The magnetocaloric effect (MCE) of La$_{0.5}$Ca$_{0.1}$Ag$_{0.4}$MnO$_3$ (LCAMO) is simulated using a phenomenological model (PM). The LCAMO MCE parameters are calculated as the results of simulations for magnetization vs. temperature at different values of external magnetic field ($H_{\text{ext}}$). The temperature range of MCE in LCAMO grew as the variation in $H_{\text{ext}}$ increased, eventually covering the room temperature at high $H_{\text{ext}}$ values. The MCE of LCAMO is tunable with the variation of $H_{\text{ext}}$, proving that LCAMO is practically more helpful as a magnetocaloric (MC) material for the development of magnetic refrigerators in an extensive temperature range, including room temperature and lower and higher ones. The MCE parameters of LCAMO are practically greater than those of some MC samples in earlier works.

Keywords: magnetocaloric effect, phenomenological model, phase transition, perovskite, entropy change

INTRODUCTION

The need to solve the problem of emission of hazard gases, which come out of conventional vapor refrigerators, results in increased interest in functioning magnetic refrigerator (MR), the idea of which depends on functioning magnetocaloric effect (MCE) (Dhahri et al., 2014; El-Sayed and Hamad, 2019a; El-Sayed and Hamad, 2019b; Ahmed et al., 2021a, Ahmed et al., 2021b; Hamad et al., 2021; Jebari et al., 2021), because the MR provides high efficiency for cooling without any negative impact on the environment and has low energy consumption, availability of mechanical stability, and fewer noise events during cooling operation (Dhahri et al., 2015; Hamad, 2015a; ErchidiElyacoubi et al., 2018a, ErchidiElyacoubi et al., 2018b; Hamad et al., 2020; Sharma et al., 2020; Belhamra et al., 2021). MCE is described as a change in magnetic entropy ($\Delta S_M$) with a variation in the external magnetic field ($H_{\text{ext}}$) exerted on the material, causing a change in temperature (Masrour et al., 2016; ErchidiElyacoubi et al., 2018a; Kadim et al., 2020, Kadim et al., 2021a, Kadim et al., 2021b). Numerous research over decades have studied various magnetic materials to discover their suitability as magnetocaloric (MC) materials suitable for the MR industry (Hamad, 2015b; Masrour et al., 2017; Jebari et al., 2021; Labidi et al., 2021). It is preferable to use MC materials that have a magnetic transition type of the second degree with a suitable Curie temperature ($\theta_C$) as appropriate for use in a wide temperature range, including room temperature (Chhoura-Maatar et al., 2020; Henchiri et al., 2020; Laajimi et al., 2020). The current efforts are directed towards the use of manganite as an effective substance in MRs due to its great chemical stability during frequent use, lack of eddy current, ease of preparation, high electrical resistance, and the possibility of improving their properties through doping and changing the oxygen content (Alzahrani et al., 2020; Chhoura-Maatar et al., 2020; Henchiri et al., 2020; Laajimi et al., 2020). Felhi et al. prepared
La$_{0.5}$Ca$_{0.1}$Ag$_{0.4}$MnO$_3$ (LCAMO) via the ceramic method and reported an increase in $H_{\text{ext}}$ and an increase in broad ferromagnetic (FM) phase transition of LCAMO covering room temperature under high $H_{\text{ext}}$ (Jeddi et al., 2020).

These results motivate us to investigate the MCE of LCAMO, expecting that the MCE of LCAMO covers a large range of temperatures, especially cryogenic temperature and room temperature. Furthermore, it is believed that LCAMO, as a manganite, has low material processing costs, high chemical stability, and high resistivity, which are advantageous for reducing the overall eddy current heating. In this research, the MCE of LCAMO is studied using a phenomenological model (PM) to simulate the isofield magnetization vs. temperature curves, concluding with simulated $\Delta S_M$, heat capacity change ($\Delta C_{P,H}$), and relative cooling power (RCP).

