Magnetocaloric Effect in La$_{0.7}$Ca$_{0.25}$Ba$_{0.05}$MnO$_3$ Nanocrystals Exhibiting the Crossover of First- and Second-Order Magnetic Phase Transformation

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In this work, we present a detailed study on the magnetocaloric effect near the first-to-second-order magnetic phase transformation of La$_{0.7}$Ca$_{0.25}$Ba$_{0.05}$MnO$_3$ nanoparticles with averaged crystallite sizes $D = 39$–79 nm. The ferromagnetic-paramagnetic phase-transition region of the bulk sample (exhibiting the first-order nature) becomes more broadened in nanoparticles (exhibiting the second-order nature). Based on isothermal magnetization data, $M(H)$, we calculated magnetic entropy change versus temperature, $\Delta S_m(T)$, of the samples under magnetic-field changes $\Delta H = 0$–30 kOe. As a result, $\Delta S_m(T)$ reaches the maximum value $|\Delta S_{m\text{max}}|$ around $T_C = 258$–262 K. With $\Delta H = 30$ kOe, $|\Delta S_{m\text{max}}|$ values obtained from the samples are located in the range 4.38–5.63 J·kg$^{-1}$K$^{-1}$, corresponding to refrigerant-capacity values $RC = 138$–141 J·kg$^{-1}$. Field dependencies of $|\Delta S_{m\text{max}}|$ and $RC$ can be expressed by a power law, with $|\Delta S_{m\text{max}}| = aH^n$ and $RC = bH^N$. Interestingly, all the $\Delta S_m(T)$ curves of the samples undergoing the second-order phase transition at different applied fields are collapsed onto a universal curve, which is obtained by normalizing the $\Delta S_m(T,H)$ curves to their respective $\Delta S_{m\text{max}}$ value, and rescaling the temperature axis above and below $T_C$, where $T_C$ is the reference temperature. [doi:10.2320/matertrans.MA201546]

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1. Introduction

Magnetic refrigeration based on the magnetocaloric effect (MCE) opens up a great opportunity for developing a new generation of refrigeration technology. The MCE-base technology shows up some advantages of energy saving, low noise and environmentally friendly. Basically, the MCE is related to the magnetic entropy change ($\Delta S_m$) of a material under the application of magnetic field change. Among MCE materials, hole-doped manganites have been widely studied.1) Particularly, these manganites give numerous advantages, such as low-production cost, simple fabrication, easily tuneable $T_C$ (the Curie temperature), and high chemical stability. Additionally, these manganites exhibit MCE comparable with Gd. For example, a maximum magnetic entropy change ($|\Delta S_{m\text{max}}|$) of $\sim$5 J·kg$^{-1}$K$^{-1}$ at $\Delta H = 10$ kOe was observed for La$_{0.7}$Ca$_{0.3}$MnO$_3$,2) while the $|\Delta S_{m\text{max}}|$ value for Gd is about 2.8 J·kg$^{-1}$K$^{-1}$.3) However, La$_{0.7}$Ca$_{0.3}$MnO$_3$ bulk compound undergoes a first-order phase transition (FOPT). Consequently, its MCE only occurs in a narrow temperature range,2) limiting the hot and cold heat exchangers. Recent studies have revealed that materials with a second-order phase transition (SOPT) have a moderate $\Delta S_m$, but their $\Delta S_m$ value is quite stable over a wide temperature range. This character makes SOPT materials more useful for magnetic refrigeration applications. For La$_{0.7}$Ca$_{0.3}$MnO$_3$, modifying its FOPT to the SOPT is known as the rounding, which can be carried out by doping4,5) and reducing crystalline size6,7) or dimensionality in the system.8) Depending on dopant types, doping content, and crystalline size, rounding results would be different. Additionally, detailed analyses for $\Delta S_m(T,H)$ data would provide important information about magnetic properties of materials.9) To get a clear idea about the performance of materials used in magnetic refrigeration devices, it is necessary to understand how their MCE evolves in desired temperature and magnetic-field ranges.

