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# Preparation and magnetocaloric effect of self-doped $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$ ( $\square$ = vacancies) polycrystal

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## Abstract

Single-phase perovskite-type manganese oxides  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  with  $x = 0.01-0.04$  have been prepared by the modified sol-gel method and the influence of the vacancy concentration in the A site on their structures and magnetocaloric properties has systematically been investigated. The experimental results revealed that the samples calcinated at 1573 K remained single phase and were constituted by submicrometre homogeneous particles without deviation from the nominal stoichiometry upon heating. For all the compositions explored in this work, the average manganese oxidation state is practically constant, at  $3.37 \pm 0.02$ . Magnetic measurement results show that an appropriate amount of vacancy concentration in the A site is favourable to both the Curie temperature and magnetic entropy change for polycrystalline  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  compounds. An approximately linear relation between Curie temperature and magnetic entropy change was observed. For  $\text{La}_{0.771}\text{Na}_{0.198}\text{Mn}_{1.000}\square_{0.029}\text{O}_{2.94}$ , the largest value of magnetic entropy change of  $3.86 \text{ J kg}^{-1} \text{ K}^{-1}$  under a field of 10 kOe and the Curie temperature of 364 K were obtained.

## 1. Introduction

Recently, perovskite manganites  $\text{A}_{1-x}\text{B}_x\text{MnO}_{3+\delta}$  (where A is a trivalent rare earth ion and B is a divalent ion such as Ca, Sr or Ba) have become a subject attracting a considerable amount of investigation due to the colossal magnetoresistance (CMR) and large magnetocaloric (MC) effects [1–13]. It has been discovered that, in some of the mixed-valent perovskite manganite materials, a metal–insulator (MI) transition is accompanied by a ferromagnetic (FM) ordering

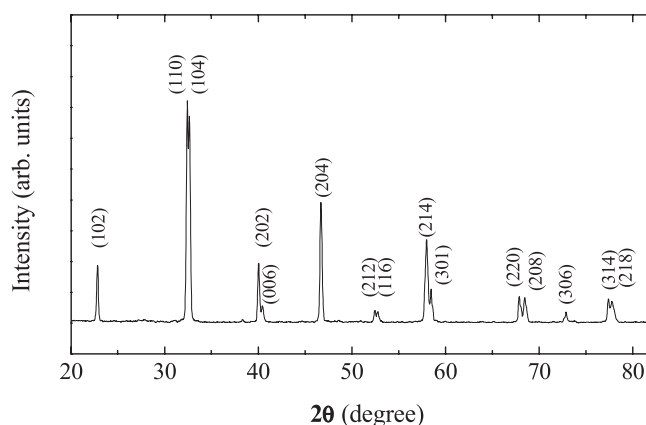
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transition. When a field is applied to these materials, the unpaired spins are aligned parallel to the field, which lowers the magnetic entropy and produces a net heat. In contrast, when the field is removed from the material, the spin tends to become random, leading to increment of the entropy and causing the material to cool down. As is well known, the MC effect in these manganese perovskites always occurs at the magnetic ordering temperature (i.e., Curie temperature,  $T_C$ ). This effect in manganese perovskites has been reported in a series of works [4, 7–13] and most of the studies were focused on the divalent and monovalent alkali-metal-doped perovskite manganese oxides. Guo *et al* [8, 9] have reported a large magnetic entropy change  $|\Delta S_M|$  of  $5.5 \text{ J kg}^{-1} \text{ K}^{-1}$  in  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  at  $T_C$  (230 K) under a field of 15 kOe. Increasing the  $\text{Ca}^{2+}$  doping level or raising the mean size of cations in the A site by substitution of  $\text{Ca}^{2+}$  with  $\text{Sr}^{2+}$  can raise the  $T_C$  of this material, but it is detrimental to the magnitude of magnetic entropy change  $|\Delta S_M|$ . Our research group [10–13] has studied the MC properties of A-(A = Na, K) substituted perovskite-type manganese oxides and discovered the improvement of the entropy change and Curie temperature in  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ . Very recently, a large magnetoresistance effect has been observed in the mixed-doped  $\text{La}_{0.7}\text{Ca}_x\text{MnO}_3$  ( $x = 0-0.3$ ) and self-doped  $\text{La}_y\text{MnO}_3$  ( $y = 0.67-0.9$ ) bulk materials [14]. We thought it interesting to study the MC effect in self-doped  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  system on a nanometre scale since the influence of doping in the A site with a vacancy (zero valance) on the MR and MC effect should be more significant than that of doping a divalent or monovalent alkali metal in the A site in these compounds. Based on our previous work [10, 13], we studied the MC effect in manganese perovskites  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  with A-site vacancies at different percentages.

