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Microwave assisted synthesis of manganese mixed oxide nanostructures using plastic templates

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Abstract

The synthesis method for obtaining sub-micrometric structures of rare earth manganese-based mixed oxide compounds is described. Pore wetting of porous polycarbonate templates with the liquid precursor was followed by a two-stage thermal treatment to obtain single phase $La_{0.325}Pr_{0.300}Ca_{0.375}MnO_3$ hollow and solid structures, with external diameter determined by the sacrificial template pore size. The first thermal stage, a microwave assisted denitration process, determines the shape of the structures. The second treatment, performed at 1073 K, allows to obtain the crystallographic structure of the compound. A variety of techniques (scanning and transmission electron microscopy, scanning probe microscopy) allowed to fully characterize the microstructure and morphology of these self-standing manganite nanostructures. For 1 μm pore size templates we obtained tubes, with external diameter around 800 nm and wall thickness around 150 nm; densely packed nanoparticles sized 20–50 nm are the building blocks of the walls. For pore size below 0.1 μm, solid nanowires were obtained, the size of constituent crystallites being around 10 nm. Overall obtained material exhibits ferromagnetic ordering below 200 K.

Keywords: Nanostructures; Complex oxides; Synthesis methods; Manganites; Magnetoresistance

1. Introduction

Complex oxides are at the center of the scenario in condensed matter physics, both for technological and basic research reasons. Desirable electrical field switching of properties in a huge variety of oxides [1] requires tailored micrometric and sub-micrometric structures to proceed. Hybrid synthesis methods provide a route to obtain such structures with different topographical and topological characteristics. Hollow structures of a variety of single oxides have been recently obtained following different methods. Vanadium oxide nanotubes using the templating effect of the surfactant molecules in a modified sol–gel process were reported by Spahr et al. [2], nanoparticle-assembled caped TiO_2 microtubes were synthesized through a freeze-drying method by Ma et al. [3], silica-based hollow nanofibers were obtained by Loscertales et al. using electrically forced coaxial nanojets [4], single-crystal gallium nitride nanotubes were obtained by CVD technique using ZnO nanowires previously grown as templates [5]. Also, ferroelectric mixed oxides [6–8] were synthesized using rigid porous materials as templates, such as alumina or silicon.

Mn oxide-based mixed valent compounds are the focus of deep interest [9] and the fabrication of solid nanowires of LaCaMnO has been recently reported,

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using anodized alumina templates [10,11]. Also, a method for obtaining nanowire frameworks using polymethyl methacrylate [12] templates was recently described. In this work we report the synthesis method for obtaining self-standing nanostructures of a Mn-based mixed oxide using a porous plastic template. The combination of pore wetting technique with the liquid precursor synthesis method followed by an appropriate microwave assisted thermal treatment allowed to obtain single phase $La_{0.325}Pr_{0.300}Ca_{0.375}MnO_3$ (LPCMO) structures with external diameter determined by the pores of the template. Wires were obtained when the pore size was below 0.1 μm and tubes for pore size above 0.2 μm. Structural and magnetic properties of hollow structures were previously reported [13].

2. Experimental

A 0.5 M stoichiometric nitric solution for LPCMO formulae was prepared by dissolution of the following analytical reagents, $Pr(NO_3)_3 \cdot 6H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ and $Ca(NO_3)_2 \cdot 6H_2O$, in pure water. To avoid the manganese oxide precipitation the solution was maintained at acidic pH. Templates of porous polycarbonate films were dipped into the nitric solution or were used as filters in an adequate system for syringe filtration. In the first option the solution fills the pores by capillary phenomena, the actual filled volume depends on the elapsed time of contact. In the second option the total volume of the pores is filled. Porous polycarbonate films were either commercial Isopore™ membrane filters from Millipore, or wet etched heavy ion irradiated films. Samples with passing through holes of 1, 0.2, 0.1 and 0.05 μm diameter were used.

The reaction to obtain the desired compound proceeds by the denitration process of the confined precursor in a microwave oven. By adjusting the time and the energy applied to the sample it is possible to accomplish this reaction without producing damage to the polycarbonate film. Fig. 1 is a scanning electron microscopy (SEM) image, showing a top view of the polycarbonate template after this treatment. Dark circular regions are the filled pores. As apparent, the template is not degraded. Microanalysis at the pores revealed the presence of Mn, La, Pr and Ca species, which are absent at the polycarbonate surface. The perovskite compound LPCMO is finally obtained and the template is sacrificed during a thermal treatment in a standard furnace at the final temperature of 1073 K. After 10 min at 1073 K the furnace goes freely to room temperature. The resulting material is a collection of sub-micrometric structures whose diameters depend on the size of the pores of the template used and their height on the way of wetting.