This paper presents a detailed analysis of $\Delta S_m(T,H)$ data near the first-to-second order phase transformation of La$_{0.7}$Ca$_{0.25}$Ba$_{0.05}$MnO$_3$ (LCBMO) nanoparticles (NPs) with different crystallite sizes ($D$). We point out that field dependencies of $|\Delta S_{m\text{max}}|$ and $RC$ values can be described by power laws, with $|\Delta S_{m\text{max}}| = aH^n$ and $RC = bH^N$. Also, by normalizing the $\Delta S_m(T,H)$ curves to their respective $\Delta S_{m\text{max}}$ value, we indicate that all these curves of the samples are collapsed onto a universal curve.

2. Experimental Details

LCBMO NPs with different $D$ were prepared by the combination of solid-state reaction and mechanical milling. First, a polycrystalline LCBMO bulk sample with the FOMT was prepared by solid-state reaction; detailed descriptions can be found elsewhere.3) After that, the LCBMO bulk sample was ground in powder, and divided into parts of 2 g for the mechanical milling with milling times $t_m = 10, 20$ and 30 minutes, used the zirconia-grinding medium supplied by SPEX-SamplePrep. The ball-to-powder mass ratio was maintained at 4.7. Obtained NPs products were checked the crystal structure by using an X-ray diffractometer (SIEMENS-D5000). Magnetization measurements versus temperature ($T$) and magnetic field ($H$) were performed on a superconducting quantum interference device (SQUID).

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Table 1 The crystallite size (D), lattice strain (ε), Curie temperature (Tc) and magnetocaloric parameters of the LCBMO samples.

<table>
<thead>
<tr>
<th>t_m</th>
<th>D</th>
<th>ε</th>
<th>Tc</th>
<th>ΔS_m</th>
<th>RC</th>
<th>n</th>
<th>n(Tc)</th>
<th>N</th>
<th>N(Tc)</th>
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<td>262</td>
<td>5.63</td>
<td>141</td>
<td>0.57</td>
<td>0.54</td>
<td>1.12</td>
<td>1.17</td>
</tr>
<tr>
<td>20</td>
<td>57</td>
<td>4.2</td>
<td>260</td>
<td>4.93</td>
<td>138</td>
<td>0.59</td>
<td>0.58</td>
<td>1.23</td>
<td>1.25</td>
</tr>
<tr>
<td>30</td>
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<td>8.7</td>
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<td>4.38</td>
<td>140</td>
<td>0.59</td>
<td>0.58</td>
<td>1.25</td>
<td>1.26</td>
</tr>
</tbody>
</table>

3. Results and Discussion

The study of X-ray diffraction patterns indicated a single phase of LCBMO samples in an orthorhombic structure (space group Pnma). Using the Williamson-Hall (W-H) method,10 the average values of both D and lattice strain (ε) were obtained, as listed in Table 1. As a result, D values are about 79, 57 and 39 nm for t_m = 10, 20 and 30 min, respectively.

Figure 1(a) shows temperature dependences of magnetization, M(T), for NPs in the field H = 100 Oe. All the samples exhibit a ferromagnetic-paramagnetic (FM-PM) transition at the Curie temperature (Tc). Their Tc values determined from the minima of dM/dT versus T curves are about 262, 260, and 258 K for D = 79, 57, and 39 nm, respectively. These values are slightly lower than Tc obtained for the LCBMO bulk/as-prepared sample (~265 K).5 Clearly, the D reduction did not change the Tc significantly, but broadened the FM-PM phase transition region. The phase-transition width determined from the full-width-at-half maximum of the dM/dT versus T curve increases from 12 to 17 K with decreasing D from 79 to 39 nm, respectively.

