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Size effect on the structural, magnetic, and magnetotransport properties of electron doped manganite $La_{0.15}Ca_{0.85}MnO_3$

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Nanocrystalline $La_{0.15}Ca_{0.85}MnO_3$ samples of various grain sizes ranging from ~17 to 42 nm have been prepared by sol-gel technique. Phase purity and composition were verified by room temperature x-ray diffraction and SEM-EDAX analysis. The bulk $La_{0.15}Ca_{0.85}MnO_3$ is known to order antiferromagnetically around 170 K and to undergo a simultaneous crystal structural transition. DC magnetization measurements on 17 nm size $La_{0.15}Ca_{0.85}MnO_3$ show a peak at ~130 K (T_N) in zero-field-cooled (ZFC) state. Field-cooled magnetization bifurcates from ZFC data around 200 K hinting a weak ferromagnetic component near room temperature due to surface moments of the nanoparticle sample. Low temperature powder neutron diffraction experiments reveal that the incomplete structural transition from room temperature orthorhombic to low temperature orthorhombic-monoclinic state also occurs in the nanoparticle sample as in the bulk. Magnetization in the ordered state decreases as particle size increases, thus indicating the reduction of the competing ferromagnetic surface moments. *© 2012 American Institute of Physics*. [doi:10.1063/1.3680246]

INTRODUCTION

There is a great deal of interest in understanding the rich fundamental properties of colossal magnetoresistance manganites as a function of grain size. In fact, systematic studies have been performed on hole-doped $R_{1-x}A_xMnO_3$ type oxides (where R = rare earth, A = divalent cation such as Ca, Sr), whereas low and electron-doped systems are not explored in detail. Recent work on an electron-doped system namely $La_{0.15}Ca_{0.85}MnO_3$ reveals an occurrence of incomplete crystal structural transition from orthorhombic (*Pnma*) to a mixed orthorhombic-monoclinic ($P2_1/m$) state at ~170 K concomitant with a paramagnetic to antiferromagnetic (AFM) phase transition. Magnetic structure of this compound further undergoes a change from G-type to C-type at ~100 K.[1,2] Neutron diffraction data indicate a competitive coexistence of antiferromagnetic and ferromagnetic interactions in the structurally phase separated state. In the present work, we attempt to understand the grain size dependent physical properties of this electron doped manganite $La_{0.15}Ca_{0.85}MnO_3$.

EXPERIMENTAL DETAILS

Nanocrystalline $La_{0.15}Ca_{0.85}MnO_3$ samples of various grain sizes ranging from ~17 to 42 nm have been prepared by sol-gel technique. The samples were sintered at a few selected temperatures for a period of 6 h. Phase purity and composition were verified by room temperature x-ray diffraction (XRD) and SEM-EDAX analysis. dc and ac magnetization measurements were carried out using commercial a vibrating sample magnetometer (Lakeshore Cryotronics, USA), SQUID magnetometer (Quantum Design, USA), and physical property measurement system (PPMS, Quantum Design) in different applied fields. Powder neutron diffraction (ND) experiments were carried out on $La_{0.15}Ca_{0.85}MnO_3$ nanoparticles of 17 nm size at a few selected temperatures between 300 K and 10 K (incident neutron wavelength 1.478961 Å, MURR, USA) to track its crystal structure and also to understand its magnetic structure. Both magnetic and crystal structures were analyzed using the FULLPROF program based on the Rietveld method.[3]

RESULTS AND DISCUSSION

Room temperature x-ray diffraction patterns revealed single phase nature of the $La_{0.15}Ca_{0.85}MnO_3$ nanoparticle samples (Fig. 1). The average crystallite size has been evaluated from the full-width at half maximum (FWHM) of the XRD peaks. The crystallite size is found to vary from 17 nm to 42 nm as the sintering temperature increases from 700 °C to 1000 °C (Table I). The crystallite size calculated from powder x-ray diffraction data, using the Scherrer formula

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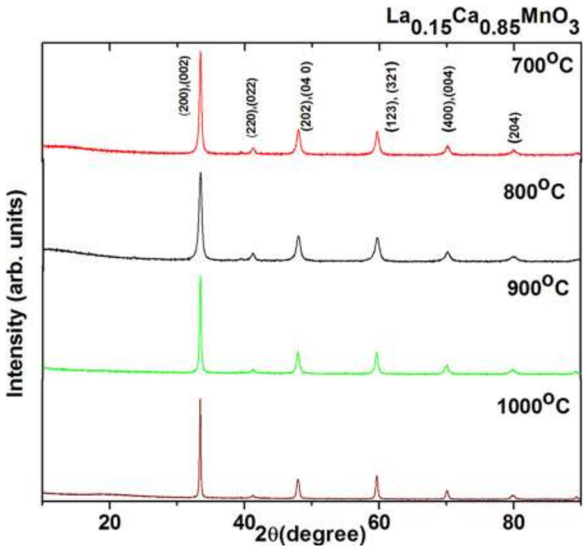

FIG. 1. (Color online) Powder x-ray diffraction pattern of $La_{0.15}Ca_{0.85}MnO_3$ samples sintered at various temperatures

could have a maximum error up to 50%.[4] The samples annealed at 700 °C and 800 °C have been characterized using high resolution transmission electron microscope (HRTEM) (Figs. 2(a) and 2(c)). The HRTEM data reveal agglomerated and elongated nature of the nanoparticles. The selected area electron diffraction (SAED) images show lattice fringes confirming the single crystalline nature of these samples (Figs. 2(b) and 2(d)).