## 2. Experimental procedure

Polycrystalline samples of  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  ( $x = 0.01-0.04$ ) with different A-site vacancies were synthesized by the modified sol-gel method as follows: stoichiometric amounts of  $\text{La}_2\text{O}_3$ ,  $\text{CaCO}_3$  and  $\text{Mn}(\text{NO}_3)_2$  were dissolved in dilute  $\text{HNO}_3$  solution at 333 K, suitable amounts of citric acid and ethylene glycol as coordinate agent were added and a completely homogeneous transparent solution was achieved. This solution was subjected to slow evaporation at 333 K until a highly viscous residual was formed, and a gel was developed during heating at 443 K. The gel was thermally treated at 873 K for 5 h for the purpose of organic precursor decomposition. After grinding, the samples were calcinated in air at 1573 K for 4 h and furnace cooled.

The phase identification and structural analysis were performed on an x-ray powder diffractometer (model D/Max-RA, Rigaku, Japan). High purity silicon powder was used as an internal standard for the lattice parameter determination. The structures and the Mn–O bond distance at room temperature were obtained from the Rietveld analysis program of the x-ray data [15]. The metal content in the sintered sample was determined by induced coupled plasma (ICP) spectroscopy (model 1100 + 2000, Jarrell-Ash, USA). The morphology and the particle size distribution of the samples were examined by direct observation via transmission electron microscopy (TEM) (model JEM-200 CX, JEOL, Japan). The oxygen content in these materials was determined by a temperature-programmed reduction (TPR) technique [16, 17]. Their magnetic properties were measured using a vibrating sample magnetometer (VSM) (model PAR155, USA). Their Curie temperature  $T_C$  was defined as the temperature of the maximum slope in  $|dM/dT|$ . Here  $T_C$  was extracted from the low field magnetization (1 kOe) versus temperature. Magnetization of the samples was measured in an isothermal regime under an applied magnetic field varying from 0 to 10 kOe. The isotherm  $M$  versus  $H$  measurements were performed around the FM ordering transition temperature ( $T_C$ ) of the samples. In the



**Figure 1.** X-ray diffraction pattern of  $\text{La}_{0.771}\text{Na}_{0.198}\text{Mn}_{1.000}\square_{0.029}\text{O}_{2.94}$ .

**Table 1.** Summary of the results of ICP and TPR measurements for  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$ .

$x$	$\langle V_{\text{Mn}} \rangle^a$	La/Mn	Na/Mn	$\langle V_{\text{Mn}} \rangle^b$	$3 + \delta$	$x^c$	Stoichiometry
0.01	3.43	0.789(5)	0.199(2)	3.35	2.96(3)	0.011	$\text{La}_{0.789}\text{Na}_{0.199}\text{Mn}_{1.000}\square_{0.011}\text{O}_{2.96}$
0.02	3.46	0.780(5)	0.202(2)	3.38	2.96(3)	0.020	$\text{La}_{0.790}\text{Na}_{0.202}\text{Mn}_{1.000}\square_{0.020}\text{O}_{2.96}$
0.03	3.49	0.771(5)	0.198(2)	3.37	2.94(3)	0.029	$\text{La}_{0.771}\text{Na}_{0.198}\text{Mn}_{1.000}\square_{0.029}\text{O}_{2.94}$
0.04	3.52	0.761(5)	0.201(2)	3.38	2.93(3)	0.038	$\text{La}_{0.761}\text{Na}_{0.201}\text{Mn}_{1.000}\square_{0.038}\text{O}_{2.93}$

<sup>a</sup> The theoretical expected values of average Mn valence for  $\text{La}_{0.8-x}\text{Na}_{0.2}\text{MnO}_3$ .

