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# The Magnetic and Magnetocaloric Properties of the Perovskite $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$

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**This paper studies the effects of the Mn-site substitution by nickel on the magnetic properties and the magnetocaloric properties of $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$ (x = 0, 0.05 and 0.1). The orthorhombic crystal structures of the samples are confirmed by the room temperature X-ray diffraction. The dependence of the Curie temperature ($T_C$) and the magnetic entropy change ($\Delta S_M$) on the Ni doping content was investigated. The samples with x = 0 had the first order phase transition, while the samples with x = 0.05 and 0.1 had the second order phase transition. As the concentration of Ni increased, the maximum entropy change ($|\Delta S_M|_{max}$) decreased gradually, from 2.78 $J\cdot kg^{-1}\cdot K^{-1}$ (x = 0) to 1.02 $J\cdot kg^{-1}\cdot K^{-1}$ (x = 0.1), in a magnetic field change of 15 kOe. The measured value of $T_C$ was 185 K, 150 K and 145 K for x = 0, 0.05 and 0.1, respectively. The phase transition temperatures became wider as x increased. It indicates that the Mn-site substitution by Ni may be used to tailor the Curie temperature in $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$.**

**Keywords :** magnetocaloric effect, manganite, magnetic properties, curie temperature

## 1. Introduction

The magnetic refrigeration based on the magnetocaloric effect (MCE), which is the temperature change of a material arising from the variation of the applied magnetic field, has attracted attention for its significant advantages when compared with the traditional gas-compression technology, with the characteristics of the higher energy efficiency and the environmental friendliness [1-4]. Physically, MCE is associated with the magnetic entropy, a parameter characteristic of the disorder in the magnetic moment. In the adiabatic conditions, the total entropy of the system is constant. When a magnetic field is applied, the magnetic entropy decreases, leading to the increase of the lattice entropy in keeping the total entropy of the material unchanged [5]. Consequently, the material heats up or cools down depending on the field effect. In the past, Gd has been considered a prime candidate refrigerant for its large magnetic entropy change and the suitable Curie temperature ($T_C$) around the room temperature. However, the amounting research has explored various new materials with the large magnetocaloric effects, including $Gd_5(Si_2Ge_2)$, $MnFeP_{1-x}As_x$, $Ni_{51.5}Mn_{22.7}Ga_{25.8}$ and $La(FeCoSi)_{13}$ [6-9]. However, the observed properties of these materials have been deemed unsuitable for the demands of the commercial applications.

It has been found that the perovskite manganites, with a chemical formula of $R_{1-x}M_xMnO_3$ (R=La, Pr, Nd, M=Ca, Sr, Ba etc.), exhibits a large magnetic entropy change comparable to that of Gd [5]. Furthermore, the working temperature range of the perovskite manganites refrigerant can be easily controlled by dopant. Various studies have focused on the A-site substitution of perovskite manganites. Recently, studies have focused on the Mn-site substitution, replaced by Fe, Co, Ni, Cu, Al and V, in finding a material with the large $\Delta S_M$ and appropriate $T_C$. Phan [5] has found that with an increase in the Co content, the $|\Delta S_M|$ values of $La_{0.7}Ca_{0.3}Mn_{1-x}Co_xO_3$ ($0 \le x \le 0.05$) are stable at 3.5 $J\cdot kg^{-1}\cdot K^{-1}$, while the value of $T_C$ is decreased from 270 K to 210 K. Zhang [10] has studied the properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_3$ ($0 \le x \le 0.05$), and the results are similar to Phan's study. Krishnamoorthi [11] has reported on the properties of $La_{0.5}Ca_{0.5}Mn_{1-x}Ni_xO_3$, suggesting that the value of $|\Delta S_M|$ is approximately 2 $J\cdot kg^{-1}\cdot K^{-1}$ with $\Delta H = 2$ T, and 6.5 $J\cdot kg^{-1}\cdot K^{-1}$ with $\Delta H = 5$ T. In this paper, we investigate the structure and the magnetic and magnetocaloric properties of $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$, in order to study the effects of the Mn-site substitution.

