Rapid synthesis of ordered manganites nanotubes by microwave irradiation in alumina templates

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Abstract

Highly ordered La\textsubscript{2/3}Ca\textsubscript{1/3}MnO\textsubscript{3} nanotube arrays were successfully synthesized by a simple and rapid process, combining nanoporous alumina template-assisted synthesis with microwave irradiation. The method offers a quick hands-on route to produce manganite bulk sample and nanotube arrays at relative low-temperatures. We obtain thin wall nanotubes of uniform diameter of 80 nm. The growth mechanism of nanotubes is briefly discussed. Magnetic measurements indicate that the ferromagnetic transition temperature $T_C$ of the nanotubes is depleted with respect to its bulk counterpart possibly due to the geometric confinement imposed by the thin wall of the nanotubes.

1. Introduction

The discovery of carbon nanotubes prompted intense research on new materials that can be synthesized in the form of nanotubes and nanowires. Such nanomaterials promise to be key components for applications in nanoscale electronics, optics and sensors, and exhibit an ever-growing importance in nanoscience and nanotechnology [1]. The techniques involved in the synthesis of nanoscale materials can be generally catalogued into chemical and physical routes and may be template-assisted. Regarding the template synthesis of nanomaterials (e.g., nanowires, nanotubes and antidots), nanoporous alumina templates (NPAT) proved to be desirable and flexible due to their easy fabrication with custom-made features, such as
pore size, interpore distance and aspect ratio variation, all controllable by adequate anodization conditions [2].

Perovskite manganites exhibit very interesting nanoscale physical properties due to their intrinsic coupling between charge, spin and lattice degrees of freedom, giving rise to renowned phenomena like colossal magnetoresistance (CMR), charge ordering and multiferroic behaviour [3,4]. The question if these phenomena remain when the materials are tailored to nanodimensions (e.g. in the form of nanotubes or nanowires) is still open, as the small size and unconventional geometries may alter the delicate balance between different phases, stabilizing new electronic/lattice/magnetic ground-states [5]. Moreover, manganites proved to be prospective candidates for a plethora of applications ranging from solid-oxide fuel cells to magnetic field sensors. The nanotube/nanowire form adds additional versatility for such applications. However, the fabrication of nanowires and nanotubes of such multicomponent oxides using template based synthesis is still a challenging issue.

Previous works reported on the template-assisted synthesis of nanowires and nanotubes of perovskite manganites via micro or nanoporous [5,6] templates, conjugated with different routes for sample preparation. Essentially all these methods are sol-gel based, using different gelling agents such as Ethylene Glycol [7] and Tetra-Ethyl-Ammonium (TEA) [8], for viscosity adjustment [9]. In addition, the routes can also differ on the type of thermal/pressure treatment to promote oxide formation, generally involving hot plate/furnace treatments [10] (at different temperatures and/or atmospheres) [11,12]. More recently, the use of microwave irradiation started to present itself as an easier, faster and more effective alternative to the common hot plate/furnace heat treatments.

Although it is well known that the details on the fabrication process are of key importance to enable the formation of nanowires and nanotubes, existing reports do not give full detail on the synthesis steps, and one is many times faced with conflicting data, yielding the synthesis reproducibility difficult [7,9,14]. Polycarbonate and nanoporous alumina membranes are the most common used templates for the growth of nanotubes. Polycarbonate templates are not, however, suitable for the production of ordered arrays since their pore structure lacks
organization and, being organic, they are destroyed during the intermediate and high temperature steps of the synthesis process, yielding nanostructured powders. Moreover, in such organic templates, mechanical confinement (if present) acts only during the low temperature stages of the synthesis process, and the system crystallization evolves mechanically free [14]. It is thus important to test if methods that proved to be valid to produce nanotubes in organic templates, apply to inorganic ones. In particular, the synthesis of nanotubes using a fast microwave assisted method was accomplished in organic polycarbonate templates. The authors showed that the membrane allows to define nanopillars of oxides and carbonates in the low temperature synthesis steps and that an additional calcination step was needed to yield the desired phase [5,8].

In this work we combined for the first time the MW irradiation with the sol-gel methods to easily and rapidly produce manganite nanotubes in alumina templates. These sustain high temperatures allowing the whole synthesis process to be performed under mechanical confinement. We show that, in contrast with the results obtained by other authors using organic templates, the desired ferromagnetic phase appears immediately after MW irradiation, achieving ordered arrays of manganite nanotubes without demanding viscosity adjustments and long calcinations times. We describe the optimum conditions to prepare thin wall La$_{1-x}$Ca$_x$MnO$_3$ [$x=1/3$] (LCMO) nanotube arrays within pores as small as 80 nm. Their magnetic and structural properties are reported.

