Tuning the microstructure and magnetocaloric properties of Na-substituted $\text{La}_{0.66}\text{Ca}_{0.33-x}\text{Na}_x\text{MnO}_3$ porous nanospheres

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+ The same contribution to this work.
Abstract

The effects of Na substituted on the microstructure and magnetocaloric properties of La$_{0.66}$Ca$_{0.33-x}$Na$_x$MnO$_3$ (x = 0, 0.05, 0.10, 0.15, 0.20) porous nanospheres synthesized by the solvothermal method were investigated. The structural analysis revealed that the substitution of Na increased the unit cell volume and distorted the lattice structure of La$_{0.66}$Ca$_{0.33-x}$Na$_x$MnO$_3$ porous nanospheres. Also, the porous nanospheres became relaxed and disintegrated with Na doping, reducing their diameter uniformity. The magnetocaloric measurements showed that an increase in the values of the Curie temperature was clearly observed upon Na doping. The maximum of the magnetic entropy change was observed to be 3.57 J/kg.K for La$_{0.66}$Ca$_{0.23}$Na$_{0.1}$MnO$_3$ and the largest relative cooling power (RCP) achieved to be 308.18 J/kg for La$_{0.66}$Ca$_{0.18}$Na$_{0.15}$MnO$_3$ under an applied field H = 5 T. The critical parameters of La$_{0.66}$Ca$_{0.33-x}$Na$_x$MnO$_3$ porous nanospheres were analyzed using the improved Arrott plot, Kouvel-Fisher method and critical isotherm, indicating significant change of critical parameters caused by Na doping. The outcomes demonstrated that Na-substituted La$_{0.66}$Ca$_{0.33-x}$Na$_x$MnO$_3$ porous nanospheres could be as promising candidates for the magnetic refrigeration near room temperature.

Keywords: Na-substituted; LCMO manganites; Critical parameters; Magnetocaloric effects
1. Introduction

With the progress and development of society, the demand for refrigeration is increasing, making refrigeration technology a hot topic of scientific research. Traditional refrigeration methods based on gas compression rely on gases such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which cause irreversible damage to the environment. Therefore, it is necessary to develop a new environmentally friendly and energy-saving refrigeration technology. Magnetocaloric effect (MCE) [1] is a magnetothermal dynamic process that can heat and cool magnetic materials through magnetization and demagnetization. The cooling effect is generated by the magnetic entropy change of the material, while the magnetic field is removed under adiabatic conditions [2]. Gadolinium (Gd) and Gd-based alloy compounds are considered to be the most active magnetic refrigerants at or near room temperature due to their huge MCE [3,4]. However, Gd has several drawbacks, including easy oxidation and high cost, which limit its use in commercial systems [5]. In addition to Gd, hundreds of MCE materials have been discovered, and many potential new materials are under study. Among these materials, perovskite manganite has received special attention due to their unique physical properties and relatively low preparation costs, making them a topic of intensive research activity [6,7]. Perovskite manganite has been widely studied as a substitute for magnetic refrigerants due to its large magnetic entropy change, high chemical stability, negligible hysteresis, high electrical resistivity, low eddy current heating, ease of preparation, adjustable phase change, and low cost [8,9]. The La$_{1-x}$AE$_x$MnO$_3$ (AE=Ca, Sr, Ba, Mg) materials,
in which La occupies the position of "A", exhibit significant MCE and colossal magnetoresistance (CMR) near the ferromagnetic-paramagnetic (FM-PM) transition temperature \( T_C \) \[10\]. The partial substitution of trivalent La\(^{3+}\) ions with divalent ions (such as Ba\(^{2+}\), Sr\(^{2+}\), Ca\(^{2+}\)) induces mixed valence states (Mn\(^{3+}\) and Mn\(^{4+}\)) of Mn ions and double exchange interactions between them. The substitution value of \( x = 0.3 \) (with the Mn\(^{3+}\)/Mn\(^{4+}\) fraction of 7/3) typically shows strong magnetism, resulting in a large magnetic entropy change \[11\]. Moreover, the crystal structure changes in the perovskite manganite can alter their physical properties, such as Jahn-Teller distortion in the MnO\(_6\) octahedra \[12\]. The static lattice distortion caused by the Jahn-Teller effect is destroyed when some Mn\(^{3+}\) ions are replaced by Mn\(^{4+}\) ions, and the dynamic Jahn-Teller effect dominates. The Mn-O bond length (\( d_{\text{Mn-O}} \)) and Mn-O-Mn bond angle (\( <\text{Mn-O-Mn}> \)) can be adjusted by the Mn\(^{3+}\)/Mn\(^{4+}\) ratio and the A-site ion radius, which affects the electronic bandwidth, DE interaction, and magnetic phase transition \[13\]. The La\(_{1-x}\)Ca\(_{x}\)MnO\(_3\) material with intermediate bandwidth \( x \approx 0.3 \) has been extensively studied due to its intriguing physical properties, such as large magnetic entropy and CMR occurring below room temperature \[14, 15\]. Previous studies have used divalent alkaline earth ions, such as Sr or Ba, to partially substitute Ca ions to obtain \( T_C \) closer to room temperature and change the critical parameters of the phase transition. The doping of monovalent K\(^{1+}\) and Na\(^{1+}\) with larger ionic radii is less studied. Additionally, when the size of magnetic materials reduced to the nanoscale, their basic magnetic properties, such as spontaneous magnetization, magnetic transition temperature and coercivity, show significant differences compared to those
of bulk materials. As the size decreases, the size effect becomes more prominent. The surface of nanoscale magnetic particles contains a magnetic dead layer composed of crystal defects and unpaired spin structures [16]. Magnetic nanoparticles exhibit changes in spin glass, superparamagnetism, coercivity, exchange bias and $T_C$. As the particle size decreases, the temperature range of magnetic entropy change tends to widen but the magnetic entropy decreases [17,18]. Based on this, we aim to find materials with high magnetic entropy change and a wide temperature range.

