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

N. Assoudi$^1$ · A. Chaabani$^2$ · Mohammed Rasheed$^3$ · I. Walha$^1$ · E. Dhahri$^1$ · Taif Alawsi$^4$ · Dikra Bouras$^5$ · R. Barille$^6$

Received: 25 March 2022 / Accepted: 6 May 2022 / Published online: 26 July 2022
© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

Abstract
In this paper, the physical characteristics of La$_{0.5}$Ag$_{0.1}$Ca$_{0.4}$MnO$_3$ and La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$MnO$_3$ compounds have been studied. Structural analysis by XRD showed that both samples crystallize in an orthorhombic structure. For the La$_{0.5}$Ag$_{0.1}$Ca$_{0.4}$MnO$_3$ sample it can be seen that there are two bands: the first is due to the stretching Mn–O bond the $v_s$ vibration mode, relates to the internal motion of a length-changing Mn–O, whereas the second corresponds to the $v_b$ bonding mode, which is sensitive to a change in the Mn–O–Mn angle. For the compound La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$MnO$_3$ the $v_b$ 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 La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$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 $\Delta S_M$ 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 La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$MnO$_3$ this value is considered significant. The magnetocaloric results indicate that the compound La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$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 $\Delta S_M$ 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 La$_{0.5}$Ag$_{0.1}$Ca$_{0.4}$MnO$_3$ and La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$MnO$_3$ compounds · Curie transition · Magnetic entropy · Landau theory · Banarjee criterion

✉ N. Assoudi
mediaassoudi@gmail.com
✉ Mohammed Rasheed
rasheed.mohammed40@yahoo.com

Extended author information available on the last page of the article
1 Introduction

Manganites of structure $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (with $\text{Ln}$: rare earths and $\text{A}$: 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 $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ ions, the average ionic radius of site A, and the magnetic and orbital disorder (Dkhilalli 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 by a divalent or monovalent element leads to oxidation of the $\text{Mn}^{3+}$ ions ([Ar] 3d$^4$) into $\text{Mn}^{4+}$ ions ([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, xxxx; 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 $v_s$, including the internal movement d caused by a change in Mn–O bond length, and the second at 420 cm$^{-1}$ corresponds to the $v_b$ 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 $v_s$.

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 $v_s$ vibration consists of the movement of Mn ion and oxygen by changing the length of the Mn–O bond while the $v_b$ binding vibration occurs when there is a change in the O$_1$–Mn–O$_2$ 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...
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 \( \text{P}_{\text{nma}} \) orthorhombic structure. It has a Curie temperature of 269 K.

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 \( \text{Mn}^{3+}/\text{Mn}^{4+} \) 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 \( \text{Mn}^{4+} \). This ferromagnetism is optimum for \( \frac{2}{3} \text{Mn}^{3+} \) and \( \frac{1}{3} \text{Mn}^{4+} \) 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 \( \text{Mn}^{3+}/\text{Mn}^{4+} = 1 \) according to the neutrality equation \( \text{Mn}^{3+}_03\text{Mn}^{4+}_05 \) and consequently 50% of \( \text{Mn}^{4+} \) while the compound \( \text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3 \) has a \( \text{Mn}^{4+} \) level of 60% according to the neutrality equation \( \text{Mn}^{3+}_04\text{Mn}^{4+}_06 \) (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,
showing a ferromagnetic behavior at $T < 261$ K for the compound La$_{0.5}$Ag$_{0.1}$Ca$_{0.4}$MnO$_3$, and $T < 270$ K for that of the compound La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$MnO$_3$.

At the Curie temperature $T_c$, the spontaneous magnetization vanishes, and the saturation magnetization increases when the temperature decreases for the compounds La$_{0.5}$Ag$_{0.1}$Ca$_{0.4}$MnO$_3$ and La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$MnO$_3$, thus confirming their ferromagnetic nature at low temperature. The values of the spontaneous magnetization $M_{sp}$ were extrapolated up to $H = 0$ T using the $M(H)$ isotherms. At temperature 10K, the saturation magnetization ($M_s$) of La$_{0.5}$Ag$_{0.1}$Ca$_{0.4}$MnO$_3$ is 94.19 emu/g and 92.8 emu/g for La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$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 270K and 261K respectively for La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$MnO$_3$ and La$_{0.5}$Ag$_{0.1}$Ca$_{0.4}$MnO$_3$.

The magnetic entropy $\Delta S_M$, which is proportional to the magnetic degrees of freedom, fluctuates according to the applied magnetic field and the sample’s magnetic order. The
Comparative examination of the physical parameters of the sol...