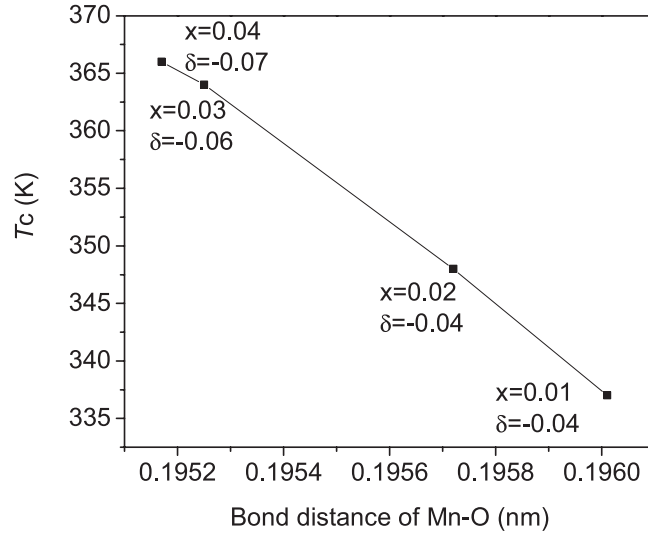
<sup>b</sup> The average manganese oxidation state calculated from electric neutrality for  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  and the ICP and TPR measurement results.

<sup>c</sup> The value calculated from ICP and TPR measurement results.

vicinity of  $T_C$ , isothermal  $M-H$  curves were obtained by steps of 10, 5, 3 and 2 K. The temperature steps were smaller near  $T_C$  and larger further away.

### 3. Results and discussion

The results of x-ray diffraction indicate that all the studied compositions,  $0.01 < x < 0.04$ , of  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  materials have the rhombohedral perovskite structure without any other secondary or impurity phase. Shown in figure 1 is a typical x-ray pattern of a selected sample,  $\text{La}_{0.771}\text{Na}_{0.198}\text{Mn}_{1.000}\square_{0.029}\text{O}_{2.94}$ . Figure 2 shows the variation of  $T_C$  with the Mn–O bond distance determined by the Rietveld analysis. One can see that  $T_C$  tends to increase when the Mn–O distance decreases. The temperature dependences of cell volume for  $x = 0.01$  and 0.03 shown in figure 3 clearly demonstrate a cell volume discontinuity of  $\Delta V/V = 31\%$  for  $x = 0.01$  and 38% for  $x = 0.03$ , respectively. TEM images show that the samples are constituted of homogeneous particles, ranging in size from 150 to 220 nm. The ICP and TPR measurement results are summarized in table 1. The theoretical expected values of average Mn valence for  $\text{La}_{0.8-x}\text{Na}_{0.2}\text{MnO}_3$  are also listed in table 1. It is worthwhile to note that unlike the theoretical expectation of  $\langle V_{\text{Mn}} \rangle$  for  $\text{La}_{0.8-x}\text{Na}_{0.2}\text{MnO}_3$ , no clear correlation between  $x$  and  $\langle V_{\text{Mn}} \rangle$  was observed in  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  according to the ICP and TPR measurement results. In fact, for all the compositions, the average manganese oxidation state  $\langle V_{\text{Mn}} \rangle$  is practically a constant, at  $3.37 \pm 0.02$ . The increase of self-doping level induces a decrease in oxygen excess. Similar phenomena have been reported in monovalent alkali-metal-doped



**Figure 2.** Curie temperature  $T_C$  as a function of Mn–O bond distance in  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$ .

