

Lanthanum cobaltite nanoparticles using the polymeric precursor method

Monica Popa*, Jose M. Calderon-Moreno*

Institute of Physical Chemistry “Ilie Murgulescu”, Romanian Academy, Splaiul Independentei 202, Bucharest, 060021, Romania

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Abstract

The present study reports the evolution of reactive lanthanum cobaltite nanoparticles obtained by a polymeric precursor route, using citric acid as chelating agent. The crystallization from amorphous precursor, particle growth and the formation of nanoparticle agglomerates at different calcination temperatures was carried out by conventional and high-resolution electron microscopy, electron diffraction and energy-dispersive X-ray analysis and Raman spectroscopy. Microstructure measurements were compared with X-ray diffraction and chemical analysis results. Electron diffraction, combined with TEM, was used to determine the proportion of amorphous phase. The presence of amorphous carbon during the decomposition of the amorphous precursor was analyzed by Raman spectroscopy. The coherent crystalline domain size and the particle size have been monitored by XRD and electron microscopy in order to determine the evolution of both crystal size and the temperature onset for the formation of polycrystalline aggregates.

The results demonstrate that at 550 °C we obtain pure single-phase equiaxed nanopowders of LaCoO₃ with crystal size of 20 nm, free of amorphous carbon and without the presence of polycrystalline aggregates.

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Keywords: LaCoO₃ powder nanoparticles; Synthesis; Polymerizable complex; Thermal evolution

1. Introduction

The synthesis/processing and characterization of nanosized mixed oxide ceramic powders have focused much interest over the last years. The use of nanometer dimension structures in the fabrication of nanoscale devices is of intense scientific and technological interest due to their crucial microstructure based properties. Powders with nanosized particles make the systems very attractive for the development of new ceramic devices, where the physical properties depend on the particle size.

LaCoO₃ perovskite-type oxides have attractive electrical and electrocatalytic properties. The importance of these materials is due to a wide variety of applications as materials for technological chemical sensors, electrocatalysts, oxygen-permeating membranes^{1–5} or electrode materials in solid oxide fuel cells.⁶ The properties and the potential applications for which they are used have generated intense research aimed both at processing and characterization. For applications it is of importance to design and prepare high quality powders with controlled

microstructure. The properties of the final materials obtained are strongly dependent on the synthesis. Solution techniques involving improvement of the synthesis conditions for obtaining pure phases have been applied with the aim of lowering the reaction temperatures and to prepare homogeneous powders.^{4,7–16}

Powder synthesis using solution techniques allows for a better mixing of the constituent elements and thus a better reactivity of the mixture to obtain pre-reaction products at lower temperatures⁷; these methods can produce chemically homogeneous powders with fine particle size and high reactivity, suitable for the preparation of dense ceramics with homogeneous microstructure. One such technique for the low temperature synthesis of oxides is the so-called amorphous complex method.^{7,11} This technique is based mainly on the formation of soluble complexes in solution, followed by elimination of the solvent, resulting in a gel that keeps the random distribution of cations of the starting solution. The organic fraction of this gel is removed by heat processing, resulting in a very fine, homogeneous and reactive crystalline oxide powder at temperatures lower than those used in the conventional solid-state reactions. It has been claimed also that the presence of excess organic material is associated with the formation of partially sintered hard agglomerates at low temperatures.

* Corresponding authors.

E-mail addresses: monicasan14@yahoo.com (M. Popa), calderon@icf.ro (J.M. Calderon-Moreno).

