ORIGINAL PAPER

Role of 5% of titanium substitution on magnetic properties of $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$

A Bouazizi¹, M Ellouze^{1*} (D, E K Hlil² and R B Jotania³

¹Faculty of Sciences of Sfax, LMEEM, University of Sfax, B.P. 1171-3000 Sfax, Tunisia

²CNRS, Grenoble INP, Institut Néel, University Grenoble Alpes, 38000 Grenoble, France

³Department of Physics, Electronics and Space Science, University School of Sciences, Gujarat University, Ahmedabad, Gujarat, India

Received: 20 September 2022 / Accepted: 22 January 2023 / Published online: 16 February 2023

Abstract: This research work focuses on analyzing how titanium substitution in site B affects the physical characteristics of La₀₆₇Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O₃. Experimental characterization was used to establish magnetic measurements and specific heat measurements for this solid–solid combination. Following magnetic measurements and those of specific heat under a magnetic field applied around $T_{\rm C}$, the magnetocaloric characteristics of this system were taken into consideration. Both the $T_{\rm C}$ transition temperature and the entropy variation produce comparable findings. The variation of the adiabatic temperature was estimated from the variation of the magnetic entropy and the specific heat. Additionally, the doping reduces the magnetocaloric characteristics of our compound, as evidenced by the relative cooling power, which is regarded as a crucial metric for magnetic refrigeration. The power law for the adiabatic temperature was used to calculate the values of b and p . Additionally, the values of the local exponent n that we calculated from the critical exponents are smaller than those obtained from the power law ($|\Delta S(H)| \propto H^n$). We discovered that α_{pure} is negative (disorder is irrelevant) by applying the Harris criterion. These results support that disorder has no significant effect on critical exponents and universality class. Besides, by calculating the variance σ^2 and following the rules of selection of the universality class according to the value of σ , we found that the critical exponents of our system belong to the mean field model. This indicates that Ti-doping changes the universality class of this kind of manganite perovskites. Finally, a comparison between the magnetocaloric effects of two compounds (father and the studied compound) was undertaken to develop a single sample with a significant magnetocaloric effect.

Keywords: Manganite; Magnetocaloric effect; Critical behavior; Phenomenological model

1. Introduction

All magnetic materials exhibit the magnetocaloric effect, which opens a wide range of research opportunities to develop active materials that are ideal for all applications. Gadolinium is the reference material for magnetic cold at ambient temperature. Due to its purity, this element also has the benefit of being a combination that is simple to acquire. It develops technologically as a result of the simplicity of implementation work made possible by its excellent ductility and malleability. As a result, it is utilized in the most. It is not, however, a viable magnetorefrigerating material for consumer applications because to its prohibitive cost (up to 3500 ϵ /kg) and limited reserves. That is why, it is crucial to locate another magnetocaloric substance, and hence the potentials of Manganites as an energetically clean alternative to remedy this problem and to be an effective alternative for magnetic refrigeration. Some of the properties of magnetic materials are highly dependent on the applied mechanical and thermal stresses, as well as the magnetic field. Also, the key requirement of magnetic refrigeration is to have proper magnetocaloric materials, which can produce a large magnetic entropy change [\[1](#page-7-0)] and a good magnetic reversibility at low magnetic fields and with a wide temperature range [[2\]](#page-7-0).

These compounds are characterized by a fairly simple crystallographic structure as well as a flexibility of substitution. Among the compounds with perovskite structures, titanate and its derivatives are the subject of several *Corresponding author, E-mail: Mohamed.Ellouze@fss.rnu.tn