**THEORETICAL CONSIDERATIONS**

According to PM, as described in Hamad (2012, 2015c, 2015d), the magnetization ($M$) vs. temperature is simulated by:

$$M(T) = \left( \frac{M_i - M_f}{2} \right) \left[ \tanh\left( \alpha (T_C - T) \right) \right] + \beta (T - T_C) + \left( \frac{M_i + M_f}{2} \right)$$

(1)
where \( M_i \) and \( M_f \) are values of magnetization at the onset and finalization of the FM paramagnetic transition as pointed out in Figure 1, respectively.

\[
\alpha = \frac{2(\beta - \gamma)}{M_i - M_f}
\]

(2)

where \( \gamma = \frac{(dM}{dT})_{T=\theta_c} \cdot \)

\[ \beta = \left( \frac{dM}{dT} \right)_{\text{average}} \] for FM phase

(3)

The numerical evaluation of \( \Delta S_M \) of LCAMO under \( H_{\text{ext}} \) variation (\( \Delta H \)) can be derived from Maxwell’s relation and derived from Eq. 1 as follows:

\[
\Delta S_M = \int_0^{H_{\text{max}}} \left( \frac{\partial M}{\partial T} \right)_H dH = \left( - (\beta - \gamma) \text{sech}^2(\alpha(\theta_C - T)) + \beta \right) \Delta H. \]

(4)

From Eq. 4, we can easily calculate \( \Delta S_M(T) \) by determining the \( M_i, M_f, \theta_c, \beta, \) and \( \gamma \) from isofield \( M(T) \) curves. Moreover, a maximum value of \( \Delta S_M(\Delta S_{\text{max}}) \), where \( T = \theta_C \), can be assessed according to the following equation:

\[
\Delta S_{\text{Max}} = \gamma \Delta H
\]

(5)
The full-width at half-maximum ($\delta T_{FWHM}$) of LCAMO can be given as follows:

$$\delta T_{FWHM} = \frac{2}{\alpha} \cosh^{-1}\left(\sqrt{\frac{2\alpha (M_i - M_f)}{\alpha (M_i - M_f) + 2\beta}}\right)$$  

(6)

A magnetic cooling efficiency of LCAMO is expected by considering the magnitude of $|\Delta S_{Max}(T, H_{max})|$ and $\delta T_{FWHM}$ (Hamad, 2012). RCP is calculated as follows:

$$RCP = \delta T_{FWHM} \times |\Delta S_{Max}(T, H_{max})|$$  

(7)

The $\Delta C_{P,H}$ of LCAMO can be given as follows (Hamad, 2012):

$$\Delta C_{P,H} = -\Delta H \alpha^2 T\left(M_i - M_f\right) \tanh(\alpha(\theta_i - T)) \sech^2(\alpha(\theta_i - T)).$$  

(8)

