Influence of Non-magnetic Ti$^{4+}$ Ion Doping at Mn Site on Structural, Magnetic, and Magnetocaloric Properties of La$_{0.5}$Pr$_{0.2}$Sr$_{0.3}$Mn$_{1-x}$Ti$_x$O$_3$ Manganites ($x = 0.0$ and $0.1$)

S. Smiy$^{1,2}$ · A. Omri$^1$ · R. Moussi$^1$ · A. Ben Ali$^2$ · S. Hcini$^1$ · B. F. O. Costa$^4$ · E. K. Hlil$^3$ · E. Dhahri$^2$

Received: 20 April 2018 / Accepted: 27 July 2018 / Published online: 30 October 2018
© The Author(s) 2018

Abstract
Polycrystalline perovskite AMn$_{1-x}$TiO$_3$ with A = La$_{0.5}$Pr$_{0.2}$Sr$_{0.3}$ ($x = 0.0$ and $0.1$) have been prepared using solid-state reaction method. X-ray powder diffraction and Rietveld refinement revealed that all samples crystallize in a rhombohedral structure with space group R$ar{3}$c. From M–T curve, we determined the Curie temperature, where the magnetization value decreases abruptly. The Curie temperature ($T_C$) decreases from 280 to 123 K when the percentage of Ti increases to 10%. The values of the magnetization $M(H)$ decrease when increasing the Ti content. Moreover, the magnetocaloric effect (MCE) was estimated in terms of isothermal entropy change ($-\Delta S_M$) using the $M(T, \mu_0 H)$ data and employing the thermodynamic Maxwell equation. In addition, using a phenomenological model, we determine magnetocaloric effect from the calculation of magnetization as a function of temperature under different external magnetic fields. Also, we can determine the relative cooling power (RCP) and the specific heat which varies from 2.803 to 7.354 J/(kg/K) for the undoped sample from $M(T, \mu_0 H)$ data at different magnetic fields theoretically.

Keywords Perovskite · Structural · Magnetic · Magnetocaloric effect · Model

1 Introduction

Manganites are compounds which have a great effect on technological development because they are widely used in magnetic refrigeration and in magnetic recording [1–3].

Manganites of type Ln$_{1-x}$A$_x$MnO$_3$, where Ln is a rare-earth cation such as La, Pr, Nd, etc. and A is an alkali or alkaline earth cation such as Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Na$^{2+}$, Pb$^{2+}$, etc. [4, 5] are characterized by a mixed valence because of the coexistence of Mn$^{3+}$ and Mn$^{4+}$ in the B site. These ions are responsible of the magnetic properties due to the double exchange theory that has been suggested by Zener [6]. Samples could be ferromagnetic-metallic, paramagnetic-insulating, ferromagnetic-insulating, or spin glass. These characteristics depend on the ratio Mn$^{3+}$/Mn$^{4+}$ which is affected by the substitution in the B site [7–14]. In this research paper, we substitute the Mn by Ti in the mother compound of La$_{0.5}$Pr$_{0.2}$Sr$_{0.3}$MnO$_3$. The choice of Ti is made for two major reasons. Firstly, Ti exists in a state of valence 4$^+$ in the structure of perovskite. So, this will affect the mixed valence between Mn$^{3+}$ and Mn$^{4+}$ resulting in the double exchange (DE) interaction between Mn$^{3+}$ and Mn$^{4+}$. Secondly, Ti$^{4+}$ is a non-magnetic ion. Therefore, influence of substitution ions 4$^+$ such as Sn$^{4+}$ and Ti$^{4+}$ for Mn in manganites has been studied [15–17]. However, there is some evidence for its influence on magnetocaloric effect. This study is expected to provide data to clarify this issue.
Fig. 1 X-ray diffraction patterns of $\text{AMn}_{1-x}\text{TiO}_3$ ($x = 0.0$ and 0.1) compounds at room temperature. All peaks of the manganite phase are indexed in the rhombohedra $\overline{R}3c$ symmetry.