studies thanks to their giant magnetic, magnetocaloric and dielectric properties. These properties encourage researchers to use it in certain applications such as industries due to the high values of the colossal magnetoresistance [[3,](#page-7-0) [4\]](#page-7-0) and giant magnetocaloric. These parameters are essential to achieve high magnetic refrigeration efficiency [\[5](#page-7-0)]. All this proprieties make them likely to be used in the field of information storage (magnetic memories and reading heads) or the development of electrical components (temperature reversible circuit breakers) [[6–10\]](#page-7-0) or used for development of material catalysts for electronic devices with low power consumption [[11](#page-7-0)]. In addition, the titanium structure is very sensitive to substitution at site A and/or at B site level, which is manifested by a great richness in the magnetic and structural phase diagrams assembling between the variations of macroscopic parameters such as temperature, pressure, size of the doping ions, elaboration method and annealing temperature. What is trusty to mention is that it is crucial to understand and master the ferromagnetic processes, microstructural evolution, and the impact of atomic flaws on the characteristics of magnetic materials. The dependencies of the universality class, which are directly tied to the dimensionality of the space and the order parameter, are a fundamental concern that is always raised and related to the dimensionality of the space and the order parameter.

The major interest of the present research work is the study of the effects of 5% of titanium substitution on the physical properties of the compound formula $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$ prepared by the solidsolid method, drawing a special attention to magnetic properties. This compound has been characterized by SQUID magnetometer for magnetization measurements at different temperatures and in different applied magnetic fields. Indeed, the variation of the specific heat was determined and that of the adiabatic temperature ΔT_{ad} is carried out by exposing a thermally insulated material to the magnetic field [\[12](#page-7-0)] and was calculated to measure the Relative Cooling Power RCP (T) to determine the magnetic properties of our material and mark it's future applicability in magnetic refrigeration technology [\[13](#page-7-0)]. We made a very low doping rate (5%) and we recorded very interesting magnetic properties. A very important relative cooling power (33.2617% J kg^{-1} per compared to Gd) which makes our sample useful in magnetic refrigeration technology although the doping rate is very low. Besides, the local exponent n was calculated from the critical exponents which are lower than those deduced from the power law $(|\Delta S(H)| \infty H^n)$.

Finally, a comparison between the magnetocaloric effect of the parent compound and the studied sample was carried out to develop a single sample with a significant magnetocaloric effect. This allows us to manufacture composites

from these two samples to have a large Curie temperature range that covers room temperature and with comparable RCP values.

2. Experimental details

The powder sample of $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$ was synthesized using the standard solid state reaction method at high temperature. All the detailed preparation procedure and basic physical properties are reported in Ref. [\[11](#page-7-0)]. The magnetization measurements were conducted using a SQUID magnetometer developed at Neel institute Laboratory in Grenoble.

3. Results and discussion

3.1. Magnetic characterization

According to Oesterreicher et al. [\[12](#page-7-0)], the dependence of the experimental data of Δ_{SM} of sample studied as a function of applied magnetic field can be determined by the relationship:

$$
|\Delta S(H)| \infty H^n \tag{1}
$$

with n as the local exponent depending on the magnetic state of the material.

The obtained values of n by a linear fit of the curves are shown in Fig. 1. The local exponent was found to be 0.78. Moreover, n can be determined locally as follows [\[13](#page-7-0)]:

Fig. 1 Variation of $Ln(\Delta S_M)$ as a function of $Ln(H)$ for $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$

$$
n = \frac{\text{d} \ \text{Ln} |(\Delta S_M)|}{\text{d} \ \text{Ln}H} \tag{2}
$$

Figure 2 represents the temperature dependence of the exponent n for the different values of the applied field. It should be noted that n evolves with the field in the entire temperature studied range. In agreement with previous experimental data $[14–17]$ $[14–17]$ $[14–17]$, the general behavior of $n(T)$ follows the following pattern: *n* close to 1 for $T < T_C$, which indicates that at these temperatures the magnetization variation does not depend on the magnetic field. Furthermore, for $T = T_{\rm C}$, *n* expects a minimum. In the mean field approximation, this is 2/3 as predicted by Osterreicher and Parker [[18\]](#page-8-0), but in the general case, n is different from this value and depends on the critical exponents. First, n gradually decreases for values close to 0.764 (for $H = 5$ T) at T_{peak} , after that it increases for values close to 2 in the PM region, which is in accordance with the Curie–Weiss law in the paramagnetic domain. Consequently, in their general behavior, these variations of $n(T, H)$ accord swell with those found in previous studies. This result indicates that the usefulness of the local exponent n gives precise information on the magnetic state, showing the inhomogeneous character existing in our material. Indeed, manganites are inhomogeneous materials even for good quality crystals [\[19](#page-8-0)]. Besides, for the studies of the local exponent n, it is very important to study the Gibbs free energy (G) to classify the transitions of the sample under study. The free energy G as a function of the total magnetization can be developed, while neglecting the terms having the very high powers in the equation that follows:

Fig. 2 Variation of the local exponent n as a function of the temperature of $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$ under different magnetic fields

$$
G(M, T) = G_0 + \frac{1}{2}A(T)M^2 + \frac{1}{4}B(T)M^4 + \frac{1}{6}C(T)M^6 - MH
$$
\n(3)

The coefficients $A(T)$, $B(T)$ and $C(T)$ express the Landau parameters that were determined from the equation quoted above by plotting μ_0H as a function of the magnetization M [\[20](#page-8-0)].

Figure 3 shows the evolution of Landau parameters A (T) , $B(T)$ and $C(T)$ as a function of temperature for our compound. As expected, $A(T)$ is positive with a minimum at $T_{\rm C}$ corresponding to a maximum at the level of susceptibility. $B(T_C) = 0$, which allows us to conclude that the transition is of a second order. $C(T_C)$ is > 0 , which is in good agreement with the Landau model [\[11](#page-7-0)]. Moreover, the variation of magnetic entropy $\Delta S(T)$ can be determined differently using the parameters $A(T)$, $B(T)$ and $C(T)$, according to the following equation:

$$
\Delta S_M(T) = S_M(T, 0) - S_M(T, H)
$$

= $-\frac{1}{2}A'(T)(M_0^2 - M^2) - \frac{1}{4}B'(T)(M_0^2 - M^4)$
 $-\frac{1}{6}C(T)(M_0^2 - M^6)$ (4)

where $A'(T)$, $B'(T)$, $C'(T)$ are the first derivatives of the

Fig. 3 Variation of Landau parameters $A(T)$, $B(T)$ and $C(T)$ whose units are T^2 kg/J, T^4 kg³/J³ and T^6 kg⁵/J⁵, respectively

coefficients $A(T)$, $B(T)$, $C(T)$ with respect to the temperature and M_0 is the value of the magnetization obtained at zero field. To complete the studies on the physical properties of our compound, we carried out measurements of the specific heat Cp carried out between different temperatures at two applied magnetic fields 1 T and 5 T (Fig. 4). It should be mentioned that the studied material is in the solid state, so one can neglect its compressibility and acquire its specific heat at constant pressure (Cp) to that at constant volume (Cv) shown in Fig. 4. The temperature dependence of the $Cp(T)$ curve shows rapid crossing at specific temperatures. Inside this curve, we have enlarged these areas. This transition confirms the Curie temperature given by the magnetic measurements of the magnetization [\[11](#page-7-0)] where the rate of change of the magnetization is quite large. This singularity is known as a lambda-like anomaly $[21, 22]$ $[21, 22]$ $[21, 22]$ $[21, 22]$ $[21, 22]$ which can be found in ferromagnetic materials where there are many magnetic interactions. The absence of extended magnetic interactions prevents the occurrence of phenomena related to magnetic properties such as lambda type transition. This peak expands with increasing magnetic field. We therefore observe a change in temperature from 206 K [\[11](#page-7-0)] to 215 K when the field goes from 1 to 5 T. This same phenomenon has already been reported for La Sr-based manganites [\[19](#page-8-0)]. In addition, the height of the peak is reduced and its width is enlarged with increasing applied field. This is a consequence of the widening of the transition zone, and the rapid decrease in the rate of change of magnetization with the applied field at the transition temperature [\[23](#page-8-0)]. This peak is also due to the particularly high values around the PM-FM transition temperature, where the rate of

