Journal of Alloys and Compounds 509 (2011) 3699–3704

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Large magnetic entropy change near room temperature in $La_{0.7}(Ca_{0.27}Ag_{0.03})MnO_3$ perovskite

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ARTICLE INFO

Article history:
Received 2 September 2010
Received in revised form
22 December 2010
Accepted 22 December 2010
Available online 30 December 2010

Keywords:
Magnetic refrigeration
Phase transitions
Magnetocaloric effect
Relative cooling power

ABSTRACT

In this paper, the magnetic properties and magnetocaloric effect (MCE) of $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$ ($x = 0$, 0.1, 0.2, 0.7, and 1) powder samples are reported. Our polycrystalline compounds were synthesized using the solid state reaction method at high temperature. Magnetization measurements versus temperature showed that all our samples exhibited a paramagnetic to ferromagnetic transition with decreasing temperature. The Curie temperature, T_C, has been found to increase from ~250 K for $x = 0$–270 K for $x = 1$. Ag doping weakens the first order phase transition, and at higher Ag doping, the phase transition is of second order. For the $La_{0.7}(Ca_{0.27}Ag_{0.03})MnO_3$ composition, the maxima of the magnetic entropy changes from the applied magnetic field (ΔS_M) at 2 and 5 T are about 4.5 and 7.75 J/kg K, respectively, at the Curie temperature of ~263 K. The relative cooling power (RCP) values without hysteresis loss are about 102 and 271 J/kg for the applied fields of 2 and 5 T, respectively. Due to the large ΔS_M, large RCP, and high Curie temperature, $La_{0.7}(Ca_{0.27}Ag_{0.03})MnO_3$ is promising for application in potential magnetic refrigeration near room temperature.

1. Introduction

Doped manganites with the general formula of $R_{1-x}M_xMnO_3$ (R = La, Pr, Nd, etc., and M = Sr, Ca, Ba, etc.) exhibit a rich variety of phenomena such as colossal magnetoresistance [1] and a large magnetocaloric effect (MCE) [2]. The latter effect, which is represented by an isothermal change in the magnetic entropy or an adiabatic change in the temperature in magnetic fields, forms the basis for magnetic refrigeration [3]. Manganites are relatively easy to synthesize, are tunable by adjustment of the doping concentration, and are considered promising candidates for magnetic refrigeration at various temperatures, as reviewed by Phan and Yu [2].

The main requirements for a magnetic material to possess a large change in magnetic entropy, $|\Delta S_M|$, are a large spontaneous magnetization as well as a sharp drop in the magnetization associated with the ferromagnetic (FM) to paramagnetic (PM) transition at the Curie temperature, T_C [4,5]. It should be noted that the magnitude of the MCE in compounds which undergo a structural transition in conjunction with the magnetic transition is increased due to the additional lattice entropy contribution [6]. Phan and Yu have provided an overview of magnetocaloric properties in perovskite manganese oxides [2]. The largest reported value of $|\Delta S_M|$ in the $La_{1-x}Ca_xMnO_3$ manganites is found to be 6.25 J/kg K at 216 K upon a magnetic field change of 1 T for $x = 0.3$, a compound which exhibits a first order paramagnetic to ferromagnetic transition [7]. According to previous reports, the $La_{0.7}Ca_{0.3}MnO_3$ compound exhibits different $|\Delta S_M|$ values depending on the elaborating technique and the oxygen stoichiometry. In fact, under a magnetic applied field of 1 T, Phan et al. [8] found that $|\Delta S_M|_{max}$ is 1.38 J/kg K at 256 K, while the maximum value of the magnetic entropy $|\Delta S_M|_{max}$ observed by Ulyanov et al. [9] reaches 7 J/kg K at 242 K.

Similarly to the doping at A site with divalent elements, monovalent substitution is expected to introduce large potential fluctuations leading to large magnetocaloric effects. Tang et al. [10] measured the MCE in $La_{0.7}Ag_{0.3}MnO_3$ compound. The $|\Delta S_M|_{max}$ was found to be 1.35 J/kg K around room temperature for a magnetic field variation, ΔH, of 1 T, while for a $La_{0.8}Na_{0.2}MnO_3$ sample, the $|\Delta S_M|_{max}$ value observed by Hou et al. [11] was found to be 0.43 J/kg K at 333 K for an applied magnetic field change of 1 T. Bejar et al. [12] measured the MCE in $La_{0.7}Ca_{0.3-x}K_xMnO_3$, and the $|\Delta S_M|_{max}$ was found to be 3.95 J/kg K at 270 K upon a magnetic field change of 2 T for $x = 0.05$, while for $La_{0.65}Ca_{0.35-x}K_xMnO_3$, the entropy change value observed by Koubaa et al. [13] was found to be 3.18 J/kg K at 310 K upon a magnetic field change of 2 T for $x = 0.2$. For their La0.7$Sr_{0.3-x}K_xMnO_3$ sample, Koubaa et al. [14] showed that