2 Experimental

Samples $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ with $x = 0.0$ and 0.1 were prepared using a solid-state reaction of $\text{La}_2\text{O}_3$, $\text{SrCO}_3$, $\text{Pr}_6\text{O}_{11}$, $\text{Mn}_2\text{O}_3$, and $\text{TiO}_2$ as precursors, all with purity of more than 99.9%. The mixture was first heated in air at 700 °C for 1 day; it is the chamottage to realize decarbonation and to eliminate all organic phases. After that, grinding will take place, and then they were reheated at 1200 °C for 24 h and reground to ensure homogenization. Then, the powder was pressed into pellet forms under 4 tonnes/cm$^2$ and sintered at 1250 °C for 1 day. The cycle of grinding sintering and pelleting is repeated several times in order to eliminate all parasitic phase. Finally, in order to determine the mesh parameters and the magnetic properties of our samples, we pass them through an X-ray diffraction (XRD) analysis (Cu-K$_\alpha$ radiation $\lambda_{\text{Cu}} = 1.5406$ Å); the X-ray diffraction measurements were conducted at the Department of Physics in the University of Coimbra, Portugal. Magnetization vs. temperature was carried out using BS2 magnetometer developed in Louis Neel Laboratory of Grenoble.

3 Results and Discussion

3.1 Structural Characterization

In order to test the purity of our compounds, we pass them on a powder X-ray diffractometer, and the diffraction spectra obtained for our samples $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.0$ and 0.1) are shown in Fig. 1. The analysis of these spectra shows that they are a single phase. This is a rhombohedral system associated with the $\overline{R}3c$ space group. It is noted that for some peaks, there is a shift toward the small 2$\theta$ for the titanium-doped sample compared with the parent compound $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$. This shift corresponds to an increase in the mesh parameters of the $\text{La}^{3+}\text{Pr}^{3+}\text{Sr}^{2+}(0.7\text{Mn}^{3+} \cdot (0.3-x)\text{Mn}^{4+}\cdot x\text{Ti}^{4+}\text{O}_3^-)$ sample. This evolution makes it possible to think that the Ti$^{4+}$ ions are well intercalated on the sites of the Mn$^{4+}$ ions which is confirmed not only by the increase of cell parameters but also by the increase of the volume of the mesh. For this reason, the intercalation of titanium instead of Mn$^{4+}$ cause the increase of the volume which varies from 347.71 Å$^3$ for $x = 0.0$ to 347.85 Å$^3$ for $x = 0.1$. Indeed, for $x = 0.0$, we have in the B site 70% Mn$^{3+}$ and 30% Mn$^{4+}$ whereas for $x = 0.1$, we have 70% Mn$^{3+}$, 20% Mn$^{4+}$, and 10% Ti$^{4+}$, and this has no influence on the rate of oxygen.

Fig. 2 Observed (circle) and calculated (continuous line) XRD patterns obtained by the Rietveld analysis for $\text{AMn}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.0$) sample. Their difference (enlarged scale) is represented at the bottom of the figure (solid line). The vertical ticks show the positions of the calculated Bragg reflections for the rhombohedral phase ($\overline{R}3c$ space group).
Table 1 Refined profile parameters for La$_{0.5}$Pr$_{0.2}$Sr$_{0.3}$Mn$_{1-x}$Ti$_x$O$_3$ ($x = 0.0$ and $0.1$) after the Rietveld refinements of X-ray powder diffraction at room temperature ($300$ K)

| $x$ | $r_B$ (Å) | $V$(Å$^3$) | $a$(Å) | $c$(Å) |
|-----|------------|------------|--------|--------|
| 0.0 | 0.6140     | 347.71     | 5.4890 | 13.3264|
| 0.1 | 0.6215     | 347.85     | 5.4893 | 13.3296|

Figure 2 discloses the X-ray powder diffraction pattern with the fitted curve for $x = 0.0$. The refined parameters found using the standard Rietveld process which is based on the use of the FULLPROF program are regrouped in Table 1. The quality of the refinement is estimated via the goodness-of-fit indicator $\chi^2$.

3.2 Magnetic Characterization

All samples AMn$_{1-x}$TiO$_3$ ($x = 0.0$ and $0.1$) present only one transition from the ferromagnetic (FM) to paramagnetic (PM) when the temperature increases (Fig. 3). This confirms the good crystallization of the samples. The Curie temperature is determined using the $dM/dT$ curve; $T_C$ is the extremum from this curve and decreases from $280$ K for $x = 0.0$ to $123$ K for $x = 0.1$. The evolution of the Curie temperature can be explained not only by the decrease of the number of Mn$^{3+}$-O$^{2-}$-Mn$^{4+}$ and consequently increase of the number of Ti$^{4+}$-O$^{2-}$-Ti$^{4+}$ chains but also by the effect of the cation size in the Mn site. We conclude that the introduction of titanium Ti$^{4+}$ causes a significant decrease of the ferromagnetic ordering temperature of the undoped system.