Fig. 4 Variation of specific heat as a function of temperature under two applied magnetic fields 2 T and 5 T for $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$

variation of the magnetization is quite large. This anomaly has also been attributed to the possible chemical inhomogeneity of the sample [[24\]](#page-8-0). Moreover, the large increase in the transition region and the reduction in the rate of change of the magnetization temperature with doping are consistent with the behavior of the specific heat anomaly. Also, this peak is explained by the fact that before the transition, the species are mainly in the form of pairs (spins, magnetic dipoles and dissimilar atoms); after the transition, they are mainly in the form of singles. Before transition, couples and singles are in balance; after the transition the pairs and singles are in balance. But during the transition, a state composed mainly of pairs changes to a state composed mainly of singles. So there is a change in the energies associated with a chemical reaction in which one mole of pairs is converted into two moles of singles. The change in magnetic entropy ΔS_{Cp} was calculated according to the following equation $[25]$ $[25]$:

$$
\Delta S_{\rm Cp}(T, H) = \int\limits_0^T \frac{\mathrm{Cp}(T, H) - \mathrm{Cp}(T, 0)}{T} \mathrm{d}T \tag{5}
$$

The magnetocaloric behavior of our system given in Fig. 5 is identical to that determined by magnetic measurements. By combining the variation of the magnetic entropy ΔS_M and the specific heat Cp at a constant magnetic field μ_0H , we can determine the variation of the adiabatic temperature ΔT_{ad} (Fig. [6\)](#page-4-0) ΔT_{ad} which is determined by [[26,](#page-8-0) [28\]](#page-8-0):

Fig. 5 Variation of magnetic entropy as a function of temperature under two magnetic fields 2 T and 5 T of $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$

Fig. 6 Variation of adiabatic temperature as a function of temperature under different magnetic fields of $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$

$$
\Delta T_{\text{ad}} = -\int_{0}^{H} \frac{T}{\text{Cp}(T,H)} \left(\frac{\partial M}{\partial T}\right)_{\text{H}} \text{d}H = -T \frac{\Delta \text{SM}(T,H)}{\text{Cp}(T,0)} \tag{6}
$$

The ΔT_{ad} variation at 5 T is 1.9 K (Table 1).

Our results are comparable with the indicated adiabatic temperature change for $La_{0.7}Sr_{0.3}MnO_3$ which is around 3 K at 5 T [\[26](#page-8-0)], 3.3 K for the compound $La_{0.8}Sr_{0.2}MnO₃$ at 7 T [\[25](#page-8-0)], and 3.33 K for $La_{0.67}Sr_{0.33}MnO_3$ [[28\]](#page-8-0). Additionally, Lin et al. [[29\]](#page-8-0) reported the case of Gd-based compounds. Ban et al. [[30\]](#page-8-0) reported that ΔT_{ad} for $Gd_{45}Tb_{55}$ is 5.8 K at $T_C = 256$ K, while for Gd, $\Delta T_{ad} = 5.6$ at 5.8 K. In Fig. [7,](#page-5-0) we represent the variation of the magnetic entropy and the adiabatic temperature as well as the specific heat for the compound at 5 T. There is a good agreement between the shapes of ΔT_{ad} and ΔS_{M} . While the FM-PM transition is well visualized even for Cp, there is a small deviation in the TC temperature. This shift is due to the measurement method and experimental error. Figure [8](#page-5-0) indicates the Variation of $\Delta T_{\text{ad}}^{\text{max}}$ as a function of the applied magnetic field of the compounds. It can be noticed that the peak of the maximum of the variation of the adiabatic temperature increases with the applied magnetic

Table 1 Values of ΔT_{ad} , RCP (T) deduced from ΔT_{ad} and the RCP (S) deduced from magnetic measurements, β , γ and σ^2 for $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$

ΔT_{ad} (K)	$RCP(T)$ $RCP(S)$		15	
0.84 (@2 T)		52.166 52.961 ($@2$ T)	0.495 1.21 1.29	
$1.9 \; (\circledcirc 5 \; T)$		135.987 136.373 (@5 T)		

field. A curve fit allows us to determine the parameters b and p of the power law defined by [[31\]](#page-8-0):

$$
\Delta T_{\text{ad}}^{\text{max}} = b(\mu_0 H)^p \tag{7}
$$

The obtained values of b and p are 0.377 and 0.967, respectively. The values of the exponent b seem to be deviated by 2/3, this is the predicted value for the mean field theory [\[11](#page-7-0)].