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doi:10.1016/j.jallcom.2010.12.169

the $|\Delta S_M|_{max}$ is about 2.15 J/kg K upon a magnetic field change of 2 T for $x = 0.15$. The entropy change value measured by the same author [15] for $La_{0.7}Sr_{0.3-x}Na_xMnO_3$ was found to be 2.04 J/kg K under a magnetic field change of 2 T. Again, they [16] measured the MCE in $La_{0.65}Ba_{0.3}M_{0.05}MnO_3$, and the $|\Delta S_M|_{max}$ was found to be 1.3, 1.43, and 1.34 J/kg K upon a magnetic field change of 2 T for M = Na, Ag, and K, respectively, while they also showed the entropy change value to be about 1.6 J/kg K for $La_{0.7}Sr_{0.1}Ag_{0.2}MnO_3$ at 315 K [17]. Finally, they [18] measured the MCE in $La_{0.65}Ca_{0.35-x}Ag_xMnO_3$, and the maximum entropy change, $|\Delta S_M|_{max}$, corresponding to a magnetic field variation of 1 T, was found to be 1.65, 1.14. 1.01, and 0.89 J/kg K for x = 0.05, 0.1, 0.15, and 0.2, respectively. It has been generally shown that the most prominent magnetic and magnetotransport properties in substituted manganites are obtained for samples having Mn^{4+} amounts around 33% [19].

In assessing the usefulness of a magnetic refrigerant material, the refrigerant capacity (RC), which is a measure of the amount of heat transfer between the cold and hot sinks in an ideal refrigeration cycle, is considered to be the most important factor, however, not the magnetic entropy change alone [20–22]. The RC depends not only on the magnitude of ΔS_M, but also on the temperature dependence of ΔS_M (e.g., the full width at half maximum of the ΔS_M (T) peak) [20,22]. In this context, a good magnetic refrigerant material with large RC requires both a large magnitude of ΔS_M and a broad width of the ΔS_M (T) curve. Most previous studies on monovalent substitution were focused mainly on exploring large MCE (large magnitudes of ΔS_M) and did not consider in detail the issues of RC and hysteretic losses. Thus, from fundamental and practical perspectives, it is essential to understand the influence of the magnetic phase transitions on both the MCE and the RC in these materials.

In the present study, we investigate the MCE related to the effects of Ag doping in $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$, which can be a suitable candidate as a working substance in magnetic refrigeration near room temperature.

2. Experimental

Powder samples of $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$ were synthesized using the standard solid-state reaction method at high temperature, by mixing La_2O_3, $CaCO_3$, Ag_2CO_3, and MnO_2 up to 99.9% purity in the desired proportions. The starting materials were intimately mixed in an agate mortar and first fired at 700 °C for 12 h. Then, the mixture was reground and again fired at 900 °C for 12 h. The mixture was ground again for a third time, pressed into pellets, and fired at 1100 °C for 12 h to obtain better crystallization. Finally, the sample was again reground, pressed into pellets, and sintered at 1350 °C for 24 h. Powder X-ray diffraction (XRD) patterns were obtained with Cu Kα radiation at room temperature. Structural analysis was carried out using the standard Rietveld method [23,24]. Magnetization measurements versus temperature in the range of 5–300 K and versus applied magnetic field up to 5 T were carried out using a physical properties measurement system (PPMS). MCE results were deduced from the magnetization measurements versus magnetic applied field up to 5 T at several temperatures.

