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La_{0.6}Ca_{0.2}Na_{0.2}MnO₃ perovskite: Structural, magnetic, critical and magnetocaloric properties

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Abstract

The results of structural, magnetic, critical and magnetocaloric characterizations of La_{0.6}Ca_{0.2}Na_{0.2}MnO₃ perovskite have been reported. XRD analysis of the sample synthesized using sol-gel method shows good crystallization in the $R\bar{3}c$ rhombohedral structure. From $M(T)$ curve, a second order ferromagnetic–paramagnetic (FM–PM) phase transition appears at the Curie temperature (T_C) around 275 K. Critical exponents (β , γ and δ) have been evaluated using different techniques such as Modified Arrott plots (MAP), Kouvel-Fisher (KF) method and critical isotherm (CI). We found that the critical exponents of the prepared sample agree well with those of the mean-field model. We have also estimated the magnetic entropy change ($-\Delta S_M$) and relative cooling power (RCP) for the sample which obey power laws as $-\Delta S_M = a(\mu_0 H)^n$ and $RCP = A(\mu_0 H)^N$, respectively. ΔS_M and RCP values were relatively higher, making the sample promising candidate for magnetic refrigeration technology. The estimated values of the magnetic-ordering parameters (n and N) are used to confirm the reliability of the evaluated critical exponent.

Keywords: Perovskites; Structural analysis; Magnetic properties; Critical behavior; Magnetocaloric effect.

1. Introduction

Cooling technologies are becoming more important. They are presented everywhere in refrigerators used in all homes up to the largest research laboratories in physics. More recently, the rapid deterioration of the ozone layer, caused in part by CFC (chlorofluorocarbon) and HCFC (hydrochlorofluorocarbons) gases used in conventional cooling systems based on gas compression and expansion cycles, as well as global warming, is driving researchers to develop more environmentally friendly cooling systems applicable to all temperature ranges, especially around the room temperature. Magnetic cooling, based on the magnetocaloric effect (MCE) materials, is a very good candidate [1, 2]. It has several advantages. The reversibility of the magnetocaloric effect during the magnetization and demagnetization cycles ensures high efficiency. In addition, it would eliminate environmentally harmful gases. Finally, the possibility of manufacturing compact cooling systems and the wide temperature range of use allows a multitude of applications thanks to magnetic refrigeration.

Since, significant and multiple advances have been made at the fundamental and applicative scale in the field of the magnetocaloric systems. Among the most commonly cited materials we found the families of Gd and Gd-Si-Ge [3, 4], $\text{LaFe}_{13-x}\text{Si}_x$ [5], $\text{MnFeP}_{1-x}\text{As}_x$ [6], and Ni-Mn-Ga [7]. The perovskite manganites represent another family which has been widely studied in the magnetic refrigeration area due to their remarkable MCE (see [1, 2] for review and references therein).

Our goal in this work is a part of this context. We have identified perovskite manganite having $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ composition. The reason for selecting such composition is essentially due to the magnetic properties of the undoped compound $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$. Indeed, the researches in the magnetic cooling field have been focusing on the search for perovskite materials that displaying larger MCE at Curie temperature (T_C)

close to room temperature. The $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ compound is one of the extensively studied manganites in the literature. This compound has a Curie temperature (T_C) relatively lower than room temperature [8-11]. On the other hand, the works made on the $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$ system reflect that the addition of Na instead La leads to the increase of its Curie temperature (see [2] for a review). Therefore, the Curie temperature for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ compound can be approached to room temperature by partial replacement of La^{3+} by Na^+ . To verify these observations, we have added in this work an amount of 20 atom % of Na instead La in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ sample. The resulting $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ compound was prepared using sol-gel method and characterized using XRD technique in order to verify its purity. The MCE of the sample was also studied by presenting its magnetic, critical and magnetocaloric properties.