In this study, we employed a mixture of glycerol and isopropanol as a solvent to successfully prepare porous $\text{La}_{0.66}\text{Ca}_{0.33-x}\text{Na}_x\text{MnO}_3$ nanospheres by a solvothermal method. We investigated the differences in crystal structure, microstructure morphology, magnetic phase transition, critical parameters and magnetic heat performance of the $\text{La}_{0.66}\text{Ca}_{0.33-x}\text{Na}_x\text{MnO}_3$ porous nanospheres with varying levels of Na doping. Additionally, we calculated the relative refrigeration capacity of the $\text{La}_{0.66}\text{Ca}_{0.33-x}\text{Na}_x\text{MnO}_3$ porous nanospheres, demonstrating their promising potential for application in the field of magnetic refrigeration.

2. Experimental

2.1 Sample preparation

To ensure the quality and purity of the chemicals used, only analytical grade reagents were employed without additional purification in this study. The nanosphere precursors were first synthesized through the solvothermal method. To replace the A-position Ca$^{2+}$, sodium nitrate and calcium nitrate tetrahydrate were adjusted in a stoichiometric ratio and served the purpose of Na$^+$ doping. Lanthanum nitrate
hexahydrate, calcium nitrate tetrahydrate, sodium nitrate and manganese nitrate were dissolved in a mixture of 35 mL propanetriol and 65 mL isopropanol, respectively, with a total of 5 mmol used and divided into five groups according to the molar ratio of La : Ca : Na : Mn = 0.66 : 0.33-x : x : 1 (x = 0, 0.05, 0.10, 0.15, 0.20). The mixture was stirred well until fully dissolved. Then, 1 g of polyvinylpyrrolidone K29-32 (PVP) was added and dissolved completely by stirring. The solution was transferred to a reaction vessel and held at 180°C for 6 hours. Once complete, the precursor was collected by centrifugation at 8000 r/min, followed by washing with ethanol and drying. Finally, the precursors were annealed in air at 700°C for 6 hours. The five groups of samples were labeled as Na-0, Na-0.05, Na-0.1, Na-0.15 and Na-0.2, according to the substitution ratio of Na. The complete chemical formula was La_{0.66}Ca_{0.33-x}Na_xMnO_3, where x = 0, 0.05, 0.10, 0.15, 0.20.

2.2 Characterization

The structure of the samples was characterized using a SmartLab SE X-ray diffractometer (XRD) diffractometer at room temperature with CuKα radiation. Phase analysis was carried out to optimize the parameters using Rietveld analysis with GSAS-II software. Furthermore, the samples were morphologically characterized using a ZEISS Sigma 300 scanning electron microscope. To observe the elemental distribution on the nanosphere surface, an energy-dispersive X-ray spectroscopy (EDS) surface sweep was also performed on the nanosphere surface using an Oxford Xplore 50 energy spectrometer. The magnetic properties of the sample were measured using a physical property measurement system (PPMS, DynaCool 9T). Zero-field cooling
(ZFC)/field cooling (FC) was tested at T = 2–300 K and H=100 Oe conditions to determine the magnetic properties. Hysteresis lines were recorded in the magnetic field range of -5~5 T at three temperatures of 300 K, 100 K and 10 K. Moreover, magnetization isotherm curves were measured every 2 K with a magnetic field ranging from 0~5 T before and after $T_c$.

3. Results and discussion

3.1 Structural properties

The phase composition, lattice parameters and dimensions of the coherent scattering zone were determined using the XRD technique with a SmartLab SE diffractometer at room temperature and CuK1 radiation ($\lambda = 0.15406 \text{ nm}$). The XRD diffractograms and phase compositions obtained via refinement fitting using the Rietveld method on GSAS-II were presented in Fig.1 [19–21]. The results indicated that all samples exhibited the Pbnm space group. The doping process did not result in the production of a secondary phase. The phase was consistent with the information provided in PDF (97-009-5246) [22]. The crystal structure parameters obtained after the structure refinement were shown in Table 1. The A-site was originally occupied by La$^{3+}$ (effective ionic radius = 1.36 Å) and Ca$^{2+}$ (1.34 Å) with coordination number (CN) = 12. The doping of Na (1.39 Å) [23,24] shared the a position. Since the radius of Na ions was larger than that of Ca ions, the ionic spacing in the cell increased when Na ions replace Ca ions, which led to an increase in cell volume. The average grain size was calculated from Scherrer's equation as [21]:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

