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# Impact of Annealing Temperature on the Physical Properties of the Lanthanum Deficiency Manganites

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**Abstract:** The lanthanum deficiency manganites $La_{0.8-x}\square_xCa_{0.2}MnO_3$ ($x$ = 0, 0.1 and 0.2), where $\square$ is a lanthanum vacancy, were prepared using the classic ceramic methods with different thermal treatments (1373 K and 973 K). The structural, magnetic, and magnetocaloric properties of these compounds were studied as a function of annealing temperature. It was noted that the annealing temperature did not affect the crystal structure of our samples (orthorhombic structure with Pnma space group). Nevertheless, a change in the variation of the unit cell volume V, the average bond length $d_{Mn–O}$, and the average bond angles $\theta_{Mn–O–Mn}$ were observed. Magnetization versus temperature study has shown that all samples exhibited a magnetic transition from ferromagnetic (FM) to paramagnetic (PM) phase with increasing temperature. However, it can be clearly seen that the annealing at 973 K induced an increase of the magnetization. In addition, the magnetocaloric effect (MCE) as well as the relative cooling power (RCP) were estimated. As an important result, the values of MCE and RCP in our Lanthanum-deficiency manganites are reported to be near to those found in gadolinium, considered as magnetocaloric reference material.

**Keywords:** vacancy manganites; thermal treatments; magnetocaloric effect

## 1. Introduction

Magnetic refrigeration technique is one of the most promising techniques in cooling technology due to the efficient and environmentally safe cooling applications, which have encouraged the experimental and the theoretical studies in this direction. Obtaining low-cost and high-performance magnetocaloric materials is not an easy target because of the related drawbacks. For instance, Gd shows a large magnetocaloric effect (MCE) in room temperature range [1], yet it is a costly element which tends to oxidation. Recent research seeks to balance the needs for technical applications by obtaining high magnetocaloric performance with fewer disadvantages by exploring several kinds of magnetic materials treated in different conditions.

In recent times, mixed valence manganites with the general formula $La_{1-x}A_xMnO_3$, where A is a divalent element (A = Ca, Sr, Ba, . . . ), have roused plenty of research thanks to their important electrical and magnetic properties, such as the colossal magnetoresistance (CMR) [2–8] and the magnetocaloric effect (MCE) [9–14]. That is why the parameter necessary for selecting magnetic refrigerants is based on the cooling power per unit volume and the relative cooling power (RCP). This parameter is a measure of the amount of heat transfer between the cold and hot sinks in a refrigeration cycle, estimating the range of operating temperature.

To ameliorate this parameter, wide-ranging research has been conducted, hence the development of many synthetic methods of producing these materials, such as solid state reaction, sol–gel, coprecipitation, high-energy ball-milling, polyol process, spark plasma sintering, etc.

Other research works have shown that the physical properties of ceramics are also sensitive to the value of the sintering temperature [15–18]. Actually, all these research works have confirmed that the electronic, magnetic, and transport properties are significantly affected by the grain size. Among the earliest reports on the effect of particle size on the physical properties, one can mention that of Mahesh et al. [19], who varied the particle size from 0.025 to 0.35 μm and found significant changes in the properties. Gupta et al. [20] reported that the saturation magnetization decreased with increase in the grain size (grain sizes 3, 14, and 24 μm), although $T_c$ (~230 K) remained constant. However, Zhang et al. [21] observed that $T_c$ decreased with increase in the grain size in the range of 24.4–240 nm. It is known that this variation of $T_c$ is controlled by the electron bandwidth W and the mobility of $e_g$ electrons [11,22,23]. In fact, the structure, magnetism, and the magnetocaloric effect are very correlated, primarily by the bandwidth W.

In addition, our original idea is to change the physical properties by simple methods including simple annealing at low temperature.

It is in this context that the present research work lies to study the effect of the sintering temperature on magnetic and magnetocaloric properties of $La_{0.8-x}\square_xCa_{0.2}MnO_3$ ($x$ = 0, 0.1 and 0.2) manganites.

## 2. Experimental Details

The $La_{0.8-x}\square_xCa_{0.2}MnO_3$ ($x$ = 0, 0.1 and 0.2) compounds were prepared by solid-state reaction and heated at a temperature of 1373 K. The preparation method as well as the structural and magnetic results were discussed in our previous research work [11]. In the present work, these samples were annealed at 973 K for 7 days in air. The structure of the samples was checked using X-ray diffraction with Cu Kα radiation (λ = 1.5406 Å) by step scanning (0.02°) in the range of $10° \leq 2\theta \leq 100°$. The magnetic measurements were performed on BS2 magnetometer developed in Louis Neel Laboratory of Grenoble.