2. Experimental

To prepare $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite, we have used the sol-gel method. This method is based on the use of citric acid as a complexing agent and ethylene glycol as polymerization agent. We have used stoichiometric proportions of $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, $[\text{Ca}(\text{NO}_3)_2]$, $[\text{NaNO}_3]$, and $[\text{Mn}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}]$ nitrates which were dissolved in distilled water, and the solution was subjected to thermal stirring at 90 °C. Thereafter, we have carefully added the ammonia in order to adjust the pH of the solution to about 7. After a certain time (~ 4 h), a viscous liquid (gel) is formed. This gel has been dried at 200 °C (for 6 h) in an oven in order to remove the residual solvent. The obtained precursor is then finely ground and the resulting powder undergoes to some cycles of grinding, pelleting and sintering. Finally, the structure of $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite was well formed at 1100 °C (for 24 h).

X-ray diffraction (XRD) pattern has been registered using "Panalytical X'Pert Pro System" two-circle automatic diffractometer operating at copper wavelength ($\lambda=1.5406 \text{ \AA}$)

with a filter of Nickel to eliminate the K_β ray. The measurement was made with 0.017° step and 18s counting time per step in angular range of $10 \leq 2\theta \leq 100^\circ$. Rietveld method using FullProf software was used for structural parameters estimation [12]. Magnetization measurements were performed using BS1 and BS2 linear extraction magnetometers. Two types of magnetic measurements were made: $M(T)$ curve under a weak magnetic field ($\mu_0 H = 0.05$ T) in the temperature range of $200 \text{ K} \leq T \leq 340 \text{ K}$; and to access the critical behavior and the variation of magnetic entropy change for the sample, the $M(\mu_0 H, T)$ isothermal magnetizations were taken as a function of temperature near T_C in $0 \leq T \leq \mu_0 H \leq 5 \text{ T}$ magnetic field interval.

3. Results and discussions

The obtained XRD diffractogram for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite is shown in **Fig. 1**. The compound is good crystallized and the majority phase is a perovskite whose diffraction peaks are indexed in $R\bar{3}c$ rhombohedral symmetry. The structural refinement for the sample is shown in the inset of **Fig. 1**, and the refined structural parameters are listed in **Table 1**. In particular, the calculated lattice constants are $a = 5.4859$ (1) Å and $c = 13.3963$ (2) Å with a cell volume of $V = 349.15$ (1) Å³. These values are smaller compared to those found for the undoped compound $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ [8]. Obviously the Na-substitution of La causes the decrease of lattice parameters in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ sample, in agreement with the results found for $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$ [13, 14]. The average crystallite size for the sample is estimated using Scherer formula as [15]:

$$D = \frac{0.9 \lambda}{\beta \cos(\theta)} \quad (1)$$

where λ is the employed X-ray wavelength, θ is the diffraction angle for the most intense peak, and $\beta = \sqrt{\beta_x^2 - \beta_{inst}^2}$ its FWHM (full width at half maximum) with β_x is the

experimental FWHM, and β_{inst} is the FWHM of a standard silicon sample. The obtained D value is about 48 nm.

Fig. 2a shows the $M(T)$ curve under magnetic field of $\mu_0 H = 0.05$ T for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite. The $M(T)$ measurement shows a FM–PM phase transition towards the T_C which is identified as the minimum of dM/dT curve (inset of **Fig. 2a**). The FM–PM phase transition occurs at $T_C = 275$ K. This value is significantly higher than the different T_C values reported for the pristine sample $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ in the literature ($T_C = 221$ K [8], 183 K [9], 180.11 K [10] and 210 K [11]). This reflects that the addition of Na instead La in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ compound leads to the increase of its Curie temperature. This correlate well with the results found for other Na–doped La perovskite systems (see [2] for a review). The inverse of magnetic susceptibility in the PM region (at $T > T_C$) is calculated as $\chi^{-1}(T) = \mu_0 H / M(T)$ and presented as a function of temperature in **Fig. 2b**. We can clearly see that the linear variation of $\chi^{-1}(T)$ obeyed the Curie Weiss (CW) law as [16]:

$$\frac{1}{\chi(T)} = \frac{T - \Theta}{C} \quad (2)$$

where C is the Curie constant and Θ is the CW temperature. Eq. (2) is used to fit the $\chi^{-1}(T)$ curve at $T > T_C$, and C and Θ values are obtained. The obtained value of $\Theta = 283$ K has a positive sign which is demonstrating dominant FM interactions between spins for the sample. Based on the obtained C value, we have determined the experimental effective paramagnetic moment μ_{eff}^{exp} of the sample as follows:

$$\mu_{eff}^{exp} = \sqrt{\frac{3 \times k_B \times C \times M_m}{N \times \mu_B^2}} \quad (3)$$

with k_B is the Boltzmann constant, M_m is the molecular mass per unit formula, N is the Avogadro number, and μ_B represents the Bohr magneton. According to Eq. (3), we found μ_{eff}^{exp} as $5.85 \mu_B$. This value can be compared with the calculated effective paramagnetic moment (μ_{eff}^{cal}) as:

$$\mu_{eff}^{cal}(\mu_B) = \sqrt{0.4 \times [\mu_{eff}^{th}(Mn^{3+})]^2 + 0.6 \times [\mu_{eff}^{th}(Mn^{4+})]^2} \quad (4)$$

where, $\mu_{eff}^{th}(Mn^{3+}) \sim 4.90 \mu_B$ and $\mu_{eff}^{th}(Mn^{4+}) \sim 3.87 \mu_B$ are respectively the Mn^{3+} and Mn^{4+} effective magnetic moments. According to Eq. (4), we have calculated μ_{eff}^{cal} value as $4.31 \mu_B$. The μ_{eff}^{cal} value is significantly lower than the experimental one. It arises from the presence of short-range FM correlation in the PM state [16].

To understand the magnetic order in $La_{0.6}Ca_{0.2}Na_{0.2}MnO_3$ perovskite, the $M(\mu_0H, T)$ isothermal magnetizations were performed at temperatures around T_C and presented in **Fig. 3a**. With similar behavior to $M(T)$ curve, the $M(\mu_0H, T)$ isotherms gradually decrease with temperature. Also, in the low temperature range, the M values increase non-linearly at low magnetic fields with a tendency to saturation at high magnetic fields reflecting a ferromagnetic behavior, and then the M values vary linearly at high temperature sign of a paramagnetic behavior. In **Fig. 3b**, we have presented M^2 vs. μ_0H/M (called as the Arrott plots) [17] which show positive slopes. According to Banerjee's criterion [18], these positive slopes of M^2 vs. μ_0H/M suggest that $La_{0.6}Ca_{0.2}Na_{0.2}MnO_3$ perovskite has the character of a second-order phase transition.

In order to study the critical behavior for $La_{0.6}Ca_{0.2}Na_{0.2}MnO_3$ perovskite near its T_C temperature, we conducted an investigation of its critical exponents (β , γ and δ). Depending on the mean field theory [19], the Arrott curves (M^2 vs. μ_0H/M) as given in **Fig. 3b** would presented around T_C as straight lines, and the isotherm corresponding to T_C should pass through the origin. From **Fig. 3b**, these two conditions are met, indicating that the mean field model is the appropriate model to study the critical behavior of $La_{0.6}Ca_{0.2}Na_{0.2}MnO_3$ perovskite. From **Fig. 3b**, the linear extrapolation of the data by intersection with the $M^{1/\beta}$ axis determines the spontaneous magnetization M_s (below T_C) and the linear extrapolation by intersection with $(\mu_0H/M)^{1/\gamma}$ axis allows to determine the values of the inverse initial

susceptibility χ_0^{-1} (above T_C). Then, the data of $M_s(T)$ and $\chi_0^{-1}(T)$ were respectively adjusted in **Fig. 4a** using the two following equations [20].