(1)
Where $K = 0.9$ was the constant corresponding to the microcrystalline shape factor. $\lambda = 0.15406$ nm was the XRD wavelength. $\beta$ was the full width at half maximum (FWHM) of the strongest-intensity diffraction peak and $\theta$ was the corresponding diffraction angle. The mean grain size of the entire sample set was consistent, measuring approximately 23 nm, as illustrated in Table 1. It was worth noting that the introduction of Na doping did not have a substantial impact on the average grain size of the specimens. The perovskite manganese oxide system relied on the DE theory, which posited that the bandwidth $W$ of the MnO$_6$ oxygen octahedron was dictated by the bond length between Mn-O, as well as the bond angle between Mn-O-Mn, as expressed below [25]:

$$W \propto \frac{\cos\left(\frac{1}{2(\pi - \langle \beta \rangle)}\right)}{d_{\text{Mn-O}}^{3.5}}$$

(2)

Here, $\beta$ was the average Mn-O-Mn bond angle. $d_{\text{Mn-O}}$ was the average Mn-O bond length. Decreasing the Mn-O-Mn bond angle and increasing the Mn-O bond length would clearly result in a decrease in the bandwidth $W$, which reduced the DE effect and $T_C$ [26]. Compared to undoped Na-0, Na doping resulted in a reduction in the Mn-O bond length and an increase in the Mn-O-Mn bond angle, leading to an increase in the system's bandwidth $W$. This increase enhanced the double exchange interaction and improved the $T_C$.

Fig.2 displayed the structure of La$_{0.66}$Ca$_{0.33-x}$Na$_x$MnO$_3$ porous nanospheres, examined through scanning electron microscopy. As evident from Fig.2 (a, f), the undoped La$_{0.66}$Ca$_{0.33}$MnO$_3$ nanospheres exhibited a porous structure with a consistent
diameter and a stable composition. This observation concurred with earlier reports on the fabrication of porous nanospheres using the glycerol solvent thermal method [27,28]. Doping with sodium resulted in the dispersion of constituent particles of nanospheres, leading to the disintegration of certain porous nanospheres. To investigate the influence of Na doping on the size and uniformity of nanospheres, the diameter of the nanospheres was measured and a diameter histogram was constructed, as presented in Fig. 2 (k-o). Subsequently, a Gaussian fit was applied to the distribution. It was noteworthy that the Gaussian peak of the sample was centered at 500-600 nm, indicating a dominant size range. Notably, the Na-0 fitting peak was comparatively narrow, indicating superior uniformity in the diameter size. However, the distribution of nanosphere diameter in the Na-doped sample became wider, as evidenced by the broadening of the fitting curve, denoting inferior uniformity in the nanosphere diameter. This phenomenon could be attributed to the partial disintegration of some nanospheres, leading to a reduction in the proportion of nanospheres with a diameter of 500-600 nm, which was particularly conspicuous in Na-0.15. Fig. 2 (p-t) showed the EDS surface scan image for Na-0.05, where a uniform distribution of all elements on the sample's surface could be observed.

3.2 Magnetic properties

Fig. 3 (a-e) showed the M vs. T curves for ZFC and FC of the samples at 100 Oe. The dM/dT curves were shown in Fig. S1. The $T_C$ of the ferromagnetic-paramagnetic transition in the samples was determined by identifying the minimum of the dM/dT curve. The values of $T_C$, irreversibility temperature ($T_{ir}$) and blocking temperature ($T_b$)
for all samples were tabulated in Table 2. The magnetic saturation ($M_s^{FC}$) of the FC curve was determined under testing conditions of 2 K and 100 Oe, which was reported in Table 2. As depicted in Fig. 3, a general decreasing trend in $M_s^{FC}$ was evident with an increasing Na doping concentration, with the exception of a slightly lower $M_s^{FC}$ of Na-0.05 relative to Na-0.1. The saturation magnetization ($M_s$) of all samples exhibited a consistent declining trend as the Na doping concentration increases. This trend was observed under the 5 T and 10 K, as shown in Fig. 3 (f). This could be attributed to the larger ionic radius of Na. Compared to Ca, which resulted in crystal structure distortion and a reduction in the long-range magnetic ordering of magnetic moments. Consequently, the magnetic coupling between adjacent ions was decreased, leading to a decline in the saturation magnetization. The difference in temperature between the blocking temperature ($T_b$) and the irreversibility temperature ($\Delta T_{irr}-T_b$), as shown in Table 2, was utilized as a gauge for nanoparticle polydispersity [29]. Furthermore, $\Delta T_{irr}-T_b$ could be used to measure the size and size distribution of the hard agglomerates of magnetic nanoparticles within the (composite) system [30,31]. For all samples except Na-0.15, $\Delta T_{irr}-T_b$ was around 20 K. In contrast, Na-0.15 had the largest $\Delta T_{irr}-T_b$ value of 69 K, indicating greater particle size variability and a wider particle size distribution. This finding was consistent with the SEM morphology characterization results mentioned above.