3. Results

3.1. Structural and magnetic properties

The phase composition and crystal structure of the samples were characterized by X-ray diffraction (XRD). The XRD patterns of the $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$ samples are shown in Fig. 1. The X-ray diffraction analysis shows that the samples with $x \leq 0.2$ are mainly composed of orthorhombic perovskite structure phases, the sample with $x = 0.7$ has two phases (perovskite structure and Ag metal phase), and the one with $x = 1.0$ has three phases (perovskite structure, Ag metal, and Mn_3O_4 phase). As might be expected, lattice parameters, as well as volume of the unit cell, are continuously enhanced with increasing x due to the substitution of large Ag^+ (1.28 Å) ions for smaller Ca^{2+} (1.18 Å) ions. Our results agree well with those obtained on the effects of K^+ doping on the physical properties of $La_{0.65}Ca_{0.35-x}K_xMnO_3$ by Koubaa et al. [13], but differ from those obtained on the effect of Ag^+ doping on the physical properties of $La_{0.65}Ca_{0.35-x}Ag_xMnO_3$ by Koubaa et al. [18]. Lattice parameters and the volume of unit cell are listed in Table 1.

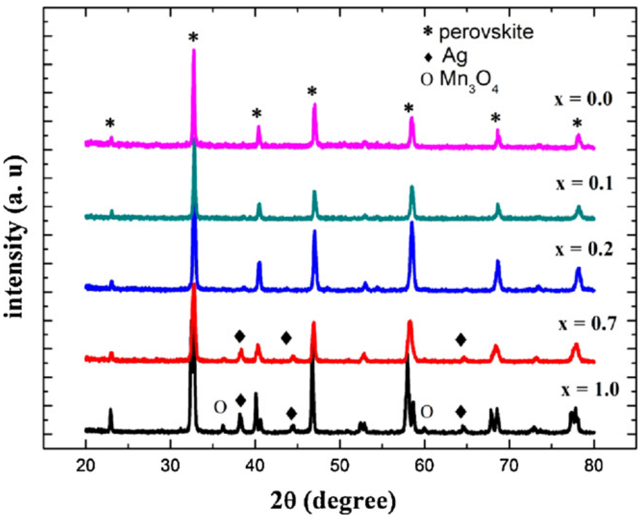

Fig. 1. XRD patterns for $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$ samples.

Table 1
Lattice parameters of the $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$ samples.

Sample (x)	a (Å)	b (Å)	c (Å)	$V_{unit\ cell}$ (Å^3)
0.0	5.47175	5.45592	7.72155	230.515
0.1	5.47760	5.47208	7.72650	231.593
0.2	5.48036	5.47446	7.74285	232.301
0.7	5.52073	5.47321	7.77363	234.889
1.0	5.54087	5.47698	7.78994	236.403

Magnetization measurements as a function of temperature in a magnetic applied field of 200 Oe (Fig. 2) showed that all our synthesized samples exhibited a paramagnetic to ferromagnetic transition with decreasing temperature. With increasing Ag content, the Curie temperature T_C increases from 250 K for $x = 0$ to 270 K for $x = 1$. As a result of increasing average ionic radius in the A site, $\langle r_A \rangle$, the values of T_C shifted to higher temperature with Ag doping content. The increasing T_C (or magnetic coupling versus double

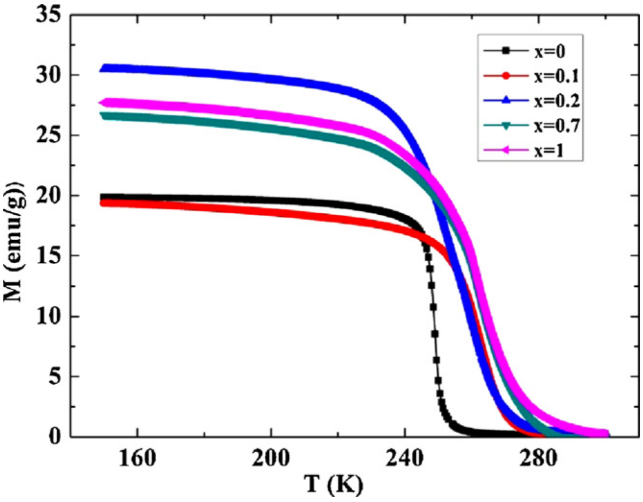

Fig. 2. Temperature dependence of magnetization at 200 Oe for $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$ samples.

