magnetic applied field of 50 mT show that all our samples exhibit a paramagnetic–ferromagnetic transition with decreasing temperature. Although K doping in our samples leads to an increase in the average ionic radius $\langle r_A \rangle$, the Curie temperature is found to remain almost constant around 330 K. From the measured magnetization data of $La_{0.8}Na_{0.2-x}K_xMnO_3$ $(0 \le x \le 0.2)$ samples as a function of magnetic applied field, the associated magnetic entropy change $|\Delta S_M|$ close to the Curie temperature T_C has been determined. The parent compound ($x = 0$) exhibits a maximum entropy change $|\Delta S_M^{Max}|$ of 1.32 J/kg K at 325 K in a magnetic applied field of 1 T. $|\Delta S_M^{Max}|$ decreases to 0.92 J/kg K at 335 K for $x = 0.2$ in the same field magnitude.

1. Introduction

The research in the perovskite manganites with general formula $Ln_{1-x}A_xMnO_3$ (Ln = Rare-earth cation, A = alkali-metal or alkaline-earth cation) has attracted much renewed attentions after the observation of large magnetocaloric effect (MCE) in these compounds [1–3]. In fact, magnetic refrigeration is becoming promising technology to replace the conventional gas-compression expansion technique [4,5]. For sub-room temperature magnetic refrigeration applications, gadolinium is the first material known to show a large MCE, since it exhibits a maximum value of magnetic entropy change, $|\Delta S_M^{Max}|$, of 5 J/kg K at 294 K under magnetic applied field change of 2 T [6]. Otherwise, manganites are also interesting for application as potential candidates in magnetic refrigeration since they have low coast, are easy to elaborate and possess tunable T_C and high chemical stability. Generally, in manganites, the large magnetic entropy change could be attributed to the variation of the double exchange interaction between Mn^{3+} and Mn^{4+} ions and the strong spin lattice coupling [7–9]. A large overview of magnetocaloric effects observed in perovskite manganites has been provided by Phan and Yu [10]. The substitution of trivalent element by monovalent alkali-metal in manganites induces less inhomogeneity (the substitution oxidizes two Mn ions from Mn^{3+} to Mn^{4+} state) and improves the physical properties [11–13]. Our research group [14–16] has widely studied the magnetocaloric properties of $La_{0.65}Ca_{0.35}MnO_3$ system where a partial calcium substitution by monovalent element is found to improve significantly the T_C value which reaches room temperature. Zhong et al. [17] have studied the magnetocaloric properties in $La_{1-x}Na_xMnO_3$ $(0 \le x \le 0.2)$ and found that for $x = 0.2$, $|\Delta S_M^{Max}|$ reaches 1.96 J/kg K upon a magnetic applied field change of 1 T. Hou et al. [18] investigated the MCE properties of $La_{0.8-x}Nd_xNa_{0.2}MnO_3$ and found that with decreasing $\langle r_A \rangle$, $|\Delta S_M^{Max}|$ decreases from 0.43 J/kg K at 333.7 K for $x = 0$–0.36 J/kg K at 295 K for $x = 0.15$ under $\Delta H = 1T$. Furthermore, the study of magnetocaloric properties in $La_{1-x}K_xMnO_3$ compounds synthesized by sol gel method has shown an enhancement in both T_C and $|\Delta S_M^{Max}|$ values reaching respectively 344 K and 2.19 J/kg K under 1.5 T for $x = 0.2$ sample [19]. More recently, Das and Dey have observed similar behavior in $La_{1-x}K_xMnO_3$ compounds synthesized by pyrophoric method with $|\Delta S_M^{Max}| = 3$ J/kg K under 1 T for $x = 0.15$ [20].

Our present study has been carried out to investigate the effect of K doping on the structural, magnetic and magnetocaloric properties of $La_{0.8}Na_{0.2-x}K_xMnO_3$ $(0 \le x \le 0.2)$ compounds with fixed Mn^{4+}/Mn^{3+} ratio equal to 2/3.

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Table 1
Refined structural parameters of $La_{0.8}Na_{0.2-x}K_xMnO_3$ ($0 \le x \le 0.2$) samples at room temperature.