perovskite manganese oxides [10, 18]. The entropy change, which results from the spin ordering (i.e., FM ordering) and is induced by the variation of the applied field from 0 to  $H_{max}$ , is given by [19]

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

From Maxwell's thermodynamic relation

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

one can obtain the following expression:

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

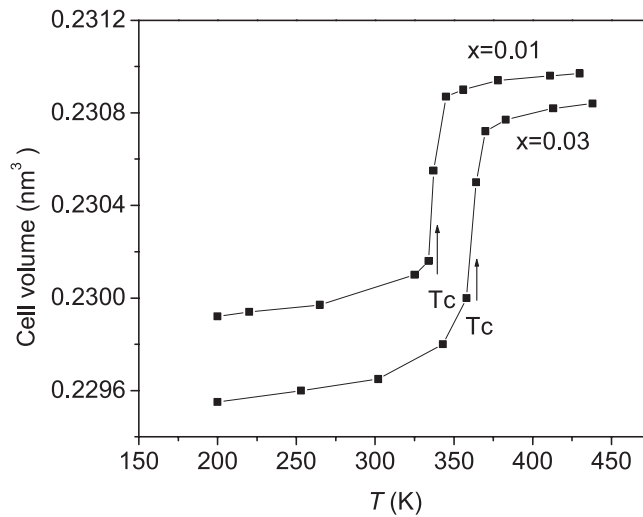
where  $H_{max}$  is the maximum external field. According to equation (3), the magnetic entropy change depends on the temperature gradient of the magnetization and attains a maximum value around the Curie temperature  $T_C$ , at which the magnetization decays most rapidly.

In fact, the magnetic entropy change  $|\Delta S_M|$  is often evaluated by some numerical methods. One method of approximation is to directly use the measurements of the  $M$ – $T$  curve under different magnetic fields. In the case of small discrete field intervals,  $|\Delta S_M|$  can be approximated from equation (3) as

$$\Delta S_M(T, H) = \sum_i \left[ \left( \frac{\partial M}{\partial T} \right)_{H_i} + \left( \frac{\partial M}{\partial T} \right)_{H_{i+1}} \right] \frac{1}{2} \Delta H_i, \quad (4)$$

where  $(\partial M/\partial T)_{H_i}$  is the experimental value obtained from the  $M$ – $T$  curve in magnetic field  $H_i$ . Another method is to use isothermal magnetization measurements. In the case of magnetization measurements at small discrete field and temperature intervals,  $|\Delta S_M|$  can be approximated from equation (3) by [20]

$$\Delta S_M(T, H) = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i. \quad (5)$$



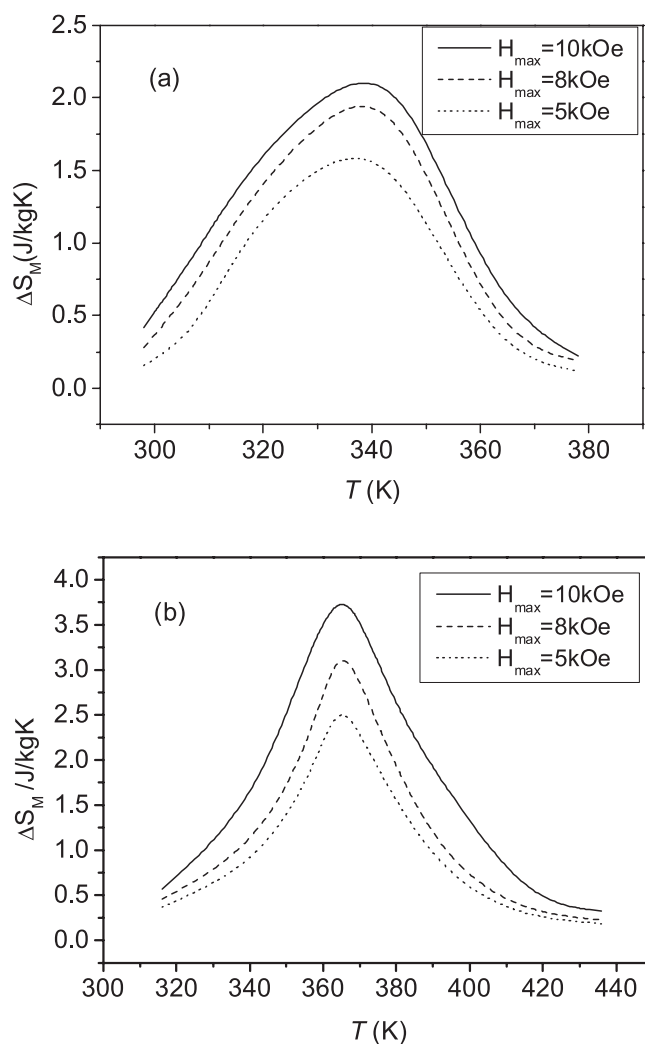
**Figure 3.** Temperature dependence of the cell volume in  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  for  $x = 0.01$  and  $0.03$ .