To investigate the magnetic behavior in the paramagnetic region above $T_C$, the molar magnetization was calculated from the FC curve. As shown in Fig. S10 (yellow line), the magnetization curve above $T_C$ was clearly linear. The high-temperature
magnetic data were fitted using the Curie–Weiss law given by Eq. (3) [32]:

\[ \chi(T) = C(T - \theta_p) \]  

(3)

Where \( \theta_p \) was the Curie–Weiss temperature and \( \theta_p \) denoted the \( T_C \) of the paramagnetic (PM) phase obtained by fitting the high-temperature region of the curve and extending the linear part to the intercept. \( C \) was the Curie constant determined by the slope of the linear curve. The effective magnetic moment (\( \mu_{\text{eff}} \)) of the PM phase could be deduced by Eq. (4) [33]:

\[ C = \frac{N_A \mu_B^2}{3k_B} \mu_{\text{eff}}^2 \]  

(4)

Where \( k_B \), \( N_A \) and \( \mu_B \) were Boltzmann's constant, Avogadro's number and Bohr magneton, respectively. The theoretical magnetic moment \( \mu_{\text{eff}} \) was obtained from the ratios of Mn\(^{2+}\), Mn\(^{3+}\) and Mn\(^{4+}\) in the chemical formula, combined with Eq. (5) [34]:

\[ \mu_{\text{PM}}(\text{Mn}) = x_{\text{Mn}^{3+}} \cdot \mu_{\text{Mn}^{3+}}^2 + x_{\text{Mn}^{4+}} \cdot \mu_{\text{Mn}^{4+}}^2 \]  

(5)

\( x_{\text{Mn}^{3+}} \) and \( x_{\text{Mn}^{4+}} \) were the corresponding manganese components. The manganese components had different effective magnetic moments, with values of Mn\(^{3+}\) = 4.90\( \mu_B \) and Mn\(^{4+}\) = 3.87\( \mu_B \). The theoretical effective magnetic moment (\( \mu_{\text{eff}}^{\text{theor}} \)) and experimental effective magnetic moment (\( \mu_{\text{eff}}^{\text{exp}} \)) values of all samples were shown in Table 3. Due to the lower valence state of Na\(^{1+}\) compared to Ca\(^{2+}\), according to the principle of electronic neutrality, as the doping level increased, more Mn\(^{3+}\) was transformed into Mn\(^{4+}\), thereby reducing the \( \mu_{\text{eff}}^{\text{theor}} \). The \( \mu_{\text{eff}}^{\text{exp}} \) also exhibited a similar decreasing trend with the increase of doping level. Fig. 4 showed the hysteresis loops of La\(_{0.66}\)Ca\(_{0.33-x}\)Na\(_x\)MnO\(_3\) at 300 K, 100 K and 10 K. The saturation magnetization (\( M_s \)) at 5 T was presented in Table 2. The relationship between magnetic moment and
saturation magnetization could be described by the fundamental magnetization equation [35]:

\[ M = \chi^m \times H \]  

(6)

According to this formula, where \( M \) represented the magnetic moment of the object, \( \chi^m \) denoted the magnetic susceptibility of the material and \( H \) stand for magnetic field intensity. It could be observed that the magnetic moment was directly proportional to the saturation magnetization. Fig.4 (f) illustrated the magnetic hysteresis loop of La\(_{0.66}\)Ca\(_{0.33-x}\)Na\(_x\)MnO\(_3\) at 10K, showed an overall decreasing trend in \( M_s \) with increasing doping concentration. The value of \( M_s \) for Na-0.15 was slightly larger than that for Na-0.1, consistent with the observed \( \mu_{\text{eff}}^{\exp} \). The magnetic hysteresis loops at 300K, 100K and 10K exhibited small \( H_C \) and displayed soft magnetic characteristics.

3.4 Critical magnetization

The isothermal magnetization curve of Na-0.05 was shown in Fig.6 (a). Below the \( T_C \), the magnetization curve saturated non-linearly and the sample was in the ferromagnetic (FM) state. However, as the temperature increased above \( T_C \), the sample entered the paramagnetic state and the magnetization intensity linearly increases with the magnetic field. According to the Banerjee standard, the slopes of the Arrott diagram \( M^2 \) vs. \( H/M \) curve below and above the phase transition temperature of all samples were positive (Fig.5, S2, S4, S6, S8 (d)), indicating that all samples exhibited a second-order magnetic phase transition. According to the scaling assumption, the critical behavior of second-order phase transitions near \( T_C \) consisted of a set of critical indices \( \beta, \gamma \) and \( \delta \) [36], which were linked to the spontaneous
magnetization strength \((M_S)\), inverse of the magnetization rate \((\chi_0^{-1})\) and critical isotherm \((H)\) \[37\], respectively. These three key parameters were used to characterize the ferromagnetic ordering \((T < T_C)\), the PM disorder \((T > T_C)\) and the phase transition critical point \((T = T_C)\) to analyze the critical behavior of the phase transition and comprehend the interaction mechanism in the magnetic phase transition, which were typically defined as \[38\]:

\[
M_S(T) = M_0 (-\varepsilon)^\beta, \quad \varepsilon < 0 \quad (7)
\]

\[
H = D M_0^\delta, \quad \varepsilon = 0 \quad (8)
\]

\[
\chi_0^{-1} = \left(\frac{H_0}{M_0}\right)^\gamma, \quad \varepsilon > 0 \quad (9)
\]

Where \(\beta\), \(\gamma\), and \(\delta\) were the critical exponents. \(\varepsilon = (T - T_C)/T_C\) was the reduced temperature. \(D\) and \(H_0/M_0\) were the critical amplitudes. For the above critical parameters, the corresponding critical values could be determined according to the Arrott-Noakes formula \[39\]:

\[
(H/M)^{1/\gamma} = \frac{a(T - T_C)}{\frac{T}{\gamma}} + b M^{1/\beta} \quad (10)
\]