## 3. Results and Discussion

The XRD patterns of $La_{0.8-x}\square_xCa_{0.2}MnO_3$ ($x$ = 0; 0.1 and $x$ = 0.2) compounds annealed at 973 K are represented in Figure 1. Similarly to the case of the annealing at 1373 K, the refinements of XRD patterns of the compounds annealed at 973 K revealed the presence of two phases. The main phase was accredited to $La_{0.8-x}\square_xCa_{0.2}MnO_3$, and the other phase was attributed to the presence of unreacted $MnO_3$.

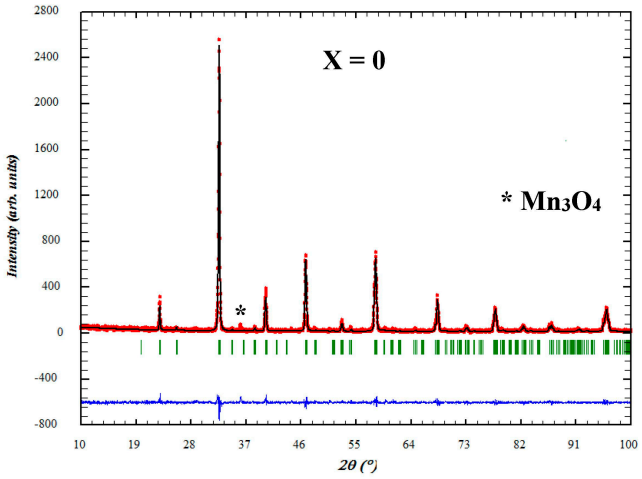


**Figure 1.** *Cont.*

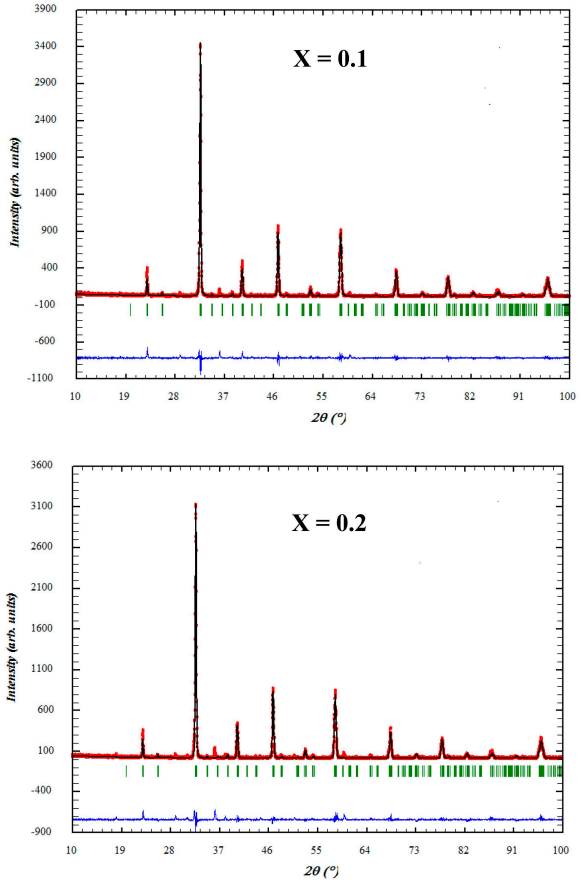


**Figure 1.** Observed (open symbols) and calculated (solid lines) X-ray diffraction pattern for $La_{0.8-x}\square_xCa_{0.2}MnO_3$ ($x$ = 0, 0.1 and 0.2) annealed at 973 K (S2). Positions for the Bragg reflection are marked by vertical bars. Differences between the observed and the calculated intensities are shown at the bottom of the diagram.

The X-ray diffraction analysis showed that all samples crystallized in the orthorhombic structure with Pnma space group.

The results of the refinement are summarized in Table 1. It is worth noting that the decrease of the annealing temperature was accompanied by a reduction of the grain size, leading to a decrease of the bond length $d_{Mn-O}$, an increase in the bond angle $\theta_{Mn-O-Mn}$, and thus a decrease in the unit cell volume.

