



Comparative examination of the physical parameters of the sol gel produced compounds $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$

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Abstract

In this paper, the physical characteristics of $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ compounds have been studied. Structural analysis by XRD showed that both samples crystallize in an orthorhombic structure. For the $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ sample it can be seen that there are two bands: the first is due to the stretching Mn–O bond the ν_s vibration mode, relates to the internal motion of a length-changing Mn–O, whereas the second corresponds to the ν_b bonding mode, which is sensitive to a change in the Mn–O–Mn angle. For the compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ the ν_b band is absent. The magnetic measurements show that the two compounds have a single transition from the PM state to the FM state with an increase in the Curie transition temperature T_c for the compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$. Similarly, the substitution of silver in calcium increases the value of the magnetization at low temperature. We also studied the magnetocaloric effect of our compounds. This study shows a significant change in magnetic entropy ΔS_M that took place around their magnetic transition temperatures T_c . Under the influence of a 5 T magnetic field. The largest fluctuation in magnetic entropy is in the order of -8.67 J/kg·K for the compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ this value is considered significant. The magnetocaloric results indicate that the compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ is the best sample which has a large RCP which suggests its good candidate in the field of magnetic cold. Based on the Banarjee criterion and Landau theory, a second-order transition is observed for both samples in the vicinity of the Curie transition T_c . The experimentally obtained value of ΔS_M is smaller than the theoretically calculated one, which proves that the transition is an unconventional transition even under the influence of a 5 T magnetic field.

Keywords $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ compounds · Curie transition · Magnetic entropy · Landau theory · Banarjee criterion

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1 Introduction

Manganites of structure $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (with Ln: rare earths and A: divalent element) have interesting physical properties and enormous technological interest in various fields of application. These intrinsic features are often described in these highly correlated electron systems by the indirect exchange interactions between the Mn^{3+} and Mn^{4+} ions, the average ionic radius of site A, and the magnetic and orbital disorder (Dkhalili et al. 2018a, b, c; Enneffati et al. 2018). In this structure manganese has a mixed valence $\text{Mn}^{3+}/\text{Mn}^{4+}$. Indeed, the trivalent element is substituted Ln^{3+} by a divalent or monovalent element leads to oxidation of the Mn^{3+} ions ($[\text{Ar}] 3d^4$) into Mn^{4+} ions ($[\text{Ar}] 3d^3$). The $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system is one of the most studied compounds in recent years due to its rich magnetic and electrical behavior (Enneffati et al. 2019). Previous studies carried out in our laboratory (Gharbi et al. 2021; Walha and Dhahri 2016) on manganites of the perovskite type of general formula $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ substituted by silver in the A site revealed that 10% silver is sufficient to destroy the state charge order and increase ferromagnetic interactions with an increase in T_c . This rise is due to the shift in the Mn–O–Mn angles caused by the overlap of the manganese ions' 3d orbitals and the oxygen ions' 2p orbitals, which is primarily responsible for the magnetic interaction in this system (Walha et al. 2004, 2009; Hamdi et al. 2017a, b; Assoudi et al. 2018a; Felhi et al. 2018). To complete and continue our work we have to study the physical properties of the compounds $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ using the sol–gel method given the important magnetocaloric properties of the compounds synthesized in this manner (Rietveld 1967; Rodriguez-Carvajal and FULLPROF, xxx; Goldshmidt 1927; Shannon 1976).

2 Results and discussion

XRD patterns for both samples were realized at room temperature and analyzed with the Rietveld refinement technique. $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ samples crystallize in the orthorhombic structure with Pbnm space group. Typical examples of the observed and calculated diffraction profiles for both samples are given in Fig. 1.

In order to determine the modes of vibrations and to identify the different types of bonds present in the structure of the samples, a study by infrared absorption spectroscopy using an FTIR Spectrum spectrometer (Fig. 2) was carried out. We observe two bands in the $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ sample: the first at 594 cm^{-1} corresponds to the Mn–O bond stretching the vibration mode ν_s , including the internal movement d caused by a change in Mn–O bond length, and the second at 420 cm^{-1} corresponds to the ν_b vibration mode, which is sensitive to a change in the Mn–O–Mn angle (Shelke and Deshpande 2017; Arulraj and Rao 1999; Shivakumara and Bellakki 2009). A single band at 590 cm^{-1} is seen in the $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ sample, which may be ascribed to the Mn–O bond stretching the s vibration mode ν_s .

The Mn ion is surrounded by six oxygen ions in the perovskite structure. A vertical axis was considered, connecting the Mn ion to the two oxygens. The ν_s vibration consists of the movement of Mn ion and oxygen by changing the length of the Mn–O₁ band while the ν_b binding vibration occurs when there is a change in the O₁–Mn–O₂ angle.