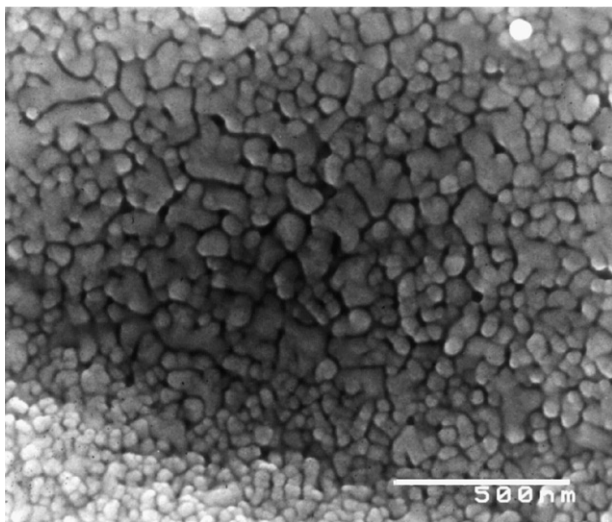
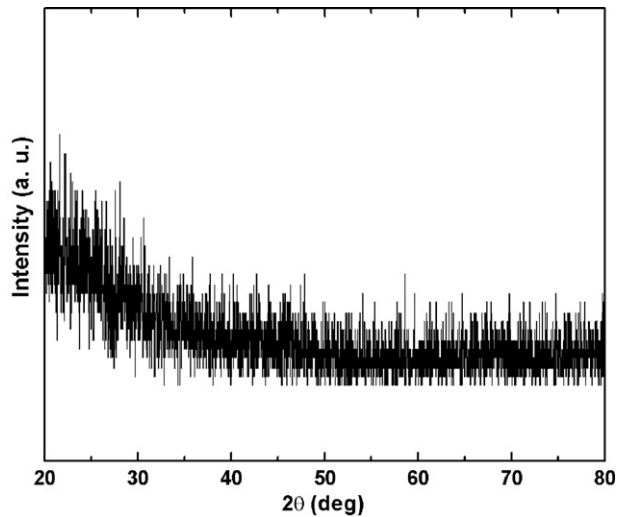


Fig. 1. XRD pattern (top) and SEM micrograph (bottom) of the amorphous precursor.

Attempts to synthesize pure single-phase powders of LaCoO_3 by the amorphous complex method and other wet-chemical routes have met with varied success, generally due to the unavoidable formation of second phases. In this context the polymerizable complex (PC) route achieves a better mixing of La and Co cations than the amorphous citrate route, thus obtaining the pure phase. Several recent reports on LaCoO_3 powder synthesis demonstrate the interest of further studies.^{17–22} However there are no studies concerning the presence of residual carbon, the calcination temperature that should be used to eliminate it, or the thermal evolution of the obtained powders: crystal size, presence of agglomerates, specific surface area. In this context, the syn-

Table 1
Proportion of amorphous phase at different calcinations temperatures.

Temperature (°C)	Amorphous (vol.%)
400	>90
450	~50
500	<10
550	–

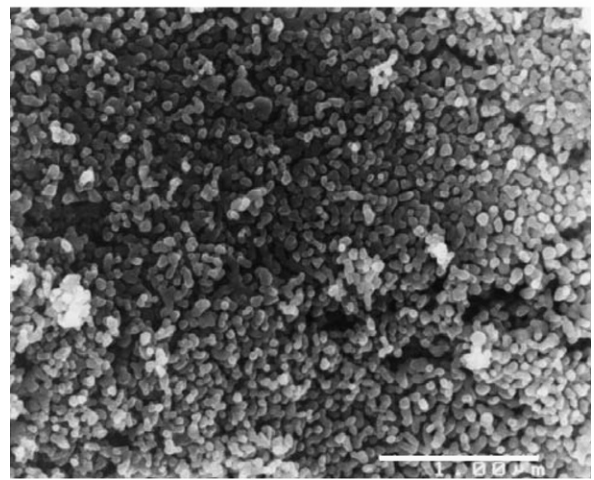
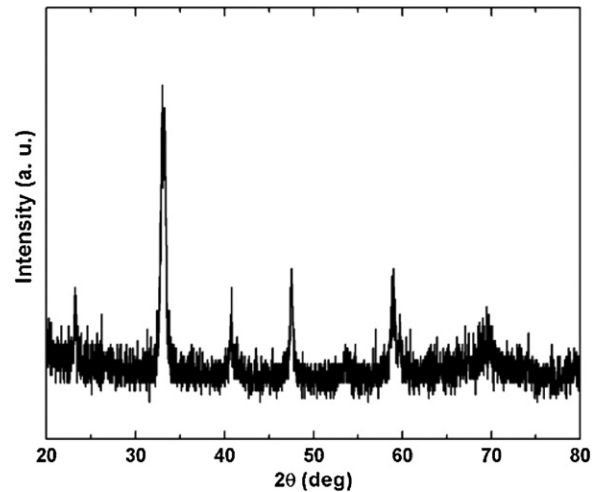


Fig. 2. XRD pattern (top) and SEM micrograph (bottom) of LaCoO_3 nanoparticles after thermal treatment of the polymeric precursor at 600 °C for 1 h.