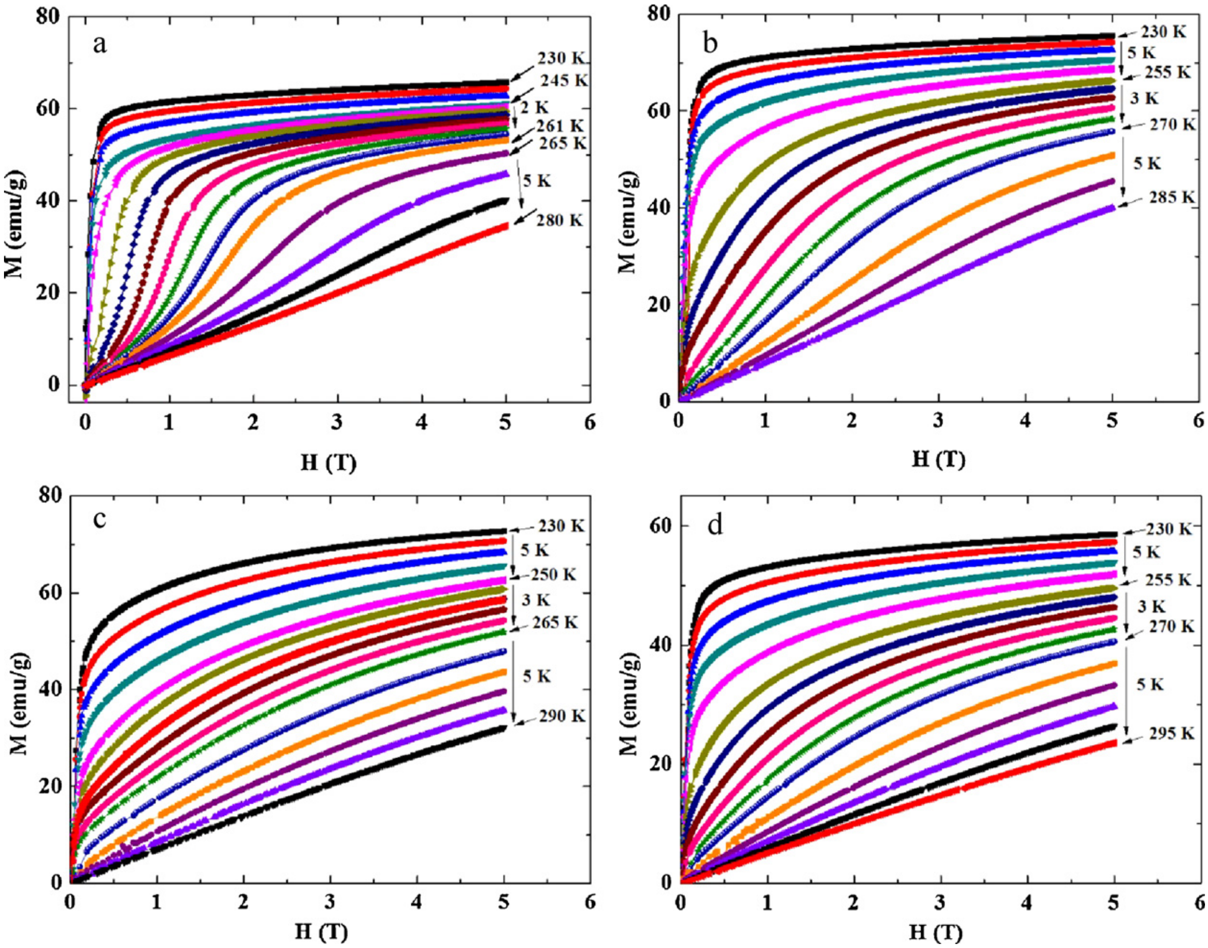

Fig. 3. Magnetization evolution versus magnetic applied field at several temperatures for $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$ samples: (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.7$, and (d) $x = 1$.

exchange interaction) can be due to increasing $\langle r_A \rangle$and an increasing Mn^{4+}/Mn^{3+} ratio. In this case, the increasing T_C is due to the first term [25].

In order to evaluate the MCE, the isothermal magnetization curves of the samples were measured with a field step of 0.05 mT in the magnetic field range of 0–5 T and over a range of temperatures around T_C. Such families of $M(H)$ curves are shown in Fig. 3a–d. It is worth mentioning that around the T_C, the samples shown in both (a) and (b) feature S-shaped magnetization, which is typical for metamagnetic materials [26], whereas this property is absent for the (c) and (d) samples. It is also worth noting that a large proportion of the changes in the magnetization occur in the relatively low field range (<2.0 T), which is beneficial for the application of MCE materials. For the samples in (a) and (b), the curves reveal a strong variation in the magnetization around the Curie temperature, indicating that there is a possibility of obtain a large magnetic entropy change associated with the FM–PM transition occurring at T_C.