To investigate the magnetic characteristics of compounds, we did magnetization measurements as a function of temperature and applied magnetic field of 0.05 T, as well as

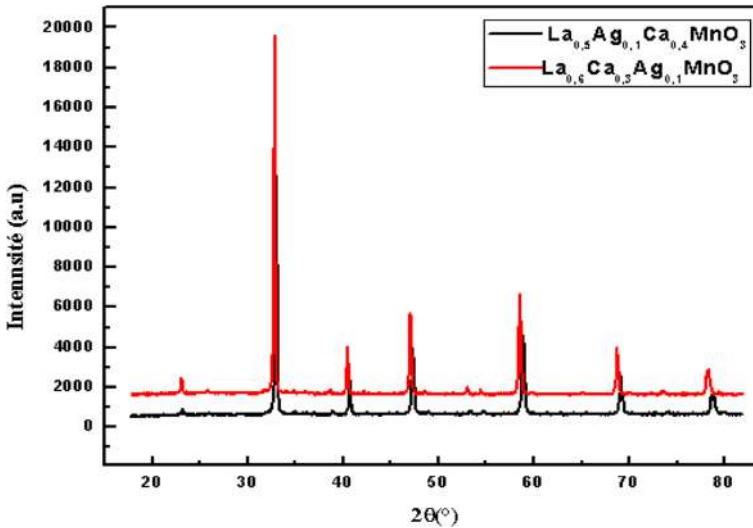


Fig. 1 X-ray diffraction patterns for both samples $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$

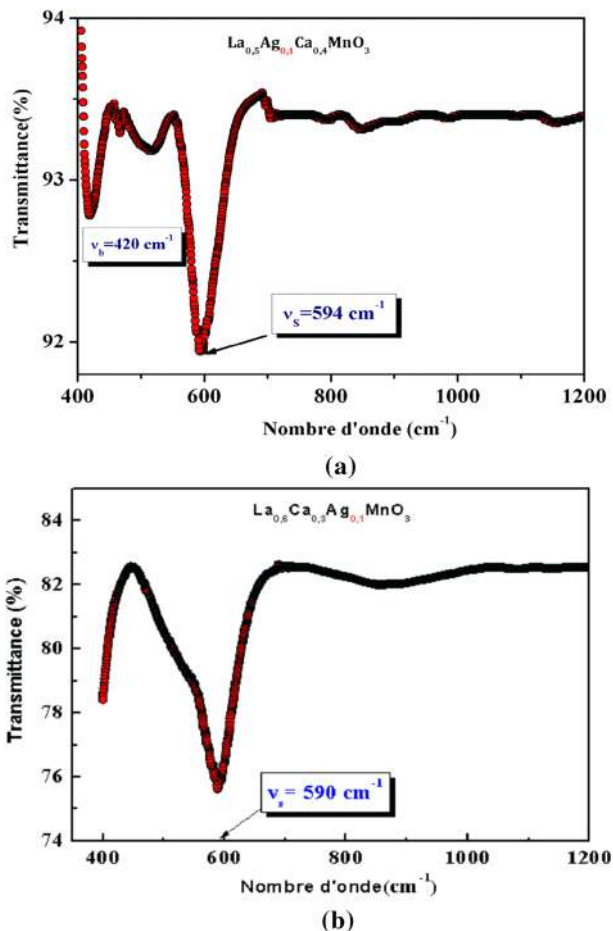
magnetization measurements as a function of applied magnetic field at various temperatures, $M(H)$. The undoped compound $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ has been studied in our laboratory (Gharbi et al. 2021). It is indexed in the P_{nma} orthorhombic structure. It has a curie temperature of 269K.

The thermal evolution of the magnetization $M(T)$ of the two samples which is represented in Fig. 3a shows that all the compounds present a continuous magnetic transition thus confirming on the one hand the good crystallization of the samples and on the other hand the homogeneous distribution of substituted ions. Additionally, the two silver-substituted compounds display a wide transition from the paramagnetic to the ferromagnetic state (FM) when the temperature lowers, and the magnetization value of the compound $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ is less than that of the compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ (Ying et al. 2011; Itoh et al. 1995).

By examining the curve Fig. 3b dM/dT in relation to temperature, we also note that silver's replacement for lanthanum causes a reduction in the (T_c) compared to that of calcium by silver. The difference between these two values can be explained by the valence effect seen by the weakening of the double exchange's ferromagnetic contacts in the molecule $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ (Baaziz et al. 2015). Indeed, the magnetic behavior of manganites is directly linked to the Mn^{3+}/Mn^{4+} ratio.