RESULTS AND DISCUSSION

At values of $H_{ext} < 5$T, there are two magnetic transitions of LCAMO, as can be observed in Figure 2, at two different temperatures variation, which is about 57% of the corresponding. It is possible that this is due to the presence of a canted FM phase in the FM matrix, which can be attributed to the additional Ag content (Jeddi et al., 2020), thus expecting two peaks in the $\Delta S_M$ curves. However, at $H_{ext} = 5$ T, it seems like a single magnetic transition of LCAMO, expecting a single peak in the $\Delta S_M$ curve. It is possible that this is due to the presence of a strong interatomic double exchange interaction at $H_{ext} = 5$ T. To simulate the MCE of LCAMO, the PM parameters ($M_i$, $M_f$, $\theta$, $\beta$, and $\alpha$) of LCAMO for each magnetic transition were determined directly from experimental data (isofield magnetization vs. temperature) as in Jeddi et al. (2020). We can see from Figure 2 that there is a good agreement between the experimental and theoretical results of $M(T)$, confirming the good fit of this model for simulating the MCE of LCAMO. This work demonstrates the good coincidence between the experimental data and the continuous curves given by PM, indicating that this model allows us to predict the MCE for LCAMO under different magnetic fields. The $M(T)$ curves of LCAMO demonstrate the magnetic transition from the FM phase to a paramagnetic one under different magnetic fields. The $\theta_C$ increases as $H_{ext}$ increases due to the increased alignment of the local spins, resulting in an increase in the interatomic double exchange interaction. As shown in Figure 3A, there are two peaks in the $\Delta S(M)$ curves when $H_{ext} < 5$ T. However, at $H_{ext} = 5$ T, there is a single peak in the $\Delta S_M$ curve due to the large interatomic double exchange interaction. $\Delta S_M$ reaches a peak of 2.75 J/kg K. Though the maximum $\Delta S_M$ is 2.75 J/kg K upon 5 T applied field variation, which is about 57% of the corresponding value of the compound that belongs to the same system as $La_{0.5}Ca_{0.2}Ag_{0.3}MnO_3$ ($\Delta S_{Max} = 4.8$ J/kg K upon 5 T), the value of RCP (273.5 J/kg upon 5 T) is larger, and the $\Delta S_M$ distribution of LCAMO is much more broad than that of $La_{0.5}Ca_{0.2}Ag_{0.3}MnO_3$ (RCP = 168 J/kg $\delta T_{FWHM} = 35$ upon 5 T), covering a wider range of temperature (Felhi et al., 2019). Figure 3B shows that $\Delta S_M(T)$ was calculated by Maxwell relation from experimental isothermal magnetization as a function of $H$ in Ref. 31, and $\Delta S_M(T)$ was calculated by PM, ranging between 240 and 270 K and covering the highest temperature transition. There is a good agreement and approach between the calculated results of both Maxwell relation and PM. Therefore, these results confirm that Eq. 4 still holds at $\Delta H$ of 0.5, 1, 3, and 5 T.
Figure 4 shows that $\Delta C_{\text{M}-\text{H}}(T)$ has an inverse change from a negative change to a positive one at around $\theta_C$ for each magnetic transition, causing a modification in the total specific heat. This oscillating temperature dependence of $\Delta C_{\text{M}-\text{H}}(T)$ at different temperatures is a reflection of $\Delta S(T)$ behavior. The behavior of $|\Delta S_m|$ and $\Delta C_{\text{M}-\text{H}}(T)$ curves suggests how the range of temperature for functioning LCAMO in the MR can be expanded. It is clear that the $|\Delta S_m|$ and $\Delta C_{\text{M}-\text{H}}$ peaks of LCAMO extend over a large temperature range. This temperature range of $|\Delta S_m|$ and $\Delta C_{\text{M}-\text{H}}$ expanded with increasing variation in $H_{\text{ext}}$ i.e., the peaks broaden, covering room temperature upon high values of $\Delta H$. This indicates that larger $|\Delta S_m|$ and $\Delta C_{\text{M}-\text{H}}$, $H$ are expected at higher values of $\Delta H$. Moreover, the variation of $H_{\text{ext}}$ allows the tuning of $\theta_C$ of LCAMO. This tunable $\theta_C$ makes LCAMO practically more helpful for the development of MRs.

Figures 5–8 show the values of $|\Delta S_m|$, $\delta T_{\text{FWHM}}$, RCP, and $\Delta C_{\text{M}-\text{H}}$ (maximum value of $\Delta C_{\text{M}-\text{H}}$) for LCAMO, respectively. It is clear that $|\Delta S_m|$, RCP, and $\Delta C_{\text{M}-\text{H}}$ show a general increase with an increase in $\Delta H$ due to enhancing the variations of alignment in the local spins with an increase in $\Delta H$, resulting in an increase in MC properties.

These large values of $|\Delta S_m|$, $\delta T_{\text{FWHM}}$, RCP, and $\Delta C_{\text{M}-\text{H}}$ in LCAMO prevailed as well in perovskite manganite due to the strong coupling between spin and lattice (Dhahri et al., 2008). Since lattice change is associated to magnetic transition in the manganite, this caused a further change in the magnetism of manganite (Dhahri et al., 2008). Furthermore, the bond distance of $<\text{Mn}–\text{O}>$ plus bond angle $<\text{Mn}–\text{O}–\text{Mn}>$ changes to favor the spin ordering with a high value of $H_{\text{ext}}$ leading to enhanced $|\Delta S_m|$, $\delta T_{\text{FWHM}}$, RCP, and $\Delta C_{\text{M}-\text{H}}$ in LCAMO (Radaelli et al., 1995; Hamad, 2015b).

Table 1 gives a comparative importance of the MCE parameters of LCAMO with those of various materials in terms of the high values of $\Delta H$ in previous works (Álvarez-Alonso et al., 2013; Hamad, 2013; Saadaoui et al., 2013; Ho et al., 2014; Bhumireddi et al., 2015; Bhumireddi et al., 2015; Boutahar et al., 2015; Jerbi et al., 2015; Gupta and Poddar, 2016; Mansouri et al., 2016; Oubla et al., 2016; Long et al., 2018; Biswal et al., 2019; El Boubekri et al., 2020). The MCE parameters of LCAMO are significantly larger than some MCE parameters of MC samples in the corresponding values of $\Delta H$ and the higher ones. From this comparative image, we conclude that LCAMO can function as a favorable MC magnet for the MR.