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

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

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

where $\partial S$ the entropy derivative, $\partial H$ the magnetic field derivative $\partial M$ the magnetization derivative, $\partial T$ temperature derivative, and $\Delta S$ 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):

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

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

$$\Delta S_M(T, \Delta \mu_0 H_j) = \sum_{j} \frac{M_{i+1}(T_{i+1}, \mu_0 H_j) - M_i(T_i, \mu_0 H_j)}{T_{i+1} - T_i} \Delta \mu_0 H_j$$ \hspace{1cm} (3)

where $\mu_0$ 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 $\Delta S_M$ (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
magnetic entropy changes $|\Delta S_{M}^{\text{Max}}|$ 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 $-\Delta S_{\text{Max}}(T)$ 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 $(-\Delta S_{\text{Max}})$ that presents a maximum in the vicinity of $T_c$ for the two compounds and that $(-\Delta S_{\text{Max}})$ is greater at the level of compound $\text{La}_{0.5}\text{Ag}_{0.1}\text{Ca}_{0.4}\text{MnO}_3$. Under the influence of a 2 T magnetic field in the vicinity of $T_c$, $\Delta S_M^{\text{Max}}$ 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 $(-\Delta S_{\text{Max}})$ is a critical requirement.
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 $\Delta S_{\text{max}}^M$ and the width at mid-height ($\delta T_{\text{FWHM}}$) 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; Rostamejjadi et al. 2011).

$$RCP = \left| -\Delta S_{\text{max}}^M \right| \times \delta T_{\text{FWHM}}$$  \hspace{1cm} (4)

where $\delta T_{\text{FWHM}}$ the full width at half maximum.
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 $La_{0.6}Ca_{0.3}Ag_{0.1}MnO_3$ are greater than those of the compound $La_{0.5}Ag_{0.1}Ca_{0.4}MnO_3$ 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 $\Delta C_P$ (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 $\Delta C_P$ quickly shifts from positive to negative (Gschneidner et al. 2005a). $\Delta C_P^{\text{min/\text{max}}}$ values grow as $\mu_0 H$ increases (Dhahri et al. 2015).
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).

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

(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 La$_{0.5}$Ag$_{0.1}$Ca$_{0.4}$MnO$_3$ and La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$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)

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

(7)
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; M'nassri et al. 2016)
\[ \Delta S(T, H) = -\frac{1}{2} \frac{\partial A}{\partial T} (M_0^2 - M^2) - \frac{1}{4} \frac{\partial B}{\partial T} (M_0^4 - M^4) - \frac{1}{6} \frac{\partial C}{\partial T} (M_0^6 - M^6) \]  

(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 \( \text{LaMnO}_3-\delta \) and discovered that the observed \( \Delta S_M \) 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 La$_{0.5}$Ag$_{0.1}$Ca$_{0.4}$MnO$_3$ and La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$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 La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$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 $\Delta S_M$ that took place around their magnetic transition temperatures $T_c$. The magnetocaloric results indicate that the compound La$_{0.6}$Ca$_{0.3}$Ag$_{0.1}$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 criterin 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 $\Delta S_M$ 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.

Funding The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Declarations

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

References

Amaral, J.S., Silva, N.J.O., Amaral, V.S.: A mean-field scaling method for first-and second-order phase transition ferromagnets and its application in magnetocaloric studies. Appl. Phys. Lett. 91(17), 172503 (2007)

Arulraj, A., Rao, C.N.R.: An infrared spectroscopic study of the insulator-metal transition and charge-ordering in rare earth manganates, (Ln$_{1-x}$A$_x$MnO$_3$, Ln=Rare Earth, A=Ca, Sr Pb. J. Solid State Chem. 145(2), 557–563 (1999)

Assoudi, N., Walha, I., Dhahri, E., Alleg, S., Hlil, E.K.: Structural, magnetic and on magnetocaloric properties near the paramagnetic to ferromagnetic phase transition in La$_{0.5}$□$_{0.1}$Ca$_{0.4}$MnO$_3$ oxide. Solid State Commun. 277, 13–18 (2018a)

Assoudi, N., Smari, M., Walha, I., Dhahri, E., Shevyrtalov, S., Dikaya, O., Rodionova, V.: Unconventional critical behavior near the phase transition temperature and magnetocaloric effect in La$_{0.5}$Ca$_{0.1}$Ag$_{0.5}$MnO$_3$ compound. Chem. Phys. Lett. 706, 182–188 (2018b)