So, to favor the existence of a ferromagnetic phase at sufficiently high temperatures, the double exchange interaction must be favored, which therefore requires a minimum fraction of Mn^{4+} . This ferromagnetism is optimum for $\frac{2}{3}Mn^{3+}$ and $\frac{1}{3}Mn^{4+}$ compositions according to the phase diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, which explains this slight increase in T_c for the compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ since it has a valence $Mn^{3+}/Mn^{4+} = 1$ according to the neutrality equation $Mn_{0.5}^{+3}Mn_{0.5}^{+4}$ and consequently 50% of Mn^{4+} while the compound $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ has a Mn^{4+} level of 60% according to the neutrality equation $Mn_{0.4}^{+3}Mn_{0.6}^{+4}$ (Walha et al. 2018). Magnetization isotherms as a function of applied field are seen in Fig. 4. As can be observed, magnetization rises as a function of the applied magnetic field and it reaches saturation at the end of a field of the order of 0.5 T,

Fig. 2 FTIR Spectra for both samples **a** $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and **b** $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$



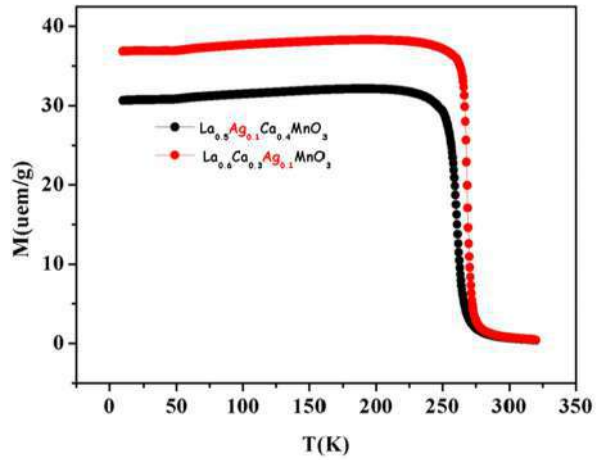
showing a ferromagnetic behavior at $T < 261 \text{ K}$ for the compound $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$, and $T < 270 \text{ K}$ for that of the compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$.

At the Curie temperature T_c , the spontaneous magnetization vanishes, and the saturation magnetization increases when the temperature decreases for the compounds $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$, thus confirming their ferromagnetic nature at low temperature. The values of the spontaneous magnetization M_{sp} were extrapolated up to $H = 0 \text{ T}$ using the $M(H)$ isotherms. At temperature 10 K , the saturation magnetization (M_s) of $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ is 94.19 emu/g and 92.8 emu/g for $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$.

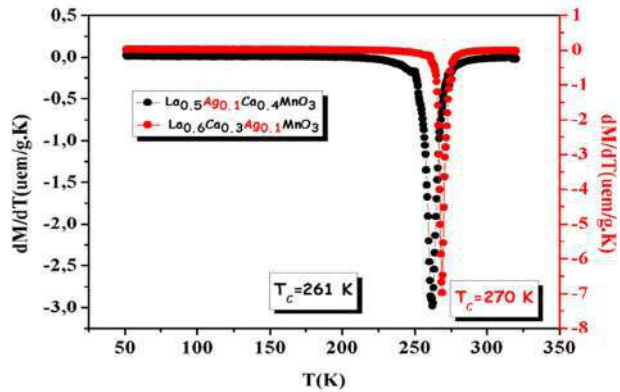
To ascertain the magnetic transition's nature, conventional Arrott plots of M^2 vs $\mu_0 H/M$ demonstrate a positive slope indicative of a second-order FM-PM transition (Fig. 5). In the vicinity of the Curie temperature, the linear curves which pass through the origin coincide with temperatures close to those deduced from the dM/dT curve. These temperatures are determined at 270 K and 261 K respectively for $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ and $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$.

The magnetic entropy ΔSM , which is proportional to the magnetic degrees of freedom, fluctuates according to the applied magnetic field and the sample's magnetic order. The

Fig. 3 a: Magnetization vs. temperature for $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ system. **b:** dM/dT vs. temperature for $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ system



(a)



(b)

magnetocaloric effect is defined by the change of Maxwell's isothermal entropy (Tlili et al. 2015; Walha et al. 2016):