In the sample doped by titanium ($x = 0.1$), we note that the FM-PM transition spreads on an important temperature range (no stiff transition). It shows that the natural magnetic order for this sample is difficult to identify with magnetization ($M$) vs. temperature ($T$) data. Therefore, it is necessary to conduct zero-field-cooled (ZFC) and field-cooled (FC) measurements.

We can observe the existence of a difference between ZFC $M (T)$ and FC $M (T)$ curves in Fig. 3 for $x = 0.1$, indicating a thermomagnetic irreversibility. In addition, the ZFC curve for the sample doped with $10\%$ titanium ($x = 0.1$) shows a clear cusp at low temperature ($32$ K), which is generally thanks to a spin-glass or a cluster-glass state. The irreversibility temperature ($T_{irr}$) of zero-field-cooled and field-cooled curves varies from $200$ K for $x = 0.0$ to $106$ K for $x = 0.1$; also, this irreversibility between ZFC $M (T)$ and FC $M (T)$ curves only illustrates the $T < T_C$, the domination of the magnetic anisotropy [18]. This anisotropy comes from a spin-orbit coupling and results in the blocking of magnetic moments by the crystalline field [19]. Therefore, to each ferromagnetic material, we define a direction of easy magnetization which depends on the crystal symmetry (cubic, orthorhombic, rhombohedral, etc.). The energy, associated with the magneto-crystalline anisotropy, is a function of the anisotropy constants ($K_1$, $K_2$, etc.). These constants depend on the materials and the turnaround time of the thermally activated magnetization which is given by the Arrhenius law [20].

$$\tau = \tau_0 \exp \frac{\Delta E_a}{K_B T}$$  \hspace{1cm} (1)

where

- $\tau_0$ is the attempt time of the order of ($10^9$-$10^{13}$);
- $\Delta E_a$ is the anisotropy energy barrier for small applied defined as: $\Delta E_a = KV$;
- $K = 25 K_B T_B/V$ [21]. $T_B$ ($T_{irr}$) is the blocking temperature, and $K_B$ is the Boltzmann constant;
- $V$ is the volume of a single particle;
- $K$ is the anisotropy constant.

In this paragraph, we are interested in studying the magnetocaloric effect of La$_{0.5}$Pr$_{0.2}$Sr$_{0.3}$Mn$_{1-x}$TiO$_3$ ($x =
The MCE is intrinsic to magnetic materials and is induced via coupling of the magnetic sublattice with the magnetic field, which alters the magnetic part of the total entropy due to a corresponding change of the magnetic field. The total entropy of a magnetic solid is the total of the lattice, electronic, and magnetic entropy ($S_L$, $S_E$, and $S_M$, respectively). The MCE can be estimated via the magnetic entropy change ($-\Delta S_M$). In addition, the MCE has a significant technological importance since magnetic materials with large values of ($-\Delta S_M$) can be employed in various thermal devices.

Figure 4a ($x = 0.0$), b ($x = 0.1$) shows the magnetization isotherms of the $(M, T, \mu H)$ curves for both samples with $\delta T = 5$ K measured at various temperatures for the $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{TiO}_3$, by measuring the magnetization as a function of magnetic field which varies from 0 to 5 T for each temperature. These curves reveal a strong variation of magnetization around the Curie temperature.

Figure 5a ($x = 0.0$), b ($x = 0.1$) presents a positive slope of the isothermal $M^2$ vs. $H/M$ curves, signaling that the FM-PM phase transitions in our samples are of the second order according to the criterion provided by Banerjee [22].

The magnetic entropy is related to the $M$, $\mu_0 H$, and absolute $T$ through the Maxwell relation [23, 24]:

$$\left(\frac{\partial S}{\partial \mu_0 H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_{\mu_0 H}$$

where $\left(\frac{\partial S}{\partial \mu_0 H}\right)_T$ is the experimental value obtained from $M(\mu_0 T)$ curves under $\mu_0 H$. 