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## 2. Experimental

The polycrystalline of $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$ ($x$=0, 0.05, 0.1) is synthesized by the standard solid state reaction method at a high temperature. The starting materials ($La_2O_3$, CaO, $NiCO_3$, $MnCO_3$) are mixed in the stoichiometric quantities in the agate mortar. The mixture is heated in air for 24 hr in temperatures up to 1,273 K, followed by the ball milling process for 2 h. After the heating process, the mixture is reground and pressed into pellets of approximately 2 mm thickness and 13 mm diameter. The pellets are then sintered at 1,573 K. The crystal structure of the samples is detected by the X-ray diffraction (XRD) at room temperature. The magnetic measurements are made by a vibrating sample magnetometer (VSM Lakeshore 7407) with the magnetic field in the range of 0-1.5 T.

## 3. Results and Discussion

The polycrystalline $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$ samples are characterized by the room temperature X-ray diffraction (XRD), indicating that all the samples are in a single phase orthorhombic crystal structure with the space group of *Pnma* (Fig. 1). With the increasing Ni content in $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$, the lattice constants first increase and then decrease (Table 1). The changes in the lattice constants are attributed to the various valences of the Ni ions with different radius ($Ni^{2+}$, 0.69 Å, $Ni^{3+}$, 0.56 Å, $Ni^{4+}$, 0.48 Å). Zhang [10] has found the presence of $Ni^{2+}$ ions in $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_3$, where the lattice constants increase with the increase in the doping Ni. Krishnamoorthi [11] has also reported the same phenomenon in $La_{0.5}Ca_{0.5}Mn_{1-x}Ni_xO_3$. However, Phan [12] has reported the existence of $Ni^{3+}$ ions in $La_{0.7}Sr_{0.3}Mn_{0.98}Ni_{0.02}O_3$. From the above studies, we may deduce that there are different valences of manganite in $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$. In our case, for $x$ = 0.05, the valence of the majority of Ni ions are bivalent; however for $x = 0.1$, the contents of the $Ni^{3+}$ ions may increase. Hence, the lattice parameters first increase due to the presence of $Ni^{2+}$, then decrease due to the increased content of $Ni^{3+}$. For $x = 0.1$, the peaks of XRD turn a little bit to the right, which means that lattice distortion exists in the manganite of $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$. The lattice distortion gets more obvious with the development of Ni. Also, the decrease in the lattice constant and the lattice volume may cause a decrease in the Mn-O-Mn bond angle and increase the Mn-O bond distance, which are important factors to the Curie temperature.

Figure 2 shows the magnetization as a function of the temperature cooled at the magnetic field of 100 Oe (FC) for $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$ ($x = 0$, 0.05, 0.1). The Curie temperature can be obtained from the figure, and the critical points of d$M$/d$T$. $T_C$ are calculated to be 185 K,

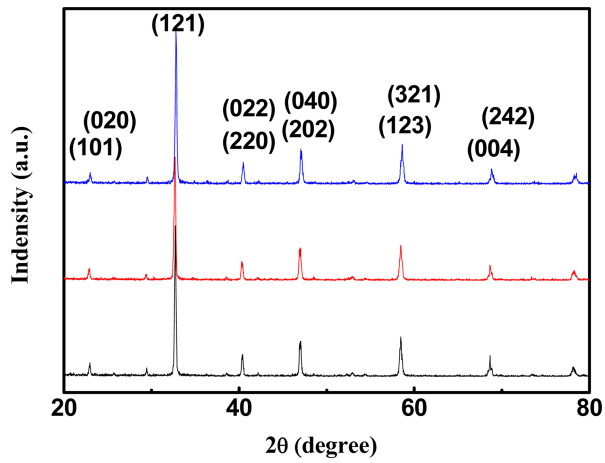


**Fig. 1.** (Color online) XRD patterns of the $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$ samples.

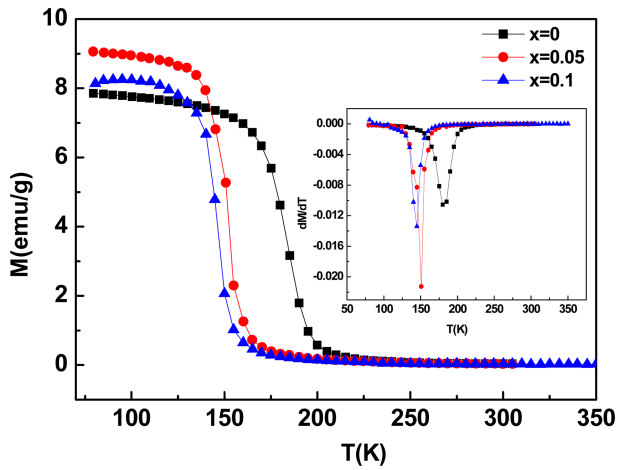


**Fig. 2.** (Color online) Temperature dependence of the field cooled (FC) magnetization curves measured at 100 Oe for $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$ ($x = 0$, 0.05, 0.1).