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \tag{1}$$

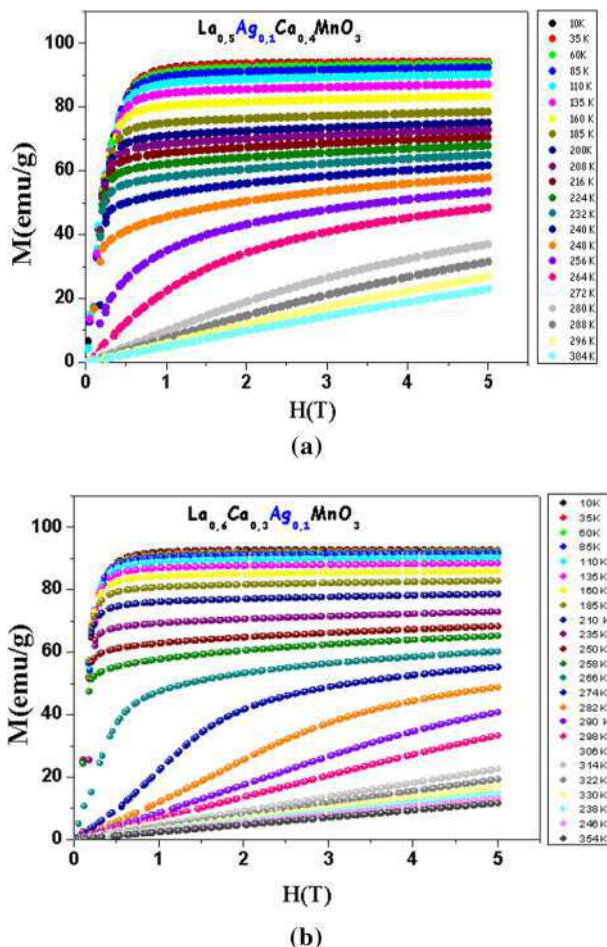
where ∂S the entropy derivative, ∂H the magnetic field derivative ∂M the magnetization derivative, ∂T temperature derivative, and ΔS the entropy change.

The following relation describes the change in the order of the spins generated by the application of a magnetic field H (Romero-Muñiz et al. 2013):

$$\Delta S_M(T, \Delta H) = S_M(T, H_2) - S_M(T, H_1) = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T}\right)_T dH \tag{2}$$

where T is the temperature, H_1 and H_2 denote the magnetic applied fields, with $H_1 \leq H_2$ because the magnetic fields H change from 1 to 5 T ($H_1 = 1, H_2 \geq 5$) if $H_1 = H_2$ this

Fig. 4 Magnetization isotherms vs. applied field at various temperatures for **a** $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and **b** $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ samples



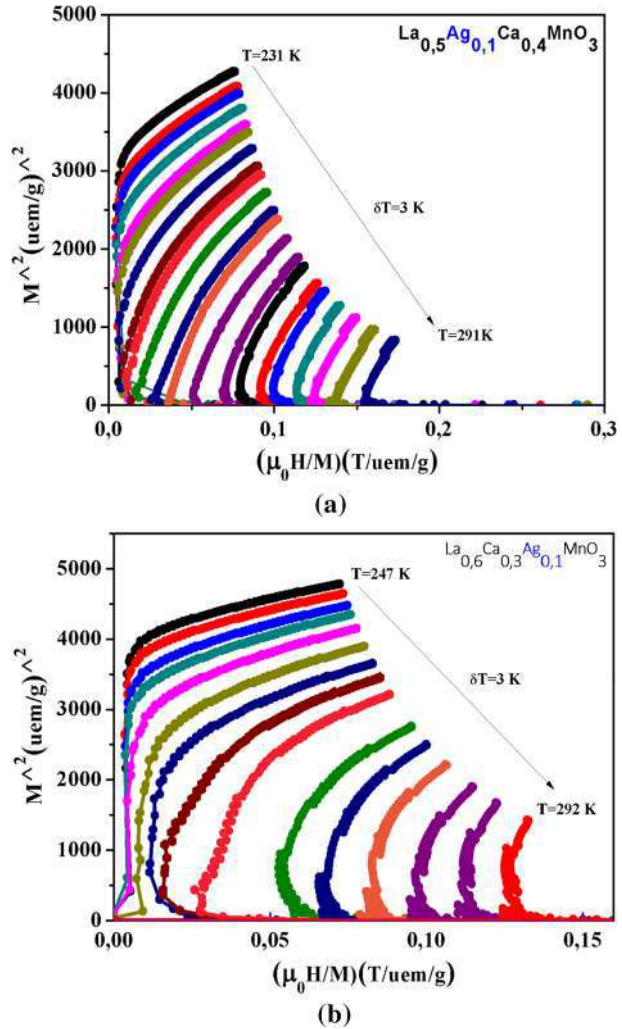
means that the integration = 0, S_M the isothermal magnetic entropy, the values of ΔS_M (the isothermal magnetic entropy change) are obtained via numerical integration of the magnetization isotherms (Ezaami et al. 2017)

$$\Delta S_M(T_i, \Delta\mu_0 H_j) = \sum_j \frac{M_{i+1}(T_{i+1}, \mu_0 H_j) - M_i(T_i, \mu_0 H_j)}{T_{i+1} - T_i} \Delta\mu_0 H_j \quad (3)$$

where μ_0 the magnetic constant (permeability of free space or vacuum permeability), M the magnetization measurement and $M(T)$ the magnetization versus temperature, the magnetization values M_i and M_{i+1} measured in a magnetic applied field H_j at temperatures T_i and T_{i+1} , respectively, and ΔS_M (the isothermal magnetic entropy change). For each temperature, the air is computed by dividing the temperature difference between the two isotherms around the temperature in question by the required field range.