$$M_s(T) = M_0(-\varepsilon)^\beta \quad (\text{with } \varepsilon < 0 \text{ and } T < T_C) \quad (5)$$

$$\chi_0^{-1}(T) = \left(\frac{h_0}{M_0}\right)\varepsilon^\gamma \quad (\text{with } \varepsilon > 0 \text{ and } T > T_C) \quad (6)$$

where M_0 , and h_0/M_0 designate the critical amplitudes, and $\varepsilon = (T - T_C)/T_C$ is the reduced temperature. The fitting results are shown in **Fig. 4a**, and the estimated values of β and γ agree well with those of the mean field model. Another estimation of the exponents' β and γ can be achieved more exactly using the Kouvel-Fisher (KF) method according the following equations [20]:

$$M_s(T) \left[\frac{dM_s(T)}{dT} \right]^{-1} = \frac{(T - T_C)}{\beta} \quad (7)$$

$$\chi_0^{-1}(T) \left[\frac{d\chi_0^{-1}(T)}{dT} \right]^{-1} = \frac{(T - T_C)}{\gamma} \quad (8)$$

Fig. 4b shows the $M_s(T) \left[\frac{dM_s(T)}{dT} \right]^{-1}$ vs. T and $\chi_0^{-1}(T) \left[\frac{d\chi_0^{-1}(T)}{dT} \right]^{-1}$ vs. T curves. The linear adjustments of these plots using Eqs. (7) and (8) allowed us to determine the β and γ values which are also very close to those of the mean field model. Concerning the third exponent (δ), it is possible to obtain it directly by adjusting the critical isotherm (CI), $M(T_C, \mu_0 H)$, according to this relation:

$$M = D(\mu_0 H)^{1/\delta} \quad (\text{with } \varepsilon = 0 \text{ and } T = T_C) \quad (9)$$

As illustrated in **Fig. 5**, we found $\delta = 3.030 \pm 0.014$. This value can be checked from the β and γ values previously determined according to Widom relation given as [21]:

$$\delta = 1 + \frac{\gamma}{\beta} \quad (10)$$

This equation gives $\delta = 3.104$ and 3.077 when the values of β and γ are taken respectively from **Fig. 4a** and **b**. These values correlate well with the δ value estimated from the CI. This

compatibility can be also supported by the state equation in the critical region given, according to Stanley's scaling hypothesis, as follows [20]:

$$M(H, \varepsilon) = |\varepsilon|^\beta f_\pm\left(\frac{\mu_0 H}{|\varepsilon|^{\beta+\gamma}}\right) \quad (11)$$

where f_+ and f_- are regular analytical functions defined at temperatures below and above T_C , respectively. By using the β and γ values obtained by KF method, we presented in **Fig. 6** the plots of $(M|\varepsilon|^{-\beta})$ vs. $(\mu_0 H|\varepsilon|^{-(\beta+\gamma)})$ which collapse into two separate branches near T_C . This is another argument which confirms the well estimation of the critical exponents of the present sample. In **Table 2**, we have compared the critical exponents of $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite (present work) with those of the theoretical models [20]. As shown in the table, the critical exponents are near the ones of the mean field model. In this case, the universality class of the magnetic phase transition for our sample which depends on the exchange interaction range can be checked by the equation of the exchange integral as follows [22]:

$$J(r) = 1/r^{d+\sigma} \quad (12)$$

where d designed the dimension of the system, and σ represents the range of interaction. It has been demonstrated that the 3D-Heisenberg exponents ($\beta = 0.365$, $\gamma = 1.336$, $\delta = 4.8$) are valid if $\sigma \geq 2$, the mean-field exponents ($\beta = 0.5$, $\gamma = 1$ and $\delta = 3$) occur if σ is less than $3/2$, however for the intermediate range $3/2 < \sigma < 2$, the exponents belong to different universality classes which depends upon σ . For our sample, the compatibility of β , γ and δ values with those of the mean field model indicates that the exchange integral for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite can be varies as $J(r) < r^{-5}$.