**Table 1.** Results of Rietveld refinements, determined from XRD patterns recorded at room temperature for $La_{0.8-x}\square_xCa_{0.2}MnO_3$ ($x$ = 0, 0.1 and 0.2) compounds annealed at 973 K (S2).

| x | 0 | 0.1 | 0.2 |
|---|---|---|---|
| **Space group** | **Pnma** | **Pnma** | **Pnma** |
| Lattice parameter | | | |
| a (Å) | 5.4503 | 5.448 | 5.446 |
| b (Å) | 7.712 | 7.709 | 7.707 |
| c (Å) | 5.474 | 5.468 | 5.463 |
| Unit cell volume (Å$^3$) | 57.522 | 57.437 | 57.412 |
| $d_{Mn-O}$ (Å) | 1.967 | 1.958 | 1.952 |
| $\theta_{Mn-O-Mn}$ (°) | 161.234 | 161.012 | 160.453 |
| $\chi^2$ (%) | 1.27 | 1.51 | 1.51 |

We have also estimated the average crystallite size D from the XRD patterns using the Scherrer formula [8]:

$$D = \frac{180}{\Pi} \frac{0.89\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the X-ray wavelength, θ and β are the diffraction angle and the full width for the most intense peak with:

$$\beta = \beta_m^2 - \beta_i^2 \quad (2)$$

$\beta_m^2$ is the experimental full width at half maximum (FWHM) and $\beta_i^2$ is the FWHM of a standard silicon sample.

The $D$ values were found to be 8.37 nm, 9.23 nm, and 10.48 nm for $x$ = 0, 0.1 and 0.2 samples, respectively. In comparison with our previous results [8], it is illustrated that with the increase in the annealing temperature, the particle size of samples increased, confirming that the annealing temperature promotes the grain growth of the samples [15–17,24,25].

It should be mentioned that a special focus was placed on how the physical properties are strongly influenced by the grain size.

Figure 2 displays an example of the temperature dependence (T) of the magnetization (M), measured at the applied magnetic field of 0.05 T, for $La_{0.8-x}\square_xCa_{0.2}MnO_3$ ($x$ = 0, 0.1 and 0.2) compounds annealed at 1373 K (S1) and 973 K (S2). For the two annealing temperatures, we can note the presence of a magnetic transition from the ferromagnetic to paramagnetic phase at the Curie temperature $T_C$, when increasing temperature for S1 and S2 compounds. Moreover, it is clearly shown that the annealing at 973 K induced an increase of the magnetization. The paramagnetic to ferromagnetic (PM–FM) transition temperatures ($T_C$) were estimated from the peak of dM/dT curves (Figure 3).