To understand the magnetic nature of the samples, a series of isothermal magnetization curves, M(H), have been measured around the FM-PM transition. From M(H) data, we performed the Arrott plots (H/M versus M^2), as shown in Figs. 1(b)–(d). The bending of these curves to two opposite directions at low magnetic fields reveals the FM-PM separation. According to Banerjee’s criteria,11 if some H/M versus M^2 curves of a material show a negative slope, it exhibits the FOPT, while a positive slope corresponds to the SOPT. Comparing with these conditions reveals the FM-PM transitions of LCBMO NPs belonging to the SOPT, see Figs. 1(b)–(d). According to the mean-field theory for FM long-range order,12 the M^2 versus H/M isotherms give a set of straight lines passing through the coordinate origin in the vicinity of Tc. However, the lack of linearity suggests the existence of FM short-range order in the samples.

Based on M(H, T) data, we have also studied the MCE of the samples. According to the thermodynamic theory, ΔS_m produced by the variation of a magnetic field variation from 0 to H is expressed by13

\[ ΔS_m(T, H) = \int_0^H \frac{dM}{dT} dH. \]

Figures 2(a)–2(c) show −ΔS_m(T) curves of the samples under the applied magnetic field changes ΔH = 5–20 kOe (with step of 2.5 kOe) and ΔH = 20–30 kOe (with step of 5 kOe). For each sample at a given temperature, |ΔS_m| increase with increasing ΔH. As a function of temperature, |ΔS_m| reaches a maximum value around Tc. With ΔH = 30 kOe, |ΔS_m| values of the samples with D = 79, 57, and...
39 nm are 5.63, 4.93, and 4.38 J·kg\(^{-1}\)·K\(^{-1}\), respectively, as shown in Table 1. In general, |∆S\(_{\text{max}}\)| values obtained from our samples are higher than those reported on \(\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3}\), \(\text{La}_{0.05}\text{MnO}_{3}\), \(\text{La}_{0.65}\text{MnO}_{3}\), \(\text{La}_{0.65}\text{MnO}_{3}\), \(\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3}\), and \(\text{La}_{0.65}\text{MnO}_{3}\) compounds.\(^{[14-16]}\)

Recently, Franco and Conde\(^{[17]}\) introduced a new method to describe \(\theta\) and \(H\) dependences of magnetic entropy change for SOPT materials. According to this method, all \(\Delta S_m(T)\) curves measured at different \(\Delta H\) values will collapse into a universal curve when \(\Delta S_m(T)\) curves are normalized to their respective peak value (i.e., \(\Delta S_m(T) / \Delta S_{\text{max}}\)) and the temperature axis above and below \(T_C\) is rescaled as

\[
\theta = (T - T_C)/(T_C - T),
\]

where \(T_C\) is the reference temperature corresponding to a certain fraction \(f\) that fulfills \(\Delta S_m(T_C) / \Delta S_{\text{max}} = f\). The choice of \(f\) does not affect the actual construction of the universal curve. In this work, we identified \(T_C\) as the temperature of the maximum magnetic entropy change, and selected \(f = 0.6\) when constructing the universal curve for each sample. Figures 2(d)–2(f) show the universal curves for the LCBMO samples measured at different \(\Delta H\). For the sample with \(D = 79\) nm (Fig. 2(d)), a breakdown at temperatures \(\theta < -1\) of the universal behaviour for the normalized entropy change can be observed. It means that the \(\Delta S_m(T)\) data of this sample do not follow a universal curve for magnetic entropy change. Meanwhile, all the \(\Delta S_m(T)\) data for samples with \(D = 57\) and 39 nm are collapsed into a unique curve in the whole temperature range, see Figs. 2(e) and 2(f).