**Experimental**

To prepare manganite nanotubes arrays, home-made NPAT with average pore diameter of 80 nm and thickness of ~200 μm were used. These were obtained by electrochemical oxidation of high-purity (>99.997%) aluminum foils. Prior to anodization, several cleaning and surface treatments were employed [15]. The substrate was first degreased in ethanol, followed by electropolishing in ethanol and perchloric acid (3:1), being then rinsed in deionised water. A two-step anodization procedure was used in order to achieve the desired pore structure organization [2]. The first anodization was performed at a constant voltage of
40 V during 4 hours. As electrolyte, a 0.3 M oxalic acid solution was used and the temperature was kept constant within 280±1 K. The resulting porous-oxide layer was then etched away in 0.5 M phosphoric / 0.2 M chromic acids mixture at 333 K for 2 hours. The second anodization was performed in the same conditions as the first one during 20 hours. In order to detach the alumina membranes from the aluminum foil underneath, a solution of copper (II) chloride in aqueous hydrochloric acid was used. To have open-through pores the barrier layer at the bottom of the pores was removed with phosphoric acid (1 M) during 45 minutes.

The sol used in the fabrication of LCMO nanotubes was prepared by dissolving in a stoichiometric ratio lanthanum oxide, calcium carbonate and manganese nitrate in water and nitric acid. The pH was adjusted with ammonia solution to the maximum stable value (pH = 4.0).

The NPAT were submerged in the LCMO precursor solution for 2 hours, filling the pores by capillarity. The microwave-hydrothermal reaction was carried out in a domestic microwave oven operating at a frequency of 2.45 GHz. The samples were irradiated for 5 minutes at 950 W and then left to cool at a natural rate. This procedure was repeated two times. The NPAT was carefully wiped to remove bulk manganite formed on the surface. Then the nanotubes and bulk samples were heated at 973 K for 5h, followed by additional 5h at 1173K. In order to observe isolated LCMO nanotubes, the NPAT were subsequently dissolved in NaOH.

Scanning Electron Microscope (SEM) analysis was obtained in a FEI Quanta 400 FEG SEM. The highly ordered arrays of LCMO nanotubes in NPAT were confirmed and isolated nanotubes were observed. Energy dispersive spectrometer (EDS) was used to determine the compositions of the as-prepared samples. X-ray diffraction (XRD) analysis was performed after microwave-hydrothermal treatment and after each thermal treatment with a Philips X-Pert diffractometer. The magnetization as a function of temperature [\(M(T)\)] and hysteresis loops [\(M(H)\)] were collected in a SQUID Quantum Design.
2. Results and discussion

As described above, highly ordered alumina templates were prepared by a two step anodization procedure. Figure 1a) shows SEM images of a typical highly ordered nanoporous alumina template with 80 nm pore diameter used as templates in the manganite synthesis.

As a comparison for each manganite sample prepared in a template its bulk counterpart was also prepared and followed similar thermal treatments. In order to observe if nanotubes were formed in the templates, alumina was partially dissolved in NaOH solution. In figure 1b) one can observe highly ordered arrays of LCMO nanotubes. The nanotubes replicate the NPAT features and grow parallel and continuous to each other, with a regularity in diameter of \( \sim 80 \) nm and length \( \sim 100 \) \( \mu \)m corresponding to the alumina template thickness, controlled by anodization time. In figure 1c) an isolated nanotube specimen can be observed confirming the high aspect-ratio of these structures and their diameter uniformity.

Figure 2 shows the EDS spectra obtained from the nanotubes still inside the alumina template. The La:Ca:Mn ratio obtained was 0.67:0.33:1, in full correspondence with the nominal composition. The aluminium (Al) and carbon (C) also found, arise, respectively, from the alumina template and the carbon glue stripe used to fix the samples inside the SEM.

At this point it is worthwhile mentioning the most relevant steps in our procedure that lead to the formation of LCMO nanotubes in NPAT. By adjusting the pH of the solution to its maximum stable value (pH = 4.0) one is able to convert the hidroxo-bridges into oxo-bridges [16]. In this way, the desired phase is formed more easily because the metal ions in the polymer are surrounded by oxo-bridges [17]. After the evaporation of the solution, hydrolysed-species condensation occurs, leading to polymerization and consequently to a viscous gel. This evaporation can be done either at a hot plate, furnace or microwave oven liberating vapours such as \( \text{H}_2\text{O} \), \( \text{NO}_x \) and \( \text{CO}_x \) [18]. This leads to an increase in the solution concentration in the pores, resulting from the dehydration and denitration processes, which keep occurring after the precipitate formation. Microwave dielectric heating originates from the natural ability of certain substances to efficiently absorb electromagnetic radiation and
then transform it into heat; it thus offers some degree of locality and selectivity [19]. If sufficient heat can be generated at local level, then chemical reactions may be initiated at a fast rate. Thus the strong microwave absorbing properties of one of the reactant oxides, leads to a rapid and highly effective synthetic pathway [17]. The use of nitrate precursors, which have high MW absorption coefficients and decompose to yield highly oxidizing NO$_2$, facilitate the formation of the Mn$^{3+}$/Mn$^{4+}$ couple, of crucial importance in manganites [11]. In our results, the appearance of the desired crystallographic phase immediately after microwave irradiation evidences the advantage of this method over other more time-consuming high temperature ($\sim$1173 K) routes for manganite preparation. Moreover, the crystallization process is done under mechanical confinement provided by the alumina template that easily stands the whole procedure. Another main advantage of using alumina templates formed by anodization processes in acidic solutions is that the pore walls are positively charged [9]. Since the sol particles after the hydrolysis reaction are negatively charged, a continuous manganite film is formed at the pore walls, corresponding to the nanotubes’ shape.