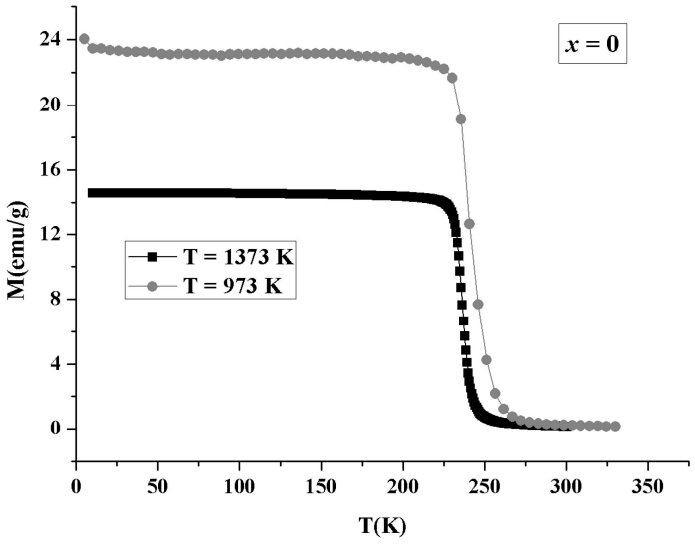


**Figure 2.** *Cont.*

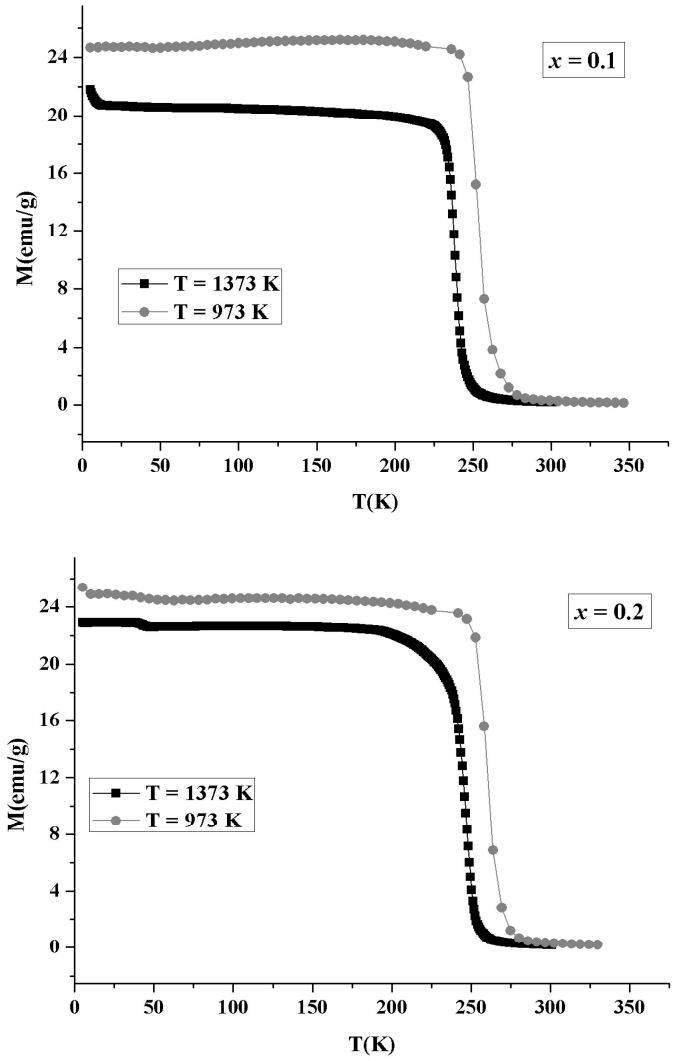


**Figure 2.** Temperature dependence (T) of the magnetization (M), measured at applied magnetic field of 0.05 T, for $La_{0.8-x}\square_xCa_{0.2}MnO_3$ ($x$ = 0, 0.1 and 0.2) compounds annealed at 1373 K (S1) and 973 K (S2).