The development of $-\Delta S_M$ (the experimental magnetic entropy change) as a function of temperature is shown in for several application industries (Fig. 6). It is noticed that when the applied magnetic field is increased, the absolute value of the maximum

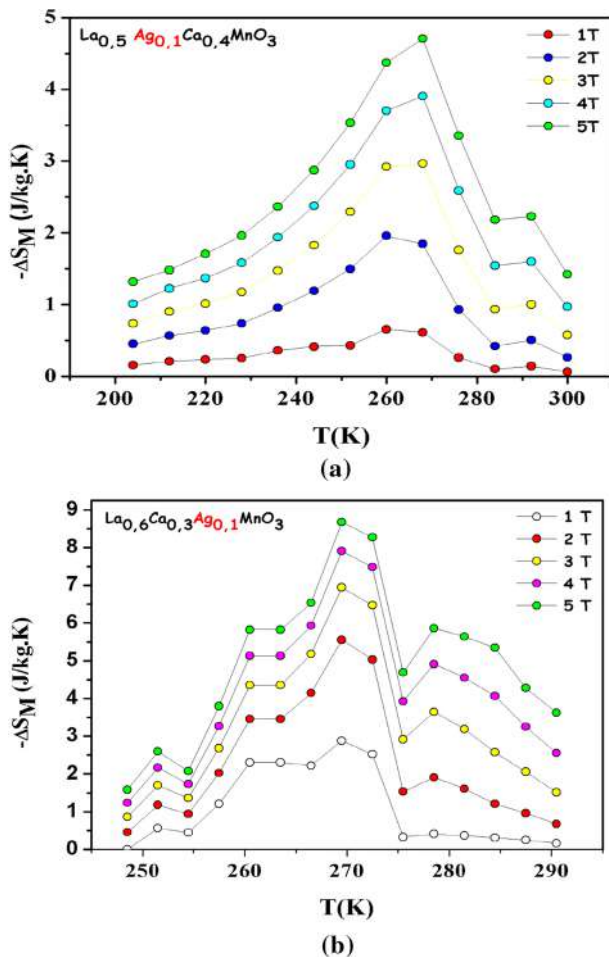
Fig. 5 Arrott plots of the **a** $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and **b** $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ samples at various temperatures



magnetic entropy changes $|\Delta S_M^{Max}|$ rises owing to the amplification of ferromagnetic interactions.

Magnetic transitions may be observed using curves plotting the change of magnetic entropy with temperature. An extremum of magnetic entropy variation can be observed around a magnetic transition following a change in the magnetic order within the material. The $-\Delta S_{Max}(T)$ curves show an increasing trend for temperatures below the Curie temperature, then reach maximum values for $T = T_c$. On the other hand, the maximum of the magnetic entropy increases with the applied magnetic field. We note $(-\Delta S_{Max})$ that presents a maximum in the vicinity of T_c for the two compounds and that $(-\Delta S_{Max})$ is greater at the level of compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$. Under the influence of a 2 T magnetic field in the vicinity of T_c , ΔS_M^{Max} reaches values of the order of 2.02 J/kg K for the compound $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ whereas that in the case of compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ is of the order of 5.55 J/kg K. This magnetic entropy maximum $(-\Delta S_{Max})$ is a critical requirement

Fig. 6 Magnetic entropy change, (ΔS_M) versus temperature for the composite system. **a** $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and **b** $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$



for categorizing a material as a suitable candidate for magnetic refrigeration, giving it the benefit of being a good candidate for magnetic refrigeration near ambient temperature.

The entropy variation between the two compounds can be interpreted by the nature of the ferromagnetic–paramagnetic transition which is much slower than that observed in the case of the compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$.

The relative cooling power, or *RCP* (Relative Cooling Power), which is defined as the product of the ΔS_M^{max} and the width at mid-height (δT_{FWHM}) of the curve $\Delta S_M(T, H)$, has been shown to be a helpful measure for assessing a material's suitability for magnetic refrigeration. The following relationship defines this metric, which represents the amount of heat that may be transported between a refrigerator's hot and cold sources (Assoudi et al. 2018b; Wang and Appl 2000; Rostamnejadi et al. 2011).

$$RCP = |-(\Delta S_M^{\text{max}})| * \delta T_{FWHM} \quad (4)$$

where δT_{FWHM} the full width at half maximum.