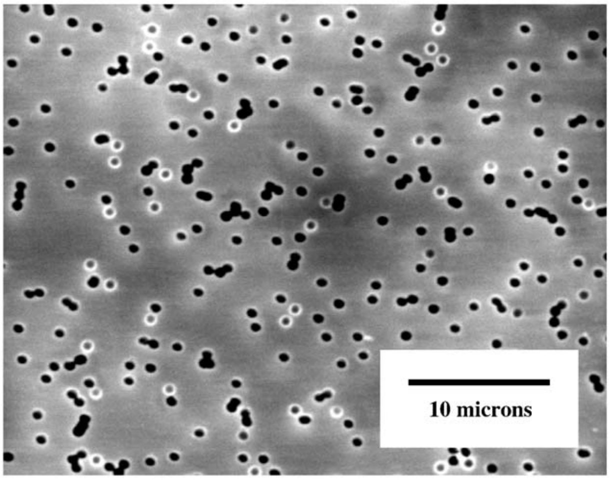

Fig. 1. SEM micrograph of the polycarbonate template with the confined precursor inside the pores, after the microwave treatment.

3. Results and discussion

X-ray powder diffraction analysis was performed after each thermal treatment with a Philips X-Pert diffractometer using Cu$K\alpha$ radiation ($\lambda = 0.154056$ nm). Fig. 2 shows data measured at room temperature at different stages of the process. The dehydration and denitration processes, in the first stage of decomposition in the microwave oven, produces a mix of single and double oxides as determined by X-ray diffraction analysis. Some of the obtained reflections could be assigned to $CaMnO_{2.5}$, $CaMn_4O_7$, La_4MnO_{11}, Pr_6O_{11} and La_2O_3. After the thermal treatment at 1073 K, the crystal structure obtained corresponds to the perovskite LPCMO ($a = 0.5446$ nm, $b = 0.7683$ nm and $c = 0.5449$ nm), without impurity phases. Also shown in Fig. 2 for comparison is the pattern obtained for a powder sample grown without using a porous template, i.e. grown in bulk following the thermal treatments previously described. Interestingly, the unconfinedly grown LPCMO compound can also be obtained in a single step, after the microwave assisted process, in agreement with previous results [14]. This fact suggests that heat released in the bulk case is enough to produce the entire reaction in one step, a situation not accomplished when the material is confined within the pores of the plastic template. Thus, a threshold volume of the pore should exist, which may allow obtaining the mixed oxide confined, without template sacrifice.

Fig. 3 shows a SEM image of isolated structures of LPCMO, obtained by freely wetting a sacrificial template with 1 μm pore size. They have an external diameter around 800 nm, and their length appears to be around 4 μm, roughly half of the polycarbonate template thickness. Although the external diameter of the tubes are rather uniform within the batch (i.e.

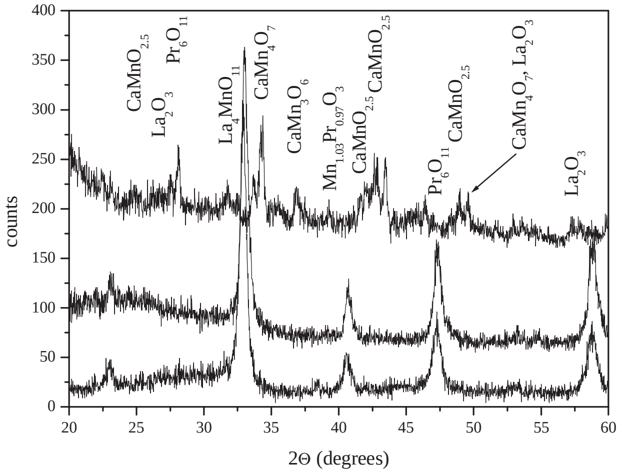

Fig. 2. X-ray diffraction patterns of nanotubes of LPCMO (template pore size 200 nm), comparing data from samples at different stages of the thermal process: after the microwave stage (upper pattern) and after the treatment at 1073 K (middle pattern). For comparison the pattern of an unconfined sample of LPCMO is shown (lower pattern).

