

Fabrication of ordered array of nanowires of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ($x=0.33$) in alumina templates with enhanced ferromagnetic transition temperature

K. Shantha Shankar, Sohini Kar, and A. K. Raychaudhuri^{a)}
Department of Physics, Indian Institute of Science, Bangalore-12, India

G. N. Subbanna^{b)}
Materials Research Centre, Indian Institute of Science, Bangalore-12, India

We report fabrication of array of crystalline nanowires (average diameter of 65 nm) of colossal magnetoresistive oxide $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO, $x=0.33$) within anodized alumina templates by filling the pores with a sol that allows formation of LCMO phase at the relatively low temperature of 600 °C. The crystalline nanowires with correct stoichiometry stabilize in the orthorhombic phase at room temperature. The nanowires are ferromagnetic at room temperature and exhibit enhanced ferromagnetic transition temperature well in excess of 300 K, which is substantially higher than that of single crystalline LCMO. This enhancement we attribute to the size induced lattice contraction in the nanowires.

Synthesis of one-dimensional nanomaterials with exotic functional properties is a field of intense activity. In addition to the well-known example of carbon nanotubes, nanowires of a number of functional materials such as GaN, GaP, TiO_2 , BaTiO_3 , and ZnO have been synthesized.^{1–3} One of the important motivations in synthesizing nanowires is the distinctive physical and chemical properties that are different from those of conventional bulk materials. In this letter, we report the fabrication of arrays of nanowires of colossal magnetoresistive oxides like lanthanum calcium manganese oxide ($\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$) (LCMO), using porous alumina templates. The nanowires (approximate diameter 60–70 nm) were found to be crystalline and most interestingly they have a ferromagnetic Curie temperature that is significantly enhanced ($T_C \approx 315$ K) compared to that of even bulk single crystal ($T_C \approx 235$ –260 K).

Rare-earth manganites of Perovskite structure with the general formula $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (where R and A are rare and alkaline earth ions, respectively) have attracted considerable attention because of their unusual magnetic and electronic properties.^{4,5} The main attraction of these materials is the large change in their electrical resistance on application of a magnetic field. An extremely important criterion for the selection of these materials for application in magnetoelectronic devices is the ferromagnetic transition temperature T_C , as magnetoresistance is prominent near T_C . Manganites with T_C close to or in excess of 300 K are most desirable for applications in devices operating at room temperature. Thus the fabrication of nanowires of LCMO with a transition temperature >300 K is an important achievement. These oxides have been prepared in various physical forms like single crystals, polycrystalline pellets, epitaxial and polycrystalline films and nanopowders. However, there are very few reports

on the nanowire preparation of these materials.⁶

The nanowires were synthesized by template aided sol-gel route^{7,8} using anodic aluminum oxide (AAO) with pores of nominal size of 100 nm and average pore density $10^9/\text{cm}^2$ as templates. We have used a sol-gel based polymer precursor route that yields highly homogeneous and stoichiometric complex oxides at moderate temperatures.^{9,10} It is also possible to control the viscosity and stability of the sol easily in polymer precursor route, which are crucial for template aided synthesis. We have synthesized nanowires using templates with diameter of 20 and 100 nm with varying chemical compositions in both Ca and Sr substituted lanthanum manganites. However, to be specific in this report we discuss the results obtained on a particular composition, namely $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO, $x=0.33$).

The sol used in the fabrication of LCMO nanowires was prepared by dissolving stoichiometric ratio of lanthanum, calcium, and manganese nitrates in required amount of water. Ethylene glycol of nearly equal volume was added and heated on a hot plate until a sol of desired viscosity forms (≈ 1 Pa s). The AAO membranes were dipped in the sol for 30–60 min and then subsequently heated to higher temperatures, after cleaning the surfaces. Heating the membranes at 600 °C was sufficient to get the desired phase.

The LCMO nanowires thus prepared were studied for structural and magnetic properties. Scanning electron microscopy was done along the cross section and compared with that of the bulk. It was evident that the pores of the membrane were almost completely filled to form uniform nanowires. Energy dispersive x-ray analysis was done to confirm the formation of nanowires of desired composition. These nanowires could not be checked for oxygen stoichiometry, however we predict that they are oxygen stoichiometric, as the nanopowders prepared starting from the same sol and prepared under similar conditions were found to be oxygen stoichiometric by redox titration analysis.¹¹

Transmission electron micrograph of an individual

^{a)} Author to whom correspondence should be addressed; electronic mail: arup@physics.iisc.ernet.in

^{b)} Deceased.