---

**Fig. 4** The field dependence of the magnetization for $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{TiO}_3$ ($x = 0.0$ (a) and 0.1 (b)) compounds measured at different temperatures around $T_C$

**Fig. 5** Arrott plots of the samples $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{TiO}_3$ ($x = 0.0$ (a) and 0.1 (b))
One can use the following expression:

$$\Delta S_M \left( \frac{T_1 + T_2}{2} \right) = \frac{1}{T_2 - T_1} \left[ \int_{T_1}^{T_2} M(T_2, \mu_0 H) \mu_0 dH - \int_{T_2}^{T_2} M(T_1, \mu_0 H) \mu_0 dH \right]$$  \hspace{1cm} (3)

The \((-\Delta S_M)\) variation was obtained by using a program carried out in our laboratory by Pr. N. Fourati and E. Dhahri and by standing on (3). We have traced the variation of the magnetic entropy changes as a function of temperature at different magnetic fields.

The spin lattice coupling in the magnetic ordering process is the reason behind this large magnetic entropy change in manganites.

### 3.2.1 Theoretical Considerations

Applying the phenomenological model [25], the variation of the magnetization as a function of temperature and \(T_C\) is given by:

$$M = \left( \frac{M_i - M_f}{2} \right) \left[ \tanh(A(T_C - T)) \right] + BT + C$$  \hspace{1cm} (4)

where \(M_i\) defines the initial value of magnetization and \(M_f\) presents the final value of magnetization at the FM-PM transition as plotted in Fig. 6.

Here,

$$A = 2 \frac{(B - S_C)}{M_i - M_f}$$  \hspace{1cm} (5)

\(B\) and \(S_C\) are respectively the magnetization sensitivity \(\frac{dM}{dT}\) at ferromagnetic state before transition, and the magnetization sensitivity \(\frac{dM}{dT}\) at \(T_C\)

$$A = \left( \frac{M_i + M_f}{2} \right) - BT_C$$  \hspace{1cm} (6)

A magnetic entropy change of a magnetic system under adiabatic magnetic-field variation from 0 to final value \(H_{\text{max}}\) is available by

$$\Delta S_M = \left( -A \left( \frac{M_i - M_f}{2} \right) \text{sech}^2 \left( A(T_C - T) \right) + B \right) \mu_0 H_{\text{max}}$$  \hspace{1cm} (7)

\(\Delta S_M\) attains the maximum at \(T = T_C\), and its value can be calculated using the following equation:

$$\Delta S_{\text{max}}^M = \left[ -A \left( \frac{M_i - M_f}{2} \right) + B \right] \mu_0 H_{\text{max}}$$  \hspace{1cm} (8)

![Fig. 6 Temperature dependence of magnetization in constant applied magnetic field](image)

![Fig. 7 Temperature dependence of magnetization for La_{0.8}Pr_{0.2}Sr_{0.3}Mn_{1-x}TiO_3 (x = 0.0 (a) and 0.1 (b))](image)
Equation (8) is a significant equation for taking into consideration the value of the magnetic entropy change to calculate magnetic cooling efficiency with its full width at half maximum.

The product between the maximum magnetic entropy change ($\Delta S_{\text{max}}^M$) and the FWHM ($\delta T_{\text{FWHM}}$) defines the RCP [26] which is a useful parameter that provides a measure of the effectiveness of magnetic materials for applications in MR.

The $\delta T_{\text{FWHM}}$ is determined by:

$$\delta T_{\text{FWHM}} = \frac{2}{A} \cosh^{-1} \sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}}$$  \hspace{1cm} (9)

The RCP is defined as

$$\text{RCP} = -\Delta S_M (T, \mu_0 H_{\text{max}}) \times \delta T_{\text{FWHM}}$$

$$= \left( M_i - M_f - 2 \frac{B}{A} \right) \mu_0 H_{\text{max}} \times \cosh^{-1} \sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}}$$

The value of the specific heat is given by [27]:

$$\Delta C_{p,H} = \frac{\delta \Delta S_M}{\delta T}$$  \hspace{1cm} (10)

According to this model [25], the specific heat can be rewritten as follows:

$$\Delta C_{p,H} = -TA^2 (M_i - M_f) \sech^2 (A (T_C - T)) \tanh (A (T_C - T)) \mu_0 H_{\text{max}}$$  \hspace{1cm} (11)

Using the phenomenological model, we can determine $\Delta \delta S_M$, $T_{\text{FWHM}}$, RCP, and $\Delta C_P$ for La$_{0.5}$Pr$_{0.2}$Sr$_{0.3}$Mn$_{0.9}$Ti$_{0.1}$O$_3$ ($x = 0.0$ and 0.1).