DC magnetization measurements on the $La_{0.15}Ca_{0.85}MnO_3$ sample annealed at 700 °C show a peak at ~130 K (T_N) in zero-field-cooled (ZFC) state (Fig. 3(a)). Field-cooled (FC) magnetization data bifurcates from ZFC data around 200 K with a hint of a weak ferromagnetic component near room temperature that could be attributed to surface moments of the nanoparticle samples. This ferromagnetic component due to surface magnetization was reported around 200 K also for the antiferromagnetic $La_{0.2}Ca_{0.8}MnO_3$ particles of size 15 to 37 nm.[5] The paramagnetic susceptibility follows Curie–Weiss law. The magnetization versus field measured at 5 K in fields up to 9 T depict a low field hysteresis superimposed on a linear increase of magnetization as a function of field indicating the competitive presence of antiferromagnetic and ferromagnetic interactions (Fig. 3(b)). However, a shift is not observed in the field-cooled curve in these samples, although exchange bias effect has been seen in nanocrystalline $La_{0.2}Ca_{0.8}MnO_3$ and $CaMnO_{3-\delta}$ particles.[5,6] Similar behavior has been observed for the sample annealed at 1000 °C with average crystallite

TABLE I. Crystallite size variation of $La_{0.15}Ca_{0.85}MnO_3$ with respect to sintering temperature, calculated from x-ray diffraction data using Scherrer formula.

Sintering temperature (in °C)	Crystallite size (nm)
700	17
800	24
900	30
1000	42

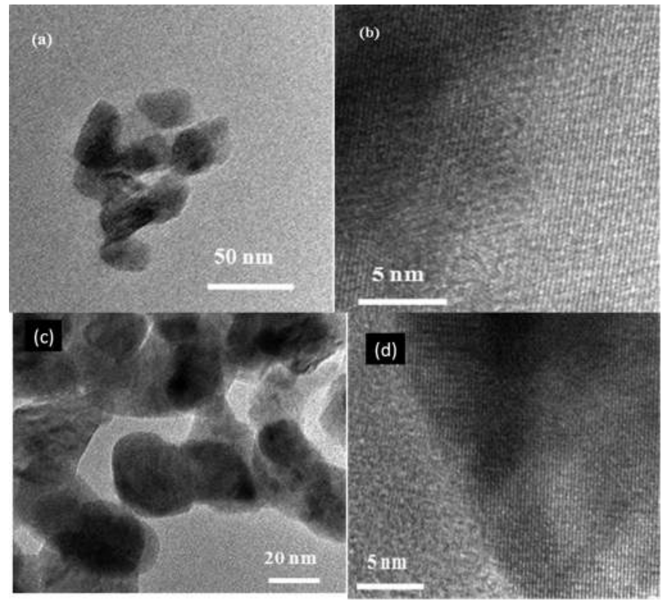

FIG. 2. (a) and (b) High resolution transmission electron microscope (HRTEM) and (c) and (d) selected area electron diffraction (SAED) images of $La_{0.15}Ca_{0.85}MnO_3$ samples sintered at 700 °C and 800 °C

size of ~42 nm (Fig. 3(c)). The cusp in the ZFC magnetization approaches that of the bulk sample. However, the overall magnetization value at 5 K, in the magnetically ordered state, is reduced (Fig. 3(d)). This could be understood as the decrease in the ferromagnetic component with increasing grain size due to the lower number of surface moments.

AC magnetic susceptibility of this compound shows a peak at T_N that shifts to higher temperatures with increasing frequency of the applied ac field indicating glassy behavior (figure not shown). This could have resulted from the competing antiferromagnetic and ferromagnetic interactions in the system. Electrical resistivity measurements on $La_{0.15}Ca_{0.85}MnO_3$ show insulating behavior for the sample as it is cooled through the magnetic transition and a maximum magnetoresistance of about 28% in 9 T is observed in the magnetically ordered state (figure not shown).

Powder neutron diffraction (ND) experiments (incident neutron wavelength 1.478961 Å, MURR, USA) have been carried out on the 17 nm size sample to verify whether the crystal structure change occurs in nanocrystalline form as in bulk. ND data acquired at selected temperatures between 300 K and 10 K reveal that indeed the incomplete structural transition from paramagnetic orthorhombic state to a low temperature orthorhombic-monoclinic state occurs in the nanoparticle sample. The lattice parameter variation as a function of temperature, obtained from ND data is plotted in Fig. 4. Thus the intrinsic structural phase separation in the magnetically ordered state of this system seems to be robust and could not be removed by particle size reduction.