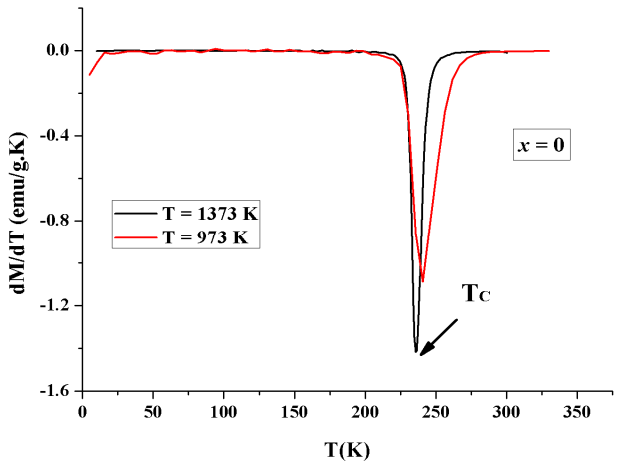


**Figure 3.** *Cont.*

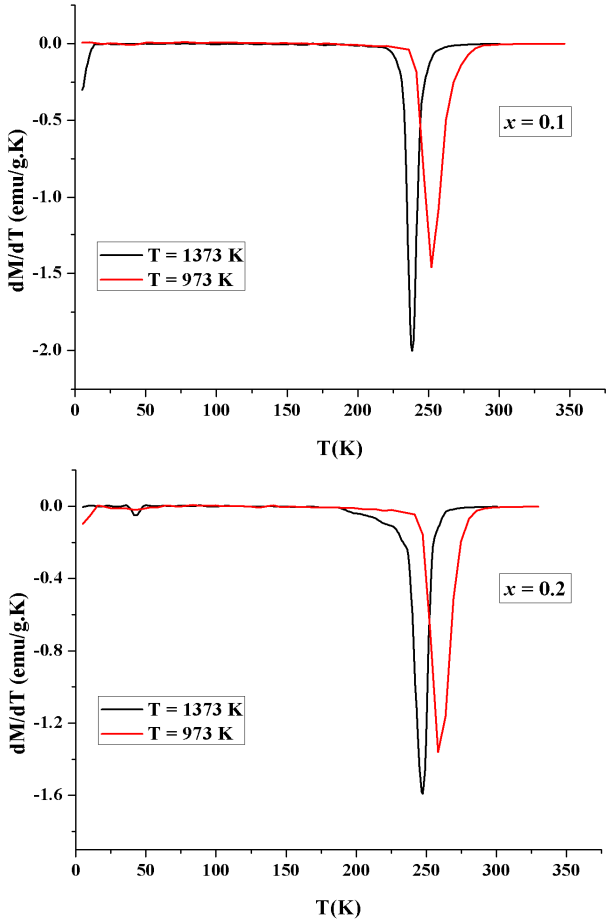


**Figure 3.** Comparison of the temperature dependence of (−dM/dT) measured for an applied magnetic field of 0.5 T for $La_{0.8-x}\square_xCa_{0.2}MnO_3$ ($x$ = 0, 0.1 and 0.2) compounds annealed 1473 K and 973 K.

The decrease of the annealing temperature was found to clearly lead to an important increase of the $T_C$ value. The increase of $T_C$ can be explained by the increase of Mn-O-Mn bond angle and the decrease of Mn-O bond length predictably with the increase of deficiency content. Both shorter Mn-O distance and larger Mn-O-Mn bonding angle lead to the increase of the electron bandwidth $W$ and the mobility of $e$g electrons, and hence the Double Exchange (DE) interaction (Table 2). Therefore, the improvement of $T_C$ can be explained by the increase of electron-one bandwidth $W$ given by:

$$W = w_0 \frac{\cos\left(\frac{\pi-\gamma}{2}\right)}{\left\langle d_{Mn-O}\right\rangle^{3,5}}$$

where $\gamma$ is the Mn-O-Mn angle, $d_{Mn\text{-}O}$ the Mn-O distance, and $W_0$ a positive constant [26].

**Table 2.** The Curie temperature ($T_C$) values for S1 and S2 compounds.

| | $T_{annealing}$ = 1373 K | | | $T_{annealing}$ = 973 K | | |
|---|---|---|---|---|---|---|
| | **x = 0** | **x = 0.1** | **x = 0.2** | **x = 0** | **x = 0.1** | **x = 0.2** |
| $T_C$ (K) | 236 | 241 | 247 | 240 | 252 | 258 |
| $W/W_0$ ($10^{-2}$ eV) | 9.05 | 9.14 | 9.28 | 9.361 | 9.498 | 9.544 |

At this level, we were interested in the most important physical property for industrial application—namely the magnetocaloric effect, which is an intrinsic property of magnetic materials. The magnetocaloric effect is a magneto-thermodynamic phenomenon in which a change in temperature of a suitable material is caused by exposing the material to a changing magnetic field. This effect is maximized when the material is near its magnetic ordering temperature (Curie temperature $T_C$).

Figure 4 shows the magnetic applied field ($\mu_0 H$) dependence of the magnetization $M$ ($T$, $\mu_0 H$) measured at different temperatures ($T$) for the $La_{0.8-x}\square_x Ca_{0.2}MnO_3$ ($x$ = 0, 0.1 and 0.2) compounds annealed at 973 K.

The magnetic entropy change $\Delta S_M$ was deduced from the $M$ ($T$, $\mu_0 H$) curves using the following equation [27]:

$$\Delta S_M\left(\frac{T_1+T_2}{2}\right) = \frac{1}{T_2-T_1}\left[\int_0^{\mu_0 H_{max}} M(T_2,\mu_0 H)\mu_0 dH - \int_0^{\mu_0 H_{max}} M(T_1,\mu_0 H)\mu_0 dH\right] \quad (3)$$