### 3.3 Simulation

In order to apply the proposed phenomenological model Fig. 7a ($x = 0.$), b ($x = 0.1$) presents the variation of the $M$ vs. $T$ in different applied magnetic fields for AMn$_{1-x}$Ti$_x$O$_3$ ($x = 0.0$ and 0.1) compounds. Although the experimental data is represented by the symbols with the solid lines showing modeled data using model parameters given in Table 2 for $x = 0.0$ and Table 3 for $x = 0.1$ it is important to mention that there is a good concordance between the experimental and the calculated results. The $M(T)$ curves demonstrate that all samples present a magnetic transition from the FM state to the PM one ($1 \leq \mu_0 H \leq 5$) when the temperature increases which is shown in Fig. 7a ($x = 0.0$, b ($x = 0.1$). Yet, the increase of the magnetic field causes an increase in the magnetization and consequently an increase in $T_C$.

Figure 8 presents the variation of the magnetic entropy change $|\Delta S_M|$ vs. temperature for AMn$_{1-x}$Ti$_x$O$_3$ ($x = 0.0$ and 0.1) in different applied magnetic fields. It can be seen that there is an agreement with the experimental result. Moreover, $|\Delta S_M|$ depends on the applied fields. The increase of the magnetic field causes a shift of the position of the peak to higher temperature (i.e. the peaks shift from 264 K for $\mu_0 H = 1$ T to 266 K for $\mu_0 H = 5$ T for the undoped sample and from 131 K for $\mu_0 H = 1$ T to 169 K for $\mu_0 H = 5$ T for the compound doped in titanium). Additionally, with increasing the magnetic field, the maximum magnetic entropy change $\Delta S_{\text{max}}^M$ shows a linear increase. This reveals a much better $\Delta S_M$ to be expected when we increase the magnetic field, hence signifying that the effect of spin-lattice coupling is associated with the change in the magnetic ordering process.

| $\mu_0 H$ (T) | $M_i$ (emu/g) | $M_f$ (emu/g) | $T_C$ (K) | $S_C$ (emu/(g/K)) | $B$ (emu/(g/K)) |
|--------------|--------------|--------------|-----------|------------------|------------------|
| 1            | 46.018       | 9.308        | 262       | -0.615           | -0.132           |
| 2            | 48.378       | 12.111       | 264       | -0.559           | -0.130           |
| 3            | 50.001       | 14.176       | 264.5     | -0.525           | -0.123           |
| 4            | 53.225       | 16.979       | 265       | -0.493           | -0.116           |
| 5            | 56.913       | 19.487       | 266       | -0.472           | -0.108           |

| $\mu_0 H$ (T) | $M_i$ (emu/g) | $M_f$ (emu/g) | $T_C$ (K) | $S_C$ (emu/(g/K)) | $B$ (emu/(g/K)) |
|--------------|--------------|--------------|-----------|------------------|------------------|
| 1            | 33.666       | 7.108        | 131       | -0.319           | -0.052           |
| 2            | 39.307       | 8.484        | 140       | -0.300           | -0.100           |
| 3            | 40.133       | 9.310        | 151       | -0.281           | -0.098           |
| 4            | 41.234       | 10.961       | 160       | -0.268           | -0.100           |
| 5            | 44.674       | 11.374       | 169       | -0.259           | -0.101           |
in the samples [28]. Also, the RCP factor which corresponds to the amount of heat transferred between the cold and the hot skins in the ideal refrigeration cycle increases by increasing the magnetic field. Figure 9a, b depicts the variation of the maximum of the change entropy $|\Delta S_{\text{max}}|$ and the variation of RCP values vs. applied magnetic field passing from 1 to 5 T, respectively. We conclude that all samples present a clear increase in the $|\Delta S_{\text{max}}|$ and RCP values when the magnetic field increases and their values decrease when introducing the titanium; for $x = 0.0$, values of RCP are more important compared with the $x = 0.1$ sample. For $H = 5$ T, samples depict not only the highest RCP values but also the important value of $|\Delta S_{\text{max}}|$. We determined the specific heat $\Delta C_p$ as a function of temperature for La$_{0.5}$Pr$_{0.2}$Sr$_{0.3}$Mn$_{1−x}$TiO$_3$ ($x = 0.0$ and 0.1) by using Eq. 11 in different magnetic fields; $\Delta C_p$ goes through an unexpected change of sign around $T_C$ with a positive value above $T_C$ and a negative value below the Curie temperature. The variation of the specific heat for $x = 0.0$ is shown in Fig. 10; $\Delta C_p,(H_{\text{max}})$ increases when the magnetic field increases.
Table 4: The predicted values of applied magnetocaloric properties for La0.5Pr0.2Sr0.3MnO3 in different applied magnetic field shifts