Fig. 7 The magnetic fields $H(T)$ dependence of the RCP for the composite system

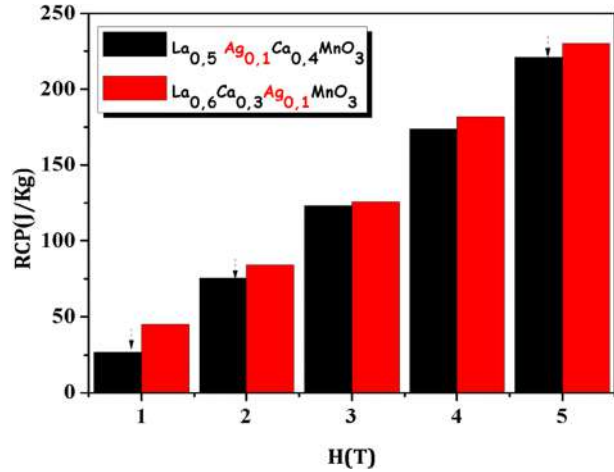


Table 1 Magnetocaloric results for our compounds compared to other materials

Materials	T_c (K)	$\mu_0 H$ (T)	RCP (J Kg ⁻¹)	References
$\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$	269	5	220,88	Gharbi et al. (2021)
$\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$	270	5	230,35	Our work
$\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$	261	5	220,94	Our work
$\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{Mn}_{0.9}\text{Cr}_{0.1}\text{O}_3$	255	5	240	Ezaami et al. (2017)
$\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$	255	5	400,01	Walha et al. (2018)
$\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$	257	5	183,16	Walha et al. (2009)

Figure 7 illustrates the variance in RCP values for all samples when subjected to magnetic fields ranging from 1 to 5 T. The values of $\mu_0 H$, RCP , and the Curie temperature T_c for the various samples obtained in the presence of a 5 T magnetic field are listed in Table 1.

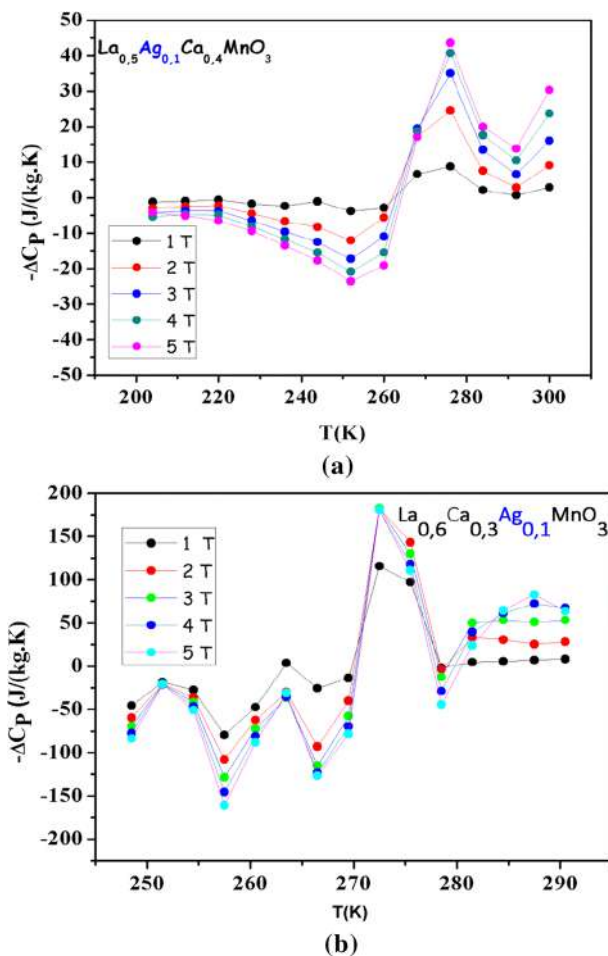
We note that the RCP values of the compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ are greater than those of the compound $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ which suggests its good candidacy in the field of magnetic cold. All the samples show an interesting factor of the RCP around the Curie transition temperature T_c . Other substances have also been reported to have this magnetocaloric action (Felhi et al. 2018; Walha et al. 2009).

The change in specific heat or heat capacity ΔC_p (heat capacity changes) was then computed for the two compounds from the entropy using the following formula.

$$\Delta C_p = -T \frac{\partial \Delta S_M}{\partial T} \quad (5)$$

The fluctuation in specific heat as a function of temperature is shown in Fig. 8 for various levels of the applied magnetic field, ranging from 1 to 5 T. It is plain to observe that as the temperature is reduced, the value of ΔC_p quickly shifts from positive to negative (Gschneidner et al. 2005a). $\Delta C_p^{\text{min/max}}$ values grow as $\mu_0 H$ increases (Dhahri et al. 2015).