3.2. Critical isotherm

For a temperature equal to Curie, the variation of the magnetization as a function of the field can be given by a power law characterized by a critical exponent δ indicated in Eq. 8:

$$
M = DH^{1/\delta} \tag{8}
$$

This critical exponent can be obtained from the Ln (M) versus Ln (H) diagram as shown in Fig. [9.](#page-5-0) According to Eq. 8, the variation of Ln (M) as a function of Ln (H) must be a straight line with a slope equal to 1/ δ . The values of δ deduced from this method are in good agreement with those found by the mean field model for our compound [\[11](#page-7-0)]. The critical exponent δ is also determined from Widom's relation [\[32](#page-8-0)] which gives a relation between the three critical exponents β , γ and δ as shown in Eq. 9 [\[33](#page-8-0)]:

$$
\delta = 1 + \gamma/\beta \tag{9}
$$

Using the values of β and γ estimated from the method of modified Arrott plots [\[11](#page-7-0)], we obtained new values of δ , which are presented in Table 1. It is necessary to point out that there is a good agreement between the experimental and calculated values of δ . Furthermore, the critical exponents found in this study obey Widom's scaling relation, confirming that the estimated values are selfconsistent and acceptable. The value of the critical exponent γ is illustrated in Table 1.

3.3. Scale behavior

The estimation of the credibility of the critical parameters can be carried out by means of the scaling law, which predicts that in the critical region, the internal field and the magnetization must confirm to universal scale behavior. Based on the equation below:

$$
\left(\frac{H}{M}\right)^{1/\delta} = \frac{T - Tc}{T1} + \left(\frac{M}{M1}\right)^{1/\beta} \tag{10}
$$

We plot the variation of $M/|\varepsilon|^\beta$ as a function of $H/|\varepsilon|^{\beta+\gamma}$ for temperatures around $T_{\rm C}$, where $\varepsilon = (T - T_{\rm C})/T_{\rm C}$ is the reduced temperature. We have arrived at two universal branches, one for temperatures below T_c and the other for those above T_c , either on a linear or logarithmic scale as

Fig. 8 Representation of Ln (M) vr. Ln (H) for $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$

shown in Fig. 9. The scaling behavior is well verified for our compound and all points are formed on two curves. This demonstrates the accuracy and good agreement of the calculated values of the critical and $T_{\rm C}$ exponents with the scaling hypothesis. The substitution of the 5% titanium in the manganese site results from a change of the critical exponents i.e., while the mother sample belongs to the 3 dimensional Heisenberg model, our system is compatible with the model of mean field. To correlate disorder with critical behavior, Fisher et al. [[34,](#page-8-0) [35\]](#page-8-0) have evaluated a computation using renormalization group theory [\[34](#page-8-0), [35](#page-8-0)], predicting that in the case of a ferromagnetic system with an exchange interaction of the form:

Fig. 9 Scale curve indicating the universal aspect one below and above T_c for $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$. Insets show the same data for a double logarithmic scale

$$
J(r) = 1/r^{d+\sigma} \tag{11}
$$

with d as a dimension of the space and σ the gap of the interaction. It is to be noted that the variance σ designates the effect of the distribution of the different cations in the Site B. This effect is called the "mismatch" effect and it is defined by [[36](#page-8-0)]:

$$
\sigma^2 = \Sigma r_i \chi_i^2 - \langle r_B \rangle^2 \tag{12}
$$

Here r_i indicates the radius of the cation i in the B site $(Mn^{3+}, Mn^{4+}$ and $Ti^{3+})$ and x_i is fraction occupancy $(\Sigma x_i = 1)$. The calculated values of the variance σ^2 are grouped in Table [1.](#page-4-0) We notice that the critical exponents of our sample belong to the mean field model.