| $\mu_0 H$ (T) | $-\Delta S_M^{\text{max}}$ (J/(kg/K)) | $\delta T_{\text{FWHM}}$ (K) | RCP (J/kg) | $\Delta C_{PH}^{\text{max}}$ (J/(kg/K)) | $\Delta C_{PH}^{\text{min}}$ (J/(kg/K)) |
|-------------|------------------|-----------------|--------|----------------|-----------------|
| 1           | 0.644            | 121.108         | 77.993 | 2.803          | -2.274          |
| 2           | 1.038            | 133.438         | 138.508| 4.497          | -3.642          |
| 3           | 1.413            | 140.596         | 198.662| 6.100          | -4.870          |
| 4           | 1.779            | 141.954         | 252.536| 7.154          | -5.571          |
| 5           | 1.962            | 145.194         | 284.870| 7.354          | -5.715          |

Table 5: The predicted values of applied magnetocaloric properties for La0.5Pr0.2Sr0.3Mn.9Ti.1O3 (x = 0.1) in different applied magnetic field shifts

| $\mu_0 H$ (T) | $-\Delta S_M^{\text{max}}$ (J/(kg/K)) | $\delta T_{\text{FWHM}}$ (K) | RCP (J/kg) | $\Delta C_{PH}^{\text{max}}$ (J/(kg/K)) | $\Delta C_{PH}^{\text{min}}$ (J/(kg/K)) |
|-------------|------------------|-----------------|--------|----------------|-----------------|
| 1           | 0.311            | 113.427         | 35.275 | 0.674          | -0.397          |
| 2           | 0.641            | 128.641         | 82.458 | 0.680          | -0.310          |
| 3           | 0.911            | 141.342         | 128.762| 0.923          | -0.426          |
| 4           | 1.175            | 151.463         | 177.969| 1.263          | -0.604          |
| 5           | 1.309            | 161.651         | 211.601| 1.296          | -0.551          |

We listed in Tables 4 and 5 the $-\Delta S_M^{\text{max}}$, $\delta T_{\text{FWHM}}$, RCP, $\Delta C_{PH}^{\text{max}}$, and $\Delta C_{PH}^{\text{min}}$ vs. applied magnetic field. It is important to note that the other method utilized to identify the transition nature from the compounds is the $|\Delta S_M|$. Figure 11a, b for temperature below and above the transition respectively for La0.5Pr0.2Sr0.3MnO3, it is viewed that $|\Delta S_M|$ changes to a positive value with the increase of the magnetic field, which corresponds to the magnetic transition from FM to PM states. We can see on Table 6 that we have a low $\Delta S_M^{\text{max}}$ compared with the other manganites listed in the table, but we have a large full width at half maximum and consequently important RCP [29, 30, 33].

In place of $M^2$ vs. $H/M$, we can obtain the nature of transition by tracing $\Delta S_M/\Delta S_M^{\text{max}}$ as a function of $\theta$, and we followed the model proposed by Franco et al. [34]. Their proposition is traced $\Delta S_M$ curves with different maximum applied fields which should collapse on the same universal curve in the case of a second-order phase transition [31–33]. In this context, the construction of this phenomenological universal curve requires the normalization of all the $\Delta S_M$ (T, $\mu_0 H$) curves with their respective peaks and to the rescale of the temperature axis as [35, 36]

$$
\theta = \begin{cases} 
-(T_C - T)/(T_{T1} - T_C)T < T_C \\
(T_C - T)/(T_{T2} - T_C)T > T_C 
\end{cases}
$$

where:

- $\theta$ is the rescaled temperature
- $T_{T1}$ and $T_{T2}$ are the temperatures of the two reference points that, in our study, have been chosen as those corresponding to $\Delta S_M^{\text{max}}$ divided by 2.