CONCLUSION

Based on thermodynamic calculation via PM, the MCE of LCAMO is simulated under different values of variation in $H_{\text{ext}}$. The MCE of LCAMO is strongly tunable with the value of the variation of $H_{\text{ext}}$. Therefore, LCAMO can be used over a wide temperature range as an effective material for MR, covering a large range of temperatures, including room temperature and lower and higher ones. The MCE of LCAMO is tunable with the variation of $H_{\text{ext}}$, proving that LCAMO is practically more helpful as a MC magnet for the development of MRs in an extensive temperature range, including room temperature. The values of the MCE parameters of LCAMO are practically greater than the MCE ones of some MC samples in earlier works.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the articleplementary material. Further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.
Theory and Monte Carlo Simulation. *J. Magnetism Magn. Mater.* 523, 167594. doi:10.1016/j.jmmm.2020.167594

Long, P. T., Manh, T. V., Ho, T. A., Dongquoc, V., Zhang, P., and Yu, S. C. (2018). Magnetocaloric Effect in La1-xSrxCoO3 Undergoing a Second-Order Phase Transition. *Ceramics Int.* 44, 15542–15549. doi:10.1016/j.ceramint.2018.05.216

Mansouri, M., Omrani, H., Cheikhrouhou-Koubaa, W., Koubaa, M., Madouri, A., and Cheikhrouhou, A. (2016). Effect of Vanadium Doping on Structural, Magnetic and Magnetocaloric Properties of La 0.5 Ca 0.5 MnO 3. *J. Magnetism Magn. Mater.* 401, 593–599. doi:10.1016/j.jmmm.2015.10.066

Masrou, R., Jabar, A., Benyoussef, A., Hamedoun, M., and Hlil, E. K. (2016). Monte Carlo Simulation Study of Magnetocaloric Effect in NdMnO 3 Perovskite. *J. Magnetism Magn. Mater.* 401, 91–95. doi:10.1016/j.jmmm.2015.10.019

Masrour, R., Jabar, A., Khilif, H., Jemaa, F. B., Ellouze, M., and Hlil, E. K. (2017). Experiment, Mean Field Theory and Monte Carlo Simulations of the Magnetocaloric Effect in La 0.67 Ba 0.22 Sr 0.11 MnO 3 Compound. *Solid State. Commun.* 268, 64–69. doi:10.1016/j.ssc.2017.10.003

Oubla, M., Lamire, M., Boutahar, A., Lassri, H., Manoun, B., and Hlil, E. K. (2016). Structural, Magnetic and Magnetocaloric Properties of Layered Perovskite La1.1Bi0.3Sr1.6Mn2O7. *J. Magnetism Magn. Mater.* 403, 114–117. doi:10.1016/j.jmmm.2015.11.076

Radaelli, P. G., Cox, D. E., Marezio, M., Cheong, S.-W., Schiffer, P. E., and Ramirez, A. P. (1995). Simultaneous Structural, Magnetic, and Electronic Transitions in\La1-xCa\textsubscript{x}MnO\textsubscript{3} with\textsubscript{x0.25 and 0.50. *Phys. Rev. Lett.* 75, 4488–4491. doi:10.1103/physrevlett.75.4488

Saadaoui, F., Koubaa, M., Cheikhrouhou-Koubaa, W., and Cheikhrouhou, A. (2013). Effects of Bismuth Doping on the Physical Properties of La0.6–xBi\textsubscript{x}Sr0.4CoO3 (0\textlesss\textless x\textlesss0.15) Cobalites. *J. Supercond. Nov. Magn.* 26, 3043–3047. doi:10.1007/s10948-013-2122-7

Sharma, P., Masrour, R., Jabar, A., Fan, L., Kumar, A., Ling, L., et al. (2020). Structural and Magnetocaloric Properties of Rare-Earth Orthoferrite Perovskite TmFeO3. *Chem. Phys. Lett.* 740, 137057. doi:10.1016/j.cplett.2019.137057

**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

**Publisher’s Note:** All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations or those of the publisher, the editors, and the reviewers. Any product that may be evaluated in this article or claim that may be made by its manufacturer is not guaranteed or endorsed by the publisher.

*Copyright © 2022 Hamad and Alamri. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.*