Where \(T\) was the temperature. \(a\) and \(b\) were constants. \(M\) was the magnetization strength and \(H\) was the magnetic field strength. The modified Arrot diagram was plotted by choosing the appropriate initial critical parameters \(\beta\) and \(\gamma\). For example: (1) mean-field model (MFM): \(\beta = 0.5, \gamma = 1.0\); (2) tricritical mean-field model (TMFM): \(\beta = 0.25, \gamma = 1.0\); (3) Ising model: \(\beta = 0.325, \gamma = 1.241\); (4) 3D-Heisenberg model: \(\beta = 0.365, \gamma = 1.336\) \[40–42\]. Fig.5, S2, S4, S6, S8 displayed the plots of \((M)^{1/\beta}\) vs. \((H/M)^{1/\gamma}\) utilizing the aforementioned model. These plots were used to select the optimal critical parameter, which was determined to be the relative slope (RS) of
Na-0.05 in Fig. 5 (i), where RS = S(T)/S(T_c). This demonstrated that the Ising model exhibited strong parallelism near the critical temperature of the phase transition. However, it should be noted that the critical temperature of the Ising model differed significantly from the T_c. The MFM model had the critical T_c closest to the experimentally measured Curie temperature T_C. To more precisely investigate the critical behavior of the sample, both Ising and MFM models were employed for the modification of critical parameters. The Na-0.1 and 0.15, which had similar circumstances, were also subjected to the Ising and MFM models. Na-0.2 exhibited superior parallelism in proximity to the critical transition temperature for the Heisenberg model. Consequently, adjustments were made to the critical parameters utilizing both the Ising and Heisenberg models. The spontaneous magnetization intensity M_S(T) and the initial magnetic susceptibility inverse \chi_0^{-1}(T) were obtained by extrapolating the axis intercept, and a new set of critical parameters was determined by fitting an exponential function. The modified Arrott plot (MAP) fitting curves for \beta and \gamma were shown in Fig. 6, S3, S5, S7, S9(c, d). In addition to MAP, the Kouvel-Fisher (KF) linear fitting method was also used for critical parameter correction [43]:

\[ M_S(T)[dM_S(T)/dT]^{-1} = (T - T_C)/\beta \quad (11) \]
\[ \chi_0^{-1}(T)[d\chi_0^{-1}(T)/dT]^{-1} = (T - T_C)/\gamma \quad (12) \]

The KF fitting curves for \beta and \gamma were shown in Fig. 6, S3, S5, S7, S9 (e, f). The new Arrott plots were plotted according to the \beta, \gamma and \delta obtained by fitting the MAP with the KF method, as shown in Fig. 5 (e), (f), (g), (h). Near critical T_C, the high-field M^{1/\beta} vs. (H/M)^{1/\gamma} showed a series of parallel straight lines, indicating that the modified
critical parameters were consistent with the Arrott-Noakes formulation. The optimal RS values for Na-0.1, Na-0.05 and Na-0.1 were KF (Ising), while the optimal RS value for Na-0.15 was KF (mean) and for Na-0.2, it was KF (Hei). The critical parameter $\delta^{exp}$ was obtained through exponential function fitting of the high-field region of the isothermal magnetization curve of the critical $T_C$. According to the Widom scaling relation equation, the reliability of $\delta$ was established if $\beta$, $\gamma$ and $\delta$ satisfy $\delta^{exp} = \delta = 1 + \gamma/\beta$ [44]. Table 3 record $\beta$, $\gamma$, $\delta^{exp}$ and $\delta$ for all samples. Based on this, the value of $\delta^{exp}$ obtained from $T_C$ calculation was smaller than the value of $\delta$ obtained through the Widom formula, even for the critical parameter $\delta$ obtained by correcting the critical $T_C$ of the mean model, which was closer to the $T_C$. Therefore, based on the evaluation of various factors such as the RS parallelism, the difference between $\delta^{exp}$ and $\delta$, and the difference between critical $T_C$ and $T_C$, the optimal set of critical parameters was marked with a superscript ※ in Table 3. The $\beta$ and $\gamma$ values for Na-0 was $\beta = 0.32642$ and $\gamma = 1.26069$, respectively, indicating a preference towards the short-range ordered Ising model. Similarly, Na-0.05 also showed a preference for the Ising model. With an increasing doping concentration, the critical parameters of Na-0.1 and Na-0.15 tended towards the long-range ordered MFM model. The critical parameters of the heavily doped Na-0.2 shift toward the short-range ordered Heisenberg model.

3.5 Magnetic entropy change

The assessment of a material's magnetic cooling ability was determined by analyzing the isothermal magnetic entropy alteration produced from isothermal
magnetization. This calculation was carried out using Maxwell's thermodynamic theory [45] and could be expressed as follows in Eq. (13):

$$\Delta S_M(T,H) = \int_0^H (\frac{\partial M(H,T)}{\partial T}) dH$$

(13)

