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

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Abstract

Polycrystalline perovskite $\text{AMn}_{1-x}\text{TiO}_3$ with $\text{A} = \text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}$ ($x = 0.0$ 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 $\text{R}\bar{3}\text{c}$. 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 $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$, 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 $\text{Mn}^{3+}/\text{Mn}^{4+}$ 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 $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$. 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.

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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 $R\bar{3}c$ symmetry

2 Experimental

Samples $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{TiO}_3$ with $x = 0.0$ and 0.1 were prepared using a solid-state reaction of La_2O_3 , SrCO_3 , Pr_6O_{11} , Mn_2O_3 , and 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

Fig. 2 Observed (circle) and calculated (continuous line) XRD patterns obtained by the Rietveld analysis for $\text{AMn}_{1-x}\text{TiO}_3$ ($x = 0.0$) 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 ($R\bar{3}c$ space group)

parameters and the magnetic properties of our samples, we pass them through an X-ray diffraction (XRD) analysis ($\text{Cu-K}\alpha$ radiation $\lambda_{\text{Cu}} = 1.5406\text{ \AA}$); 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 $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{TiO}_3$ ($x = 0.0$ 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 $R\bar{3}c$ space group. It is noted that for some peaks, there is a shift toward the small 2θ 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 $\text{La}^{3+}\text{Pr}^{3+}\text{Sr}^{2+}(0.7\text{Mn}^{3+}(0.3-x)\text{Mn}^{4+}_x\text{Ti}^{4+}\text{O}_3^{2-})$ 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 $347.71\text{ \AA}^3$ for $x = 0.0$ to $347.85\text{ \AA}^3$ 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.

Table 1 Refined profile parameters for $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.0$ and 0.1) after the Rietveld refinements of X-ray powder diffraction at room temperature (300 K)

	r_B (Å)	V (Å ³)	a (Å)	c (Å)
$x = 0.0$	0.6140	347.71	5.4890	13.3264
$x = 0.1$	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 χ^2 .

3.2 Magnetic Characterization

All samples $\text{AMn}_{1-x}\text{TiO}_3$ ($x = 0.0$ 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 $\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{4+}$ and consequently increase of the number of $\text{Ti}^{4+}\text{-O}^{2-}\text{-Ti}^{4+}$ 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.

Fig. 3 Temperature dependence of magnetization of $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{TiO}_3$ as measured in a field of 0.01 T (red symbols for zero-field cooling (ZFC) and black symbols for field cooling (FC)). The inset indicates the dM/dT (T) curves used to determine T_C

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].

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

where

- τ_0 is the attempt time of the order of $(10^9\text{--}10^{13})$;
- ΔE_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 Boltzman 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 $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{TiO}_3$ ($x =$

0.0 and 0.1). 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 , μH) 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]:

$$\left(\frac{\partial S}{\partial \mu_0 H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_{\mu_0 H} \quad (2)$$

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:

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

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:

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

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,

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

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

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

Fig. 6 Temperature dependence of magnetization in constant applied magnetic field

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

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

ΔS_M attains the maximum at $T = T_C$, and its value can be calculated using the following equation:

$$\Delta S_M^{\max} = \left[-A \left(\frac{M_i - M_f}{2} \right) + B \right] \mu_0 H_{\max} \quad (8)$$

Fig. 7 Temperature dependence of 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))

Table 2 Model parameters for $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$ ($x = 0.0$) in different applied magnetic fields

$\mu_0 H$ (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

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 ($\Delta S_M^{\max}$) and the FWHM (δT_{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 δT_{FWHM} is determined by:

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

The RCP is defined as

$$\begin{aligned} \text{RCP} &= -\Delta S_M(T, \mu_0 H_{\max}) \times \delta T_{\text{FWHM}} \\ &= \left(M_i - M_f - 2\frac{B}{A} \right) \mu_0 H_{\max} \times \cosh^{-1} \\ &\quad \sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}} \end{aligned}$$

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

$$\Delta C_{P,H} = \frac{\delta \Delta S_M}{\delta T} \quad (10)$$

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

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

Using the phenomenological model, we can determine $\Delta \delta S_M$, T_{FWHM} , RCP, and ΔC_P for $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.0$ and 0.1).

