

# Effect of Crystallite Size on the Thickness of Nonmagnetic Shell and Magnetic Properties of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$

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**Abstract**  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  compounds with the crystallite size of  $D = 45\text{--}200$  nm were synthesized by utilizing the solid-state reaction and mechanical ball milling methods. The reduction of the crystallite size ( $D$ ) resulted in the decrease of both  $T_C$  and magnetization, broadening of the phase transition region, and appearance of Griffiths phase features in the materials. The temperature dependence of saturation magnetization ( $M_S$ ), the variations of the coercivity ( $H_C$ ), and the deviation of magnetization from expected Bloch's law  $T^{3/2}$  for these samples were also investigated. Based on the core-shell model, the core diameter and the nonmagnetic shell thickness for the samples were determined.

**Keywords** Nanocrystals · Perovskite manganites · Magnetic properties · Core/shell-like structure

## 1 Introduction

Recently, the effect of crystallite size reduction on the physical properties of hole-doped manganites has attracted lots of interest of scientists for both fundamental and application aspects [1–5]. Owing to finite-size effect and inter-particle interactions, remarkable new phenomena were

observed in nano-materials [1]. The inter-particle interaction was found to be strongly modifying the magnetic response of nanoparticle systems; e.g., the dc susceptibility obeys the Curie-Weiss law rather than the Curie law at high temperatures. Moreover, the magnetic behavior of the particle surface differs from that of the core [2, 3]. Higher magnetic disorder that is usually present in the surface layer is known as a dead magnetic layer. Before one investigates the magnetic behavior of manganites in nanoscales, one has to prepare nanomaterials through a variety of synthesis methods. However, almost authors have used the bottom-up approach (e.g., sol-gel, mechanochemical milling, interactive milling, or sputtering methods) to prepare nanostructured samples. In this work, instead, we have used a simple preparative method that is the top-down approach to prepare nano-polycrystalline  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  (LCMO) samples and have investigated their magnetic properties.

## 2 Experiment

First, LCMO ceramic samples were prepared by conventional solid-state reaction. High-purity powders  $\text{La}_2\text{O}_3$ ,  $\text{CaCO}_3$ , and Mn were used as starting materials. These powders were ground and mixed well, and then heated in air at  $1,200^\circ\text{C}$  for 24 h. After heating, the obtained powder was re-ground, pressed into pellets, and sintered at  $1,400^\circ\text{C}$  for 24 h in air. These pellets were then used for mechanical ball milling (by using a Spex 8000D system) with the mass ratio of ball/powder = 4.1/1. The milling time ( $t_m$ ) was varied from 0 to 30 min (denoted as LC0, LC10, LC20, and LC30 for  $t_m = 0, 10, 20,$  and 30 min, respectively). Their structure was checked by using an X-ray diffractometer (Siemens D5000, with  $\lambda = 1.5406 \text{ \AA}$ ). The surface morphology of samples has been observed by

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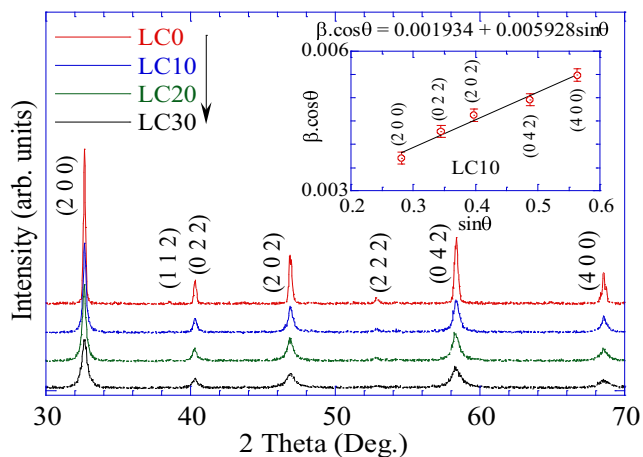
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scanning electron microscopy (SEM). The  $M(T)$  and  $M(H)$  curves were measured via a SQUID magnetometer.