**Table 1.** Lattice parameter (a, b, c), volume (V), Curie temperature (TC), maximum magnetic entropy change ($|\Delta S_M|_{max}$) and RCP in $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$.

| Nominal composition | $a$(Å) | $b$(Å) | $c$(Å) | $V$(Å$^3$) | $T_C$(K) | $\Delta S_M$(J·kg$^{-1}$·K$^{-1}$) | RCP(J·kg$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $La_{0.7}Ca_{0.3}MnO_3$ | 5.4517 | 5.4653 | 7.7280 | 230.26 | 185 | 2.78 | 77.8 |
| $La_{0.7}Ca_{0.3}Mn_{0.95}Ni_{0.05}O_3$ | 5.4479 | 5.4692 | 7.7319 | 230.38 | 150 | 1.62 | 72.9 |
| $La_{0.7}Ca_{0.3}Mn_{0.9}Ni_{0.1}O_3$ | 5.4410 | 5.4630 | 7.7040 | 229.50 | 145 | 1.02 | 55.1 |

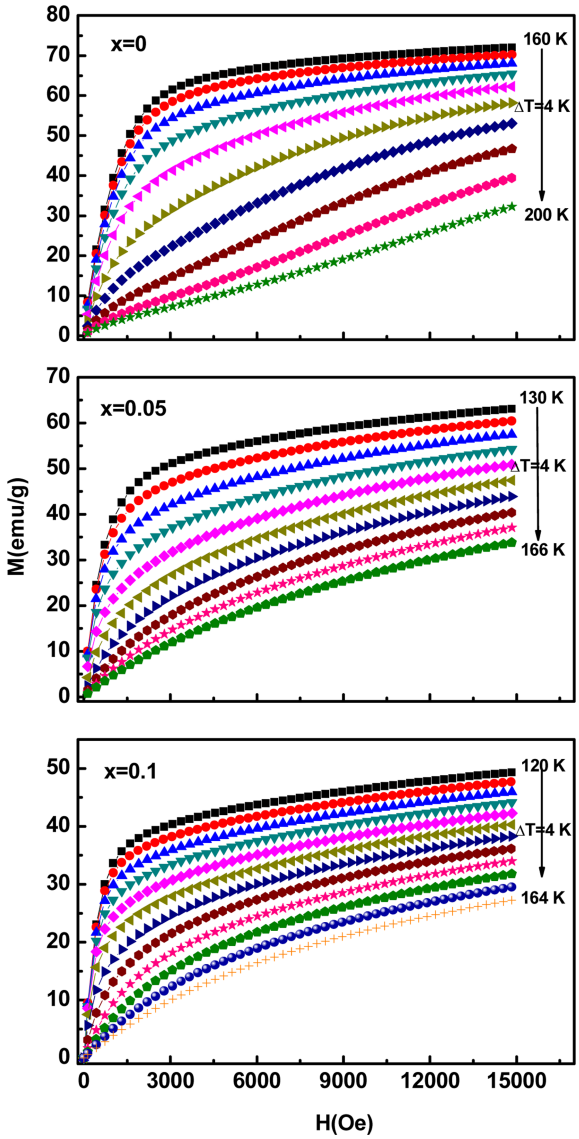


**Fig. 3.** (Color online) Isothermal magnetization curves of $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$ ($x = 0$, 0.05, 0.1) observed at different temperatures.