Fig. 8 Heat Capacity Changes (ΔC_p) vs. temperature for **a** $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and **b** $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ samples



By altering the magnetic field $\mu_0 H$ as a function of the magnetization, the temperature dependence of the Landau coefficients $A(T)$, $B(T)$, and $C(T)$ is derived (Gschneidner et al. 2005b; Regmi et al. 2009).

$$\mu_0 H = A(T)M + B(T)M^3 + C(T)M^5 \quad (6)$$

where A , B and C are temperature-dependent expansion coefficients or the Landau coefficients. The results of this adjustment are shown in Fig. 9 for the two compounds $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$. As predicted, A is positive near T_c (Curie temperature) and the value of B is positive at T_c , confirming the transition's second order nature.

By differentiating the magnetic component of the free energy with respect to temperature, one may derive the appropriate magnetic entropy (Pankratov et al. 2019)

$$S(T, H) = \frac{1}{2}A'(T)M^2 + \frac{1}{4}B'(T)M^4 + \frac{1}{6}C'(T)M^6 \quad (7)$$

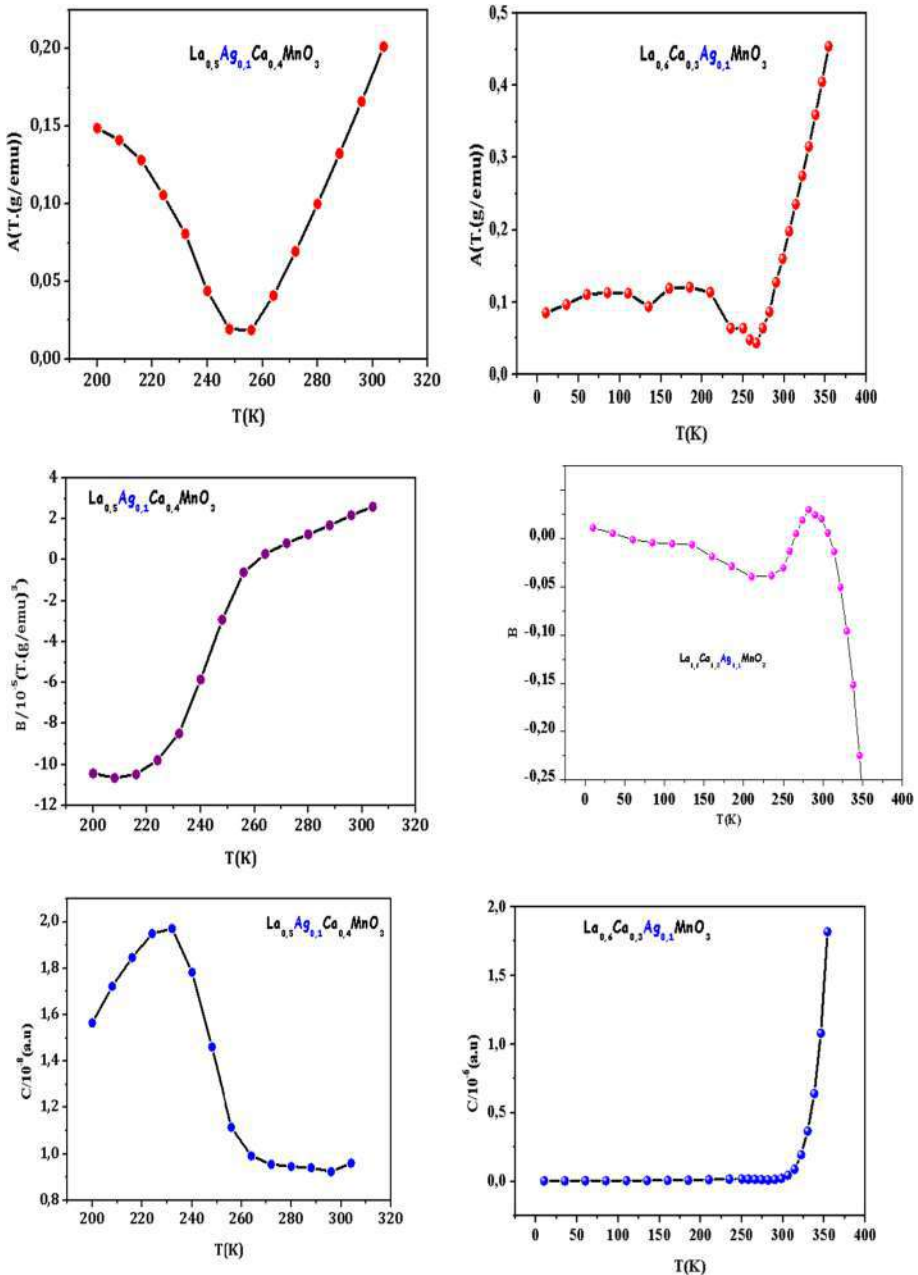


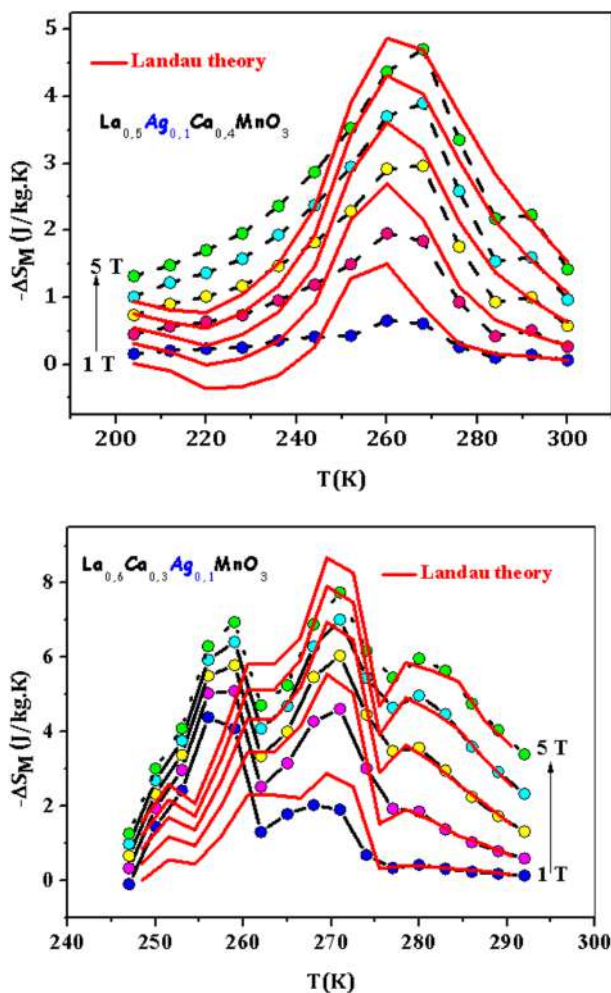
Fig. 9 Variations of landau coefficients $A(T)$, $B(T)$, and $C(T)$ as a function of temperature

where $A'(T)$, $B'(T)$ and $C'(T)$ are the temperature derivatives of the expansion coefficients $A(T)$, $B(T)$ and $C(T)$, respectively, which have been derived from fitting $M(H)$ isotherms. The following equation describes the variation of the magnetic entropy $\Delta S_M(T)$ (Amaral et al. 2007; Mⁿassri et al. 2016)

$$\Delta S(T, H) = -\frac{1}{2} \frac{\partial A}{\partial T} (M_0^2 - M^2) - \frac{1}{4} \frac{\partial B}{\partial T} (M_0^4 - M^4) - \frac{1}{6} \frac{\partial C}{\partial T} (M_0^6 - M^6) \quad (8)$$

with M_0 being the value of the magnetization measured in the absence of a magnetic field. The findings indicate that our materials display a magnetic transition of second order. Figure 10 illustrates the theoretical findings and actual data for various applied magnetic fields. The research indicates unequivocally that magnetoelastic coupling and electron interaction both contribute significantly to magnetic entropy and its temperature dependence for both