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Synthesis and electron spin resonance of $La_{2/3}Ca_{1/3}MnO_3$ nanowires

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$La_{2/3}Ca_{1/3}MnO_3$ (LCMO) nanowires were prepared using a sol-gel process and an anodically oxidized aluminum template. Scanning electron microscopy (SEM) shows that the nanowires are almost parallel and their diameter is around 40 nm. The temperature dependence of the electron spin resonance (ESR) linewidth is similar to that observed for the case of nanostructured LCMO. From this dependence, the determined magnetic transition temperature, T_C, of the LCMO nanowires, is of the order of 120-130 K.

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1. Introduction

The quasi one dimensional materials have attracted much attention due to their significant technological applications in optical [1], electrical [2] and magnetic [3] devices. Many different techniques have been employed to fabricate such materials, such as electroless plating [4], chemical vapor deposition [5] and sol-gel [6].

Regarding the template for the array growth, the porous alumina membrane (Al_2O_3) has received a great deal of attention because of its self organized, cylindrical, and uniform holes, of which size can be controlled.

Plenty of efforts have been expended on the synthesis of nanoscale materials of various elements and compounds. Up to now the synthesis of nanowires of multi – component oxides is still a challenging issue [7 - 9].

The perovskite manganites are well-known compounds for their colossal magnetoresistive (CMR) properties. Recently, CMR manganites with nanometer-scale dimensions have became of great interes for their potential technological applications. These nanostructured materials could exhibit enhanced electronic and magnetic properties compared to their conventional microscale counterparts [10].

In the present work, we have successfully prepared perovskite-like $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) nanowires by using porous Al_2O_3 membrane as a template. The scanning electron microscopy (SEM) was used to evaluate the mean diameter of the nanowires.

Electron Spin Resonance (ESR) Spectroscopy is ideally suited in probing the dynamics of spins over a wide temperature range in nanostructured CMR [11]. Here, we have investigated the temperature dependence of the ESR linewidth in order to get informations about the ferromagnetic-paramagnetic transition temperature (T_C) of LCMO nanowires.

2. Experimental

A 99.99% aluminum plates (0.1 mm) were degreased in carbontetrachloride and acetone, washed in distilled water and electrochemically polished (Na_2CO_3, 15%, Na_3PO_4,5%, 30V, 15 minutes). After polishing, the plates were washed with water and dipped in chromic acid solution, to desmudge. We have anodized Al plates in a H_2SO_4 solution (15%), at 8° C, 22V, getting the pored Al_2O_3 coating 30-40 μm in thickness. At the bottom of the pores there is a thin oxide layer, adjacent to aluminum substrate, called barrier layer.

In order to obtain LCMO nanowires we have followed the procedure described in Ref. [7]. Stoichiometric amounts of La_2O_3 and $CaCO_3$ were dissolved in hot nitric acid. In this solution a measured amount of $Mn(NO_3)$ was introduced under stirring to form a homogenous mixed nitrate solution. After that, the nitrate solution is diluted by deionized water to a pH level of about 2.5. For obtaining an array of nanowires, first of all, we removed aluminum substrate (etched by: 20% HCl+ 0.1M $CuCl_2$), and then the barrier layer. The etchant used was a 4% phosphoric acid. After etching of the barrier layer, the Al_2O_3 membrane was washed with water and dried at room temperature.

The Al_2O_3 membrane was put into a culture dish, containing a proper amount of above- mentioned mixed nitrate solution. The culture dish was kept at 80˚C for gradual removal of water in solution. Due to the hydrolysis of metals cations (La^{3+}, Ca^{2+}, Mn^{2+}) a transparent viscous sol was formed upon evaporation of the water. The Al_2O_3 template in which the sol was incorporated into the channels was put into a tube furnace. The temperature of the furnace was ramped from the room temperature to 400 °C with a rate of 2˚C/min and kept at this temperature for 1h. After firing at 800 °C for 2h the power of furnace was turned off.

3. Results and discussion

The resulting material is a membrane formed by submicrometric structures whose diameters and morphologies are determined by the size of the pores of the Al_2O_3 template (Fig. 1).