Figure 12 presents the magnetic entropy change of the La0.5Pr0.2Sr0.3MnO3, measured for the maximum
Table 6 Maximum entropy change $-\Delta S_M^{\text{max}}$ and relative cooling power (RCP) occurring at the Curie temperature $T_C$ at magnetic field $\Delta \mu_0 H$ for La$_{0.5}$Pr$_{0.2}$Sr$_{0.3}$Mn$_{1-x}$TiO$_3$ ($x = 0.0$ and 0.1) samples (present work; PW) compared to several materials considered for magnetic refrigerations.

| Samples                  | $-\Delta S_M^{\text{max}}$ (J/kg/K) | RCP (J/kg) | $\Delta \mu_0 H$ (T) | $T_C$ (K) | Ref. |
|--------------------------|-----------------------------------|------------|----------------------|-----------|------|
| Gd                       | 9.5                               | 410        | 5                    | 293       | [29] |
| La$_{0.7}$Sr$_{0.3}$Mn$_{0.95}$Ti$_{0.05}$O$_3$ | 2.44                             | –          | 2                    | –         | [30] |
| La$_{0.67}$Sr$_{0.33}$Mn$_{0.95}$Fe$_{0.05}$O$_3$ | 2.8                              | 307        | 1.2                  | –         | [31] |
| La$_{0.35}$Sr$_{0.275}$Ca$_{0.375}$MnO$_3$    | 2.94                             | 37.2       | 1                    | 215       | [32] |
| La$_{0.5}$Pr$_{0.2}$Ba$_{0.3}$MnO$_3$         | 3.9                              | 371.45     | 5                    | 295       | [33] |
| La$_{0.5}$Pr$_{0.2}$Sr$_{0.3}$MnO$_3$         | 1.969                            | 284.87     | 5                    | 280       | PW   |
| La$_{0.5}$Pr$_{0.2}$Sr$_{0.3}$Mn$_{0.9}$Ti$_{0.1}$O$_3$ | 1.309                           | –          | 5                    | 123       | PW   |

applied fields which varies from 1 to 5 T; all the curves are overlaid on a single axis. This confirms the second-order transition.