All samples were displayed in Fig. 7 as temperature-dependent magnetocaloric entropy change graphs of H vs $|\Delta S_M|$ vs T. It could be observed that the magnetic entropy change ($|\Delta S_M|$) peak graph increased with the increase of the magnetic field and increased and then decreased with the temperature, exhibiting a maximum value of $|\Delta S_M|$ around the phase transition temperature. The temperature at which maximum magnetic entropy change ($|\Delta S_M^{\text{max}}|$) was maximum was $T_{MCE}$, and the $T_{MCE}$ under low-field conditions was smaller than that under high-field conditions. N.A. Liedienov et al. [46] had proposed that this might be attributed to the contribution of SPM nanoparticles to the acceleration of magnetization rate under low-field conditions. It was also possible that this stemmed from the competition between magnetic ordering and thermal fluctuations in the material. In low magnetic fields, thermal fluctuations dominated, leading to a reduction in magnetic ordering and thus a decrease in magnetic entropy. As the temperature decreased, magnetic ordering became stronger and magnetic entropy increased. In high magnetic fields, magnetic ordering dominated, resulting in $|\Delta S_M^{\text{max}}|$ at higher temperatures [47]. The maximum magnetic entropy change ($|\Delta S_M^{\text{max}}|$) values under 1~5 T magnetic fields were shown in Table 4. As the concentration of Na doping increased, there was a notable trend in $|\Delta S_M^{\text{max}}|$, whereby it initially increased before decreasing. Among the various doping concentrations, Na-0.1
exhibited the highest $|\Delta S_{M_{\text{max}}}|$, which was recorded at 3.57 J/kg K (5 T). On the other hand, Na-0.15 exhibited the lowest $|\Delta S_{M_{\text{max}}}|$, which was recorded at 2.62 J/kg K (5 T). This may be attributed to the disintegration of Na-0.15’s nanospheres and the loosening of particles. This led to a weakening of the particle magnetic correlation, ultimately resulting in a decrease in the system's $|\Delta S_{M_{\text{max}}}|$. The relative cooling power (RCP) was another important factor in evaluating the magnetothermal effect, specified by the following equation [48]:

$$RCP = \int_{T_1}^{T_2} |\Delta S|dT$$

(14)

Where $T_1$ and $T_2$ were the temperatures at half the maximum magnetic entropy change. The RCPs of all samples at a 1~5 T magnetic field were shown in Table 4. Compared to the undoped Na-0, the RCP of Na-doped samples showed a slight decrease with increasing doping concentration, which may be due to the decrease in the temperature difference of the $|\Delta S_{M_{\text{max}}}|$ peak width. As shown in the entropy peak diagram in Fig.7, the entropy of the sample decreased significantly when the temperature was higher than $T_{MCE}$, which was the paramagnetic temperature range. Under a magnetic field of 1~5 T, although the phase transition temperature and $|\Delta S_{M_{\text{max}}}|$ of Na-0.15 were relatively low, it had a large RCP, with the maximum RCP of Na-0.15 being 308.18 J/kg at 5 T. This was because Na-0.15 has a large $|\Delta S_{M_{\text{max}}}|$ both before and after the phase transition temperature, and $|\Delta S_{M_{\text{max}}}|$ decreased less as the temperature increases. This resulted in a larger half-width of the $|\Delta S_{M_{\text{max}}}|$ peak for Na-0.15, which enhanced its relative cooling power. The relative cooling power of Na-0.15 could reach 75% of the conventional Gd metal refrigerant currently in use.
In summary, La\(_{0.66}Ca_{0.33-x}Na_xMnO_3\) showed potential for application in the field of magnetic refrigeration.

4. Conclusions

Based on the above, Na-doped La\(_{0.66}Ca_{0.33-x}Na_xMnO_3\) porous nanospheres were successfully prepared by changing the ratio of Na and Ca ions by the solvent-thermal method. Characterization of the morphology of La\(_{0.66}Ca_{0.33-x}Na_xMnO_3\) showed that Na doping caused the structure of the nanospheres to loosen and disintegrate, reducing the uniformity of their diameter. Na doping had resulted in an increase in the unit cell volume of La\(_{0.66}Ca_{0.33-x}Na_xMnO_3\), shortening of the Mn-O bond length due to lattice distortion, increasing the Mn-O-Mn bond angle, enhancing the system's \(T_C\), and making it closer to room temperature. Specifically, the \(T_C\) of Na-0.15 was lower than that of Na-0 due to the weakened magnetic correlation caused by the dispersion of magnetic nanoparticles. Na-0.15 exhibited the smallest \(|-\Delta S_{M}^{\text{max}}|\) of 2.62 J/kg K (5T) among all other samples. The most considerable \(|-\Delta S_{M}^{\text{max}}|\) of 3.57 J/kg K (5T) was observed in Na-0.1. Notably, Na-0.15 had demonstrated the highest RCP of 308.18 J/kg (5T), mainly due to its broad temperature range of FWHM. Analysis had been carried out using the improved Arrott plot, Kouvel-Fisher method and critical isotherm. The critical parameters induced by doping had been more obvious. The critical parameters \(\beta\) and \(\gamma\) of Na-0 and Na-0.05 had tended to the Ising model, while those of Na-0.1 and Na-0.15 had tended to the mean-field model. The critical parameters \(\beta\) and \(\gamma\) of Na-0.2 had tended towards the Heisenberg model.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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La_{0.66-x}Ca_{0.33-y}Mn_{1+x+y}O_3 porous nanospheres: Structure, critical behavior, magnetocaloric effects and a first-order reversal curve analysis, Ceramics International. (2023). https://doi.org/10.1016/j.ceramint.2023.04.058.


Fig. 1 XRD diagram of $\text{La}_{0.66}\text{Ca}_{0.33-x}\text{Na}_x\text{MnO}_3$. 

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**Fig. 2.** The SEM images of Na-0 (a, f), Na-0 (b, g), Na-0.1 (c, h), Na-0.15 (d, i) and Na-0.2 (e, j).