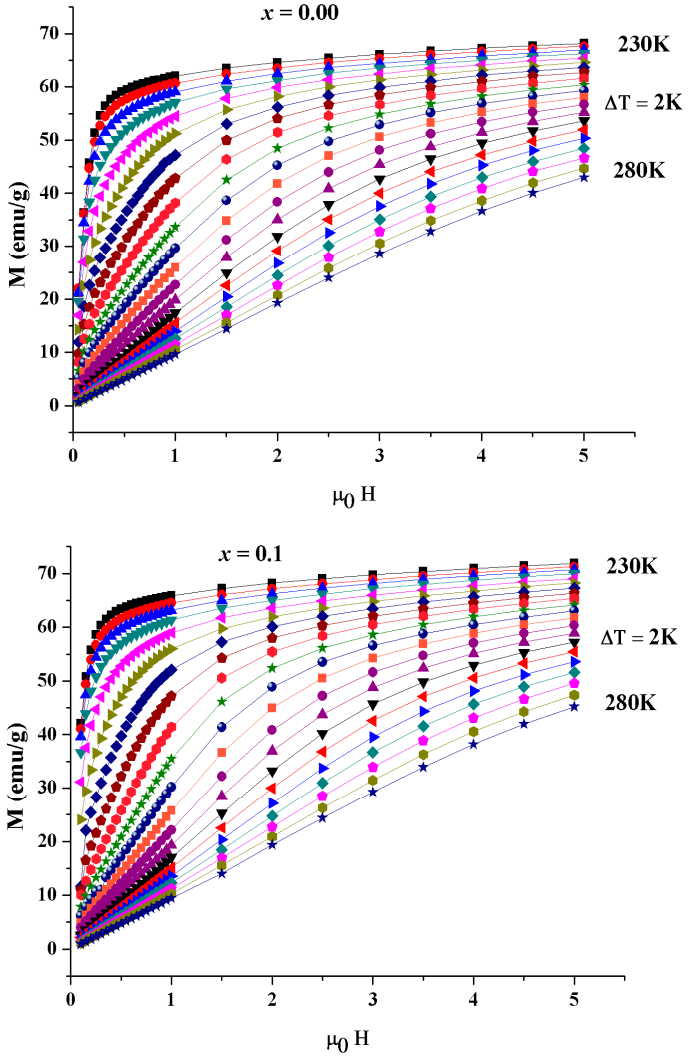


**Figure 4.** *Cont.*

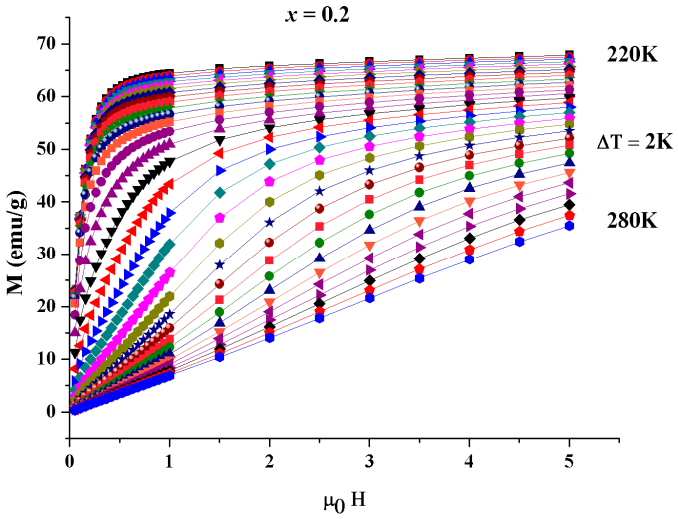


**Figure 4.** Temperature ($T$) dependence of the magnetization M (T, $\mu_0 H$) measured at different magnetic applied field ($\mu_0 H$) for the $La_{0.8-x}\square_x Ca_{0.2}MnO_3$ ($x$ = 0; 0.1 and $x$ = 0.2) compounds annealed at 973 K.

Figure 5 shows the temperature dependence of the magnetic entropy change ($-\Delta S_M$) measured for an applied magnetic field of 2 T for $x$ = 0.00 and 0.2 samples annealed at 1373 and 973 K.