3.4. Study of disorder

Harris [[37\]](#page-8-0) discussed the effect of disorder on the critical behavior of magnetic systems When the pure critical exponent α_{pure} of the pure system is positive, the disorder acts on the critical exponents and results in a modification of the critical behavior governed by a new random fixed critical point. Conversely, if α_{pure} is negative, the disorder is irrelevant. The exponent for the α_{pure} system is deter-mined by the Rushbrooke scaling relation [[38\]](#page-8-0) given by:

$$
\alpha_{pure} + 2\beta + \gamma = 2 \tag{13}
$$

Based on this relationship, we found that the value of α_{pure} is negative ($\alpha_{pure} = -0.19$). So, clutter is irrelevant, which explains the mean field class obtained for our compound. Besides, the value of the local exponent n can be determined from the critical exponents β and γ using the following equation [\[38](#page-8-0)]:

$$
n(T_{\rm C}) = 1 + \frac{\beta - 1}{\beta + \gamma} \tag{14}
$$

and the relation (14) can be written as follows

$$
n(T_{\rm C}) = 1 + \frac{1}{\delta} \left(1 - \frac{1}{\beta} \right) \tag{15}
$$

Some researchers have reported that for materials exhibiting second-order phase transitions n, they should be described by the mean-field model, such as $n = 2/3$ [\[14](#page-7-0), [39](#page-8-0)], and any deviation from this value must be justified by the Curie temperature distribution of the sample [\[38](#page-8-0), [40](#page-8-0)]. The values of critical exponents for the parent sample agree with those of a 3D-Heisenberg. However, with the substitution of Ti^{4+} ions, the critical exponent β increased up to the value characteristic of the mean field model, and the critical exponent γ decreased and became closer to the mean-field value. These results indicate that Ti-doping changes the universality class of the manganite perovskites. In fact, the obtained value of n is 0.71. From Fig. 10, we can deduce that with the increase of Ti substitution, the maximum of $-\Delta S_M$ versus T decreases. Previous results have confirmed that the change in maximum entropy decreases with doping and followed by a decrease in the critical transition temperature T_{C} . Furthermore, this decreases in $-\Delta S_M^{\text{Max}}$ remains relatively high, which favors the possibility of making compounds useful for magnetic refrigeration in different temperature. This decrease is linked to the decrease in double exchange interactions between Mn^{4+} and Mn^{3+} ions. According to Othmani et al. [\[41](#page-8-0)] annealing at low temperature increases the maximum value of the variation of entropy. Besides, from the curve $-\Delta S_M(T)$ we can deduce the type of the magnetic transition. In fact, a first-order transition is characterized by a narrow magnetic transition and a large

 ΔS_{MAX}^{M} La_{0.67}Ba_{0.22}Sr_{0.11}MnO₃ 2.5 $\mu_0 H = 5T$ $a_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$ 2.0 ΔS (J. kg ^{-1}K $^{-1})$ dT_{EWHM} 1.5 1.0 0.5 0.0 200 300 350 150 250 400 $T(K)$

Fig. 10 Temperature dependence of the magnetic entropy change $(-\Delta S_M)$ at different measured for an applied field 5 T for compounds $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$ and $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Ti_{0.05}O_3$

value of $-\Delta S_M^{\text{Max}}$. Nevertheless, a second-order transition shows a large magnetic transition (high value of ΔT_{FWHM}), yet with a small maximum of the magnetic entropy variation (Fig. 10). The obtained results confirm those obtained in the studies of isotherms using the Banerjee criterion [[42\]](#page-8-0).

It is known that magnetic refrigeration works most efficiently near the Curie temperature of the working substance. In order to increase the temperature range of magnetic refrigeration, a refrigerator can be constructed from a variety of substances with comparable physical and chemical properties. Next, we can use composites that have magnetocaloric compound properties, where a series of magnetocaloric materials with comparable RCP value are combined for the purpose of forming a composite refrigerant. This situation can be well satisfied by considering a mixture of the same compounds annealed at two different temperatures (1373 K $[11]$ $[11]$ for father sample and 1400 K for our compound) for refrigeration over the temperature range. This new method of preparing composites with magnetocaloric properties compounds presents an important advantage based on the synthesis of a single series of compounds annealed at different temperatures or in the same annealing temperature. Additionally, it should be noted that the RCP values of the mother and studied compound are comparable, which prompts us to reconsider the possibility of creating a multilayer composite that functions as a magnetic cooler over a large temperature range. To create a single sample with a strong magnetocaloric effect, we will also compare the magnetocaloric effects of two different substances. This enables us to create composites from these samples to have a wide Curie temperature range that covers the ambient and with