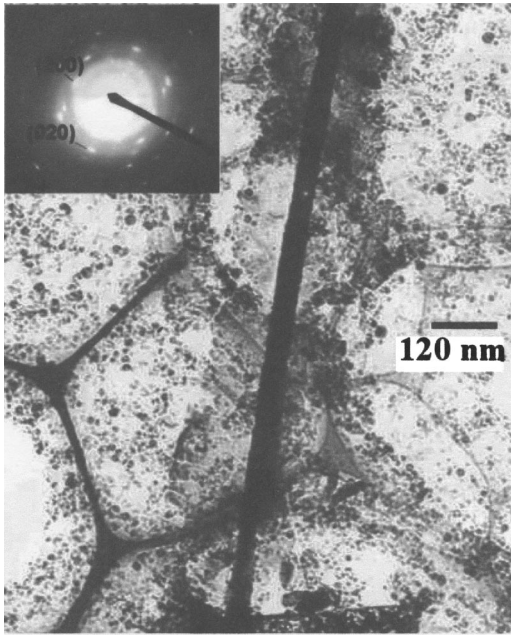


FIG. 1. Transmission electron microscopy image on a LCMO nanowire freed from the template and the inset shows the SAED image recorded on the nanowire.

LCMO nanowire removed from the supporting template is shown in Fig. 1. Most of the nanowires are around 60–70 nm in diameter and tens of microns in length. This shrinkage is expected as the nanowires are prepared by heat treating the sol-filled membranes. We have carried out detailed selected area electron diffraction (SAED) studies on the nanowires and found that they crystallize in the orthorhombic structure [consistent with the x-ray diffraction (XRD) results]. The rings corresponding to (002) and (020) planes are marked in the SAED image shown in the inset.

XRD data were recorded on the nanowires freed from the membrane by dissolving in dilute NaOH [shown in Fig. 2(a)]. In the same graph we show the XRD pattern of a conventional LCMO ($x=0.33$) sample prepared by solid state reaction routes [Fig. 2(c)]. The pattern for the nanowire could be indexed to an orthorhombic cell with lattice param-

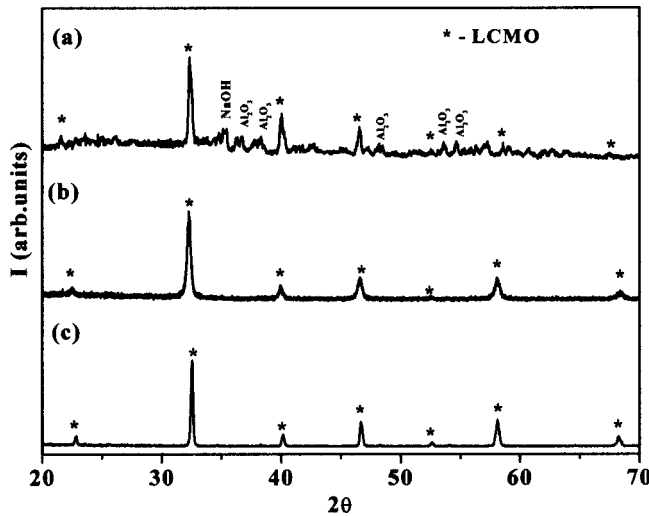


FIG. 2. XRD pattern of (a) LCMO nanowire, (b) LCMO nanopowder (average particle size of 30 nm), and (c) microcrystalline powder prepared by conventional solid state reaction.

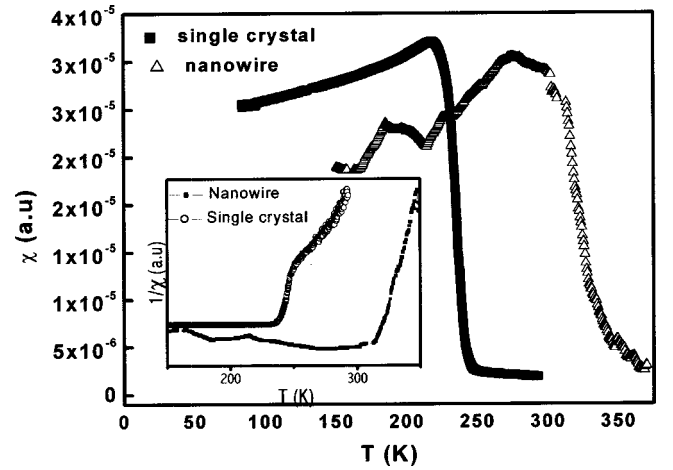


FIG. 3. Plot of magnetic susceptibility vs temperature of LCMO nanowires and bulk single crystal. Inset gives the Curie–Weiss plot.