As mentioned above, all the LCBMO NPs undergo the SOPT because the \(H/M\) versus \(M^2\) curves exhibit positive slopes (Figs. 1(b)–(d)), whereas the LCBMO bulk sample undergoes a FOPT.\(^{[5]}\) In addition, Franco and Conde\(^{[17]}\) suggested that the overlap of all the \(\Delta S_m(T)\) curves into a unique curve is an additional confirmation of the general validity of the treatment in SOPT materials. From these reasons, clearly, the samples with \(D = 39–57\) nm are SOPT materials, while the sample with \(D = 79\) nm is located in between the FOPT and SOPT materials (i.e., the crossover of the first-to-second-order phase transformation). The suppression of FOMT, and the crossover of first and second order phase transition in manganite NPs were also observed and reported.\(^{[2,8]}\) In general, it has been accepted that the presence of quenched disorder forces fluctuation-driven first-order transitions to become continuous. This can be explained basing on the core-shell model.\(^{[7]}\) In case of NP systems, the core part can retain the intrinsic FOMT of the bulk compound, while the disordered shell part is more likely to undergo the SOMT, from the disordered state into the PM.\(^{[23]}\) The order parameter may diminish continuously at the shell part leading to divergence of the correlation lengths as in a second order material, and that the first order transition in the core part is masked by a second order transition at the disordered shell part.\(^{[6,8]}\) It means that there is a crystalline critical size \(D_{\text{crit}}\) for the establishment of the SOMT, which can be strongly influenced by the nature of the surface of NPs. The influence of surface effects on the nature of phase transition in NPs has been also invoked to explain the destabilization of the FOMT, detailed descriptions could be found elsewhere.\(^{[2,6–8]}\) In our case, the divergence of the \(\Delta S_m(T) / \Delta S_{\text{max}}\) versus \(\theta\) curves at \(\theta < -1\) for the \(D = 79\) nm sample indicates the magnetic inhomogeneity and coexistence of FOPT and SOPT properties. This means that there is a value of \(D_{\text{crit}}\) for the FOPT-SOPT transformation in LCBMO NPs. We suggest the \(D_{\text{crit}}\) value for these NPs to be about 79 nm. A similar result was also found for \(\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3}\) NPs with \(D_{\text{crit}} = 60–70\) nm.\(^{[18]}\)

For \(\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3}\) NPs prepared by the sol-gel method, the particle critical diameter \(d_{\text{crit}}\) has been also determined by SEM of \(d_{\text{crit}} = 60–95\) nm\(^{[19]}\) and \(d_{\text{crit}} = 160\) nm.\(^{[3]}\)

According to Franco and Conde,\(^{[17]}\) magnetic-field dependences of \(|\Delta S_{\text{max}}|\) and refrigerant capacity \((RC)\) in the SOPT materials can be expressed by the power laws \(|\Delta S_{\text{max}}| = a \cdot H^n\), and \(RC = b \cdot H^\delta\), respectively, where \(a\) and \(b\) are coefficients, \(n\) and \(N\) are the field exponents, respectively. Here, the \(RC\) is defined as \(RC = |\Delta S_{\text{max}}| \times \delta T_{\text{FHWM}}\), where \(\delta T_{\text{FHWM}}\) is the full-width-at-half maximum (FWHM) of the \(\Delta S_m(T)\) curve. Depending on \(D\), \(\delta T_{\text{FHWM}}\) is found to be \(25, 28,\) and \(32\) K, corresponding to the values \(RC = 141, 138,\) and \(140\) J·kg\(^{-1}\) for \(D = 79, 57,\) and 39 nm, respectively. One can see that with the reduction of \(D\), the value of \(|\Delta S_{\text{max}}|\) decreases significantly, while \(RC\) values are almost unchanged. This can be related to the compensation effect that broadens the phase-transition temperature range, which is likely attributed to a large size distribution in the samples.