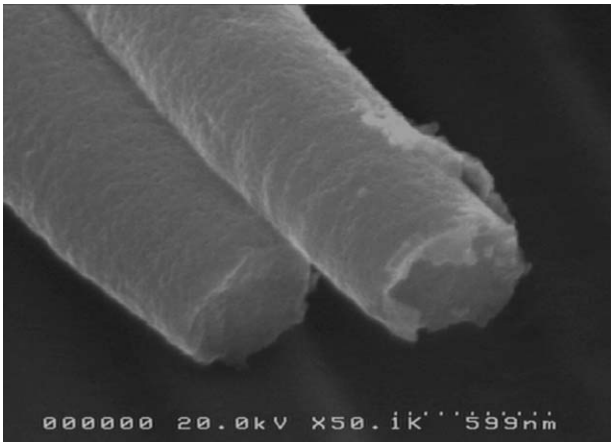

Fig. 3. SEM micrograph of sub-micrometric tubular structures of LPCMO grown in a 1 μm pore size polycarbonate template.

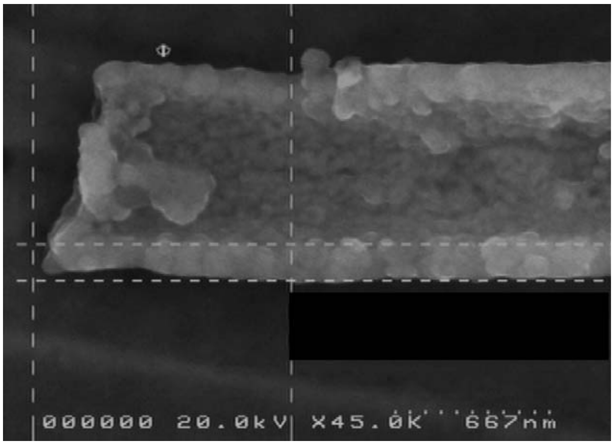

Fig. 4. SEM micrograph of a broken tube of LPCMO grown in a 1 μm pore size polycarbonate template.

variations lower than 10%, probably due to the original pore width distribution), the length of the tubes has a distribution suggesting that full wetting of the pores was not completed or that they were broken during sample preparation. External walls appear quite smooth on the micrometer length scale.

Remarkably, these nanometric structures are hollow. In Fig. 4 a SEM image of a partially broken tube is shown, unveiling both a cross-section view of the walls, and the inner surface of the tube. The formation of straight and uniform walls 150 nm thick is apparent. This view of the inner face of the walls allows to distinguish that they are formed by nanoparticles sized around 50 nm, a fact that was not apparent in Fig. 3.

The hollow structure is formed during the microwave treatment of the liquid precursor confined in the template. A thin surface film of solution covers the walls of the pores by wetting phenomena. The increase of the solution concentration on the walls results from the dehydration process, which continues until the nitrates begin to precipitate on them. The denitration process takes place simultaneously, and a mix of different double oxides appears on the inner walls of the pores. When the sample is further annealed, these preformed oxide-based structures evolve towards the LPCMO compound and the sacrificial polycarbonate template is burned. The morphology of the nanoparticle assembly is thus mainly determined during the microwave-assisted treatment. The external diameter of the obtained tubes is slightly smaller (10–20%) than the original pore size, due to a contraction process during annealing.

The topography of the walls was further studied by means of atomic force microscopy using a commercial MDT tip in tapping mode. Fig. 5 shows images obtained from the inner (Fig. 5a) and outer (Fig. 5b) faces of the walls of the same structure depicted in Fig. 4. As apparent, in both cases the grains that form the walls are sized around 40 nm. These building blocks appear to be compactly packed, in agreement with the cross-section view of the walls shown in Fig. 4. While the appearance of the external face might be determined by the confinement produced by the template, the inner side of the tube should reflect unconstrained growth. However, in both cases the morphology appears to be dominated by the nanograins, probably due to the grain growth kinetics in these thermal processes. Transmission electron microscopy (TEM) images of these structures were obtained using a CM 200 Philips microscope with an acceleration voltage of 200 kV. We observed that walls are formed by crystallites around 30 nm size using the dark field TEM technique, as shown in Fig. 6. Smaller bright regions are individual crystallite specimens, while bigger ones are presumably agglomerates of