Baaziz, H., Tozri, A., Dhahri, E., Hlil, E.K.: Effect of particle size reduction on the magnetic phase transition and the magnetocaloric properties in ferromagnetic insulator La$_{0.9}$Sr$_{0.1}$MnO$_3$ nanoparticles. Chem. Phys. Lett. 625, 168–173 (2015)
Chandra, S., Biswas, A., Datta, S., Ghosh, B., Siruguri, V., Raychaudhuri, A.K., Phan, M.H., Srikanth, H.: Evidence of a canted magnetic state in self-doped LaMnO$_3$+$\delta$(0.04): a magnetocaloric study. J. Phys. Condens. Matter 24(36), 366004 (2012)

Dhahri, A., Jemmali, M., Taibi, K., Dhahri, E., Hlil, E.K.: Structural, magnetic and magnetocaloric properties of La$_{0.9}$Ca$_{0.1}$Sr$_{0.1}$Mn$_{1-x}$Cr$_x$O$_3$ compounds with $x = 0.005$ and 0.1. J. Alloys Compd. 618(2015), 488–496 (2015)

Dkhilalli, F., Megdiche, S., Guidara, K., Rasheed, M., Barillé, R., Megdiche, M.: AC conductivity evolution in bulk and grain boundary response of sodium tungstate Na$_2$WO$_4$. Ionics 24(1), 169–180 (2018a)

Dkhilalli, F., Megdiche Borchani, S., Rasheed, M., Barillé, R., Guidara, K., Megdiche, M.: Structural, dielectric, and optical properties of the zinc tungstate ZnWO$_4$ compound. J. Mater. Sci. Mater. Electron. 29(8), 6297–6307 (2018b)

Ezaami, A., Sellami-Jmal, E., Cheikhrouhou-Koubaa, W., Cheikhrouhou, A.: Enhanced magnetocaloric properties with a tunable Curie temperature in (1–$x$)La$_{0.55}$Sr$_{0.1}$Ca$_{0.35}$MnO$_3$/$x$La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$ system (0≤ $x$≤ 1). J. Mater. Sci.: Mater. Electron. 28(22), 16741–16746 (2017)

Felhi, H., Smari, M., Walha, I., Dhahri, E., Valente, M.A., Bessais, L.: Influence of insoublility of silver on the Hirshfeld surface analyses and magnetic behavior of La$_{0.75}$Ca$_{0.15}$Ag$_{0.4}$MnO$_3$ compound. Chem. Phys. Lett. 691, 262–270 (2018)

Goldschmidt, V.M., Geochemische verteilungsgesetze der element, VII, VIII (1927) 1928.

Gschneidner, Karl A., V. K. Pecharsky, and A. O. Tsokol. "Recent developments in magnetocaloric materials" Reports on progress in physics 68, no. 6 (2005a): 1479.

Gschneidner, Karl A., Pecharsky, V.K., Tsokol, A.O.: Recent developments in magnetocaloric materials. Rep. Prog. Phys. 68(6), 1479–1539 (2005b)

Hamdi, R., Tozri, A., Smari, M., Dhahri, E., Bessais, L.: Structural, magnetic, magnetocaloric and electrical studies of Dy$_{0.5}$Sr$_{0.5}$Ca$_{0.1}$MnO$_3$ manganites. J. Magn. Magn. Mater. 444, 270–279 (2017a)

Hamdi, R., Tozri, A., Smari, M., Dhahri, E., Bessais, L.: Resistivity, I-V characteristics and hall effect in Dy$_{0.3}$Sr$_{0.7}$Ca$_{0.1}$Mn$_{0.5}$O$_3$ manganites. Mater. Res. Bull. 95, 525–531 (2017b)

Itoh, M., Natori, I., Kubota, S., Motoya, K.: Hole-doping effect on magnetic properties of La$_{1-x}$Sr$_x$CoO$_3$ (0.0≤5≤0.5). J. Magn. Magn. Mater. 140, 1811–1812 (1995)

Mnasri, R., Chniha Boudjada, N., Cheikhrouhou, A.: Nearly constant magnetic entropy change involving the enhancement of refrigerant capacity in (La$_{0.9}$Ba$_{0.1}$Sr$_{0.1}$MnO$_3$)$_{1-x}$/(Co$_2$O$_3$)$_x$ composite. Ceram. Int. 42(6), 7474–7485 (2016)

Pankratov, N.Y., Mitsiuk, V.I., Ryzhkovskii, V.M., Nikitin, S.A.: Direct measurement of the magnetocaloric effect in MnZnSb intermetallic compound. J. Magn. Magn. Mater. 476, 46–49 (2019)

Regmi, R., Tackett, R., Lawes, G.: Suppression of low-temperature magnetic states in Mn$_3$O$_4$ nanoparticles. J. Magn. Magn. Mater. 321(15), 2296–2299 (2009)

Rietveld, H.M.: Line profiles of neutron powder-diffraction peaks for structure refinement. Acta Crystallogr. A 22(1), 151–152 (1967)

Rodriguez-Carvajal, J.: FULLPROF: a program for rietveld refinement and profile matching analysis of complex powder diffraction patterns (ILL, unpublished).