samples. Additionally, the experimentally determined value of S_M is less than the theoretically estimated value, indicating that the transition is an unusual one even when a 5 T magnetic field is supplied. Chandra et al. (2012) recently investigated the magnetic and magnetocaloric characteristics of $\text{LaMnO}_{3.6}$ and discovered that the observed ΔS_M is less than the predicted one. This model does not account for the Jahn–Teller distortion, and the exchange interactions accurately predict the observed change in magnetic entropy as a

Fig. 10 The theoretical findings and actual data for various applied magnetic fields



function of temperature. It is thus necessary to include these interactions into the magnetocaloric effect estimated using the indirect technique in order to modify this model.

3 Conclusion

In this paper, we studied the physical properties of $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ compounds. Structural analysis by XRD showed that both samples crystallize in an orthorhombic structure. The magnetic measurements show that the two compounds have a single transition from the PM state to the FM state with an increase in the Curie transition temperature T_c for the compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$. Similarly, the substitution of silver in calcium increases the value of the magnetization at low temperature.

We also studied the magnetocaloric effect of our compounds. This study shows a significant change in magnetic entropy ΔS_M that took place around their magnetic transition temperatures T_c . The magnetocaloric results indicate that the compound $\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$ is the best sample which has a large RCP which suggests its good candidate in the field of magnetic cold. based on the Banarjee criterion and Landau theory, a second-order transition is observed for both samples in the vicinity of the Curie transition T_c . The experimentally obtained value of ΔS_M is smaller than the theoretically calculated one, which proves that the transition is an unconventional transition even under the influence of a 5 T magnetic field.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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