	$x = 0$	$x = 0.05$	$x = 0.1$	$x = 0.15$	$x = 0.2$
a (Å)	5.483(2)	5.485(8)	5.493(5)	5.497(9)	5.505(1)
b (Å)	5.483(2)	5.485(8)	5.493(5)	5.497(9)	5.505(1)
c (Å)	13.314(2)	13.326(1)	13.342(5)	13.357(4)	13.378(5)
V (Å^3)	346.67	347.29	348.71	349.65	351.13
Mn–O (Å)	1.947(5)	1.949(5)	1.951(5)	1.951(6)	1.954(5)
Mn–O–Mn (°)	166.44(4)	165.87(4)	166.03(4)	166.86(4)	166.99(3)
χ^2 (%)	0.978	0.913	0.968	0.928	0.982
$\langle r_A \rangle$ (Å)	1.366	1.378	1.391	1.403	1.416
σ^2 (Å^2)	0.14×10^{-3}	3.71×10^{-3}	6.96×10^{-3}	9.91×10^{-3}	12.54×10^{-3}

2. Experimental techniques

Powder samples of $La_{0.8}Na_{0.2-x}K_xMnO_3$ ($0 \le x \le 0.2$) have been synthesized using the standard solid state reaction method at high temperature. The starting materials were intimately mixed in an agate mortar and then heated in air up to 1000 °C for 60 h. The obtained powders were then pressed into pellets (of about 1 mm thickness and 13 mm diameter) and sintered at 1100 °C in air for 60 h with intermediate regrinding and repelling. Finally, these pellets were rapidly quenched to room temperature in air in order to freeze the structure at the annealed temperature. Phase purity, homogeneity and cell dimensions were determined by powder X-ray diffraction at room temperature. As our samples have been synthesized in air, they are consequently stoichiometric in oxygen [21]. Structural analysis was carried out using the standard Rielveld technique [22,23]. The amount of Mn^{4+} ions has been quantitatively checked by iodometric titration. Magnetization measurements versus temperature in the range 20–400 K and versus magnetic applied field up to 8 T were carried out using a vibrating sample magnetometer. MCE were deduced from the magnetization measurements versus magnetic applied field up to 8 T at several temperatures.