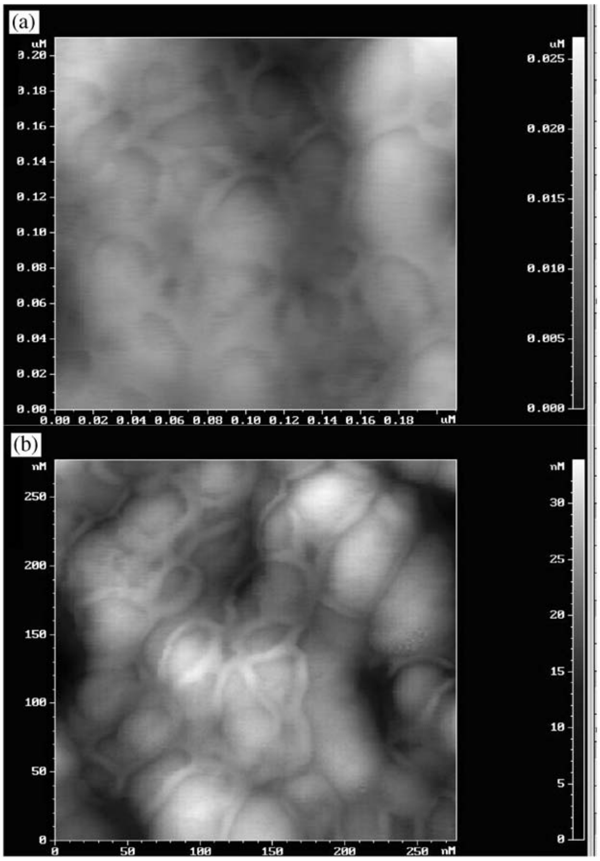

Fig. 5. Atomic force microscopy image of the same isolated nanotube shown in Fig. 4: topographic details of the internal (5a) and external (5b) walls.

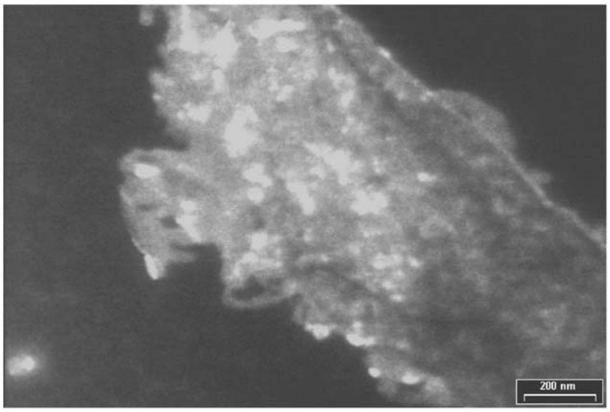

Fig. 6. Dark field TEM image of an isolated tubular structure grown in a 1 μm pore size polycarbonate template. Bright regions correspond to individual grains.

neighbor crystallites with similar orientation. These crystallites have no preferential orientation, i.e., the walls of the tubes have no texture, as the diffraction pattern of the nanotubes exhibits concentric rings [13].

Magnetization data of the obtained material was collected using a commercial vibrating sample magnetometer between 80 and 300 K. Powder formed by a collection of structures exhibit ferromagnetic ordering, with Curie temperature around 200 K. A magnetization vs. applied magnetic field loop performed at 80 K is shown in Fig. 7, where their soft ferromagnetic behavior including hysteresis is depicted.

Similar results, i.e., hollow tubular structures of the LPCMO compound were obtained using polycarbonate templates with pore size 0.2 μm and following the same procedure. Obtained nanotubes have external diameter around 200 nm, wall thickness 60 nm, and nanograins sized around 30 nm as building blocks. Depending on the diameter of the pore the structure obtained can be hollow or solid. For pore size 0.1 and 0.05 μm, we obtained LPCMO wires instead of tubes. This fact was confirmed by TEM images, as shown in Fig. 8a for a structure obtained from a 50 nm pore size template. As expected, decreasing the pore size while keeping the other synthesis parameters constant favors the deposited material on opposite sides of the pore to overlap, thus forming a solid structure. Interestingly, constituent crystallites of solid nanowires are sized around 5–10 nm, as shown in the dark field TEM image of a wire obtained from a 0.1 μm size pore (Fig. 8b).

