

Relationship between the synthesis parameters and the morphology of manganite nanoparticle-assembled nanostructures

A.G. Leyva^{a,b}, H.E. Troiani^c, C.J. Curiale^c, R.D. Sanchez^{c,*}, P. Levy^a

^a*Departamento de Física, Centro Atómico Constituyentes, CNEA, Av. Gral. Paz 1499, (1650) San Martín, Prov. de Buenos Aires, Argentina*

^b*Escuela de Ciencia y Tecnología, UNSAM, San Martín, Buenos Aires, Argentina*

^c*Centro Atómico Bariloche and Instituto Balseiro (UNCuyo), CNEA, Av. Bustillo 9500 (R8402AGP), S.C. de Bariloche, RN, Argentina*

Abstract

Nanoparticles assembled into nanostructures (NAN) of manganese perovskite oxides for different compositions and diameters have been synthesized following a template-assisted method. We discuss the relationship among geometrical, structural and nanostructural parameters observed when synthesizing LaMnO_3 , $\text{La}_{0.66}\text{Sr}_{0.33}\text{MnO}_3$, $\text{La}_{0.66}\text{Ca}_{0.33}\text{MnO}_3$ and $\text{La}_{0.325}\text{Pr}_{0.300}\text{Ca}_{0.375}\text{MnO}_3$ manganite based complex oxides. For all the studied compounds, the structures are composed of an assembly of small (some few tens of nanometers) grains. They form nanotubes above some threshold diameter of the template, and nanowires below it. Here we focus on the correlation between grain size and the diameter at which the tube to wire crossover occurs. The threshold for this tube to wall crossover seems to depend on the specific compound. We present evidence from TEM observations that allow a rationalization of several phenomena in the synthesis process.

© 2007 Elsevier B.V. All rights reserved.

PACS: 61.46.+w; 81.07.De; 81.20.-n

Keywords: Complex oxides; Nanostructures; Manganites

1. Introduction

Complex oxides exhibiting multifunctional properties are nowadays intensively studied. We have recently reported a straightforward method to produce nanoparticle-assembled nanostructures (NAN) of manganese oxide-based perovskites exhibiting magnetic properties. The template strategy we followed allows to obtain either hollow tubes or solid wires, and to select their diameter. The method, due to the possibility of tuning several parameters associated with these structures as length, diameter and wall thickness, is reliable for massive production, a key point when applications are envisaged. Potential uses of NANs cover from magnetoresistive devices in spintronics to fuel cells [1].

Obtained NANs are composed of small (some few tenths of nanometer) grains. They exhibit interesting features at different scales: these grains are assembled into walls, which form hollow structures (nanotubes) above some threshold diameter of the template, and solid nanowires below it. These NANs exhibit different magnetic properties as compared with bulk materials [2–4].

In previous studies, the synthesis and characterization of NANs having some few microns length for the $\text{La}_{0.325}\text{Pr}_{0.300}\text{Ca}_{0.375}\text{MnO}_3$ (LPCMO) and $\text{La}_{0.66}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) compounds has been reported [2,3]. Here we present the comparison between both of them with the LaMnO_3 (LMO) and $\text{La}_{0.66}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO) manganite-based complex oxides. We focus on the correlation among composition (number of species involved), grain size, the diameter at which the tube to wire (i.e. hollow to solid) transition occurs. We show scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

*Corresponding author. Tel.: +54 2944 445158; fax: +54 2944 445299.
E-mail address: rodo@cab.cnea.gov.ar (R.D. Sanchez).

evidence establishing a mechanism for the synthesis process, and we discuss the possibility of tuning several typical lengths, thus having control on the magnetic behavior and effective surface area exposed.

2. Experimental

The synthesis method for obtaining perovskite NANs is based on the pore wetting technique applied into porous polycarbonate sacrificial templates. Briefly, it consists in an initial wetting stage (using the template films as filters in a syringe filtering device) followed by a couple of thermal treatments [3,4]. We used commercial polycarbonate templates with nominal pore diameters ranging from 50 to 1000 nm. TEM experiments were performed with a CM 200 Philips equipment equipped with an ultratwin objective lens. The acceleration voltage was 200 keV. NANs were mixed with an inert solvent and small drops of the slurry were put on commercial ultra-thin carbon support films on Cu grids. For the SEM experiments a Philips XL30 equipment was used.

3. Results

We have applied the above-described synthesis method to obtain NANs of some few manganese oxide-based perovskite compounds having different chemical compositions and different number of cations, i.e. LMO, LSMO, LCMO and LPCMO, for several template pore diameters.