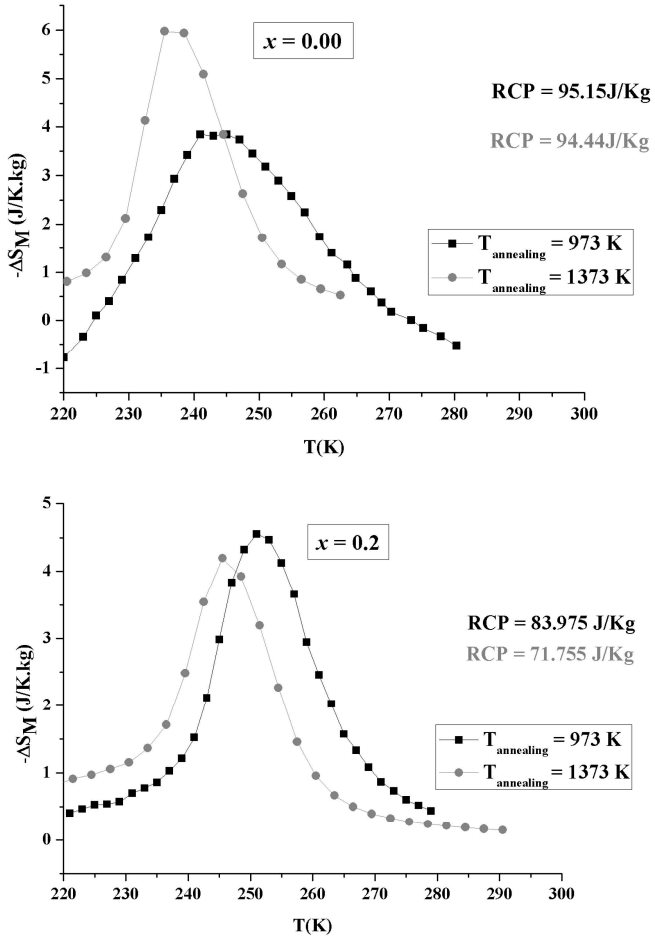


**Figure 5.** Temperature dependence of the magnetic entropy change ($-\Delta S_M$) measured for an applied magnetic field of 2 T for $x$ = 0.00 and 0.2 samples annealed at 1373 and 773K. RCP: relative cooling power.

From these curves, it can be deduced that the annealing at low temperature (973 K) changed the value of the maximum of the magnetic entropy change ($-\Delta S_{\mathrm{M\,max}}$) and the full width at half maximum ($\delta T_{FWHM}$). For example, for $x$ = 0, under H = 2 T, $\Delta S_{\mathrm{M\,max}}$ is equal to 5.96 and 3.84 J $Kg^{-1}$ $K^{-1}$ at $T_{annealing}$ = 1373 and 973 K, respectively.

The cooling efficiency of magnetic refrigerants was evaluated by means of the so-called relative cooling power (RCP) factor, corresponding to the amount of heat transferred between the cold and hot sinks in the ideal refrigeration cycle and defined as [28]:

$$RCP = -\Delta S_{Max} \times \delta T_{FWHM} \quad (4)$$

where $\Delta S_{Max}$ is the maximum of magnetic entropy change and $\delta T_{FWHM}$ is a full width at half maximum.

We can clearly deduce that the annealing at low temperature (973 K) enhanced the value of the relative cooling power (RCP) factor for both samples (Figure 5).

Table 3 exhibits the comparison between the obtained results and those of other magnetocaloric materials. From the comparison with Gd data and from a technological point of view, our data emphasize that our material can be considered as a relevant potential candidate to be used in cooling systems based on magnetic refrigeration. From an industrial point of view, this material presents beneficial parameters such as low cost, lacking rare earths, low weight, no corrosion, ease of synthesis, and chemical stability. For all these reasons, the suggested material can be considered as a substantial candidate for magnetic refrigeration.

**Table 3.** Comparison of reported values of the maximum magnetic entropy change ($-\Delta S_{\mathrm{M\,max}}$) and RCP values at the Curie temperature ($T_c$) under a magnetic field ($\mu_0 H$) for various manganites and the Gd magnetic refrigerant material.

| Materials | $T_C$ (K) | $\mu_0 H$ (T) | $-\Delta S_{\mathrm{M\,max}}$ (J/K kg) | RCP (J/kg) | References |
|---|---|---|---|---|---|
| Gd | 299 | 2 | 5 | 196 | [29] |
| $La_{0.7}Na_{0.2}MnO_3$ | 335 | 2 | 2.83 | 76.91 | [23] |
| $La_{0.8}Na_{0.15}\square_{0.05}MnO_3$ | 320 | 2 | 2.97 | 96.06 | [23] |
| $La_{0.8}Na_{0.1}\square_{0.1}MnO_3$ | 295 | 2 | 2.97 | 96.06 | [23] |
| $La_{0.8}Ca_{0.2}MnO_3$ | 240 | 2 | 3.84 | 95.15 | This work |
| $La_{0.7}\square_{0.1}Ca_{0.2}MnO_3$ | 252 | 2 | 2.98 | 96.17 | This work |
| $La_{0.6}\square_{0.2}Ca_{0.2}MnO_3$ | 258 | 2 | 4.56 | 83.97 | This work |

The change of magnetic entropy can be also calculated from the field dependence of the specific heat by the following integration [30]:

$$\Delta S_M(T,H) = \int_0^T \frac{C_p(T,\mu_0 H) - C_p(T,0)}{T}\,\mathrm{dT} \quad (5)$$

The change of specific heat $\Delta C_p$ associated with a magnetic field variation from 0 to $H$ can be calculated using Equation (5) as:

$$\Delta C_P(T,\mu_0 H) = C_P(T,\mu_0 H) - C_P(T,0) = \frac{T\delta\Delta S_M(T,\mu_0 H)}{\delta T} \quad (6)$$