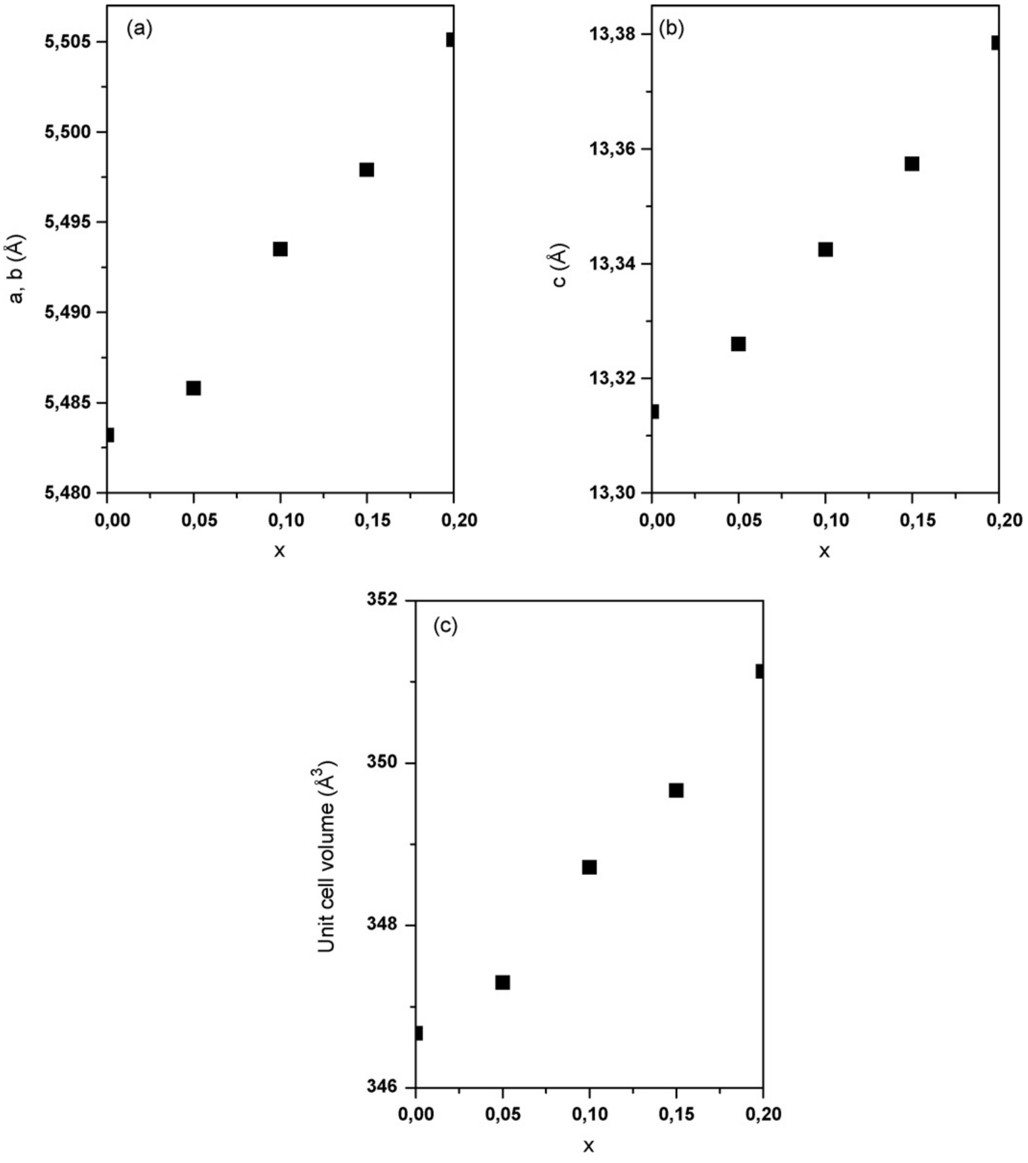

Fig. 1. (a) Unit cell parameters a and b, (b) unit cell parameter c and (c) unit cell volume evolution versus K content for $La_{0.8}Na_{0.2-x}K_xMnO_3$ ($0 \le x \le 0.2$) compounds.

3. Results and discussion

The results of the X-ray diffraction (XRD) studies at room temperature of $La_{0.8}Na_{0.2-x}K_xMnO_3$ ($0 \leq x \leq 0.2$) compounds indicate that all our samples were found to be single phase and have the same perovskite structure. As the potassium content increases there is a shift in the intense diffraction peak to the lower angle. This result indicates an increase in the volume of the unit cell with potassium content. The structural parameters of the samples are refined by the Rietveld profile-fitting method. The profile refinement is started with scale and background parameters followed by the unit cell parameters. Then, the peak asymmetry and preferred orientation corrections are applied. Finally, the positional parameters and the individual isotropic parameters are refined. It has been found that all our samples can be indexed in the rhombohedral system with $R\bar{3}c$ space group. The final refinement values of the structural parameters and χ^2 values of the Rietveld analysis are summarized in Table 1. In this table the average size of A-site cations ($\langle r_A \rangle$) and the mismatch size (σ^2) at the A-site are also listed. With increasing K content, the lattice parameters *a*, *b* and *c* increase leading to an increase of the unit cell volume (Fig. 1). In our synthesized samples, the Mn^{4+}/Mn^{3+} ratio is fixed and this structural evolution can be explained rather by an increase of $\langle r_A \rangle$ induced by the substitution of smaller Na^+ ($r_{Na^+} = 1.39$ Å) ions by larger K^+ ($r_{K^+} = 1.64$ Å) ions [24]. The average crystallite size can be estimated from the XRD data using the Scherer relation [25]. The values of the effective particle size are found to be in the range 30–40 nm.

Magnetization measurements as a function of temperature in the range 20–400 K and in a magnetic applied field of 50 mT showed that our synthesized samples exhibit a paramagnetic to ferromagnetic transition with decreasing temperature as can be shown in Fig. 2 for $La_{0.8}Na_{0.05}K_{0.15}MnO_3$ compound. Although K doping in our samples leads to an increase in the average ionic radius $\langle r_A \rangle$, the Curie temperature T_C (defined as the temperature at which dM/dT shows a minimum) is found to remain almost constant and equal to 330 K. The similar low temperature reduction of magnetization and constant Curie temperature values have been also reported for $La_{0.67}Ca_{0.33}Mn_{1-x}V_xO_3$ manganites [26]. The authors showed that V would not have gone completely to the substitutional site leading to the existence of multiphase compound. In our structural study no second phase has been detected, so this behavior could be rather explained by the antagonist competition between the mismatch effect and $\langle r_A \rangle$ [27–29]. For all our samples, in the paramagnetic phase ($T > T_C$), the temperature dependence of the magnetic susceptibility follows the Curie–Weiss law, $\chi = C/T - \theta_P$, where *C* is the Curie constant and θ_P is the Curie–Weiss temperature (inset Fig. 2). The values of θ_P are found to be 328.4 K, 330.1 K and 329.1 K, 329.6 K and 330.5 K for $x = 0$, 0.05, 0.1, 0.15 and 0.2 respectively. The Curie constant values calculated from the line slopes of the reciprocal susceptibility versus temperature curve, $\chi^{-1}(T)$, have been used to estimate the experimental effective paramagnetic moment μ_{eff}^{exp}. We found the μ_{eff}^{exp} value to be $3.66\mu_B$, $3.46\mu_B$, $3.87\mu_B$, $3.94\mu_B$ and $3.28\mu_B$ for $x = 0$, 0.05, 0.1, 0.15 and 0.2 respectively lower than the therotically predicted value of $4.5\mu_B$.