In this paper, we adopt the latter method to evaluate the entropy change associated with the applied field variation.

Figure 4 shows the temperature dependence of magnetic entropy change  $|\Delta S_M|$  under different external fields in  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  for  $x = 0.01$  and  $0.03$  samples. The peak temperature of  $|\Delta S_M|$  is the same as  $T_C$ . The dependence of the Curie temperature  $T_C$  and entropy change  $|\Delta S_M|$  on the A-site vacancy concentration  $x$  for  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  is shown in figure 5. It is clear that both  $T_C$  and  $|\Delta S_M|$  increase at first with increasing  $x$  when  $0.01 \leq x \leq 0.03$  and then keep approximately constant when  $x > 0.03$ . An approximately linear relation between  $|\Delta S_M|$  and  $T_C$  is observed as shown in figure 6. This phenomenon means that it is possible to enhance both the entropy change and the Curie temperature by doping a small number of vacancies in the A site for polycrystalline  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  compounds.

Until now, two different parameters have been considered to be relevant concerning the electronic and magnetic properties of these compounds, namely, the concentration of  $\text{Mn}^{4+}$  or the average manganese oxidation state (directly related to the concentration of carriers in the  $e_g$  orbital) and the mean size of cations in A positions,  $\langle r_A \rangle$ . From table 1, the average manganese oxidation state is practically constant, at  $3.37 \pm 0.02$  for these four samples; the effect of the increase in vacancy concentration is a decrease of the oxygen excess. This means the first parameter (the concentration of  $\text{Mn}^{4+}$ ) keeps constant for these four samples, thus the second parameter (the mean size of cations in A positions) is responsible for the magnetic behaviours of the compounds. It is well known that the Mn–O bond distance and the cell volume of the samples are directly related to the variation of the mean size of cations in A positions. From the lattice analyses of XRD we can see that the Mn–O bond distance decreases with the increase of A-site vacancy concentration  $x$  for  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  (figure 2). According to the double-exchange interaction theory, shorter Mn–O distance in this structure corresponds to larger Mn–O–Mn bonding angle, leads to a stronger interaction and gives higher  $T_C$ .

From equation (3), a larger  $M$  and  $\partial M/\partial T$  could give a larger  $|\Delta S_M|$ . The four samples have a similar structure, which exhibits a first-order ferromagnetic–paramagnetic phase transition, associated with the discontinuous variation in the volume at  $T_C$  [21]. The