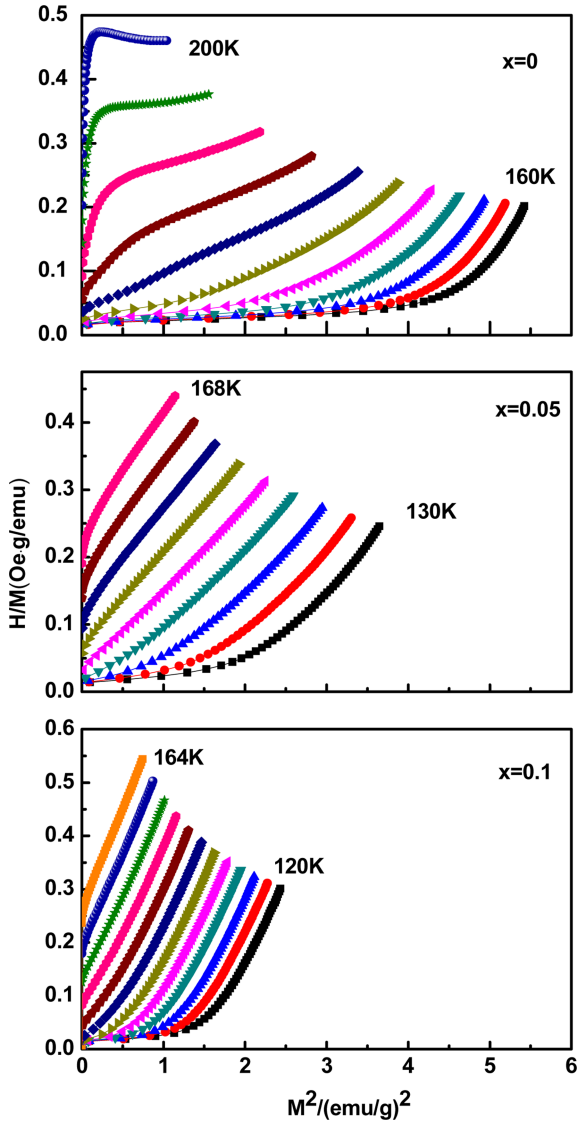


**Fig. 4.** (Color online) Arrott plots (H/M versus $M^2$) of $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$ ($x = 0$, 0.05, 0.1) at different temperatures.

150 K and 145 K for $x = 0$, 0.05 and 0.1, respectively. The value of $T_C$ drops gradually, with the increasing Ni content. The value of $T_C$ for $La_{0.7}Ca_{0.3}MnO_3$ is lower than that reported, due to the different preparation methods [13]. The tendency of $T_C$ is in a good agreement with the earlier reports of the Ni doped $La_{0.5}Ca_{0.5}MnO_3$ compounds [11]. Debnath [14] has reported that in the $La_{0.7}Ca_{0.3}Mn_{1-x}$-$Ni_xO_3$ perovskite, the Curie temperature is decided by the double exchange interaction between the $Mn^{3+}$ and $Mn^{4+}$ ions. The double exchange interaction is weakened due to the substitution of Ni, so that the value of $T_C$ is decreased. Therefore, the more the content of Ni doped, the smaller the $T_C$.

The isothermal magnetization curves of the samples are measured in the magnetic field change of 1.5 T at different temperatures around $T_C$ (Fig. 3). The feature can be divided into two regions. The first region, which is nonlinear, shows the FM phase; and the second linear region is associated with the PM phase. In order to observe clearly the types of phase transition in $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$, we performed the Arrott curves of H/M versus $M^2$, as shown in Fig. 4. Zhang [10] reports that $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_3$ undergoes the second order phase transition. Debnath [14] also suggests the negative slopes in $La_{0.7}Ca_{0.3}Mn_{0.95}Ni_{0.05}O_3$, showing the presence of the first order phase transition. In our samples of $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$, when $x = 0$, the negative slope is clearly observed according to the Banerjee

criterion (Fig. 4), proving the occurrence of the first order magnetic transition. In $x = 0.05$ and 0.1, the positive slope is found, indicating the presence of the second order magnetic transition. There is a strong influence of the lattice effects in the samples at $x = 0$, which reflects the first order character. In $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$, the anomalous volume change at $T_C$ is depressed by the decrease of the unit cell volume, supporting the second order character [14]. In $x = 0.05$ and 0.1, the presence of the second order magnetic transition may be attributed to the change of the unit cell volume, which influences the anomalous volume change at $T_C$. It suggests that there are two types of magnetic transitions in $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$.