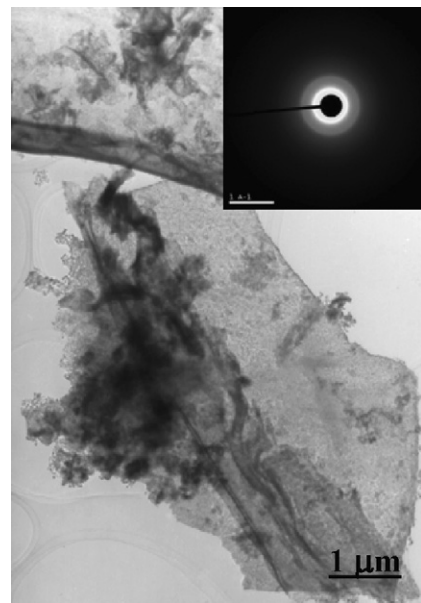


Fig. 3. TEM micrograph of the polymeric precursor calcined at 400 °C for 1 h and (inset) ED pattern showing a single diffuse ring. The amorphous flake-like material has no crystalline seed or internal features.

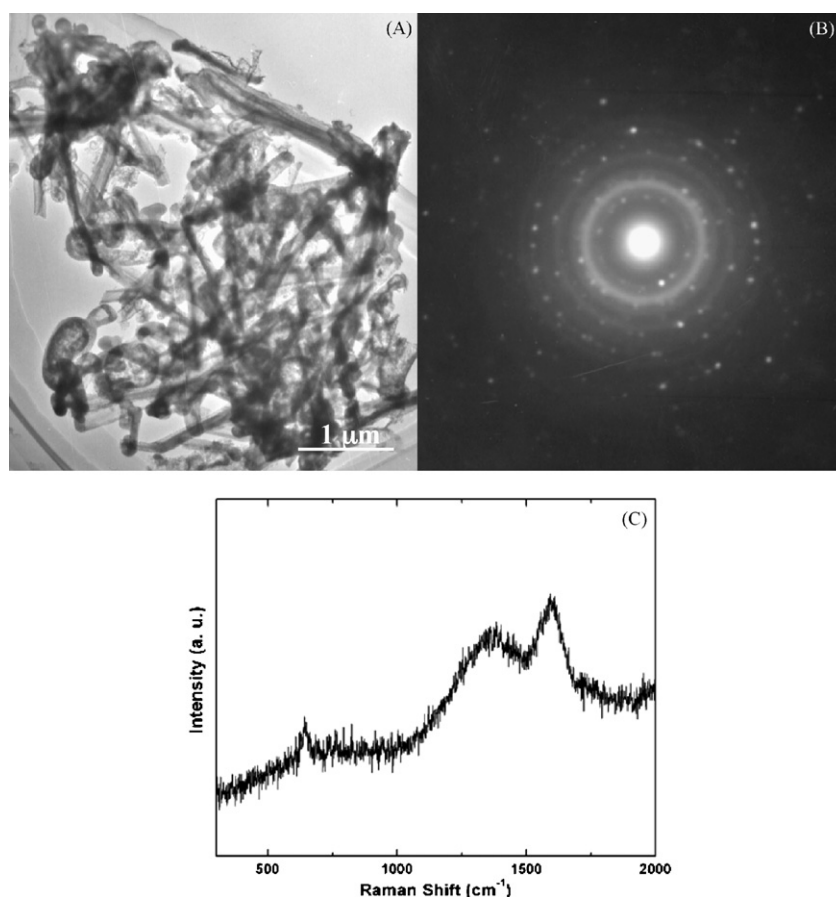


Fig. 4. (A) TEM micrograph of the precursor after thermal treatment at 450 °C for 1 h, showing LaCoO₃ nanocrystallites embedded in the amorphous precursor. (B) Electro-diffraction pattern. (C) Visible Raman spectroscopy detected the presence of amorphous carbon, indicated by broad peaks at 1340 and 1587 cm⁻¹, along with the peaks of the LaCoO₃ nanocrystals.

thesis of crystalline powders by methods that involve the use of organics, such as the amorphous complex method and the polymerizable complex method (PC method) at low temperature, based only in X-ray diffraction evidence, ignores the presence of residual carbon and the formation of hard polycrystalline agglomerates.¹²