To understand the nature of the magnetic transition of the samples, Arrott plots of M^2 versus H/M covering a broad temperature range around T_C are plotted in Fig. 4. Clearly, an inflection point and negative slopes are observed in Fig. 4a and b, indicating the occurrence of a first order magnetic transition. Neither an inflection point nor negative slopes are observed in Fig. 4c and d proving the occurrence of a second order magnetic transition. Therefore, it is expected that doping with Ag weakens the first order magnetic phase transition and that at higher Ag doping, the nature of the phase transition is second order.

3.2. Magnetocaloric properties

The entropy change as a function of temperature in different magnetic fields ranging from 0 to 5 T for the samples $x = 0.0$, 0.1, 0.7, and 1 are shown in Fig. 5. The maximum values of ΔS_M corresponding to an external field of 2 T for those samples are about 5.71, 4.5, 2.47, and 2.59 J/kg K, respectively, and 7.528, 7.63, 5.04, and 4.83 J/kg K, respectively, for a 5 T magnetic field. $|\Delta S_M|$ exhibits a linear rise with increasing field, as shown in Fig. 5, which indicates that a much larger entropy change is to be expected at higher magnetic field, satisfying thereby the effects of spin-lattice coupling associated with changes in the magnetic ordering process in the samples [27]. Besides, we note that for the $La_{0.7}(Ca_{0.3})MnO_3$ and $La_{0.7}(Ca_{0.27}Ag_{0.03})MnO_3$ samples, the maximum magnetic entropy change (5.71 at 251 K and 4.5 J/kg K at 263 K for a 2 T field) is larger, about 90% of that for pure Gd for a 2 T field change [28], and also larger than for many other perovskite materials [14–16,18,25,29–31], but smaller than for the most conspicuous magnetocaloric material, $Gd_5(Si_2Ge_2)$ [28]. In particular, these values are larger than the values reported by Koubaa et al. [15–17,19]. An abrupt variation in the magnetization and a sharp volume change at T_C are two of the key conditions required for a large ΔS_M. For the samples with $x = 0.7$ and 1.0, the transitions are of second order, so the above-mentioned conditions are not present, and therefore, ΔS_M falls considerably. The giant magnetic entropy changes in these magnetic materials suggest that they could be potential candidates for magnetic refrigerants. However, before magnetic refrigeration becomes a viable cooling