4 Conclusion

In this research paper, we investigated the effect of substitution in the B site on the structural, magnetic and magnetocaloric properties of AMn$_{1-x}$Ti$_x$O$_3$ with $x = 0.0$ and 0.1 synthesized using the solid-state method. The refinement proves that all samples crystallize in the rhombohedral structure with $R\overline{3}c$ space group. In addition, samples present a second-order ferromagnetic to paramagnetic phase transition which takes place at the $T_C$. Furthermore, based on phenomenological model. A detailed investigation of our magnetic and magnetocaloric properties samples have been studied; we can note that there is an agreement between measured magnetic entropy change and those calculated theoretically of $M(T)$ and $-\Delta S_M^{\text{max}}$ at different applied fields For $x = 0.0$, sample presents an important $-\Delta S_M^{\text{max}}$ and RCP comparable with other manganites. These materials can be considered good candidates for magnetic refrigeration at low temperatures.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. Gschneidner, K.A., Jr., Pecharsky, V.K.: Int. J. Refrig. 31, 945 (2008)
2. Phan, M.H., Yu, S.C.: J. Magn. Magn. Mater. 308, 325 (2007)
3. Awana, V.P.S., Tripathi, R., Kumar, N., Kishan, H., Bhalla, G.L., Zeng, R., Sharth, L.S., Ganesan, CV., Habermeier, H.U.: vol. 107
4. Von Helmolt, R.: Phys. Rev. Lett. 71, 2331 (1993)
5. Chadra, K. et al.: Appl. Phys. Lett. 63, 1990 (1993)
6. Zener, C.: Phys. Rev. 82, 403 (1951)
7. Joncker, G.H.: J. Appl. Phys 37, 1424 (1966)
8. Omri, A., Bejar, M., Sajieddine, M., Dhahri, E., Hili, E.K., Es-Souni, M.: Physica B 407, 2572 (2012)
9. Omri, A., Bejar, M., Dhahri, E., Es-Souni, M., Valente, M.A., Graça, M.F.P., Costa, L.C.: J. Alloys Compd. 536, 173–178 (2012)
10. Dhahri, R., Omri, A., Bejar, M., Bekri, M., Dhahri, E., Sajieddine, M.: J. Supercond. Nov. Magn. 26, 3099–3104 (2013)
11. Gayathri, N., Raychaudhuri, A.K., Arularj, A., Rao, C.N.R.: Phys. Rev. B. 56, 1345 (1997)
12. Joncker, G.H.: Physica B 22, 707 (1956)
13. Rao, G.H., Sun, J.R., Kattwinkel, A., Schmitt, E., Gmelin, E.: Physica B 269, 379 (1999)
14. Tlili, M.T., Dhahri, E., Sajieddine, M., Hili, E.K.: vol. 62 (2011)
15. Kallel, N., Dhahri, J., Oumezzine, M., Vincent, H.: J. Magn. Mater. 261, 56 (2003)
16. Bohigas, X., Tejada, J., del Barco, E., James, W.J., Sales, M.: J. Phys.: Condens. Matter 10, 263 (1998)
17. Dhahri, J., Dhahri, A., Oumezzine, M., Dhahri, E.: J. Magn. Mater. 320, 2613 (2012)
18. Lui, L., Lui, Y., Miao, J., Lu, Z., Wang, Y., Y Sui, Z., Lui, Q., Hunag, D., Shang, W.: J. Alloys Compd. 427, 368 (2007)
19. Vollhardt, B.D.: Introduction to magnetic material. Addison-Wesley, New York (1972)
20. Dormann, J.L., Fiorani, D., Tronc, E.: Adv. Chem. Phys. 98, 283 (1997)
21. Céline, PORTEMONT: Etude De L’anisotropie D’échange Dans Des AgriGats De Cobalt NanoméTraques, These, Université Joseph-Fourier, Grenoble I, France (2006)
22. Banerjee, B.K.: Phys. Lett. 12, 16 (1964)
23. Nisha, P., Darbandi, A., Misra, A., Suresh, K.G., Varma, M.R., Hahn, H.: J. Phys. D Appl. Phys. 43, 135001 (2010)
24. Foldeaki, M., Chahine, R., Bose, T.K.: J. Appl. Phys. 77, 3528 (1995)
25. Hamad, M.A.: Phase Transition. 85(10), 6–12 (2012)
26. Hamad, M.A.: Nov. Magn. https://doi.org/10.1007/s10998-013-2260-y (2013)
27. Hamad, M.A.: J. Therm. Anal. Calorim. https://doi.org/10.1007/s10973-012-2505-1 (2012)
28. Hamad, M.A.: J. Adv. Ceram. 1(4), 290 (2012)
29. Pecharsky, V.K., Gschneidner, K. A., Jr.: Phys. Rev. Lett. 78, 4494–4497 (1997)
30. Dui, N.V., Son, D.V., Yu, S.C., Bau, L.V., Hong, L.V., Phuc, N.X., Nam, D.N.H.: Phys. Status Solidi (b) 244, 4570–4573 (2007)
31. Nisha, P., Savitha Pillai, S., Darbandi, A., Varma, M.R., Suresh, K.G., Hahn, H.: Mater. Chem. Phys. 136, 66–74 (2012)
32. Phan, M.H., Chandra, S., Bingham, N.S., Srikanth, H., Zhang, C.L., Cheong, S.W., Hoang, T.D., Chinh, H.D.: Appl. Phys. Lett. 97, 242506–242506-3 (2010)
33. Tozri, A., Khelif, J., Dhahri, E.: Mater. Chem. Phys. 149–150, 728–733 (2015)
34. Franco, V., Blazquez, J.S., Conde, A.: J. Appl. Phys. 103, 07B316 (2008)
35. Dhahri, J., Dhahri, A., Oumezine, M., Dhahri, E.: J. Magn. Mater. 320, 2613 (2008)
36. Bellouz, R., Oumezine, M., Hlil, E.K., Dhahri, E.: J. Magn. Mater. 375, 136 (2015)