Fig. 1 shows a SEM micrograph of a typical bundle of NANs for the LSMO composition. In our samples, the grains are tightly assembled to form self-standing structures. The histogram shown in the inset of Fig. 1 reveals the grain size distribution for the LSMO (200 nm pore) case, from TEM data. SEM images were formed with a secondary electron detector. This type of detector reveals mainly topographic features, but does not allow the precise

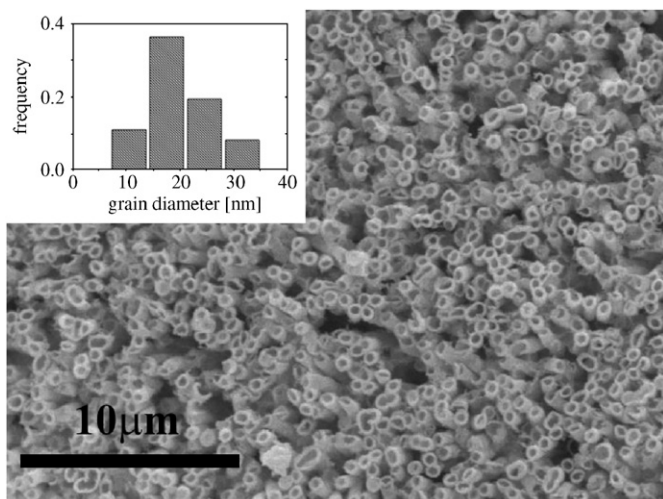


Fig. 1. SEM micrograph of LSMO nanotubes. Inset: grain size histogram with values obtained from TEM images (see text).

measurement of the grain size. On the other hand, TEM diffraction contrast images, either bright- or dark field, both reveal the true granular structure and size of component grains. The size of component grains was found to have a dependence on both composition and diameter of the NAN.

For example, when using 1000 nm nominal template pore diameter, LPCMO NANs exhibit typical grain size around 35 nm. Instead for the LCMO, LSMO and LMO compositions the grain size is approximately 25 nm. We emphasize that in all cases the same synthesis parameters were used. Overall obtained size data is summarized in Table 1.

It is also evident from Table 1 that a reduction of the nanograin size is produced as a function of the nominal pore diameter. This fact suggests a correlation relating the pore size and the grain forming mechanism on one side to the hollow or solid nature of the NANs on the other one.

Table 1
Median grain size as a function of nominal template pore diameter (ϕ), for LMO, LSMO, LCMO and LPCMO compositions

ϕ (nm)	Grain size (nm)			
	LMO	LSMO	LCMO	LPCMO
50				$7 \pm 3(w)$
100		$18 \pm 7(w,t)$		$10 \pm 4(w)$
200	$19 \pm 6(t)$	$19 \pm 7(t)$	$21 \pm 8(w,t)$	$28 \pm 9(w,t)$
600		$26 \pm 7(t)$		
1000	$26 \pm 7(t)$	$24 \pm 6(t)$	$25 \pm 8(t)$	$35 \pm 9(t)$

Letters w and t refer to nanowires and nanotubes, respectively, and they define the nanowire nanotube transition.

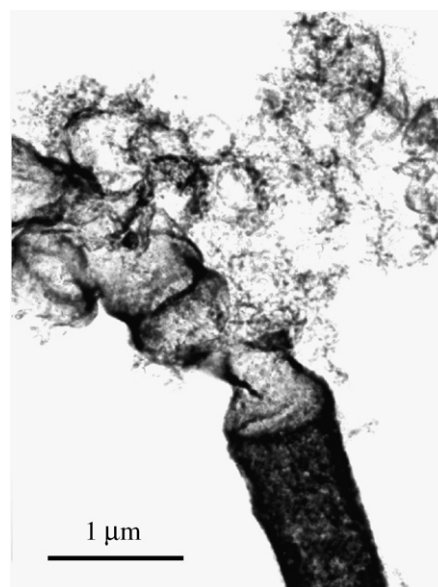


Fig. 2. Bright field TEM image for an LSMO hollow NAN. Attached to its end, the tip shows a structure resembling bubbles, suggesting the escaping of gases during the evaporation of the precursor while the thermal treatment is taking place.

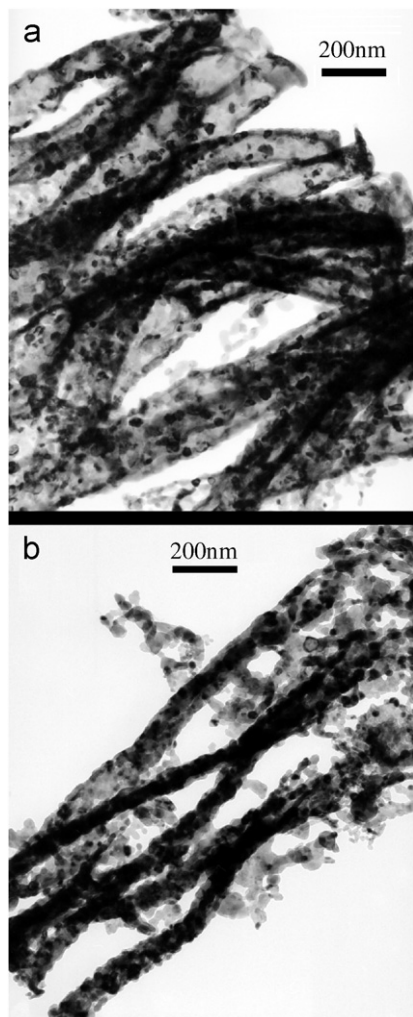


Fig. 3. Dark field TEM images detailing the tube to wire transition, for two NANs of LCMO composition obtained from the same batch (nominal 200 nm template pore diameter): (a) hollow NAN (i.e. nanotube) and (b) solid NAN (i.e. nanowire).