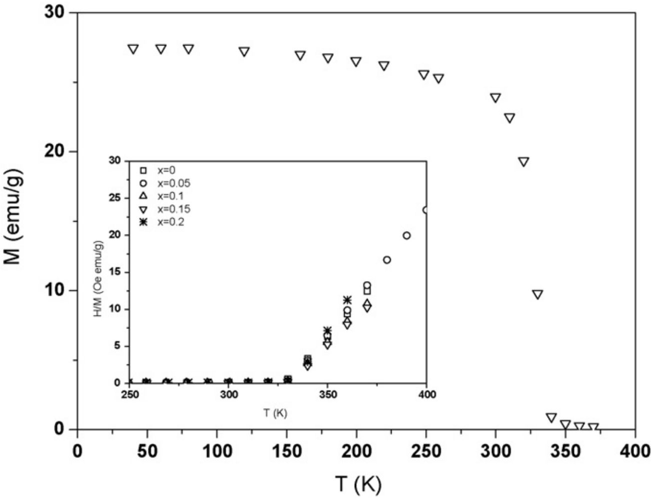

Fig. 2. Temperature dependence of the magnetization at $\mu_0H = 50$ mT for $La_{0.8}Na_{0.05}K_{0.15}MnO_3$ compound. The inset shows the temperature dependence of reciprocal magnetic susceptibility for $La_{0.8}Na_{0.2-x}K_xMnO_3$ ($0 \leq x \leq 0.2$) compounds.

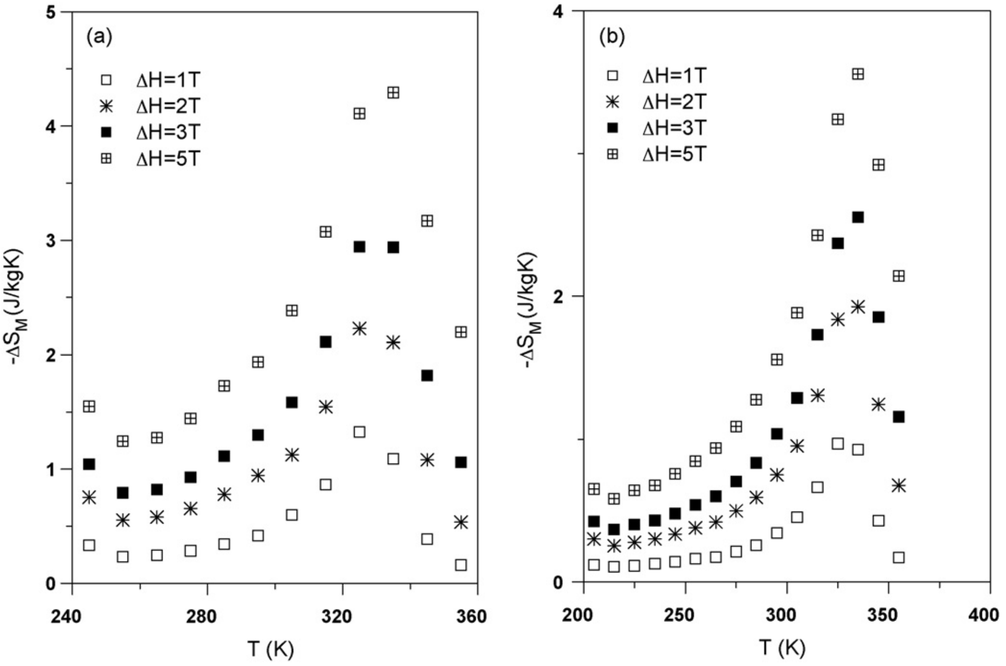

Fig. 3. Magnetic entropy change $|\Delta S_M|$ as a function of temperature at several magnetic applied fields for (a) $La_{0.8}Na_{0.2}MnO_3$ and (b) $La_{0.8}K_{0.2}MnO_3$ samples.