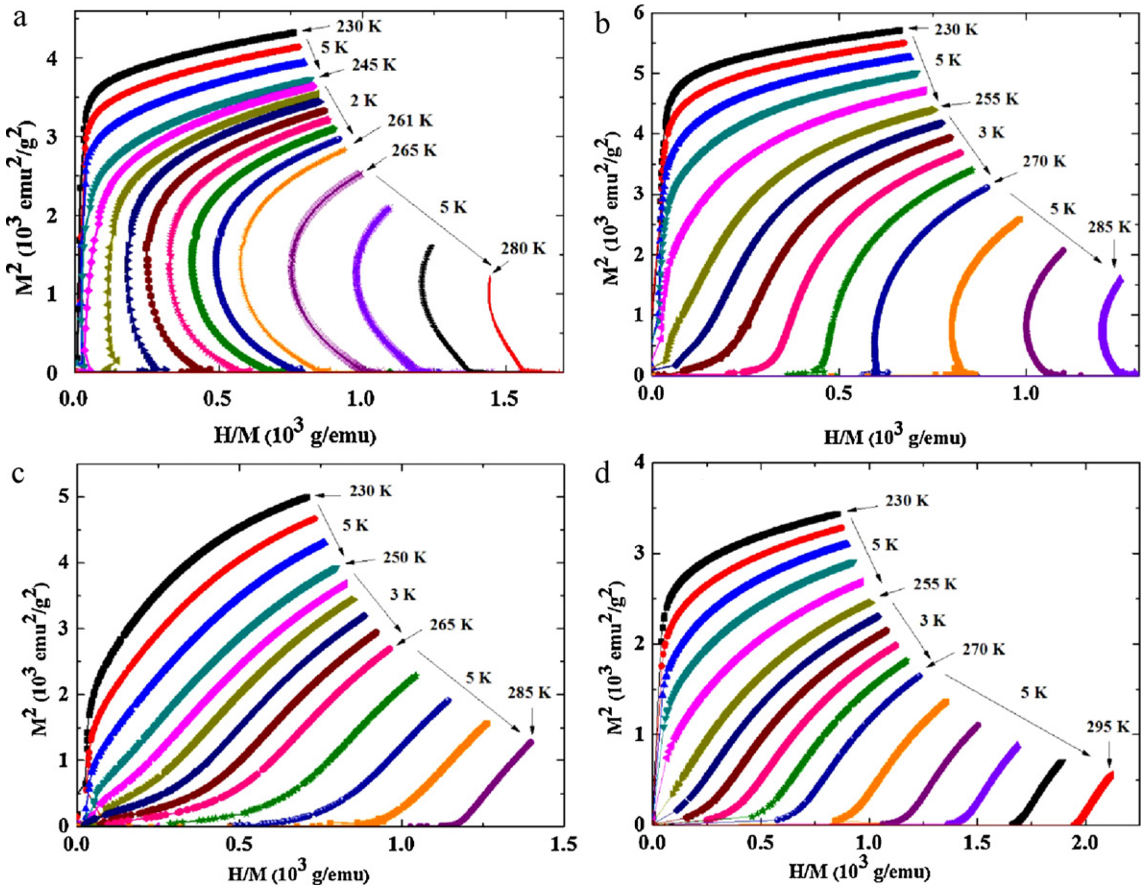

Fig. 4. M^2 versus H/M curves of isotherms for $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$ samples: (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.7$ and (d) $x = 1$.

technology, one must reduce the applied magnetic field, so as to allow the use of permanent magnets instead of superconducting magnets as the magnetic-field source. Therefore, a very important task is to search for novel magnetic materials possessing giant low-field induced MCEs. Our results provide a possibility for the development of magnetic refrigerant substances that are operable with a permanent magnet rather than a superconducting one as the magnetic field source.

On the other hand, the cooling efficiency of magnetic refrigerants is evaluated by means of the so-called relative cooling power (RCP), which corresponds to the amount of heat transferred between the cold and the hot sinks in the ideal refrigeration cycle defined by $RCP = |\Delta S_M| \times \delta T_{FWHM}$, where δT_{FWHM} means the full width at half-maximum of the magnetic entropy change curve. The RCP values for the $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.7}Ca_{0.27}Ag_{0.03}MnO_3$ and the $La_{0.7}Ag_{0.3}MnO_3$ samples exhibit an almost linear rise with increasing field, as shown in Fig. 6a. The RCP values of $La_{0.7}Ca_{0.27}Ag_{0.03}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ are 270.8 J/kg and 218 J/kg for a 5 T field change. These values are, however, lower than the RCP value reported for Gd, although they are high enough compared with many perovskite materials. From Fig. 6a, we can conclude that even though at low field the ΔS_M value of $La_{0.7}Ca_{0.3}MnO_3$ is slightly higher than that of $La_{0.7}Ca_{0.27}Ag_{0.03}MnO_3$, the value of RCP for the $La_{0.7}Ca_{0.27}Ag_{0.03}MnO_3$ is much higher than for the $La_{0.7}Ca_{0.3}MnO_3$, and this is only due to the uniform distribution of the ΔS_M, which is desirable for an Ericsson-cycle magnetic refrigerator.

Furthermore, we recall that hysteretic losses (magnetic and thermal hysteresis) are often involved in first order magnetic phase transitions [26] which would again justify the calculated RC values. Because these hysteretic losses are the costs in energy to drive one cycle of the magnetic field, they must be considered when calculating the usefulness of a magnetic refrigerant material being subjected to field cycling [21]. To evaluate possible hysteretic losses involved in the magnetic phase transitions in $La_{0.7}Ca_{0.3}MnO_{3,}$ $La_{0.7}Ca_{0.27}Ag_{0.03}MnO_3$, and the $La_{0.7}Ag_{0.3}MnO_3$ samples, we measured the M–H curves at temperatures around T_C. Fig. 6b shows, for example, the $M(H)$ curves measured at 260 K (near T_C). Interestingly it can be seen that even though $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Ca_{0.27}Ag_{0.03}MnO_3$ show a first order phase transition, the hysteresis loss is almost negligible, so the effective refrigeration capacity (RC_{eff}) is same as the RC value, which is therefore desirable for an efficient magnetic refrigerant cycle.