Diameter histogram of porous nanospheres obtained from SEM images statistics, red curve obtained by Gaussian fitting (Na-0 (k), Na-0 (l), Na-0.1 (m), Na-0.15 (n) and Na-0.2 (o)). The

Surface element distribution mapping of Na-0.5 (p~t).
Fig. 3. FC curves of $\text{La}_{0.66}\text{Ca}_{0.33-x}\text{Na}_x\text{MnO}_3$ (a). FC and ZFC curves of Na-0 (b), Na-0.05 (c), Na-0.1 (d), Na-0.15 (e) and Na-0.2 (f), respectively.
Fig. 4. The hysteresis lines of Na-0 (a), Na-0.05 (b), Na-0.1 (c), Na-0.15 (d) and Na-0.2 (e) at 300K, 100K and 10K, respectively. The hysteresis lines of La$_{0.66}$Ca$_{0.33-x}$Na$_x$MnO$_3$ at 10K (f).
Fig. 5. \( (M)^{1/\beta} \) vs \( (H/M)^{1/\gamma} \) plots of Na-0.05 (a, b, c, d, e, f, g, h). The RS plot of Na-0.05 (i).
Fig. 6. (a) The isothermal magnetization curve $M(H)$ for Na-0.05. (b) Exponential plot $\ln(H)$ vs $\ln(M)$ of the high field region of the isothermal magnetization curve for Na-0.05. (c, d) The spontaneous magnetization $M_S(T)$ (left axis) and inverse susceptibility $\chi^{-1}$ (right axis) versus temperature for Na-0.05. Red lines are fits according to Eqs. (7) and Eqs. (9), respectively. The Kouvel–Fisher plots for Na-0.05. Red lines are the fits of the model according to Eqs. (11) and Eqs. (12), respectively.
Fig. 7. 3D $|\Delta S_M|_{\text{max}}$ diagrams of Na-0 (a), Na-0.05 (b), Na-0.1 (c), Na-0.15 (d) and Na-0.2 (e).
Table 1. Structural parameters of the La$_{0.66-x}$Ca$_{0.33-y}$Mn$_{1+x+y}$O$_3$ obtained from Rietveld refinement of X-ray diffraction data.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Na-0</th>
<th>Na-0.05</th>
<th>Na-0.1</th>
<th>Na-0.15</th>
<th>Na-0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (nm)</td>
<td>24.7</td>
<td>26.1</td>
<td>23.3</td>
<td>24.9</td>
<td>21.1</td>
</tr>
<tr>
<td>a</td>
<td>5.4943</td>
<td>5.5018</td>
<td>5.4850</td>
<td>5.5096</td>
<td>5.5018</td>
</tr>
<tr>
<td>b</td>
<td>5.4644</td>
<td>5.4635</td>
<td>5.4780</td>
<td>5.4525</td>
<td>5.4635</td>
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<tr>
<td>c</td>
<td>7.7189</td>
<td>7.7316</td>
<td>7.7430</td>
<td>7.7504</td>
<td>7.7316</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>231.7507</td>
<td>232.4048</td>
<td>232.6526</td>
<td>232.8305</td>
<td>232.4048</td>
</tr>
<tr>
<td>(B)Mn$^{3+/4+}$ -O$_2^-$</td>
<td>1.9600</td>
<td>1.9424</td>
<td>1.9452</td>
<td>1.9471</td>
<td>1.9456</td>
</tr>
<tr>
<td>(A)Ca$^{2+}$/La$^{3+}$/Na$^{1+}$ -O$_2^-$</td>
<td>2.8260</td>
<td>2.6375</td>
<td>2.7870</td>
<td>2.5924</td>
<td>2.5772</td>
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<tr>
<td>(B)Mn$^{3+/4+}$ -O$_2^-$ -Mn$^{3+/4+}$</td>
<td>159.9220</td>
<td>168.6589</td>
<td>168.7080</td>
<td>168.6710</td>
<td>168.7610</td>
</tr>
<tr>
<td>(A)Ca$^{2+}$/La$^{3+}$/Na$^{1+}$ -O$_2^-$ -Mn$^{3+/4+}$</td>
<td>88.0594</td>
<td>95.5818</td>
<td>90.2458</td>
<td>90.3762</td>
<td>84.4361</td>
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<td>$R_{wp}$ (%)</td>
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<td>6.820</td>
<td>7.664</td>
<td>8.673</td>
<td>7.713</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>1.07</td>
<td>1.43</td>
<td>1.61</td>
<td>1.74</td>
<td>1.67</td>
</tr>
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Table 2. $T_C$ of $\text{La}_{0.66}\text{Ca}_{0.33-x}\text{Na}_x\text{MnO}_3$, PM Curie temperature ($\theta$), experimental magnetic moments $\mu_{\text{eff}}^{\text{exp}}$, theoretical magnetic moments $\mu_{\text{eff}}^{\text{theor}}$, blocking temperature $T_b$, irreversible temperature $T_{ir}$, $\Delta T_{ir}-T_b$. Mean field model phase-change temperature $T_{\text{MFM}}$, phase change temperature $T_{\text{MAP}}$ from modified Arrott plot (MAP) curve fit. Phase change temperature $T_{\text{KF}}$ from Kouvel-Fisher (KF) linear fit. The models used for fitting are recorded in parentheses.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Na-0</th>
<th>Na-0.05</th>
<th>Na-0.1</th>
<th>Na-0.15</th>
<th>Na-0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_C$ (K)</td>
<td>244</td>
<td>248</td>
<td>252</td>
<td>232</td>
<td>267</td>
</tr>
<tr>
<td>$\theta$ (K)</td>
<td>256.75</td>
<td>258.66</td>
<td>265.84</td>
<td>252.29</td>
<td>273.36</td>
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<tr>
<td>$\mu_{\text{eff}}^{\text{exp}}$ ($\mu$B)</td>
<td>7.13</td>
<td>5.31</td>
<td>4.36</td>
<td>4.65</td>
<td>4.09</td>
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<td>$\mu_{\text{eff}}^{\text{theor}}$ ($\mu$B)</td>
<td>4.58</td>
<td>4.54</td>
<td>4.49</td>
<td>4.44</td>
<td>4.38</td>
</tr>
<tr>
<td>$T_b$ (K)</td>
<td>227</td>
<td>228</td>
<td>235</td>
<td>168</td>
<td>242</td>
</tr>
<tr>
<td>$T_{ir}$ (K)</td>
<td>250</td>
<td>250</td>
<td>253</td>
<td>237</td>
<td>265</td>