In order to confirm the ferromagnetic behavior of our samples at low temperatures, we performed magnetization measurements versus magnetic applied field up to 8 T at several temperatures. The experimental value of the spontaneous magnetization $M_{sp}(\mathrm{exp})$ determined by extrapolation of the $M(H)$ data in the high field regions to zero field is found to be $3.37\mu_B$/Mn, $3.32\mu_B$/Mn, $3.37\mu_B$/Mn, $3.41\mu_B$/Mn and $2.73\mu_B$/Mn for $x = 0$, 0.05, 0.1, 0.15 and 0.2 respectively. The theoretical value of the spontaneous magnetization $M_{sp}(\mathrm{Th})$ determined by assuming full spin alignment of Mn ions ($4\mu_B$ for Mn^{3+} and $3/2\mu_B$ for Mn^{4+}) is found to be $3.6\mu_B$/Mn. For $La_{0.8}K_{0.2}MnO_3$ sample, the discrepancy between $M_{sp}(\mathrm{exp})$ and $M_{sp}(\mathrm{Th})$ arises from the disorder in the A-site cation.

For all our samples, Arrott plots above T_C show a linear behavior which indicates that a second order magnetic transition occurs [30]. The critical exponent γ deduced from the magnetization measurements as a function of the magnetic applied field up to 8 T at several temperatures is found to remain almost constant and equal to 0.34 for all compounds.

The magnetic entropy change, $|\Delta S_M|$, induced by the magnetic field change can be calculated according to the classical thermodynamic theory based on Maxwell's relations [31]. Fig. 3 shows $|\Delta S_M|$ evolution of $La_{0.8}Na_{0.2}MnO_3$ and $La_{0.8}K_{0.2}MnO_3$ samples as a function of temperature for different external magnetic applied fields. Upon a magnetic field change of 1 T, the maximum entropy change, $|\Delta S_M^{Max}|$, of $La_{0.8}Na_{0.2}MnO_3$ sample reaches 1.32 J/kg K at 325 K. This value of $|\Delta S_M^{Max}|$ is found to be higher than that reported recently by Hou et al. in $La_{0.8-x}Nd_xNa_{0.2}MnO_3$ ($x = 0$) sample [18]. This difference may be caused by the difference in the elaborating