Romero-Muñiz, C., Franco, V., Conde, A.: Influence of magnetic interactions between phases on the magnetocaloric effect of composites. Appl. Phys. Lett. 102(8), 082402 (2013)

Rostamnejadi, A., Venkatesan, M., Kameli, P., Salamati, H., Coey, J.M.D.: Magnetocaloric effect in La$_{0.67}$Sr$_{0.33}$MnO$_3$ manganese above room temperature. J. Magn. Magn. Mater. 323(16), 2214–2218 (2011)

Shannon, R.D.: Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. Sect. Cryst. Phys. Diffr. Theor. Gen. Crystallogr. 32(5), 751–767 (1976)
Shelke, A.R., Deshpande, N.G.: Effect of the cation substitution on the structural, electrical and magnetic properties in the electron-doped manganese. Ferroelectrics 516(1), 98–105 (2017)

Shivakumara, C., Bellakki, M.B.: Synthesis, structural and ferromagnetic properties of La$_{1-x}$K$_x$MnO$_3$ (0.0 ≤ x ≤ 0.25) phases by solution combustion method. Bull. Mater. Sci. 32(4), 443–449 (2009)

Tili, R., Hammouda, R., Bejar, M., Dhahri, E.: Theoretical investigation of the magnetocaloric effect on La$_{0.7}$(Ba, Sr)$_{0.3}$Mn$_{0.9}$Ga$_{0.1}$O$_3$ compound at room temperature. J. Magn. Magn. Mater. 386, 81–84 (2015)

Walha, I., Dhahri, E.: Magnetic and electrical properties induced by the substitution of divalent by monovalent in the La$_{0.5}$Ca$_{0.5}$MnO$_3$ compound. J. Supercond. Novel Magn. 29(12), 3001–3007 (2016)

Walha, I., Ehrenberg, H., Fues, H., Cheikhrouhou, A.: Structural and magnetic properties of La$_{0.6}$Ca$_{0.4}$Mn$_x$O$_3$ (0 ≤ x ≤ 0.2) perovskite manganite. J. Alloys Compd. 485(1–2), 64–68 (2009)

Walha, I., Dhahri, E., Hilil, E.K.: Magnetocaloric effect and its correlation with critical behavior in La$_{0.5}$Ca$_{0.5}$Te$_{0.1}$MnO$_3$ manganese oxide. J. Alloys Compd. 680, 169–176 (2016)

Walha, I., Smari, M., Mnasri, T., Dhahri, E.: Structural, magnetic, and magnetocaloric properties of Ag-doped in the La$_{0.5}$Ca$_{0.5}$MnO$_3$ compound. J. Magn. Magn. Mater. 454, 190–198 (2015)

Walha, I., Boujelben, W., Koubaa, M., Cheikh-Rouhou, A., Haghiri-Gosnet, A.M.: Deficiency effects on the physical properties of the lacunar La$_{0.5}$Ca$_{0.5-x}$MnO$_3$ manganese oxides. Phys. Status Solidi (a) 201(7), 1416–1420 (2004)

Wang, Z.: Appl. Phys. Lett. (2000) 77:928

Ying, Y., Eom, T.W., Dai, N.V., Lee, Y.P.: Magnetic properties and Griffiths singularity in La$_{0.45}$Sr$_{0.55}$Mn$_{1−x}$Co$_x$O$_3$. J. Magn. Magn. Mater. 323(1), 94–100 (2011)

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

Authors and Affiliations

N. Assoudi$^1$ · A. Chabani$^2$ · Mohammed Rasheed$^3$© · I. Walha$^1$ · E. Dhahri$^1$ · Taif Alawsi$^4$ · Dikra Bouras$^5$ · R. Barille$^6$

$^1$ Applied Physics Laboratory, Sfax Faculty of Sciences, University of Sfax, B.P. 802, 3018 Sfax, Tunisia

$^2$ University of Kairouan, 3100 Kairouan, Tunisia

$^3$ Applied Sciences Department, University of Technology, Baghdad, Iraq

$^4$ Technical Engineering College, Al-Ayen University, Thi-Qar, Iraq

$^5$ Laboratory of Active Components and Materials (LCAM), University of Larbi Ben M’hidi, 04000 Oum El Bouaghi, Algeria

$^6$ MOLTECH-Anjou, Université d’Angers/UMR CNRS 6200, 2 Bd Lavoisier, 49045 Angers, France