No hysteresis loss indicates that the MCE is fully reversible. It does also mean the presence of strong magnetoelastic coupling and no magnetoplastic coupling in the substances. So we would like to say, there should be no potential work hardening of the material for cycling 1 order transitions. The heat flow through the cooling engine is the mass of working medium times the cycle frequency times the Curie temperature times the entropy change. We know that Ag has the highest thermal conductivity of any metal. So we guess the heat conductivity of the substance should be increased. A further effort has been taken on the thermal conductivity measurements of these materials.

4. Discussion

A change in the nature of the magnetic transition suggests a variation in the nature of the magnetic coupling. Goodenough has suggested that in manganites, the static-cooperative Jahn–Teller (JT) distortions are replaced in the ferromagnetic phase by dynamic JT distortions that introduce vibrational modes into the spin-spin

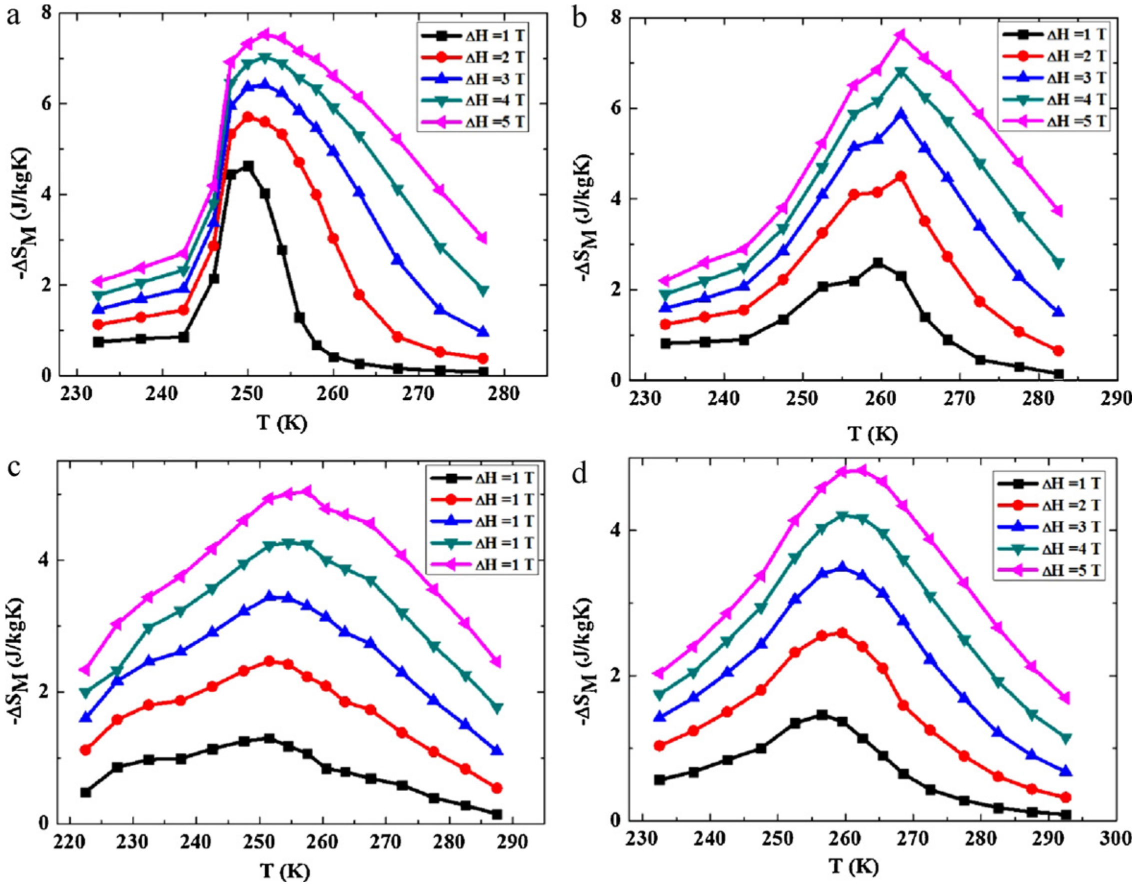

Fig. 5. Magnetic entropy change of $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$ samples: (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.7$, and (d) $x = 1$ samples as a function of temperature from different magnetic field intervals.