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 $\text{AMn}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.0$ 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 ($x = 0.00$, 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 $\text{AMn}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.0$ 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 $\Delta S_M^{\max}$ shows a linear increase. This reveals a much better ΔS_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

Table 3 Model parameters for $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ($x = 0.1$) in different applied magnetic fields

$\mu_0 H$ (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

Fig. 8 Variation of the magnetic entropy change vs. temperature at different applied magnetic fields magnetic 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)). The solid lines are predicted results, and symbols represent experimental data

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 $|\Delta S_{\max}|$ 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 $|\Delta S_{\max}|$ 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 $H = 5\text{ T}$, samples depict not only the highest RCP values but also the important value of $|\Delta S_{\max}|$. We determined the specific heat ΔC_P as a function of temperature for $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{TiO}_3$ ($x = 0.0$ and 0.1) by using Eq. 11 in different magnetic fields; ΔC_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

Fig. 9 a Magnetic field dependence of the maximum entropy change ($-\Delta S_{\text{M}}^{\max}$) and b relative cooling power values (RCP) for the $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{TiO}_3$ ($x = 0$ and 0.1) compounds

$x = 0.0$ is shown in Fig. 10; $\Delta C_{P,H(\max)}$ increases when the magnetic field increases.

Fig. 10 Temperature dependence of specific heat (ΔC_P) under different magnetic field variations 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)) samples

Table 4 The predicted values of applied magnetocaloric properties for $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$ in different applied magnetic field shifts

$\mu_0 H$ (T)	$-\Delta S_M^{\max} (\text{J}/(\text{kg}/\text{K}))$	δT_{FWHM} (K)	RCP (J/kg)	$\Delta C_{\text{P,H(max)}}$ (J/(kg/K))	$\Delta C_{\text{P,H(min)}}$ (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 $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Ti}_{0.1}\text{O}_3$ $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ($x = 0.1$) in different applied magnetic field shifts

$\mu_0 H$ (T)	$-\Delta S_M^{\max} (\text{J}/(\text{kg}/\text{K}))$	δT_{FWHM} (K)	RCP (J/kg)	$\Delta C_{\text{P,H(max)}}$ (J/(kg/K))	$\Delta C_{\text{P,H(min)}}$ (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

Fig. 11 Variation of the magnetic entropy change vs. maximal field applied for $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$ ($x = 0.0$) perovskite as selected temperatures below or above transition, respectively

We listed in Tables 4 and 5 the $-\Delta S_M^{\max}$, δT_{FWHM} , RCP, $\Delta C_{\text{P,H(max)}}$, and $\Delta C_{\text{P,H(min)}}$ 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 $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$, 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 $\Delta S_M^{\max}$ 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 $\Delta S_M/\Delta S_M^{\max}$ as a function of θ , and we followed the model proposed by Franco et al. [34]. Their proposition is traced ΔS_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 ΔS_M (T , $\mu_0 H$) curves with their respective peaks and to the rescale of the temperature axis as [35, 36]

$$\begin{cases} \theta = -(T_C - T)/(T_{r1} - T_C)T < T_C \\ \theta = (T_C - T)/(T_{r2} - T_C)T > T_C \end{cases}$$

where:

- ✓ θ is the rescaled temperature
- ✓ T_{r1} and T_{r2} are the temperatures of the two reference points that, in our study, have been chosen as those corresponding to $\Delta S_M^{\max}$ divided by 2.

Figure 12 presents the magnetic entropy change of the $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$, measured for the maximum

Table 6 Maximum entropy change $-\Delta S_M^{\max}$ and relative cooling power (RCP) occurring at the Curie temperature T_C at magnetic field $\Delta\mu_0 H$ for $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.0$ and 0.1) samples (present work; PW) compared to several materials considered for magnetic refrigerations

Samples	$-\Delta S_M^{\max}$ (J/(kg·K))	RCP (J/kg)	$\Delta\mu_0 H$ (T)	T_C (K)	Ref.
Gd	9.5	410	5	293	[29]
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.95}\text{Ti}_{0.05}\text{O}_3$	2.44	—	2	—	[30]
$\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{0.95}\text{Fe}_{0.05}\text{O}_3$	2.8	307	1.2	—	[31]
$\text{La}_{0.35}\text{Sr}_{0.275}\text{Ca}_{0.375}\text{MnO}_3$	2.94	37.2	1	215	[32]
$\text{La}_{0.5}\text{Pr}_{0.2}\text{Ba}_{0.3}\text{MnO}_3$	3.9	371.45	5	295	[33]
$\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$	1.969	284.87	5	280	PW
$\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Ti}_{0.1}\text{O}_3$	1.309	161.651	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 $\text{AMn}_{1-x}\text{Ti}_x\text{O}_3$ with $x = 0.0$ and 0.1 synthesized using the solidstate method. The refinement proves that all samples crystallize in the rhombohedral structure with $R\bar{3}c$ 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 $-\Delta S_M^{\max}$ at different applied fields. For $x = 0.0$, sample presents an important $-\Delta S_M^{\max}$ and RCP comparable with

other manganites. These materials can be considered good candidates for magnetic refrigeration at low temperatures.

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Fig. 12 Normalized entropy change $\Delta S_M(T, \mu_0 H)/\Delta S_M^{\max}$ vs. θ (rescaled temperature) for $\text{La}_{0.5}\text{Pr}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$ ($x = 0.0$) compound at different applied magnetic field change interval

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