

Characterization of Sol-Gel Nanoparticles of Magnetoresistive $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3+\delta}$

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ABSTRACT

We have synthesized nanoparticles of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3+\delta}$ by the sol-gel method, using urea as gelificant agent. The gel was decomposed at 250 °C and the resulting powders were calcined at temperatures up to 1000 °C. Starting crystallization of the perovskite was observed at 500°C and it is complete near 600°C. The Rietveld method was used in order to extract structural and microstructural parameters. Transmission electron micrographs reveal elongated particles which polar (long) axis size increases from 40 to 300 nm with the calcination temperature.

Magnetic properties show two behaviours: the smaller particles are superparamagnetic, while the larger ones are ferromagnetic. We have related it with mono- and multi-domain particles. Above Curie temperature, we have also observed the presence of coercive fields in a range larger than 500 K. In comparison to conventional ceramic routes, larger magnetorresistances were observed for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3+\delta}$ nanoparticles.

INTRODUCTION

In the last three years a lot of works have been published in thin films [1-4] and ceramic samples [5] of perovskite manganates, $\text{R}_{1-x}\text{B}_x\text{MnO}_{3+\delta}$ (where R = La, Pr, Nd, Sm, and B = Ca, Sr, Ba, Pb), showing giant magnetoresistance behaviour. These materials have quite interesting magnetotransport properties [6-9] and great potential applications as magnetic sensors or magnetic recording heads.

$\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3+\delta}$ crystallizes in a structure which shows a orthorhombic distortion respect to the ideal cubic perovskite ABO_3 , belonging to space group Pbnm [10]. This orthorhombic distortion of the unit cell is due to a cooperative buckling of corner-shared octahedra in order to optimize the A-O bond lengths, enlarging the unit cell and decreasing the cation-anion-cation angle ϕ from 180° [11].

The sol-gel process has the potential advantage over the other methods not only for achieving homogeneous mixing of the components on atomic scale, but also for the possibility of forming films or fibers from gels which are of technological importance [12]. Other goals of the sol-gel route are lower processing temperatures and short annealing times required, high purity of the materials, good control of the stoichiometry, size and shape of the particles, and particle sizes well below 100 nm for lower processing temperatures.

In the present work we describe the synthesis of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3+\delta}$ particles via sol-gel technology and calcined at several temperatures in order to study the effect of the calcination temperature on their structural, magnetic and magnetotransport properties.

EXPERIMENTAL SECTION

All reagent-grade chemicals were provided by Aldrich Chemical Co (Steinheim, Germany), unless $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ which was provided by Fluka Chemie AG (Buchs, Switzerland). $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and La_2O_3 were dried in a vacuum desiccator and stored in an inert glove box before use, because they are highly hygroscopic. $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was kept refrigerated, due to its low melting point (around 25 °C), and handled in an inert glove box. In order to obtain a polycrystalline reference pattern, $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3+\delta}$ was synthesized by solid state reaction from stoichiometric amounts of La_2O_3 , CaO and Mn_2O_3 . This mixture was pelletized applying a pressure of 5000 kg/cm² and then annealed at 1200 °C in two steps of 24 and 72 h, and after at 1300 °C in two steps of 24 and 72 h, with intermediate grindings in an agate mortar after each step.

For the synthesis of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3+\delta}$ via sol-gel technology urea was used as gelificant agent. As starting materials, stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used due to their high solubility in water. The initial concentrations were 0.2*2/3 M in La(III), 0.2*1/3 M in Ca(II) and 0.2 M in Mn(II) and the urea concentration was fixed at $\psi = 10$, with $\psi = \frac{[\text{urea}]}{[\text{La(III)}] + [\text{Ca(II)}] + [\text{Mn(II)}]}$. The reasons for using this value of ψ are given

elsewhere [13]. The solvent was evaporated directly on a hot plate with continuous stirring at temperatures ranging between 75 and 137 °C, which corresponds to the melting point of urea. When cooling down, a pink gel appeared, which was decomposed in an oven at 250 °C in air for 3 h, yielding to a quite porous precursor. After milling in an agate mortar, the precursor was calcined at several temperatures (ranging between 300 and 1000 °C) in order to study the effect of the particle size on their structural, magnetic and magnetotransport properties.