The isothermal variation of the magnetic entropy (ΔS_M) was calculated from the experimental isothermal magnetizations curve $M(H, \mu_0 H)$ by the application of the following Maxwell relation [2]:

$$\Delta S_M(T, \Delta \mu_0 H) = \int_0^{\mu_0 H} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (13)$$

where $\mu_0 H$ is the applied magnetic field. The results obtained for applied fields of 1 to 5 T are shown in **Fig. 7a** for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite. The magnetic entropy change reaches a maximum peak near the order temperature as $|\Delta S_M^{max}| = 3.09 \text{ J.kg}^{-1}.\text{K}^{-1}$ at $\Delta\mu_0 H = 5 \text{ T}$. This value is significantly high. As a result, the sample can be used in magnetic refrigeration technology. For comparison, the $|\Delta S_M^{max}|$ values of certain perovskites [23-31] are given in **Table 3**.

In other part, concerning the magnetic-field correlation of ΔS_M for samples having second-order PM-FM magnetic phase transitions, Oesterreicher and Parker [32] have dismantled that this correlation can be expressed as:

$$-\Delta S_M = a(\mu_0 H)^n \quad (14)$$

where a is a constant, and n is an exponent which depends on the magnetic state of the sample. For a ferromagnetic material, $n=2$ above its Curie temperature T_C , and $n=1$ below its T_C . According to the mean field approach, the $\Delta S_M(\mu_0 H)$ obeys a power function with $n=2/3$ at T_C . Moreover, the exponent n can be expressed at T_C versus the critical exponents (β , γ and δ) as [33]:

$$n(T_C) = 1 + \frac{\beta-1}{\beta+\gamma} \quad (15)$$

and

$$n(T_C) = 1 + \frac{1}{\delta} \left(1 - \frac{1}{\beta}\right) \quad (16)$$

By adjusting the $\Delta S_M(\mu_0 H, T_C)$ isothermal using Eq. (14) in **Fig. 7b**, the n value is estimated as $n=0.675 \pm 0.015$. The obtained n -value is close to the mean field prediction ($n=2/3$). On the other hand, taking into account the values of β and γ previously determined from KF method (**Fig. 4b** and **Table 2**), and the δ -value deduced from the CI (**Fig. 5** and **Table 2**), the n -values are found as 0.664 and 0.666 by using Eqs. (15) and (16), respectively. These values are very close to that obtained at T_C using Eq. (14). These results confirm the well estimation

of the critical exponents for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ sample. The relative cooling power (RCP) of a material is defined as the integrated area under the $\Delta S_M(T)$ curve with the temperatures corresponding to the half-height values of the magnetic entropy variation peak (δT) as bounds of integration. The RCP values at different applied fields are estimated according the following relation [2]:

$$RCP = |\Delta S_M^{max}| \times \delta T_{FWHM} \quad (17)$$

For $\Delta\mu_0 H = 5$ T, the RCP value is about 214 J kg^{-1} . This value is reported in **Table 3** besides those of some perovskite materials at the same magnetic applied field. It has been shown that the magnetic-field variation of the RCP can be expressed as the following power law [34]:

$$RCP = A(\mu_0 H)^N \quad (18)$$

where N is the critical exponent of the magnetic transition. The estimated N -value from the $RCP(\mu_0 H)$ for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ sample is found as $N = 1.335 \pm 0.004$ (see the fit in **Fig. 7b**). This value is higher than those previously found for other systems [34-36] and the one reported for Gd alloy ($N = 1.16$) [37]. According to V. Franco et al. [38]:

$$N = 1 + \frac{1}{\delta} \quad (19)$$

From Eq. (19) and using the estimated N -value, we calculated the value of δ exponent as $\delta = 2.985$. This value agrees well with those estimated from the CI $M(T_C, \mu_0 H)$ and Widom relation. This result confirms the well correlation between the critical behavior and MCE analyses performed for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite.