Figures 3(a)–(c) shows magnetic-field dependences of \(n(T, H)\) and \(RC\) for LCBMO samples. The solid lines are fitting curves of the \(|\Delta S_{\text{max}}|\) and \(RC\) data to the power laws \(|\Delta S_{\text{max}}| = a \cdot H^n\), and \(RC = b \cdot H^\delta\), respectively. The field exponents determined for samples with \(D = 39–79\) nm are \(n = 0.57–0.59\) and \(N = 1.12–1.25\), as shown in Table 1. Alternatively, the field exponents can be also locally calculated through the following expression\(^{[17]}\)

\[
n(T, H) = \frac{d \ln |\Delta S_m(T, H)|}{d \ln H}
\]

where \(n(T, H)\) is the field exponent calculated from the \(\Delta S_m(T, H)\) data, \(n = 2\) for \(T \gg T_C\), \(n = 1\) for \(T \ll T_C\), and \(n\) has a minimum at \(T = T_C\).

\[
N = 1 + \frac{1}{\delta}
\]

Where \(\delta\) is the critical exponent associated with the critical isotherm\(^{[11]}\)

\[
M(T = T_C) = DH^{1/\delta}
\]

Figures 3(d)–(f) show temperature dependences of \(n\) calculated from eq. (3) based on \(\Delta S_m(T, H)\) data for \(\Delta H = 5–30\) kOe (with step of 5 kOe). One can see that \(n\) approaches to \(1\) in the FM phase at \(T \ll T_C\), and to \(2\) in the PM phase at \(T \gg T_C\). With \(\Delta H = 30\) kOe, the values of \(n\) at \(T = T_C\) [denoted as \(n(T_C)\)] are about 0.54–0.58 for samples with \(D = 39–79\) nm (Table 1). For the critical exponent \(\delta\), we can obtain its value by fitting the critical isotherm, \(M(H, T = T_C)\), to eq. (5). Thus, \(\delta\) values found are 5.93, 3.95, and 3.91 for \(D = 79, 57,\) and 39 nm, respectively. Therefore, the exponent \(N\) value obtained by using eq. (4) [denoted as \(N(T_C)\)] is 1.17, 1.25, and 1.26 for \(D = 79, 57,\) and 39 nm, respectively. Clearly, the \(n(T_C)\) and \(N(T_C)\) values are very close to those obtained by fitting to the power laws, see Table 1. This
Fig. 3 (a)–(c) Field dependences of $|\Delta S_{\text{max}}|$ and $RC$, and (d)–(f) temperature dependences of the field exponent $n$ obtained at different fields for the LCBMO samples, where (a) and (d); (b) and (e); (c) and (f) for $D = 79$, 57, 39 nm, respectively. Figure 3

reflects that the field exponents $n$, $N$, $n(T_C)$ and $N(T_C)$ determined as described above are reliable.

4. Conclusion

We have investigated the MCE near the first-to-second order phase transformation of LCBMO NPs with $D = 39–79$ nm. Experimental results indicated the broadening of the FM-PM phase transition region when $D$ decreases, making LCBMO compounds more useful for magnetic refrigeration applications. We pointed out that the overlap of all $\Delta S_{\text{eff}}(T)$ curves onto a unique master curve is an additional confirmation of the general validity of the treatment in the SOPT materials. Meanwhile, all the $\Delta S_{\text{eff}}(T)$ curves do not overlap at temperatures below $T_C$ indicating a first-to-second order phase transformation. Besides, the field dependences of magnetic entropy change were also investigated in detail.

Under an applied magnetic field change of 30 kOe, $|\Delta S_{\text{max}}|$ values are 5.63, 4.93, and 4.38 J·kg$^{-1}$·K$^{-1}$, corresponding to $RC = 141, 138,$ and 140 J·kg$^{-1}$, for $D = 79, 57$, and 39 nm, respectively. Interestingly, the $|\Delta S_{\text{max}}|$ and $RC$ values obtained obey to the power laws, $|\Delta S_{\text{max}}| = aH^n$ and $RC = bH^p$, respectively. Using the universal curve and the power laws, we could extrapolate the $|\Delta S_{\text{max}}|$ and $RC$ values of the SOPT materials at any temperature and magnetic field ranges for the FM-PM phase transition in order to assess their applicability in cooling devices.

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