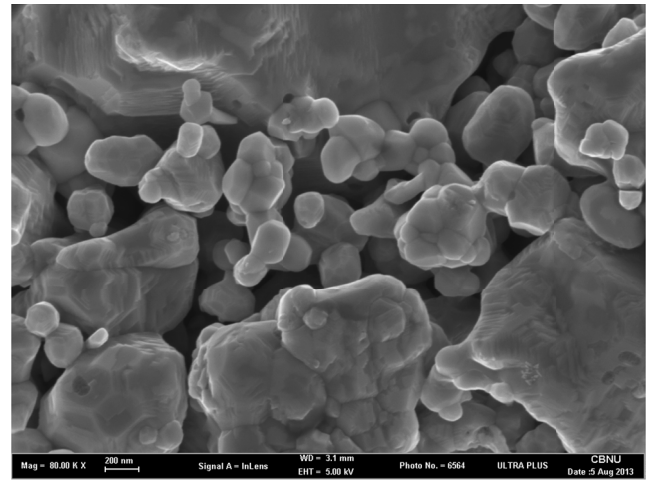
### 3 Results and Discussions

Figure 1 shows the X-ray diffraction (XRD) patterns for the LCMO samples with various  $t_m$  values. Our detailed analyses, i.e., identifying the Miller-indexed peaks, reveal that they are single phase in an orthorhombic structure, with the lattice parameters  $a \approx 5.48 \text{ \AA}$ ,  $b \approx 7.75 \text{ \AA}$ , and  $c \approx 5.46 \text{ \AA}$ . The lattice parameters were almost independent of  $t_m$ . Using the Williamson-Hall (W-H) method [6], the average values of both the crystallite size ( $D$ ) and strain ( $\varepsilon$ ) parameters could be obtained from the relation  $\beta \cos \theta = (K\lambda / D) + 2\varepsilon \sin \theta$  where  $\beta$  is the full width at a half maximum of an XRD peak,  $\theta$  is the Bragg angle, and  $K = 0.9$  is the shape factor. The W-H analysis for LC10 is representatively shown in the inset of Fig. 1. The crystallite size obtained for  $t_m = 0, 10, 20,$  and  $30$  min are  $D = 200, 72, 54,$  and  $45$  nm, and  $\varepsilon = 0.002, 0.003, 0.003,$  and  $0.010$ , respectively. Notably,  $D = 200$  nm is herein an estimated value for the as-prepared sample ( $t_m = 0$ ), and its real value can be larger because the W-H method is more accurate for the size of nanoparticles smaller than  $100$  nm. Figure 2 shows the SEM image for a representatively sample, LC10. In comparison with the SEM image, the  $D$  values deduced from W-H method are in good agreement.

Figure 3a shows the temperature dependence of field-cooled (FC) and zero-field-cooled (ZFC) magnetizations of the samples in the field of  $H = 100$  Oe. The  $T_C$  values determined from the minima of the  $dM/dT$  vs.  $T$  curves are  $252, 252, 248,$  and  $246$  K for  $D = 200, 72, 54,$  and  $45$  nm, respectively. Here, the reduction in  $D$  did not change the  $T_C$  significantly, but it broadened the phase transition region.

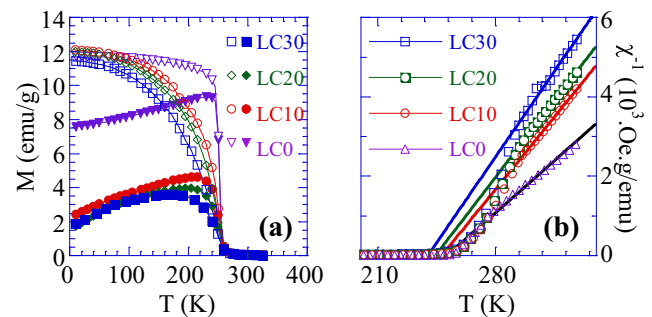


**Fig. 1** XRD patterns for LCMO samples. The inset shows a detailed W-H analysis for the LC10 sample



**Fig. 2** SEM image for LC10 sample

The width of the FM-PM phase transition ( $\Delta T_C$ ) determined from the full width at half maximum of the  $dM/dT$  vs.  $T$  curve increases from  $6$  to  $34$  K with decreasing  $D$  from  $200$  to  $45$  nm. In Fig. 3b, we showed the  $\chi^{-1}(T)$  curves deduced from  $M_{ZFC}(T)$  data. One can see that in the high-temperature region,  $\chi^{-1}$  varies almost linearly with temperature following the Curie-Weiss law [7],  $\chi(T) = C/(T - \theta)$ , where  $C$  is the Curie constant, and  $\theta$  is the ordering temperature. Here,  $\theta$  decreases gradually in the temperature range of  $251$ – $240$  K with decreasing  $D$ . This confirms that the strength of FM interaction decreases in LCMO nanoparticles with a smaller crystallite size. Notably,  $\chi^{-1}(T)$  data at high-temperature regions obey the Curie-Weiss law well for LC0 sample with  $D = 200$  nm, whereas for samples with smaller crystallite sizes ( $D = 72, 54,$  and  $45$  nm), the Curie-Weiss law is not satisfied in the full PM temperature range. That is because there are obviously sharp downturns in  $\chi^{-1}(T)$  curves well above  $T_C$ , which is the characteristic of the Griffiths singularity [8]. It means that the Griffiths phase exists in LCMO nanoparticles. This could be explained by higher degree of disorder in nanoparticle