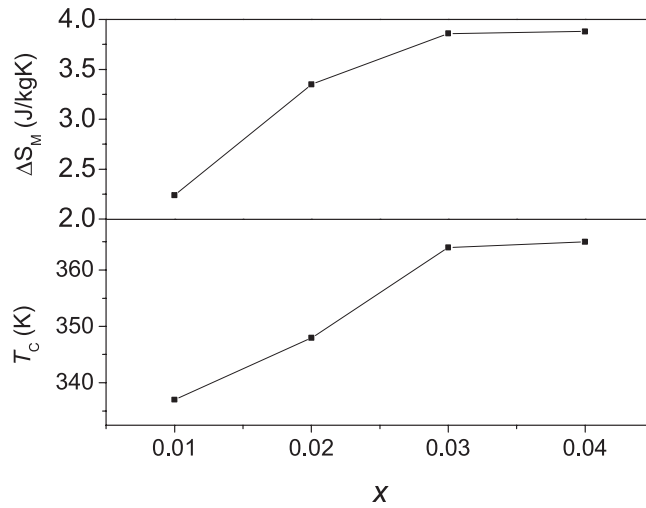


**Figure 4.** Temperature dependence of  $|\Delta S_M|$  under different fields in  $\text{La}_{0.8-x}\text{Na}_{0.2-x}\square_x\text{MnO}_{3+\delta}$  for  $x = 0.01$  (a),  $x = 0.03$  (b).

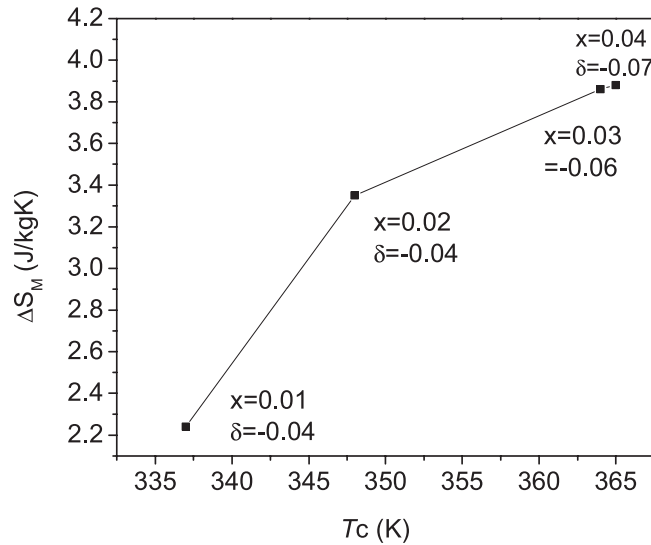
variation in the volume causes an additional change in magnetism, and is beneficial to larger  $|\Delta S_M|$ . The doping of small numbers of vacancies in the La–Na–Mn–O system reduces the cell volume and enlarges the discontinuity of the volume change at  $T_C$  (figure 3), and therefore gives a sharper change in magnetization, leading as a result to a larger  $|\Delta S_M|$ .

#### 4. Conclusions

High purity and homogeneous polycrystalline  $\text{La}_{0.8-x}\text{Na}_{0.2-x}\square_x\text{MnO}_{3+\delta}$  ( $x = 0.01\text{--}0.04$ ) perovskites were synthesized by a modified sol–gel technique. For all the compositions, the average manganese oxidation state is practically a constant, at  $3.37 \pm 0.02$ . The increase of self-doping level induces a decrease in oxygen excess. The measurement results show that an appropriate amount of vacancy concentration in the A site is favourable to both



**Figure 5.** Plot of Curie temperature  $T_C$  and entropy change  $|\Delta S_M|$  as a function of A-site vacancy concentration  $x$  for  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$ .



**Figure 6.** Plot of  $|\Delta S_M|$  versus  $T_C$  for  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$ .

the Curie temperature and magnetic entropy change for  $\text{La}_{0.8-x}\text{Na}_{0.2}\square_x\text{MnO}_{3+\delta}$  compounds. The maximum magnetic entropy change of  $|\Delta S_M| = 3.86 \text{ J kg}^{-1} \text{ K}^{-1}$  and the high Curie temperature of  $T_C = 364 \text{ K}$  were obtained in  $\text{La}_{0.771}\text{Na}_{0.198}\text{Mn}_{1.000}\square_{0.029}\text{O}_{2.94}$ .

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