4. Conclusion

$\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite has been synthesized using sol-gel method. XRD measurement shows a perovskite phase whose diffraction peaks are well indexed in the $R\bar{3}c$ rhombohedral symmetry. The sample presents a second order FM-PM magnetic phase transition at Curie temperature equal to 275 K. The critical exponents study for the sample shows that the critical behaviour is described in the mean field model with an exchange integral varying as $J(r) < r^{-5}$. The estimated values of magnetic entropy and RCP indicate that the sample can be used in the magnetic refrigeration technology. Finally, the magnetic field variations of ΔS_M and RCP were used to confirm the reliability of the critical exponents estimated for the sample.

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Table legends

Table 1: Rietveld refinement of the structural parameters for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite. The numbers in parentheses are estimated standard deviations to the last significant digit.

<i>Sample</i>		$\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$	
<i>Space group</i>		$R\bar{3}c$	
<i>Cell parameters</i>	<i>a</i> (Å)		5.4859 (1)
	<i>c</i> (Å)		13.3963 (2)
	<i>V</i> (Å ³)		349.15 (1)
<i>Atoms</i>	La/Ca/Na	Wyckoff Positions	6a
		Site Symmetry	32
		Atomic Positions	(<i>x</i> , <i>y</i> , <i>z</i>)
		Isotropic Debye-Waller factor <i>B</i> _{iso} (Å ²)	0.81 (1)
	Mn	Wyckoff Positions	6b
		Site Symmetry	-3
		Atomic Positions	(<i>x</i> , <i>y</i> , <i>z</i>)
		Isotropic Debye-Waller factor <i>B</i> _{iso} (Å ²)	0.58 (1)
	O	Wyckoff Positions	18e
		Site Symmetry	2
		Atomic Positions	(<i>x</i> , <i>y</i> , <i>z</i>)
		Isotropic Debye-Waller factor <i>B</i> _{iso} (Å ²)	1.56 (1)
<i>Structural parameters</i>		Bond length	<i>d</i> _{Mn-O} (Å)
		Bond angle	<i>θ</i> _{Mn-O-Mn} (°)
		Average crystallites size	<i>D</i> (nm)
<i>Agreement factors</i>	Profile factor	<i>R</i> _p (%)	5.91
	Weighted profile factor	<i>R</i> _{wp} (%)	8.48
	Structure factor	<i>R</i> _F (%)	3.52
	Goodness of fit	<i>χ</i> ² (%)	3.44

Table 2: Comparison of the critical exponents values of $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite (present work) with those of the theoretical models.

<i>Material</i>	<i>Technique</i>	T_c (K)	β	γ	δ	<i>Ref.</i>
Mean-field model			0.5	1.0	3.0	[20]
3D- Heisenberg model			0.365 ± 0.003	1.336 ± 0.004	4.80 ± 0.04	[20]
3D- Ising Model			0.325 ± 0.002	1.24 ± 0.002	4.82 ± 0.02	[20]
Tricritical mean-field model			0.25	1.0	5.0	[20]
$\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$	<i>Modified</i>	274.69 ± 0.74	0.481 ± 0.009	-	-	Present work
	<i>Arrott</i>	274.19 ± 0.56	-	1.012 ± 0.012	-	
	<i>plots</i>					
	<i>Kouvel-</i>	274.87 ± 0.14	0.492 ± 0.004	-	-	Present work
	<i>Fisher</i>	274.63 ± 0.19	-	1.022 ± 0.001	-	
	<i>method</i>					
	<i>Critical</i>	-	-	-	3.030 ± 0.014	Present work
	<i>isotherm</i>					

Table 3: Magnetocaloric parameters at $\mu_0 H = 5$ T for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite (present work) compared with those found at the same applied magnetic field for other perovskite systems.