Based on the thermodynamic theory, the isothermal magnetic entropy changes associated with the magnetic-field variation is given by,

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^H \left(\frac{\partial S}{\partial H}\right) dH \qquad (1)$$

From Maxwell's thermodynamic relation,

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

one can obtain the following expression

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^H \left(\frac{\partial S}{\partial H}\right) dH \qquad (3)$$

The magnetic entropy change is calculated by the general method. In the case of the magnetization measurements at small discrete field and temperature intervals, $\Delta S_M$ can be approximated as,

$$\Delta S_M = \Sigma\left[\frac{(M_i - M_{i+1})_{H_i}}{T_{i+1} - T_i}\right]\Delta H_i \qquad (4)$$

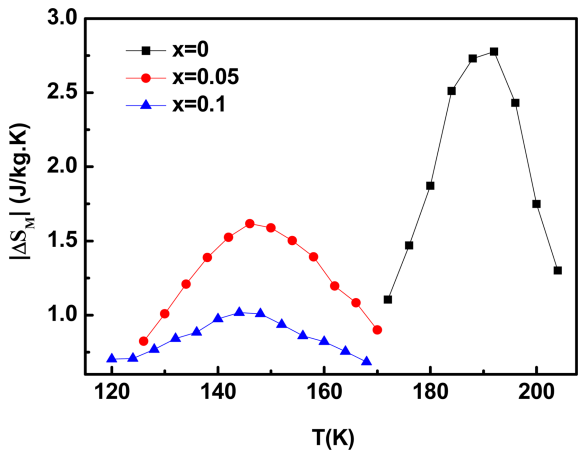


**Fig. 5.** (Color online) Magnetic entropy change $\Delta S_M$ as a function of the temperature for $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$ ($x = 0$, 0.05, 0.1).

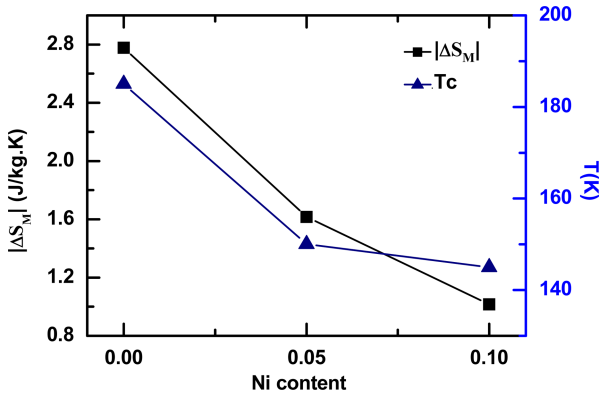


**Fig. 6.** (Color online) The maximum magnetic entropy change $\Delta S_M$ and the Curie temperature ($T_C$) as a function of the Ni content.

where $M_i$ and $M_{i+1}$ are the experimental data of magnetization at $T_i$ and $T_{i+1}$, respectively, under a magnetic field $H_i$. The $\Delta S_M$ can be calculated from the isothermal M-H curves at a series of temperatures using Eq. (4).

The magnetic entropy change $\Delta S_M$ as a function of the temperature is obtained using Eq. (4). The temperature dependence of $\Delta S_M$ according to the change in the magnetic field of 1.5T is shown in Fig. 5. As we can see, the values of $|\Delta S_M|_{max}$ achieved for $x = 0$, 0.05, 0.1 are 2.78 $J \cdot kg^{-1} \cdot K^{-1}$, 1.62 $J \cdot kg^{-1} \cdot K^{-1}$ and 1.02 $J \cdot kg^{-1} \cdot K^{-1}$, respectively. What's more, the $T_C$ and $\Delta S_M$ plots, which are shown in Fig. 6, suggest the similar reduction tendency with the increase of the Ni content. The results are explained as follows: for the perovskite $La_{0.7}Ca_{0.3}MnO_3$, the ferromagnetic double exchange interaction of the $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$ pair is predominant while the anti-ferromagnetic super exchange interactions of the $Mn^{3+}$-$Mn^{3+}$ and $Mn^{4+}$-$Mn^{4+}$ pairs are subordinate. When Ni is doped into $La_{0.7}Ca_{0.3}MnO_3$, the content of the Mn ions is decreased, so that the double exchange interaction of the $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$ pair is weakened, leading to the decrease in the $T_{C\ value}$. Zhang [10] suggests that the super exchange interaction pairs of $Mn^{3+}$-$Mn^{3+}$, $Mn^{4+}$-$Mn^{4+}$, $Ni^{2+}$-$Ni^{2+}$, $Ni^{2+}$-$Mn^{3+}$ and $Ni^{2+}$-$Mn^{4+}$ compete strongly with the $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$ ferromagnetic phase, leading to the development of the anti-ferromagnetic phase in $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_3$. The doping of Ni also leads to the presence of the $Ni^{2+}$ ions, which strengthens the anti-ferromagnetic phase as the additive contributes to the super exchange interaction. Hence the $T_C$ of $La_{0.7}Ca_{0.3}Mn_{0.95}Ni_{0.05}O_3$ drops quickly. When the doping value of Ni reaches to 0.1, the content of $Ni^{3+}$ ions increases. Phan [12] reports that a substitution of $Ni^{3+}$ for $Mn^{3+}$ in $La_{0.7}Sr_{0.3}MnO_3$ may weaken the double exchange in the ferromagnetic interaction of $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$. In our sample, the decrease in $T_C$ may have attributed to the