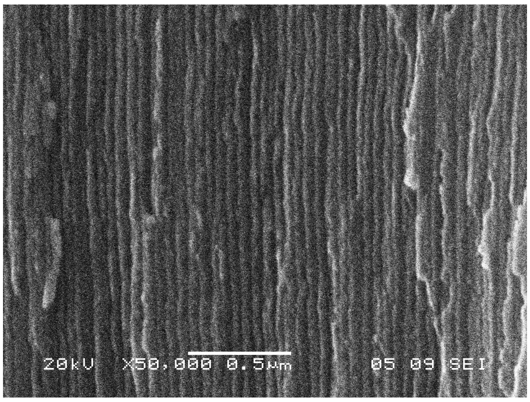

Fig.1. SEM micrograph of LCMO nanowires obtained using Al_2O_3 template.

One could observe that the channels are parallel with a uniform diameter. The mean diameter of the nanowires is around 40 nm. Although the lengths of nanowires are in this picture about 2 µm, it does not mean that the nanowire are only so short, because this image is only a section of the membrane. The evaluated value of the mean diameter is comparable with the reported one (≈ 30 nm) in Ref. [7].

X-Band ESR investigations, carried out in the 80-300 K temperature range, have revealed a single line with g ≈ 2 similar to that observed for the case of LCMO nanoparticles [8]. A typical ESR spectra is given in Fig. 2.

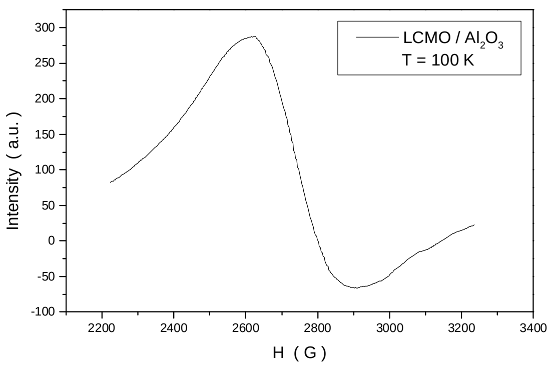

Fig. 2. X-Band ESR spectra at T = 100 K of $La_{2/3}Ca_{1/3}MnO_3$ nanowires.

In the following we discuss the temperature dependence of the ESR linewidth, $\delta H_{1/2}$. In Fig.3, the linewidth temperature dependence of LCMO nanowires is presented and compared to that corresponding to LCMO nanoparticles annealed at T_A = 1073 K. As a general feature for bulk and nanostructured CMR manganites, the linewidth goes through a minimum at $T_{min} \approx (1.1\text{-}1.2)\ T_C$ [12]. In the paramagnetic regime, $T > T_{min}$, the linewidth increases with increasing temperature and could be well described by the small polaron hoping model [13]. Its increase below T_{min} could be attributed to the usual critical slowing down in ferromagnets.

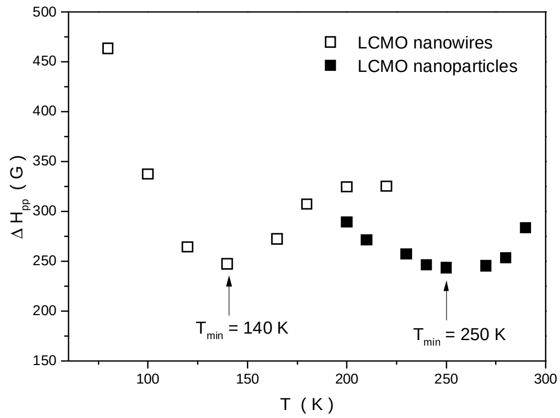

Fig. 3. Temperature dependences of the ESR linewidth, ΔH_{pp}, for LCMO nanowires (□) and sol – gel LCMO nanoparticles annealed at T_A = 1073 K (■).

As one can see from Fig. 3, the temperature T_{min} is smaller than the corresponding one for LCMO nanoparticles. It implies a smaller T_C and in accordance with the empirical relation between T_{min} and T_C, we estimated for LCMO nanowires a T_C value in the range of 120-130 K. The observed decrease of T_C is most likely due to the different oxygen stoichiometry of the samples.

4. Conclusions

We have synthesized nanowires of $La_{2/3}Ca_{1/3}MnO_3$ using a sol-gel procedure and Al_2O_3 as template. SEM micrographs reveal that the nanowires were nearly uniform in size with a diameter of around 40nm. ESR investigation revealed a similar behavior to that corresponding to CMR nanoparticles. From the temperature dependence of the ESR linewidth a magnetic transition temperature, T_C, of the order of 120-130 K, was evaluated.

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