Composition	T_c (K)	ΔH (T)	$ \Delta S_M^{max} $ ($\text{J.Kg}^{-1}.\text{K}^{-1}$)	RCP (J.Kg^{-1})	Ref.
$\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$	275	5	3.09	214	Present work
$\text{La}_{0.6}\text{Pr}_{0.1}\text{Ba}_{0.3}\text{MnO}_3$	215	5	1.97	230	[23]
$\text{La}_{0.6}\text{Pr}_{0.1}\text{Ba}_{0.3}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$	162	5	1.31	123	[23]
$\text{La}_{0.78}\text{Dy}_{0.02}\text{Ca}_{0.2}\text{MnO}_3$	312	5	7.10	214.78	[24]
$\text{Pr}_{0.8}\text{K}_{0.2}\text{MnO}_3$	160	5	7.23	274.13	[25]
$\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$	269	5	6.59	221	[26]
$\text{La}_{0.6}\text{Ca}_{0.3}\text{Ag}_{0.1}\text{MnO}_3$	267	5	8.24	264	[26]
$\text{Nd}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$	145	5	3.91	265	[27]
$\text{Nd}_{0.67}\text{Ba}_{0.33}\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_3$	134	5	2.97	242	[27]
$\text{La}_{0.67}\text{Ba}_{0.33}\text{Mn}_{0.95}\text{Fe}_{0.05}\text{O}_3$	271	5	2.54	246	[28]
$\text{Pr}_{0.67}\text{Ba}_{0.33}\text{Mn}_{0.95}\text{Fe}_{0.05}\text{O}_3$	128	5	3.09	287	[28]
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.95}\text{Al}_{0.05}\text{O}_3$	332	5	4.4	-	[29]
$\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{0.95}\text{Ni}_{0.05}\text{O}_3$	-	5	3.2	-	[30]
$\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$	290	5	3	132	[30]
$\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_3$	328	5	5.00	200	[31]

Figure captions

Fig. 1: Main panel: X-ray diffraction pattern for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite. All peaks of the perovskite phase are indexed in the hexagonal setting of the rhombohedral $R\bar{3}c$ symmetry. The inset shows the Rietveld analysis of XRD pattern. The bottom line (blue) represents the difference between the XRD data (red) and calculated fit (black), and the green lines are Bragg positions.

Fig. 2: (a) Temperature dependence of magnetization and graph of dM/dT vs. T under magnetic field of $\mu_0 H = 0.05$ T for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite. (b) Temperature dependence of the inverse of magnetic susceptibility fitted using the Curie Weiss law.

Fig. 3: (a) M ($\mu_0 H$, T) curves and (b) Arrott plots around T_c for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite.

Fig. 4: (a) Spontaneous magnetization $M_s(T)$ (left-axis) and inverse initial susceptibility $\chi_0^{-1}(T)$ (right-axis) as a function of temperature fitted according to Eqs. (5) and (6), respectively for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite. (b) Kouvel-Fisher plots for the spontaneous magnetization $M_s(T)$ (left-axis) and the inverse initial susceptibility $\chi_0^{-1}(T)$ (right-axis) fitted according to Eqs. (7) and (8), respectively.

Figs. 5: Isothermal $M(T_c, \mu_0 H)$ plot at log-log scale for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite adjusted following Eq. (9).

Figs. 6: Scaling plots for La_{0.6}Ca_{0.2}Na_{0.2}MnO₃ perovskite below and above T_c using β and γ determined by the Kouvel-Fisher method. The inset represents the same plot in log-log scale.

Fig. 7: (a) Temperature dependence of the magnetic entropy change at various applied magnetic fields for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Na}_{0.2}\text{MnO}_3$ perovskite. (b) $|\Delta S_M^{\max}|$ vs. $\mu_0 H$ curve fitted using $\Delta S_m = a(\mu_0 H)^n$ power law, and RCP vs. $\mu_0 H$ curve fitted using $RCP = A(\mu_0 H)^N$ power law.