The samples were characterized by X-ray powder diffraction, using a diffractometer Philips PW-1710 with Cu anode (radiation CuK_α of $\lambda = 1.54186 \text{ \AA}$). Transmission electron microscopy was carried out with a Philips CM-12 working at 80kV. The magnetic properties of the samples were measured with a DMS 1660 vibrating sample magnetometer (VSM) between 100 and 900 K. Electrical resistivity, as a function of temperature and external magnetic field, was carried out with the standard DC four-probe method between 77 and 300 K; the powders obtained from the sol-gel method were pressed at $6 \cdot 10^3 \text{ kg/cm}^2$ into disks of 13mm-diameter.

RESULTS AND DISCUSSION

The initial aqueous solution has a slightly acid pH (~5.2). This pH remains acid during most of the evaporation process, increasing a little bit as far as water is removed due to the decomposition of urea reaching neutral pH values. The small increase in pH is an indication that urea decomposes in low proportions. This decomposition releases hydroxide ions which favour the hydrolysis of cations [14]. The hydrolysis leads to the formation of small amounts of a precipitate. The X-ray diffraction pattern of the dried precipitate indicates the presence of $\text{La}_2\text{O}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ (JCPDS-ICDD Card No. 28-512) and, in lower percentages, of hexagonal $\text{La}(\text{CO}_3)\text{OH}$ (JCPDS-ICDD Card No. 26-815). We observe only lanthanum compounds in the precipitate due to the larger acidity of the La(III) ions comparing to the other cations present in the solution: Ca(II) and Mn(II) [14].

When the mixture is enough concentrated the temperature raises up to the melting point of urea, around 137 °C. This temperature increase leads to a larger extent of urea decomposition raising the pH. At this stage the mixture is taken out from heating and, when it cools down, a large

increase on viscosity is observed leading to the formation of a gel. Metallic ions will be then located in the gel network with an statistical distribution according to the stoichiometric amounts of these ions in the starting solution.

Sol-gel samples of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3+\delta}$ show an incipient crystallization at 500 °C and complete crystallization takes place about 600 °C. Below this temperature we can observe very small peaks of calcite (rhombohedral CaCO_3 , JCPDS-ICDD Card No. 5-586), as it can be observed in Fig. 1.

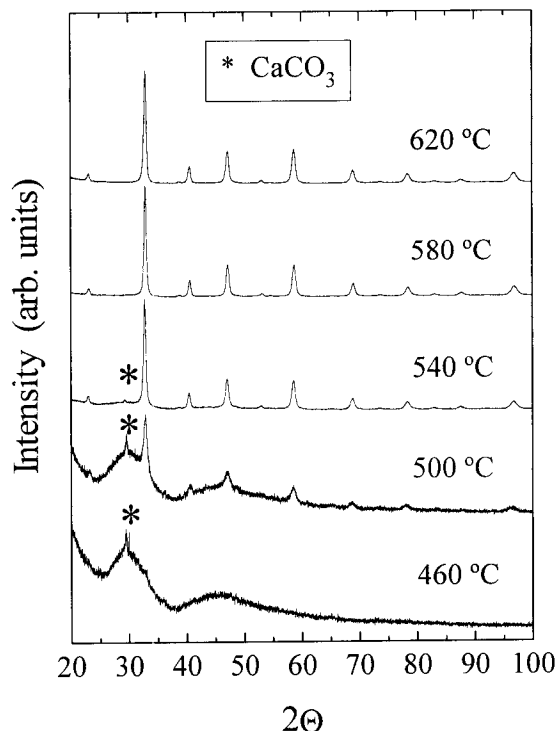


Fig. 1 : X-ray diffraction patterns of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3+\delta}$ samples as a function of the calcination temperature. Around 600 °C the crystallization is complete.