The magnetic entropy change near T_N is calculated from the field dependent magnetization data, and a weak, inverse magnetocaloric effect is observed signifying the antiferromagnetically ordered state (figure not shown). This observation is in agreement with the recent report on the magnetocaloric properties of nanocrystalline $La_{0.125}Ca_{0.875}MnO_3$ of particle

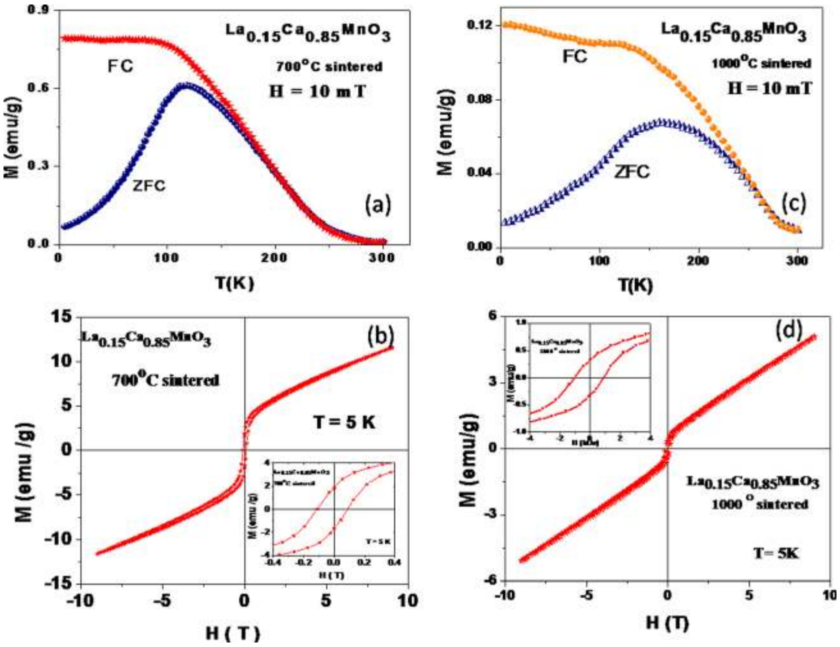

FIG. 3. (Color online) (a) to (d) Magnetization vs temperature obtained in zero-field-cooled (ZFC) and field-cooled (FC) conditions and Magnetization vs field at 5 K for the $La_{0.15}Ca_{0.85}MnO_3$ samples sintered at 700 °C and 1000 °C.

sizes between 60 nm to 70 nm.[7] Earlier reports on bulk and nanocrystalline $La_{0.2}Ca_{0.8}MnO_3$ system revealed monotonous increase of weak ferromagnetism with reduction in particle size and also the coexisting magnetic interactions and hence the glassy nature.[5] Similar behavior is observed in the present composition although it is in the cross-over region of the structure-magnetic phase diagram. In addition the nanocrystalline $La_{0.15}Ca_{0.85}MnO_3$ system retains the incomplete structural phase transition as in the bulk.

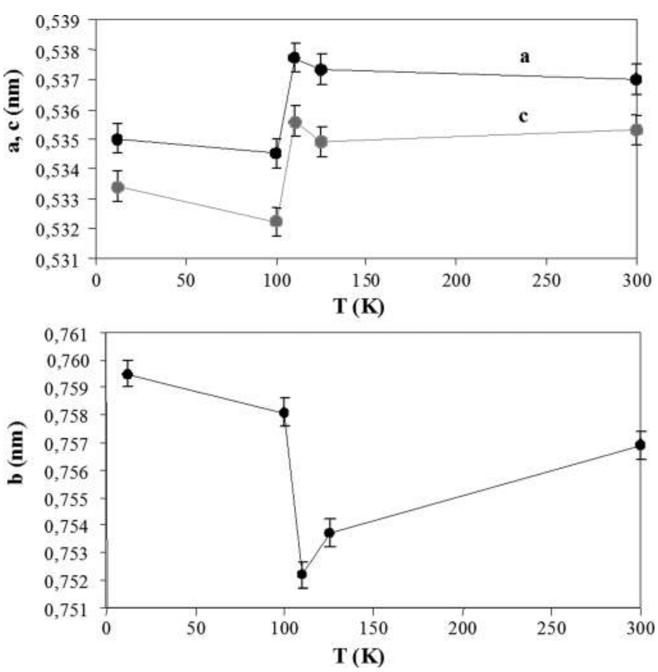

FIG. 4. Lattice parameter variation as a function of temperature as obtained from powder neutron diffraction data for the 700 °C sintered $La_{0.15}Ca_{0.85}MnO_3$.

CONCLUSIONS

Nanocrystalline electron doped manganites $La_{0.15}Ca_{0.85}MnO_3$ of 17 nm size have been extensively studied for their structural and magnetic properties. The nanoparticle samples retain the room temperature crystal structure of the bulk. These undergo antiferromagnetic transition as the bulk and show evidence for surface moments. Neutron diffraction data on the 17 nm size nanoparticle sample confirms the occurrence of incomplete crystal structural transition through the magnetic transition temperature as the bulk sample.

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