</tr>
<tr>
<td>$\Delta T_{ir}-T_b$</td>
<td>23</td>
<td>22</td>
<td>18</td>
<td>69</td>
<td>23</td>
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<td>$M_{SFC}$</td>
<td>14.43</td>
<td>15.19</td>
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<td>$M_S$ (10K)</td>
<td>90.99</td>
<td>86.69</td>
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<td>74.50</td>
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<td>$M_S$ (100K)</td>
<td>84.93</td>
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<td>$M_S$ (300K)</td>
<td>19.65</td>
<td>17.34</td>
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<td>$T_{\text{MFM}}$ (K)</td>
<td>231</td>
<td>232</td>
<td>246</td>
<td>196</td>
<td>252</td>
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<tr>
<td>$T_{\text{Ising}}$ (K)</td>
<td>233</td>
<td>232</td>
<td>248</td>
<td>202</td>
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<td>$T_{\text{Heisenberg}}$ (K)</td>
<td>233</td>
<td>234</td>
<td>248</td>
<td>200</td>
<td>254</td>
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<td>$T_{\text{MFM}}$ (K)</td>
<td>247</td>
<td>246</td>
<td>260</td>
<td>220</td>
<td>206</td>
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<td>$T_{\text{MAP}}$ (K)</td>
<td>227 (Ising)</td>
<td>232 (Ising)</td>
<td>248 (Ising)</td>
<td>190 (Ising)</td>
<td>248 (Ising)</td>
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<td></td>
<td>243 (Mean)</td>
<td>244 (Mean)</td>
<td>256 (Mean)</td>
<td>224 (Mean)</td>
<td>250 (Mean)</td>
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<tr>
<td>$T_{\text{KF}}$ (K)</td>
<td>235 (Ising)</td>
<td>232 (Ising)</td>
<td>246 (Ising)</td>
<td>198 (Ising)</td>
<td>252 (Ising)</td>
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<td>247 (Mean)</td>
<td>242 (Mean)</td>
<td>254 (Mean)</td>
<td>216 (Mean)</td>
<td>262 (Mean)</td>
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</table>
Table 3. According to the initial critical parameters of the model, the critical parameters $\beta$, $\gamma$, $\delta^{\exp}$ and the scalar theory $\delta$ obtained by using the KF, MAP. Initial model in parentheses. The $\delta^{\exp}$ of the first row of each sample is derived from the isothermal magnetization curve fit where the Curie temperature is located.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\delta^{\exp}$</th>
<th>$\delta$</th>
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<tr>
<td>Na-0</td>
<td>0.23726</td>
<td>1.23442</td>
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<td>MAP(Ising)</td>
<td>0.32642</td>
<td>1.26069</td>
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<td>KF(Ising)</td>
<td>0.40336</td>
<td>1.10458</td>
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<td>MAP(Mean)</td>
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<td>1.01404</td>
<td>2.98518</td>
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<td>Na-0.05</td>
<td>0.31872</td>
<td>1.2068</td>
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<td>4.78640</td>
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<td>MAP(Ising)</td>
<td>0.30873</td>
<td>1.22307</td>
<td>4.82374</td>
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<td>KF(Ising)</td>
<td>0.4527</td>
<td>1.0055</td>
<td>3.23269</td>
<td>3.22112</td>
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<td>3.43626</td>
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<td>MAP(Ising)</td>
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<td>3.61006</td>
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<td>KF(Ising)</td>
<td>0.32445</td>
<td>1.20184</td>
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<td>0.52331</td>
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<td>2.64900</td>
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<td>5.47441</td>
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<td>MAP(Hei)</td>
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<td>KF(Hei)</td>
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</table>

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Table 4. The maximum magnetic entropy change (-ΔSₘ) and the relative cooling power (RCP) at 1–5T.

<table>
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<tr>
<th>Samples</th>
<th>-ΔSₘ (J/kg K)</th>
<th>RCP (J/kg)</th>
</tr>
</thead>
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<td>1T</td>
<td>2T</td>
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<tr>
<td>Na-0</td>
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<td>1.63</td>
</tr>
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<td>1.71</td>
</tr>
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<tr>
<td>Na-0.2</td>
<td>0.84</td>
<td>1.56</td>
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