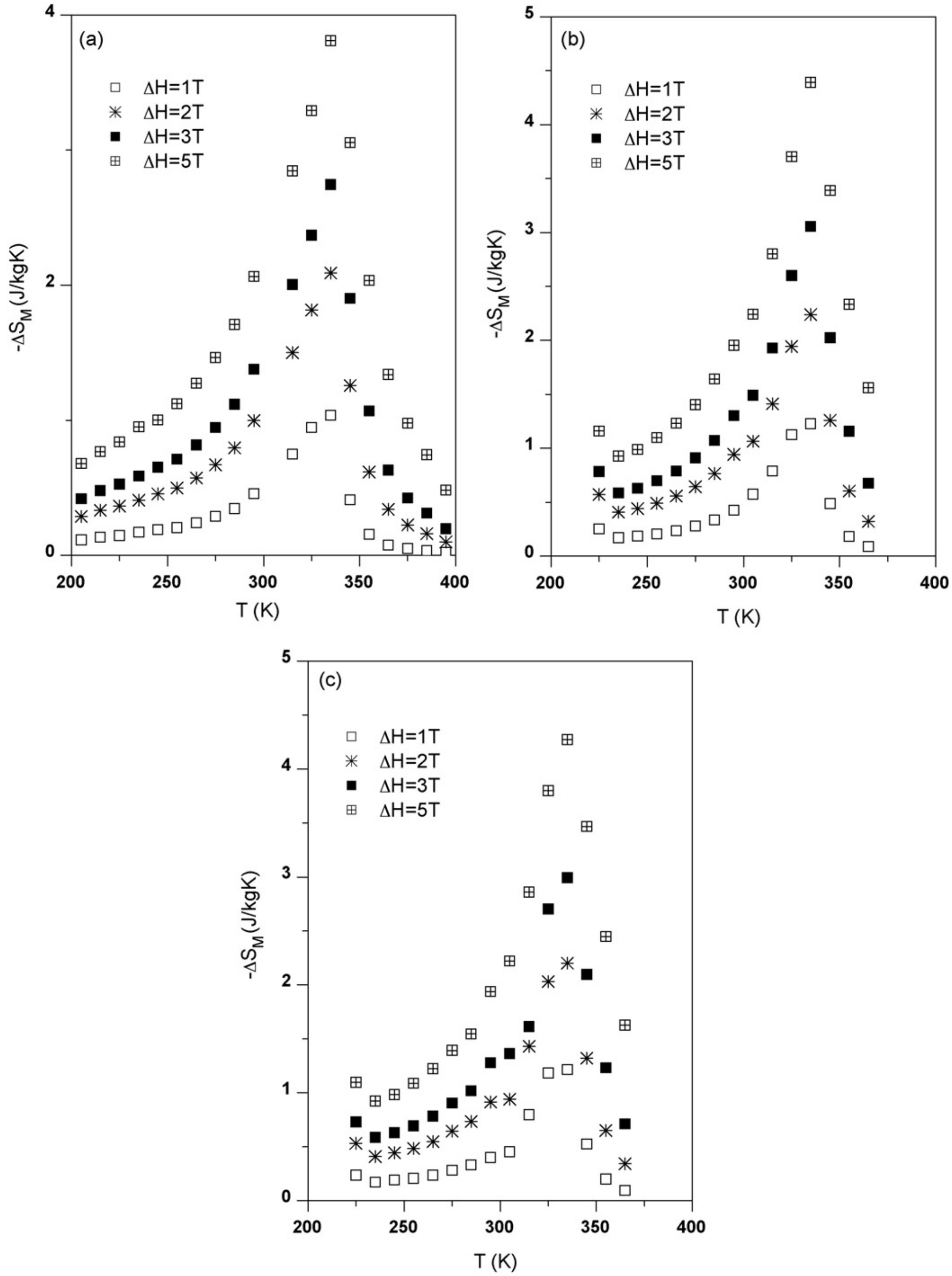

Fig. 4. Magnetic entropy change $|\Delta S_M|$ as a function of temperature at several magnetic applied fields for $La_{0.8}Na_{0.2-x}K_xMnO_3$ ($0.05 \le x \le 0.15$) samples.

method which influences strongly the grain size of the samples [32]. Upon the same magnetic applied field of 1 T, $|\Delta S_M^{Max}|$ decreases to 0.92 J/kg K at 335 K for $La_{0.8}K_{0.2}MnO_3$ sample.

Fig. 4a–c shows the $|\Delta S_M|$ evolution versus temperature, for field change up to 5 T, in $La_{0.8}Na_{0.2-x}K_xMnO_3$ ($0.05 \leq x \leq 0.15$) samples. The $|\Delta S_M^{Max}|$ values corresponding to a magnetic field variation of 2 T are found to be 2.09 J/kg K, 2.24 J/kg K and 2.20 J/kg K for $x = 0.05$, 0.1 and 0.15 respectively.

The relative cooling power (RCP) is evaluated as $RCP = -\Delta S_M^{Max}(T, H) \times \delta T_{FWHM}$ where δT_{FWHM} is the full-width at half-maximum of $|\Delta S_M|$ versus temperature [33]. For our samples, the RCP values are respectively 88.3 J/kg, 107.5 J/kg, 91.3 J/kg, 86.6 J/kg and 85.2 J/kg at 2 T for $x = 0$, 0.05, 0.1, 0.15 and 0.2 respectively. Our results may be interesting enough, compared to materials considered as good for applications in magnetic refrigerators, opening a way for investigations of materials useful for magnetic refrigeration.

4. Conclusions

In summary, we have presented a study of $La_{0.8}Na_{0.2-x}K_xMnO_3$ ($0 \leq x \leq 0.2$) powder samples through X-ray and magnetic measurements. The structural study shows that all our synthesized samples crystallize in the rhombohedral structure with $R\bar{3}c$ space group. The lattice parameters as well as the unit cell volume increase with potassium content. All our samples exhibit a paramagnetic–ferromagnetic transition with decreasing temperature. Large MCE has been obtained in all samples at the Curie temperature and $|\Delta S_M^{Max}|$ reaches the highest value of 2.24 J/kg K for the sample with $x = 0.1$ upon a magnetic applied field change of 2 T. They may be alternative candidates for active magnetic refrigerants working above room temperature. The relative cooling power of $La_{0.8}Na_{0.05}K_{0.15}MnO_3$ is 107 J/kg under a magnetic field of 2 T, which is comparable to other reported magnetic refrigerants.

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