Fig. 11 Temperature dependence of the magnetic entropy change $(- \Delta S_M)$ at different measured for an applied field 5 T for composites

comparable RCP values (Fig. 11). Our initial goal was to create a single sample with a significant magnetocaloric effect. However, by annealing at various temperatures, we were able to produce a set of samples with the same composition, but with different magnetic transition temperatures (T_C) . This allows us to fabricate multilayers from these samples to have a wide Curie temperature range that covers room temperature and with comparable RCP values.

4. Conclusions

The present research work was intended to develop and characterize new materials with potential of application in the field of magnetic cold, information storage. We then developed a system using the classic ceramic production method based on the sintering technique. The physical properties of these materials strongly depend on the elaboration conditions (sintering, annealing, etc.) on the one hand and on the purity of the samples elaborated on the other. In a subsequent step, it is noted that the specific heat variation is positive prior to the transition and negative following it, and that it only deviates from zero in the vicinity of T_{C} .

Besides, we have calculated the variation of the adiabatic temperature ΔT_{ad} and the cooling power RCP (T), which reveal values slightly greater than those determined from the measurements of the magnetic isotherms (RCP(S)). However, we found that the values of the local exponent n derived from the critical exponents are less than those deduced from the power law ($|\Delta S(H)| \propto H^n$). In addition, using the Harris criterion, we discovered that α_{pure} is negative (disorder is irrelevant). These findings confirm that the critical exponents and universality class are not significantly impacted by disorder.

Moreover, by calculating the variance σ^2 and following the rules of selection of the universality class according to the value of σ , we found that the critical exponents of our system belong to the mean field model. These results indicate that Ti-doping changes the universality class of the manganite perovskites. Finally, in future research, we intend to conduct a comparison between the magnetocaloric effects of two compounds to develop a single sample with a significant magnetocaloric effect.

Author contributions AB: Synthesis of materials, preparing Original draft preparation, data analysis, graphics, formal analysis, investigation. ME: Mentor, Conceptualization, Data curation, Investigation, Writing, modification and Editing, language editing, manuscript submission. EKH: Data curation and analysis, Draft modification, Investigation, final analysis. RJ: Investigation, Draft and graph modification, writing-review and editing.

Funding The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Conflict of interest The authors have no relevant financial or nonfinancial interests to disclose.