The aim of our present study is to report on the effect of calcination temperature on the powders microstructure. Within this framework, we report the microstructure evolution of nanosized LaCoO₃ powders prepared from the La–Co metal polymeric precursor by means of a simple Pechini-type polymerizable complex (PC). The present research focuses the crystallization process, nucleation and growth of LaCoO₃ from the amorphous precursors during thermal treatment and the formation of grain boundaries and local sintering behavior above the crystallization temperature. We demonstrate with detailed electron microscopy and electron diffraction measurements the direct transformation from the amorphous precursor into perovskite LaCoO₃ nanocrystals, the percentage of transformation from amorphous at each temperature and the temperatures at which the sample is free of amorphous precursor and also free of amorphous carbon, a byproduct of the method whose presence is never mentioned in other reports and that we have monitored by Raman spectroscopy. Results determine the suitability and advantages of

the use of PC method to provide homogeneous small particle size powders with high sinterability to prepare ceramics at low temperatures.

2. Experimental

The powder preparation method has been described elsewhere.⁴ Citric acid was dissolved in water, followed by the addition of La₂O₃ · 3H₂O and CoCO₃. The mixture was stirred in order to obtain in the solution the stable metal–CA complexes and ethylene glycol (EG) was added. The temperature of the solution was increased to 70 °C and kept at this temperature until the formation of a viscous and transparent light yellow gel occurred. The poly-esterification reaction between CA and EG occurs in the solution and immobilizes the metal ions in the polymeric network. The beaker was transferred to a mantle heater, and the temperature increased and kept at 300 °C for 3 h. Heating the organic parts results in a dark brown ash which was ground into a powder, referred to as the “precursor” hereafter. The “precursor” powder was ground and calcined in air in the temperature range from 400 to 900 °C, at a heating rate of 10 °C min⁻¹, for 5 min to 8 h, using sintered alumina boats, generating fine powders. The products obtained at different stages were characterized by different techniques.