Microstructural information was derived from the Philips PC-APD software by fitting individual reflexions. An average crystallite size, D_{hkl} , was determined by applying the Debye-Scherrer's formula using the full-width-at-half-maximum (FWHM), β , of the several X-ray diffraction peaks: $D_{hkl} (\text{\AA}) = \frac{k \cdot \lambda}{\beta(\text{size}) \cdot \cos\Theta}$, where k is the shape factor which normally ranges

between 0.9 and 1.0 (in our case $k=0.9$), λ is the X-ray wavelength and Θ the Bragg angle. $\beta(\text{size})$ is the difference in profile widths of broadened and standard peaks: $\beta(\text{size}) = \beta_{\text{sample}} - \beta_{\text{standard}}$. As standard it was used a KCl sample sieved between 25 and 40 μm .

More accurate structural and microstructural parameters were extracted from the X-ray data using the program LS1, based in the Rietveld method [15,16] and written in Microsoft Professional BASIC 7.0 by Lutterotti *et al* [17]. Peak profile was modelled by pseudo-Voigt functions corrected for instrumental assymetry. The background is reproduced by a polynomial expression and, if amorphous phase halos are present in the diffraction pattern, they are modelled inserting very broad Gaussians. Because the Caglioti formula cannot reproduce all these possible broadening effects [18],

the authors have developed a model to connect profile width and shape directly to crystallite size (column length) and microstrain, along the various crystallographic directions, using conditions on cosine Fourier coefficients and their derivatives [18,19].

X-ray data were collected in the 2Θ range $20-100^\circ$ ($12-100^\circ$ for samples calcined below 600°C) with a step interval of 0.020° and a time step of 10 s.

Lattice parameters, unit cell volume and density for the various samples are shown in Fig. 2. Below 600°C we observe a decrease of all lattice parameters up to 530°C remaining almost constant in the range $530-600^\circ\text{C}$. The initial decrease is due to calcium segregation as calcite, so the material has not the right stoichiometry 67% La : 33% Ca but more percentage of La (III) ions which are larger than Ca (II) ions (1.15 and 1.05 Å for octahedral coordination, respectively) [20]. For well-crystallized samples, it is observed a significant increase of all parameters with the calcination temperature between 600 and 700°C and above this temperature a slow decrease. This slow decrease of the unit cell volume above 700°C is due to a better compactation of the structure, so the density increases slightly.

We have no clear explanation for the sharp increase between 600 and 700°C but there are several factors which can affect the lattice parameters as the Mn(IV) content, the size of the crystallite domains or changes in stoichiometry.

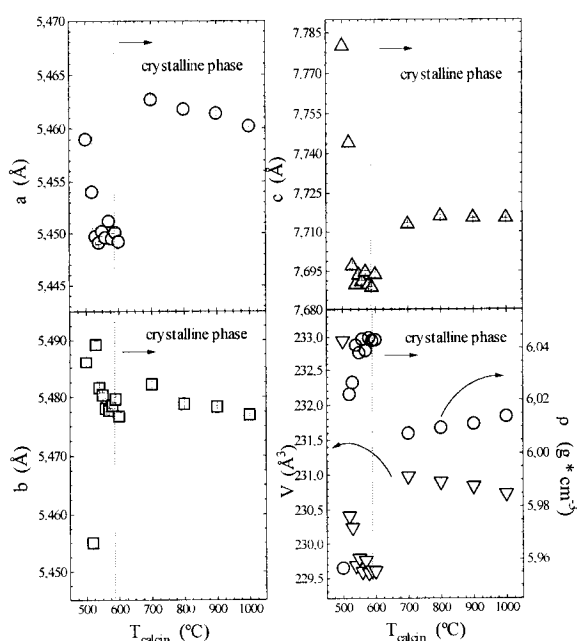


Fig. 2 : Unit cell parameters, volume and density of the sol-gel samples as a function of the calcination temperature.