The advantage of this microwave assisted synthesis method is the fine grain nature of the powder obtained. The reactivity and sinterability of nanometer sized grains is well known, this fact makes possible to obtain homogenous and stoichiometric complex oxides at relatively low temperature. It is worth mentioning that the plastic substrate can be totally eliminated without any leftover material by the final thermal treatment, yielding roughly aligned nanostructures [13]. Also, other

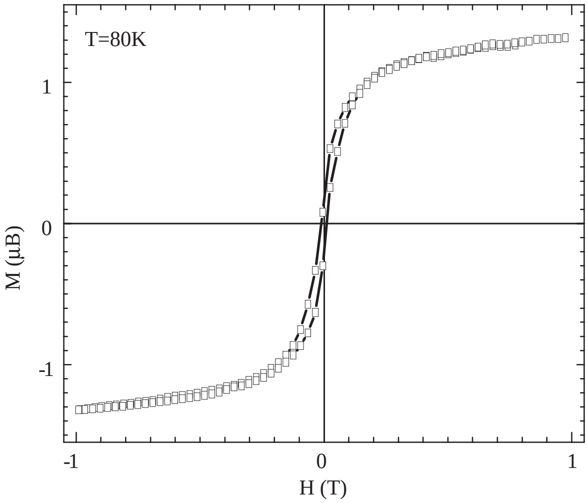

Fig. 7. Hysteresis loop performed after zero-field cooling to 80 K a collection of LPCMO nanostructures grown in a 1 μm pore size polycarbonate template.

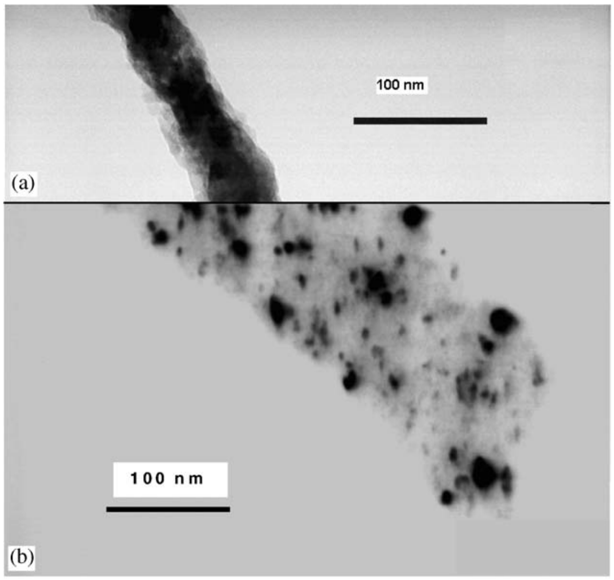

Fig. 8. (a) TEM image of an isolated solid structure grown in a 0.05 μm pore size template. (b) Negative dark field TEM image of an isolated solid structure grown in a 0.10 μm pore size template.

related stoichiometric compounds were successfully obtained using this method.

Interest in manganese oxide-based materials relies on their spin polarized charge transport, colossal magnetoresistance, and memory capabilities [9]. Confined electronic transport and junctions could be studied using manganite nanowires. The possibility of taking profit of the nanotubular shape of complex oxide-based structures for device applications was recently emphasized in the literature [15]. As clearly shown in Fig. 4, the obtained structures reported here are hollow and have very high surface-to-volume ratio. We envisage the possibility of tuning or modifying magnetic and transport properties of these tubes by changing their constitutive nanoparticle grain size by a recrystallization process. As strain and anisotropy play a definite role in manganites, this change in grain size could introduce interesting modifications to their properties. Besides, solid oxide fuel cells using manganese oxide-based compounds as cathodes have been proposed, as hollow structures take advantage of the low impedance for gas to flow through them. The microwave assisted method may provide a way to grow the cathode materials on the electrolyte surface.

Summarizing, we have shown the feasibility of assembling nanograins to form hollow and solid nanostructures composed of the mixed valent $La_{0.325}Pr_{0.300}Ca_{0.375}MnO_3$ complex oxide. The synthesis method takes benefit of a two stage thermal treatment. During the first one, the shape of the structures is defined, while during the second one the crystallographic structure of the desired compound is obtained, and the template is completely eliminated. A morphological characterization was given using a variety of microscopic techniques. The significance of this hybrid synthesis method is based on its simplicity, reproducibility, and the applicability to other complex oxides. Clearly, further work needs to be done for a complete topographic, microstructural, electric and magnetic characterization of the obtained products.

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