weakening of the double exchange interaction.

When the doping content of Ni increases, the magnetic entropy changes in $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$ decrease gradually. Because the type of phase transition changes from the first order phase transition in $La_{0.7}Ca_{0.3}MnO_3$ to the second order phase transition in $La_{0.7}Ca_{0.3}Mn_{0.95}Ni_{0.05}O_3$, the value of $|\Delta S_M|_{max}$ drops from 2.78 $J\cdot kg^{-1}\cdot K^{-1}$ to 1.62 $J\cdot kg^{-1}\cdot K^{-1}$. The magnetic entropy change of the first order phase transition contains the lattice entropy; and as such, $|\Delta S_M|_{max}$ of $La_{0.7}Ca_{0.3}MnO_3$ is larger than that of $La_{0.7}Ca_{0.3}Mn_{0.95}Ni_{0.05}O_3$. When the doping content of Ni reaches to 0.1, the effects of the magnetic dilute, which reduces the magnetic moment in the material, lead to the decrease of the spontaneous magnetization in $La_{0.7}Ca_{0.3}Mn_{0.9}Ni_{0.1}O_3$. Because the non-paired electrons of $Ni^{3+}$ ions are 3, which is less than that of $Mn^{3+}$ which are 4, the spontaneous magnetization of $La_{0.7}Ca_{0.3}Mn_{0.9}Ni_{0.1}O_3$ is less than that of $La_{0.7}Ca_{0.3}Mn_{0.95}Ni_{0.05}O_3$. The decrease of spontaneous magnetization contributes to the decrease of $\Delta S_M$.

If we observe the features of the $\Delta S_M$ curves carefully, we find that the width of the $\Delta S_M$ curves increases gradually with the increasing doping. The relative cooling power (RCP) value is defined as RCP = $|\Delta S_M|_{max} \times \delta T_{FWHM}$, where $\delta T_{FWHM}$ is the width of half the maximum $\Delta S_M$ versus the $T$ curve [15, 16]. The RCP values of 77.8, 72.9 and 55.1 $J\cdot kg^{-1}$, for $x$=0, 0.05 and 0.1, respectively, are shown (Table 1). The width of the curves is important to the increase of the RCP. Because the phase transition changes from the first order to the second order for $x = 0$ to $x = 0.1$, the curve of $\Delta S_M$ becomes wide as associated with the large RCP. The double exchange interaction and the super exchange interaction also lead to the wide temperature transition range. The large value of RCP is of benefit to the capacity of the refrigeration.

## 4. Conclusion

We have studied the structure, the magnetic properties and the magnetocaloric effect of $La_{0.7}Ca_{0.3}Mn_{1-x}Ni_xO_3$ in the orthorhombic crystal structure. It is found that the Curie temperature and the magnetic entropy changes gradually decrease with the increase in the Ni content, and that the samples are of the second-order phase transition. With the Ni doping, the contents of $Mn^{3+}$ and $Mn^{4+}$ change, so that the double exchange interaction is weakened, resulting in the decrease of $T_C$ and $\Delta S_M$. Through the decrease of the $\Delta S_M$, the temperature transition range becomes wider, which in turn leads to the relatively large RCP.

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