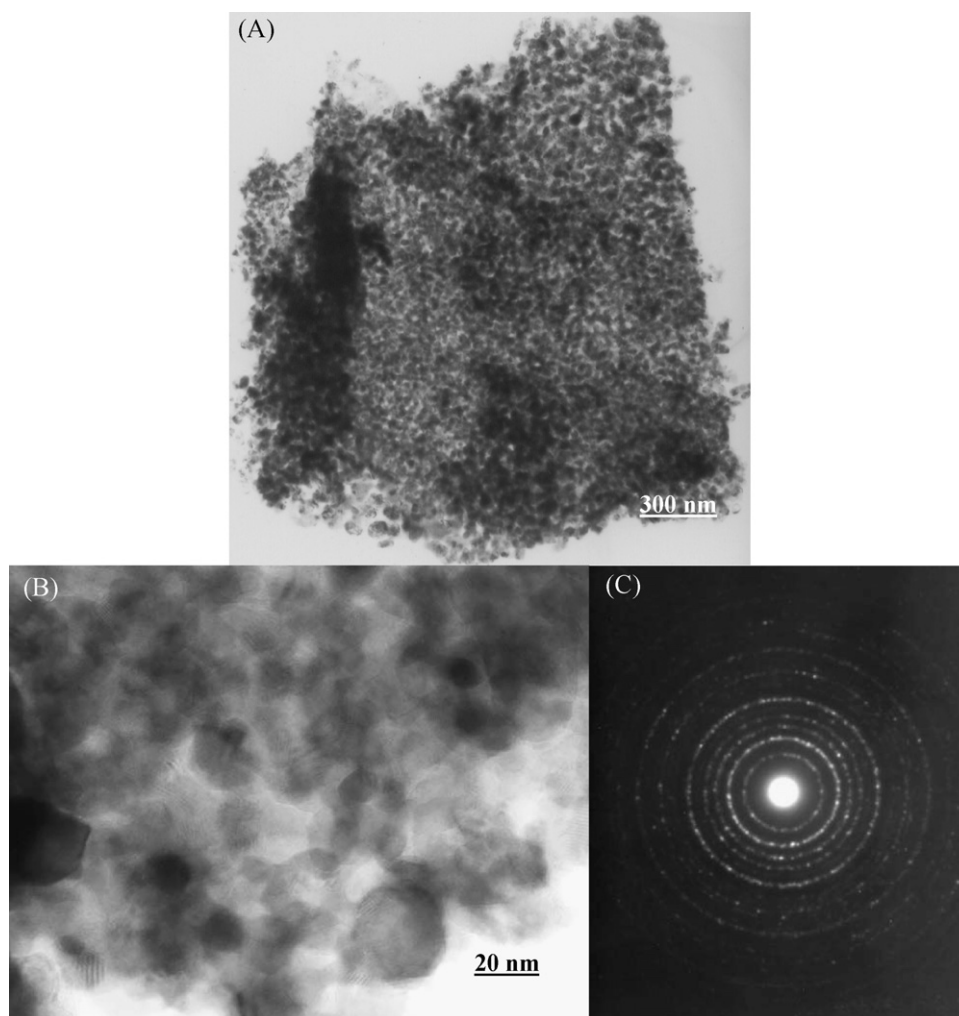


Fig. 5. (A) TEM micrographs of the LaCoO_3 nanocrystallites calcined at 450°C for 1 h. (B) HRTEM micrograph showing the lattice image of the nanocrystallites. (C) The electro-diffraction pattern showed clear diffraction rings of single-phase rhombohedral LaCoO_3 .

The precursor was characterized by thermal analysis (TG-DTA) in static atmosphere air between 30 and 900°C , with a heating rate of $10^\circ\text{C min}^{-1}$, using 7.5 mg of sample in Pt crucible. The precursor and the calcined LaCoO_3 powders were characterized by XRD, in a 2θ range from 15° to 75° with scanning speed of $0.75^\circ \text{min}^{-1}$, at room temperature using $\text{Cu K}\alpha$ radiation (Siemens D-500). The calcined powders were characterized by Raman spectroscopy (Model Jobin Yvon T-64000) with a CCD detector cooled with liquid nitrogen; the 514 nm line of an Ar^+ laser was used as excitation source. The spectra were collected at 25°C , with a laser power of 10 mW to avoid any laser ablation. The powder morphology was observed by scanning electron microscopy (SEM) (Hitachi 4100FE) and transmission electron microscopy (TEM) (Hitachi H800MT and JEOL 2010) equipped with electron diffraction (ED). The composition of the amorphous precursors and powders was studied by energy-dispersive X-ray analysis (EDX) (KeveX).

The present study determines, using electron microscopy techniques, the solid reaction products at different temperatures, the nucleation of lanthanum cobaltite nanoparticles from the polymeric precursor during thermal treatment; the amount of amorphous or carbon phases present; the crystalline phases in

the powders; the grain growth with temperature and the formation of grain boundaries and local sintering behavior above the crystallization temperature.

3. Results and discussion

The ash of the gel after thermal treatment at 300°C in the mantle heater or “precursor” material shows an amorphous character. Fig. 1 shows a SEM micrograph and the XRD pattern of the amorphous precursor. After thermal treatment of the precursor, the formation of LaCoO_3 nanocrystalline powders was observed. Fig. 2 shows a SEM micrograph and the XRD pattern of LaCoO_3 nanoparticles calcined at 900°C for 1 h. The lowest calcination temperature to obtain the LaCoO_3 crystalline phase is 450°C , although amorphous phase remains, identified by the presence of a broad peak between 20 and 40° (Fig. 1). Table 1 indicates the proportion of amorphous phase after each calcination temperature. Fig. 3 shows a TEM micrograph of the precursor calcined at 400°C . At this temperature the La–Co amorphous precursor has lost all its organic part but no crystalline seed or internal structure could be observed in the flake-like material. The ED pattern showed a single diffuse

ring (inset in Fig. 3). The calculated chemical composition from EDX measurements revealed almost stoichiometric [La]:[Co] ratios and a high carbon content (C atomic %: ~60%). Therefore, the sample calcined at 400 °C is composed of a mixture of amorphous carbon and amorphous lanthanum cobaltite.