Additional insight into the grain assembling forming mechanism was obtained from images depicted in Figs. 2 and 3. Fig. 2 shows a bright field TEM image of a single LSMO 800 nm nanotube, whose tip is attached to a frozen structure that resembles a set of bubbles, which were found to be formed by the same LSMO material forming the dense NANs.

This unique nanotube was “quenched” at an intermediate stage of the nanoparticle-assembling process. Such specimens are scarcely found in typical batches. We understand that the synthesis mechanism of the nanotubes is evidenced by this image.

Fig. 3 shows bright field TEM images of a set of LCMO NANs corresponding to the same synthesis experiment, obtained using a 200 nm nominal pore size template. Interestingly, for this nominal pore diameter both tubes and wires were simultaneously obtained from the same batch. While Fig. 3(a) shows nanotubes, Fig. 3(b) shows nanowires of smaller diameter than those of the tube.

We speculate that this fact is due to the unavoidable statistical distribution of diameter size of the pores in the mold. Quite remarkably, for other nominal mold diameters, above 200 nm only nanotubes are obtained.

In the LPCMO case, when templates of 200 nm are used, a coexistence of tubes and wires are observed. Above this pore diameter only nanotubes are obtained while for diameters below 200 nm only wires are formed.

4. Discussion and conclusions

Taking into consideration Figs. 2 and 3, our representation of the synthesis process is the following: when the diameter of the pore is large enough, the hollow structure is the natural consequence of the mechanism by which the synthesis process occurs. The precursor solvent finds its way as an escaping gas out along a central channel of the pore. The material acquires a tubular structure due to the fact that the condensed remaining material wets the inner walls of the template. It is also seen in Fig. 2 that escaping gas bubbles can also drag material, which further favors the tubular structure.

When the diameter of the mold is reduced beyond a certain threshold (which was found to depend on the specific compound) the structures does not acquire a hollow tubular geometry, forming solid wires instead. This fact is evidenced in Fig. 3 for LCMO NANs obtained from a sacrificial template with nominal pore diameter of 200 nm. We stress at this point that images in Fig. 3a and b correspond to the same batch, i.e. the same template and synthesis parameters all along the process.

Thus, when the typical size of the mold pore is smaller than a certain threshold value, component grains and the overall structure forms in a different way. If the grains have similar size to the mold pores, just some few grains would occupy the whole cross section of the pore, making the synthesis process difficult to proceed. As a consequence the synthesis proceeds along a different route, i.e. reducing the typical grain size. In this case, the need of evaporating gases acting as the driving force for the change. The decomposition gases evolve during the synthesis promoting crystalline boundaries (due to the solid and gaseous phase coexistence) in a small channel. Smaller grain sizes allow for the formation of many internal channels in the forming NAN which result necessary for the escaping of the gaseous products gases. In this way a solid wire assembled by smaller grains is formed. It is remarkable that the system offers the possibility of tuning the grain size at constant temperature.

The chemical composition is another interesting synthesis variable which might influence the grain size. Although (for a fixed mold pore) the threshold for the solid structure formation and grain size seem to depend on the specific compound, further experiments are needed in order to understand the role of the type and number of cations.

In summary, in the template-assisted synthesis of NANs for several complex oxides, different grain sizes are

observed depending on the solid or hollow nature of the product. We suggest that this fact is undoubtedly related to the underlying synthesis mechanism.

Acknowledgments

This work was partially supported by ANPCyT PICT03-13517, PAV-MaN, RN3 M, PICT-2004 21372, U.N. Cuyo 06/C203; PIP-CONICET 5250.

References

- [1] L. Hueso, N. Mathur, *Nature* 427 (2004) 301.
- [2] J. Curiale, R. Sánchez, H. Troiani, G. Leyva, P. Levy, *Appl. Phys. Lett.* 87 (2005) 043113.
- [3] A.G. Leyva, P. Stoliar, M. Rosenbusch, V. Lorenzo, P. Levy, C. Albonetti, M. Cavallini, F. Biscarini, H.E. Troiani, J. Curiale, R.D. Sánchez, *J. Solid State Chem.* 177 (2004) 3949.
- [4] J. Curiale, R.D. Sánchez, H. Troiani, A.G. Leyva, P. Levy, *Appl. Surf. Sci.* 2007, in press.