Using Equation (6), $\Delta C_p$ of the $La_{0.8-x}\square_x Ca_{0.2}MnO_3$ ($x$ = 0 and 0.2) compounds annealed at 1373 and 973 K versus temperature for an applied magnetic field of 2 T is displayed in Figure 6. As the figure shows, anomalies are observed in all curves around the Curie temperature $T_C$, due to the magnetic phase transition. The value of $\Delta C_p$ undergoes a sudden change of sign from positive to negative around $T_C$ with a negative value below $T_C$ and a positive value above $T_C$. For example, for $x$ = 0.2, the maximum/minimum values of $\Delta C_p$ exhibit a steady increase with the decrease of annealing temperature, which proves that the annealing temperature is an alternative method to ameliorate the value of the change of specific heat in manganites.

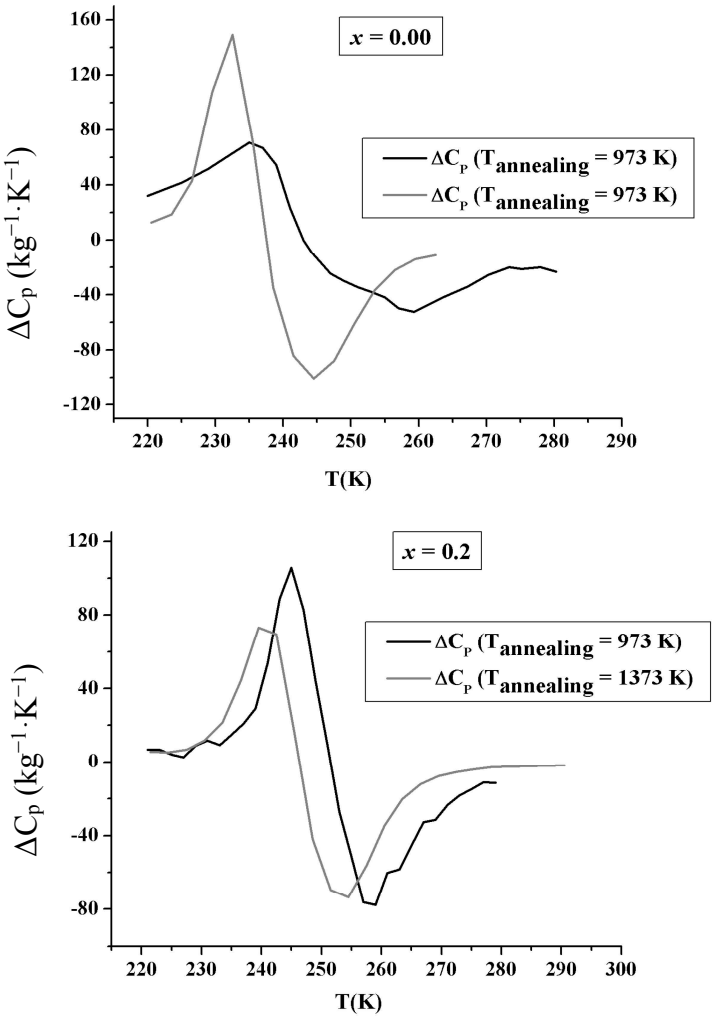


**Figure 6.** Change of specific heat ΔCp as a function of temperature calculated for an applied magnetic field of 2 T for $La_{0.8-x}\square_xCa_{0.2}MnO_3$ ($x$ = 0, 0.1 and 0.2) samples annealed at 1373 and 773 K.

## 4. Conclusions

The present work has undertaken the study of the important role of the annealing temperature effects on the structural, magnetic, and magnetocaloric properties of $La_{0.8-x}\square_xCa_{0.2}MnO_3$ ($x$ = 0; 0.1 and $x$ = 0.2) samples. The decrease of the annealing temperature from 1373 (S1) to 973 K (S2) was found to decrease the grain size, leading to: (i) a decrease of the lattice parameters and the unit cell volume, (ii) an increase of magnetization as well as of Curie Temperature $T_c$, (iii) an increase of the value of the (RCP) factor.

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**Author Contributions:** Ridha Skini analyzed the data and wrote the paper, Hlil El Kebir performed the experiments, Essebti Dhahri provided with the samples.

**Conflicts of Interest:** The authors declare no conflict of interest.

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