According to thermo-gravimetric measurements the combustion of the organics in the powder precursor occurs between 180 and 470 °C. Fig. 4 shows the precursor after thermal treatment at 450 °C, the onset temperature of crystallization of the LaCoO₃ nanopowder, shown by the appearance of LaCoO₃ crystallites embedded in the amorphous precursor. The amorphous flakes kept their irregular shape even after thermal treatment, however, the density of LaCoO₃ crystallites varied between the flakes. The XRD patterns alone cannot confirm the presence of carbon from the organic matrix, but Raman scattering can readily indicate the presence of amorphous carbon.^{23,24} Our Raman spectroscopy measurements detected the presence of amorphous carbon, indicated by broad peaks at 1340 and 1587 cm⁻¹ (Fig. 4C). EDX studies indicated that the ratios of [La]:[Co]:[C] in the polymeric precursor were similar to those in the untreated amorphous material. The ED pattern in Fig. 5 shows the LaCoO₃ nanocrystallites formed at 450 °C and the characteristic ring pattern of polycrystalline LaCoO₃. The crystallites have typical sizes between 15 and 40 nm, with a mean particle size of 26 nm, calculated from over 200 LaCoO₃ nanocrystals. The proportion of amorphous phase, estimated from TEM measurements is ~50%.

After calcination at 500 °C, most of the amorphous part disappeared (Fig. 6) and only LaCoO₃ crystallites remained. Powders synthesized by wet-chemical methods that use organic chelates, like the amorphous complex method or the polymerizable complex method, often result in agglomerates of nanoparticles partially sintered during the thermal treatment applied to remove the organic matrix. Since large amounts of carbon lead to an excessive release of heat during its combustion, it is desirable to

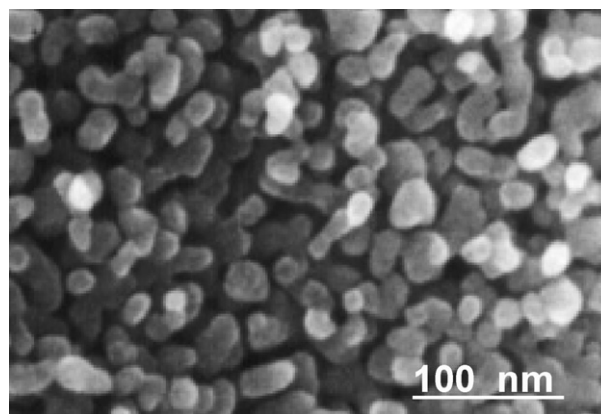


Fig. 6. SEM micrograph of a sintered agglomerate formed after calcination of LaCoO₃ nanocrystallites at 600 °C for 1 h. The grains in the agglomerate show a homogeneous size, with an average grain size ~40 nm.

decrease as much as possible the presence of carbon in the system in order to avoid the partial sintering of the highly reactive particles. Citric acid was used as the chelating agent to this end to reduce the amount of organics during the process. Raman, TEM and EDX measurements showed the presence of carbon up to 550 °C. Pure single-phase LaCoO₃ nanocrystallites were obtained after burnout of the residual carbon by calcination for 1 h at 550 °C. Samples calcined at 550 °C showed good homogeneity after the complete removal of the organic part, without the presence of agglomerates or partial sintering; LaCoO₃ particle sizes were similar to that of the powders calcined at 450 °C. The main difference after thermal treatment at 550 °C was the disappearance of the amorphous flakes and the complete elimination of carbon presence, as confirmed by elemental chemical analysis. These results indicate a strong tendency of LaCoO₃ for isolated nucleation from the amorphous precursor at low temperature.