eters of $a=5.435(0.04)$ Å, $b=7.699(0.03)$ Å, and $c=5.450(0.09)$ Å and $V=228$ Å³, unit cell anisotropy defined as $\delta \equiv (b/(a^2+c^2)^{0.5}) - 1$ is equal to 0.00027 ($\delta=0$ for cubic cell). The lattice parameters and the unit cell anisotropy parameter are smaller compared to those of bulk microcrystalline powder [$a=5.4687(0.002)$ Å, $b=7.775(0.001)$ Å, and $c=5.484(0.0019)$ Å, with the cell volume of 233.18 Å³ and $\delta=0.00391$.] Such lattice volume contraction on particle size reduction is reported on other nanomaterials.¹² In nanocrystalline LCMO with particle size of 30 nm [XRD data given in Fig. 2(b)], prepared by sol-gel method, we find similar lattice contraction and reduction in δ .¹¹ Compared to the nanopowders, the δ has reduced further in nanowires implying that the structure of the nanowire sample is more symmetric.

Figure 3 shows the plot of magnetic susceptibility versus temperature of the nanowire sample freed from the membrane along with that of a single crystal of LCMO (of same composition) prepared by float zone technique. The inset shows the Curie–Weiss plot. The ferromagnetic-paramagnetic transition is at 315 K for the nanowire sample and is 235 K for the single crystalline sample. The substantial shift in T_C to higher temperatures (by ~ 80 K), in the nanowire samples, is definitely the most noteworthy effect of size reduction.

In view of the enhancement of T_C in both the nanowires and nanocrystalline powders¹¹ of LCMO, we would like to conclude that this is a general consequence of the size reduction. We propose that the T_C enhancement arises mainly from the hardening of the Jahn–Teller (JT) phonon mode Ω_{ph} as the size is reduced. This is the stretching mode of the MnO₆ octahedra and in LCMO ($x=0.33$) $\Omega_{ph} \approx 78$ meV. In the presence of the JT distortion, $T_C \approx \Delta \exp(-\gamma E_{JT}/\Omega_{ph})$,¹³ where Δ = bandwidth (2 eV), γ = dimensionless coupling constant (0.3–0.4), E_{JT} = JT energy (1 eV). The numbers in brackets are the values for a typical manganite like LCMO ($x=0.33$) with $T_C \sim 250$ –300 K. Ω_{ph} increases with application of pressure¹⁴ and has a mode Gruniesen parameter $\Gamma \equiv -\partial\Omega_{ph}/\partial V \approx 2$. The cause of T_C enhancement on size reduction can thus be traced to the sensitivity of the phonon mode Ω_{ph} . Taking the reduction in cell volume of nearly 2.6% (in the nanowire sample) and $\Gamma \approx 2$, we get

$\delta\Omega_{\text{ph}}/\Omega_{\text{ph}} \approx 5.2\%$ and $\delta T_C \approx 60$ K assuming that other parameters remain unchanged. ($\delta T_C \approx 80$ K needs only a $\delta\Omega_{\text{ph}}/\Omega_{\text{ph}} \approx 6.5\%$). An additional enhancement $\delta T_C \approx 10\text{--}15$ K is expected from a 5% increase in Δ which arises due to the decrease in both the unit cell anisotropy δ and the unit cell volume. The observed enhancement is thus likely to be caused by both enhancement of Δ and predominantly an increase in Ω_{ph} . The explanation given above has a close parallel to the pressure induced T_C enhancement in manganites, wherein $dT_C/dP \approx 12\text{--}15$ K/GPa for $P < 3$ GPa for LCMO (0.33).¹⁵ However, the pressure induced enhancement saturates at $\delta T_C \approx 30\text{--}40$ K. We believe that this difference is mainly due to the difference between the externally applied hydrostatic pressure and the surface pressure,¹⁶ caused by the size reduction. The surface pressure is expected to have a significant non-hydrostatic component particularly in long nanowires.

To conclude, we have prepared nanowires of LCMO by a template-aided sol-gel process. This method can be extended to the nanowire fabrication of many multicomponent materials. The T_C of the nanowires was significantly enhanced above that of the single crystals.

One of the authors (K.S.S.) acknowledges CSIR for research associateship and A.K.R. thanks the department of Science and Technology, Government of India for a sponsored project.

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