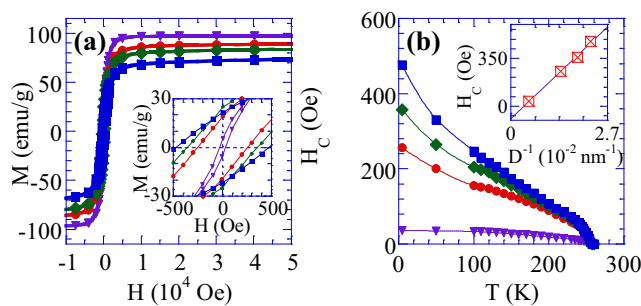


**Fig. 3** a ZFC (solid symbols) and FC (open symbols)  $M(T)$  curves with  $H = 100$  Oe. b  $\chi^{-1}(T)$  data fitted to the Curie-Weiss law (solid lines)

samples than that in as-prepared sample (LC0). According to Salamon et al. [8], the disorder due to the bending of Mn-O-Mn bond induces the formation of Griffiths phase in the  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  system.

Figure 4a shows hysteresis loops of  $M(H)$  curves measured at 5 K. One can see that the magnetization value was reduced in the smaller LCMO nanoparticles. This reduction is related to the nonmagnetic layer or spin disorder on the surface; its thickness increases with decreasing  $D$ . The coercivity ( $H_C$ ) value substantially increases when the crystallite size decreases see the inset in Fig. 4a. A monotonic decrease of  $H_C$  with increasing temperature in the range of 5–240 K becomes more rapid when temperature increases above 240 K see Fig. 4b. This is associated with the FM-PM phase transition, where magnetic moments located within FM domains/clusters become disordered due to thermal agitation. At temperatures above  $T_C$ , the value of  $H_C$  is thus almost 0, in good agreement with the above  $M(T)$  analyses. Interestingly, the  $H_C$  observed below  $T_C$  increases with decreasing  $D$ . The  $H_C$  at 5 K as a function of the surface/volume ratio ( $D^{-1}$ ) is shown in the inset of Fig. 4b. In general, when  $D$  is reduced,  $H_C$  increases and reaches a maximum value at some critical diameter ( $D_{cr}$ ) of the single domain state, and then, it decreases with further decrease in the crystallite size [7]. The solid line in the inset of Fig. 4b is a fit of our experimental  $H_C$  data to the function  $H_C = m + n/D$ , where  $m$  and  $n$  are constants [7]. This indicates that our LCMO systems are close to a multidomain structure [9]. It means that the  $D$  values are larger than  $D_{cr}$  values of the single domain state, which makes the anisotropy energy smaller. Hence, the  $H_C$  value decreases monotonically with increasing  $D$  as shown in the inset of Fig. 4b.

We have also determined the saturation magnetization ( $M_S$ ) for the samples at different temperatures. From  $M^2(H)$  curves, the linear extrapolation from high fields to the intercepts with the  $M^2$ -axis gives the values of

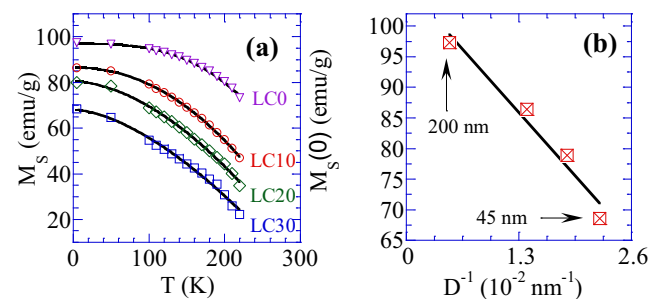


**Fig. 4** **a**  $M$  vs.  $H$  measured at 5 K. The inset shows the zoom-in view of the region between  $H = -500$  and  $500$  Oe. **b**  $H_C$  as a function of  $T$ . The inset shows  $D^{-1}$  dependence of  $H_C$  at 5 K. Here, triangles, circles, diamonds, and squares indicate LC0, LC10, LC20, and LC30 samples, respectively