Figure 3 shows XRD pattern of the as-prepared LCMO bulk sample showing that the method indeed yields the desired manganite phase. All peaks can be indexed to the expected orthorhombic Pbnm cell with lattice constants of $a=0.5504$ nm, $b=0.5474$ nm and $c=0.7673$ nm. The continuous line is a pattern matching performed using fullprof software.

The M(T) measurements were performed under a constant magnetic field of $H = 50$ Oe from $T = 5$ K to room temperature. These followed the Zero Field Cooling (ZFC) procedure: the sample was cooled, with $H = 0$, to $T = 5$ K, after which the measuring field of 50 Oe was applied. The study was carried out in annealed (973 K for 5 h followed by 1173 K for 5 h) and as-irradiated samples (bulk and nanotubes). Figure 4 illustrates the influence of thermal treatment on the magnetic properties of bulk samples and ordered arrays of nanotubes. The as-irradiated samples have a much lower saturation magnetization values and a lower critical temperature, $T_c$ (table 1). Moreover, the as-irradiated samples have a much broader para-to-ferromagnetic phase transition. After the annealing process at 1173 K, the samples already
exhibit an abrupt change in magnetization indicating good magnetic homogeneity. The bulk powders, as well as the walls of the nanotubes are formed by magnetic nanograins, which are enlarged by the annealing processes. The differences observed in the phase transition of the as-irradiated and annealed samples are associated with the different magnetic grain sizes.

The magnetic susceptibility of the samples was also calculated using the $M(T)$ values ($M = \chi H$). At high enough temperatures, the thermal variation of $1/\chi$ follows the linear Curie-Weiss law. The Curie-Weiss temperatures of the as-irradiated samples are much lower than the corresponding critical temperatures ($T_C$), indicating that anti-ferromagnetic (AFM) correlations must be present. This effect can be attributed to grain boundary mediated AFM interactions between ferromagnetic (FM) grains. After annealing, the grain size increases, thus increasing the size of the FM grains with a correspondent decrease of AFM correlations. This is further supported by the low values of the saturation magnetic moment $\mu_{sat}$ (much lower than the spin only theoretical values of $\mu_{sat}^{th} = 3.67 \mu_B$). Table 1 summarizes the magnetic parameters ($T_C$, $\theta$; $\mu_{sat}$) found for these samples. Comparing the magnetic properties of the ordered arrays of manganite nanotubes with the ones of their bulk counterparts one can see that the geometric confinement induced by the nanotube thin walls depletes $T_C$, as expected due to the reduction of nearest neighbours as one goes from 3D to 2D [13]. A similar effect occurs when one prepares manganite thin films [20, 21].

In addition, one notices that geometric confinement seems to prevent full ferromagnetic alignment as one infers from the magnetization saturation measurements (up to 5 T, not shown) where no clear saturation is observed.

### 3. Conclusions

In summary, we have successfully produced ordered arrays of LCMO thin wall nanotubes with diameters as small as 80 nm using a template-assisted method combined with microwave irradiation. The nanotubes are uniform and present very high aspect ratio. We have found evidence for geometric confinement effects on the nanotube magnetic properties.
The proposed nanotube preparation method has shown to be very effective to rapidly produce ordered nanotube arrays of reduced diameter and offers major advantages compared with the other routes, namely simplicity, fastness and cost-effectiveness. In this work we have used this method to produced LCMO nanotubes, however, it is considered to be fully possible to use the same method to fabricate nanotubes of other mono and multi-component oxides.

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References
Figure 1. SEM images of: a) the surface of nanoporous alumina template; b) the La2/3Ca1/3MnO3 nanotube arrays after removal of the alumina and c) isolated nanotube.
Figure 2. EDS Spectrum of La$_{0.66}$Ca$_{0.33}$MnO$_3$ nanotubes in nanoporous alumina templates.

Figure 3. Room temperature X-ray diffraction pattern for the bulk sample as-irradiated. The observed pattern (dots), calculated (solid line) and reflection of the corresponding phase, Pbnm (tick marks) are shown.
Figure 4. Field cooling magnetization versus temperature for the produced samples. For the nano-as-irradiated and bulk-as-irradiated samples the magnetization values was multiplied by 4. In the case of the nanotubes-samples, the magnetization was normalized to the mass of the template.