In Fig. 3 we represent the results obtained by the Rietveld method for crystallite sizes and we compare them with those extracted from the Philips PC-APD software.

Transmission electron micrographs show elongated particles which polar (long) axis size increases from 40 to 300 nm as the calcination temperature increases. The fact that TEM sizes are two or three times larger than that obtained by X-ray diffraction is due to the presence of twinning and, perhaps, other kind of defects as vacancies, dislocations, etc.

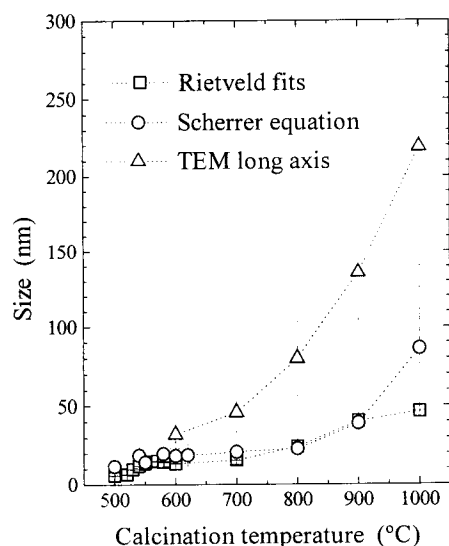


Fig. 3 : Comparison of sizes obtained by X-ray diffraction, using the Rietveld method and the Debye-Scherrer equation, and by transmission electron microscopy. The dot lines are a guide to eye.

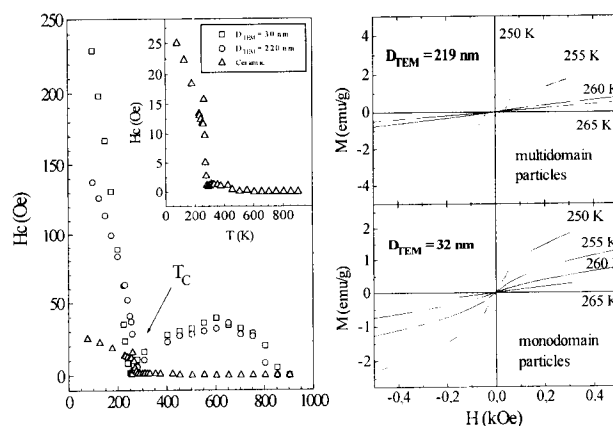


Fig. 4 : Coercive fields of the sol-gel samples measured between 100 and 900 K, obtained from the hysteresis loops.

Two kind of magnetic behaviours were observed: for the larger particles (above an average particle size of about 80 nm) the coercive field drops continuously up to the bulk Curie point, $T_C = 265$ K, and behave as paramagnetic above this critical temperature; in the case of the smaller ones (below an average particle size of about 50 nm), the samples are superparamagnetic below T_C , between 230 and 265 K (Fig 4). This results lead us to consider the smaller particles as single domains, while the larger ones behave as usual ferromagnetic multidomains. Using a theoretical relation we have determined the critical size of spherical grains below which they are single domains [21]. The critical size was 80 nm, which is in good agreement with our experimental results. In the small particles we have observed the presence of coercive fields above the Curie point in a range of 500 K (Fig. 4). This behaviour could be associated to the presence of magnetic

clusters, larger than those with sizes of ~ 12 Å, recently reported by De Teresa *et al.* in ceramic samples [22]. More systematic studies are in progress in order to clarify this assumption.

The particle size has also a great influence in the magnetoresistance, $\frac{\Delta R}{R_0} = \frac{(R_H - R_0)}{R_0}$, as it can be observed in Fig. 5 : at 1 kOe, the ceramic sample shows a MR change of 5%, while the sol-gel sample prepared at 700 °C, 12% [21,23].

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