$M_S^2(T, 0)$ . The obtained  $M_S(T)$  data are plotted in Fig. 5a. A power law form of  $M_S(T) = M_S(0)[1 - BT^\epsilon]$  [7] is used to fit the data with  $M_S(0) = 97.0, 86.4, 78.9,$  and  $68.6$  emu/g,  $B = 1.46 \times 10^{-6}, 4.05 \times 10^{-4}, 3.17 \times 10^{-3},$  and  $7.30 \times 10^{-3} \text{ K}^{-\epsilon}$ ; and  $\epsilon = 3.07, 2.13, 1.77,$  and  $1.61$  for  $D = 200, 72, 54,$  and  $45$  nm, respectively. One can see that the temperature dependence of the magnetization do not follow Bloch’s law, but obeys a  $T^\epsilon$  law with  $\epsilon$  increasing from 1.61 to 3.07 when  $D$  increases from 45 to 200 nm (see the solid lines in Fig. 5a). The variation tendency of the exponent  $\epsilon$  for our samples is quite similar to a previous report [10]. Additionally, the  $M_S(0)$  value obtained is smaller than that of the LCMO bulk single crystal ( $M_S(0) = 97.5$  emu/g) [11]. The  $M_S(0)$  values for the samples are reduced linearly with  $D^{-1}$  (see Fig. 5b). This result is consistent with that reported by Lopez-Quintela et al. [12], confirming that the magnetization is actually influenced by the particle surface. We used a model of the core-shell structure [13] to determine the core diameter ( $d_C$ ) for magnetic particles in the samples. The LCMO particles are assumed to have a spherical shape, and each of them is composed of an ideal single-crystalline core with the saturation magnetization of the core,  $M_C = 97.5$  emu/g [11], and the density of  $\rho_C = 5.9 \text{ g/cm}^3$  [14]. For a particle of radius  $r$ , consisting of a core surrounded by a shell of thickness  $d_{\text{shell}} \ll r$  (with the corresponding  $\rho_S$  value roughly assigned to be  $4 \text{ g/cm}^3$  [3]), the core diameter ( $d_C$ ) can be found from [13]

$$d_C = D \cdot \left[ \frac{\rho_S/\rho_C}{\rho_S/\rho_C + (M_C - M_S)/(M_S - M_{\text{Shell}})} \right]^{\frac{1}{3}} \quad (1)$$

By using (1), while assuming a nonmagnetic shell ( $M_{\text{Shell}} = 0$ ), the  $d_C$  values obtained are 199.5, 67.9, 48.9, and 38.3 nm for  $D = 200, 72, 54,$  and  $45$  nm, respectively. Clearly, the nonmagnetic shell thickness, which can be estimated by  $d_{\text{shell}} = (D - d_C)/2$ , increases from 0.25 to 3.35 nm with decreasing  $D$ . The increase in  $d_{\text{shell}}$  and decrease in  $D$  (or the increase in  $D^{-1}$ ) are the main reason for the reduction in the strength of FM inter-particle



**Fig. 5** **a**  $M_S$  vs.  $T$  for the samples (symbols) is fitted to a power law  $T^\epsilon$  (solid lines). **b**  $D^{-1}$  dependence of  $M_S(0)$

interactions and in the  $M_S$  for LCMO nanoparticles, as mentioned above.

#### 4 Conclusion

The analyses of the magnetic properties were performed for LCMO nanoparticles with the crystallite size of  $D = 45$ – $200$  nm. Based on  $\chi^{-1}(T)$  curves, the existence of Griffiths phase in LCMO nanoparticles was observed, which implied the higher degree of disorder in nanoparticle samples. The results show that the  $D$  values of our LCMO samples are larger than the  $D_{cr}$  of the single domain state. Therefore,  $H_C$  value increases monotonically with decreasing  $D$ . Also, the temperature dependence of magnetization in this case obeys a power law  $T^\varepsilon$ , with  $\varepsilon > 3/2$ . The reduction in  $M_S$  vs.  $D$  is mainly due to the formation of a nonmagnetic surface shell surrounding the nanoparticles, which increases from  $0.25$  to  $3.35$  nm when  $D$  is decreased from  $200$  to  $45$  nm.

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