References

- [1] A S Erchidi Elyacoubi, R Masrour, A Jabar, M Ellouze and E K Hlil J. Mater. Res. Bull. 99 132 (2018).
- [2] A S E Elyacoubi, R Masrour and A Jabar J. Solid State Commun. 271 39 (2018).
- [3] R von Helmholtz, J Wocker, B Holzapfel, M Schultz and K Samwer Phys. Rev. Lett. **71** 2331 (1993).
- [4] K Chahara, T Ohno, M Kasai and Y Kozond Appl. Phys. Lett. 63 1990 (1993).
- [5] A S Erchidi Elyacoubi, R Masrour and A Jabar J. Appl. Surf. Sci. 459 537 (2018).
- [6] H L Ju, C Kwon, Q Li, R L Green and T Venkatesan Appl. Phys. Lett. **65** 2108 (1994).
- [7] S S P Parkin Annu. Rev. Mater. Sci. 25 357 (1995).
- [8] V Goldschmidt Geochemistry (Oxford University Press) (1958)
- [9] S Geller J. Chem. Phys. 24 1019 (1956).
- [10] S Belhamr, R Masrour, A Jabar and E K Hlil J. Polyhedron 193 114891 (2021).
- [11] A Bouazizi, M Ellouze, S Labidi, E K Hlil and R B Jotania J. Mat. Sci. Mat. Electronics. 32 13099 (2021).
- [12] R Masrour, A Jabar, H Khlif, F Ben Jemaa, M Ellouze and E K Hlil J. Solid State Commun. 268 64 (2017).
- [13] P Sharma, R Masrour, A Jabar, J Fan, A Kumar, L Ling, C M C Wang and H Yang J. Chem. Phys. Lett. 740 137057 (2020).
- [14] H Oesterreicher and F T Parker J. Appl. Phys. **55** 4334 (1984).
- [15] T D Shen, R B Schwarz, J Y Coulter and J D Thompson J. Appl. Phys. 91 5240 (2002).
- [16] V Franco, A Conde, M D Kuzmin and J M Romero-Enrique J. Appl. Phys. 105 07A917 (2009).
- [17] C Flores, V Franco, A Conde, Q Y Dong and H W Zhang J. Magn. Mang. Mater. 804 322 (2010).
- [18] M Nasri, M Triki, E Dhahri and E K Hlil J. Alloys Compd. 546 84 (2013).
- [19] A Tozri, E Dhahri, E K Hlil, M Sajieddine and M Valente Solid State Comm. **151** 4 315 (2011).
- [20] H Osterreicher and F T Parker J. Appl. Phy. 55 4334 (1984).
- [21] J M De Teresea, M R Ibarra, P Algarabel, L Morellon, B Garcia-Landa, C Marquina, C Ritter, A Maignan, C Martin, B Raveau, A Kurbakov and V Trounov Phys. Rev. B 65 100403 (2002).
- [22] K De, S Majumdar and S Giri J. Magn. Magn. Mater. 322 102 (2010).
- [23] A M Tishin, K A Gschneidner and V K Pecharsky Phys. Rev. B 59 503 (1999).
- [24] R J Thorn J. Chem. Thermodyn. 34 973 (2002).
- [25] A Szewczyk, M Gutowska, B Dabrowski, T Plackowski, N P Danilova and Yu P Gaidukov Phys. Rev. B 71 224432 (2005).
- [26] D N H Nam, N V Dai, L V Hong, N X Phuc, S C Yu, M Tachibana and E Takayama-Muromachi J. Appl. Phys. 103 043905 (2008).
- [27] A M Tishin and Y I Spichkin J. Condensed Matter Phys. 214 33214 (2003).
- [28] A Rostamnejadi, M Venkatesan, P Kameli and H Salamati J. Magn. Magn. Mater. 323 2214 (2011).
- [29] G C Lin, Q Wei and J X Zhang J. Magn. Magn. Mater. 300 392 (2006).
- [30] V Ban, «Matériaux magnétoréfrigérants à large zone de travail». (France: Thesis at Henri Poincaré University) (2011). <https://hal.univ-lorraine.fr/tel-01746398/document>
- [31] V Franco, A Conde, J M Romero-Enrique, Y I Spichkin, V I Zverev and A M Tishin J. Appl. Phys. 106 103911 (2009).
- [32] M Nasri, M Triki, E Dhahri and E K Hlil J. Alloys Compd. 84 546 (2013).
- [33] S Nair, A Banerjee, A V Narlikar, D Prabhakaran and A T Boothroyd Phys. Rev. B 68 132404 (2003).
- [34] J S Kouvel and M E Fisher *Phys. Rev. A* 136 1626 (1964).
- [35] M E Fisher, S K Ma and B G Nickel Phys. Rev. Lett. 917 29 (1972).
- [36] F Damay, C Martin, A Maignan and B Raveau J. Appl. Phys. 82 6182 (1997).
- [37] A B Harris *J. Phys. C* 7 1671 (1974).
- [38] V Franco and J S Blazquez Appl. Phys. Lett. 89 222512 (2006).
- [39] V Franco and A Conde Int. J. Refrig. 33 465 (2010).
- [40] V Franco and A Conde Sci. Mater. **67** 594 (2012).
- [41] S Othmani, M Bejar, E Dhahri and E K Hlil J. Alloys Compd. 46 475 (2009).
- [42] S K Banerjee *Phys. Lett.* **12** 1 16 (1964).

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.