interaction, giving rise to an extra superexchange term [32,33]. That is, in our case, there is a strong influence of lattice effects in the samples at $x = 0$ and 0.1, which is reflected in strong variations in several physical properties supporting the first order character of the transition [34]. The large magnetic entropy change in perovskite manganites is believed to originate from the role of spin–lattice coupling in the magnetic ordering process [35]. Due to strong coupling between spin and lattice, significant lattice change accompanying the magnetic transition in perovskite manganites has been observed [36,37]. The lattice structural change in the Mn–O bond distances and Mn–O–Mn bond angles would in turn favour the spin ordering. Therefore, a more abrupt change in magnetization near T_C occurs and results in a large magnetic entropy change. From the observation of large magnetic entropy change and the fact that a strong spin–lattice coupling exists in perovskite manganites, a conclusion can be drawn that a strong spin–lattice coupling in the magnetic transition process would lead to an additional magnetic entropy change near T_C and consequently favour the MCE.

Again the larger size of the Ag ion compared to the Ca ion causes the A-site average ionic radius $\langle r_A \rangle$ to increase. This leads to a change in the Mn–O bond length and the Mn–O–Mn bond angle.

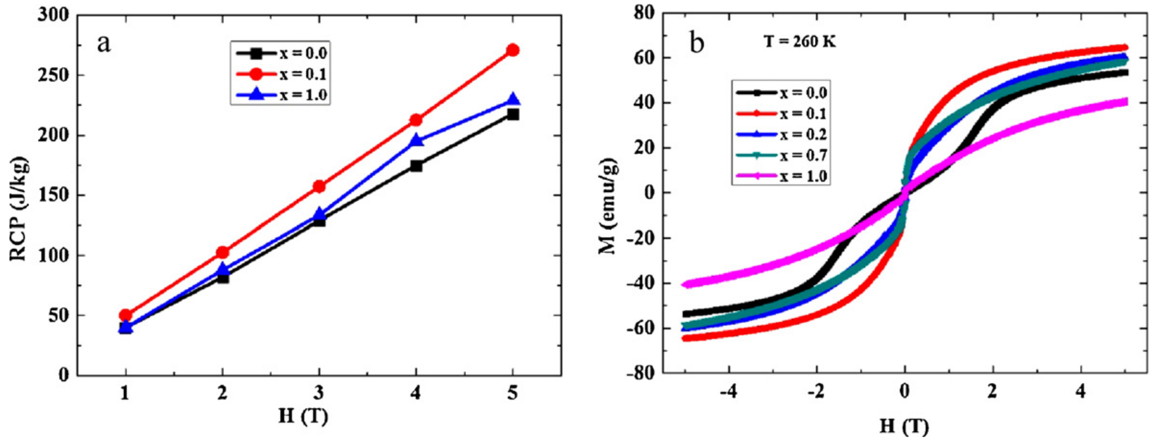

Fig. 6. (a) Relative cooling power values (RCP) versus applied magnetic field for $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.7}Ca_{0.27}Ag_{0.03}MnO_3$, and the $La_{0.7}Ag_{0.3}MnO_3$ samples. (b) Isothermal magnetization for $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$ samples measured at 260 K.

Consequently, it increases the t—tolerance factor and the electron bandwidth W, which both contribute to increase the transition temperature and have a strong influence on the high-field magnetic entropy change. The larger internal stress caused by the larger $\langle r_A \rangle$ may result in a lower rotation of MnO_6 and a smaller volume of thermal expansion, accompanied by an increase in the magnetization at T_C. A larger MCE is consequently observed.

Large low-field induced MCEs with negligible hysteresis loss of these materials provide a possibility for the development of magnetic refrigerant substances that are operable with a permanent magnet rather than a superconducting one as the magnetic field source.

5. Conclusions

In this work, we have studied the MCE for $La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3$ compounds. Doping with monovalent Ag increases the Curie temperature and weakens the first order phase transition, so that at higher Ag doping levels, the nature of the phase transition is second order. The Ag doped $La_{0.7}Ca_{0.27}Ag_{0.03}MnO_3$ compound showed an increase in ΔS_M of 4.5 J/kg K at a 2 T and of 7.63 J/kg K at a 5 T field change, respectively, at the Curie temperature of 263 K, as well as a higher RC value (270.8 J/kg) without any hysteresis loss. These results indicate that $La_{0.7}Ca_{0.27}Ag_{0.03}MnO_3$ may be a good candidate as a potential working material for magnetic refrigeration.

Acknowledgements

This work was supported by the Australian Research Council (DP0879070).

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