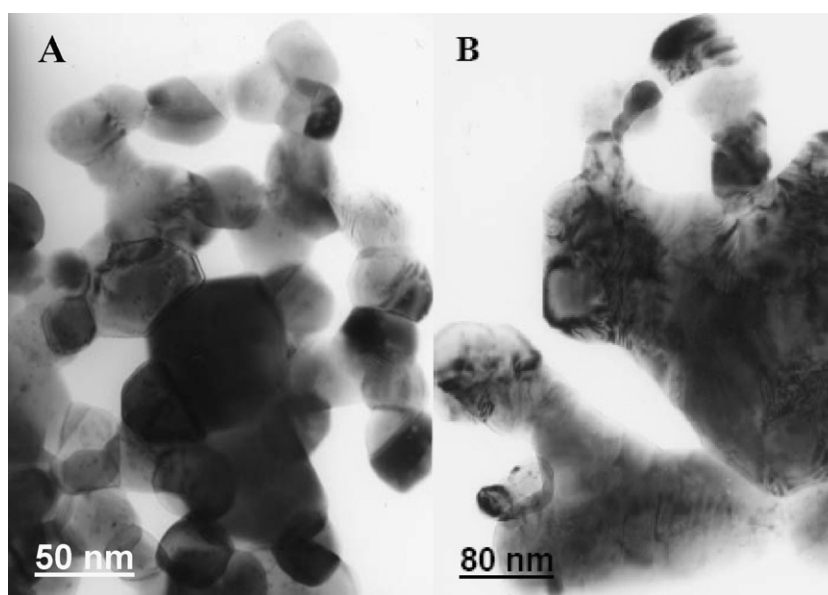


Fig. 7. TEM micrographs of the LaCoO₃ nanoparticles calcined at (A) 700 °C and (B) 900 °C for 1 h, showing partial sintering by the formation of grain boundaries and grain boundary networks; the internal features inside the grains indicate defects associated with grain boundaries and the formation of domains inside the grains.

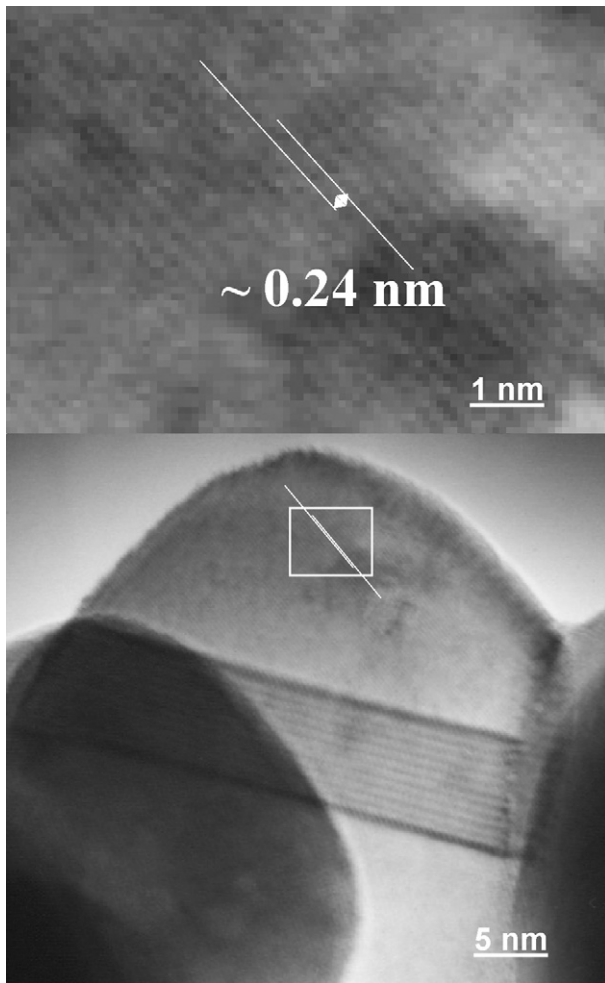


Fig. 8. (Bottom) HRTEM micrograph after thermal treatment at 900 °C showing dislocation networks associated to the grain boundaries and (top) the detail of the lattice image inside the LaCoO₃ nanocrystallite. The lattice misalignment is clearly seen at the grain boundary, and a dislocation network indicates the formation of ferromagnetic domains with different orientation inside the nanocrystallite.

Increasing temperatures led to the formation of grain boundaries and sintering. Despite the relatively low calcination temperature, it is possible to observe in the SEM images (Fig. 6) of the sample calcined at 600 °C that the powder was partially sintered. The beginning of grain growth was also observed at 600 °C. Fig. 7 shows formation of grain boundaries and grain boundary networks after thermal treatment at 700 and 900 °C. TEM measurements after thermal treatment at 900 °C show partial sintering by the formation of grain boundaries and dislocation networks associated with the grain boundaries. Features associated with domain formation can be clearly distinguished inside the crystallites. Fig. 8 is a HRTEM micrograph of a small agglomerate formed during partial sintering at 600 °C; the lattice image shows a good crystalline order inside in the LaCoO₃ particles, in agreement with the XRD patterns, as well as dislocations networks associated to the grain boundaries.

Fig. 9 shows the evolution with temperature of the measured average particle from SEM and TEM micrographs and of the coherent crystalline domain size obtained from XRD mea-

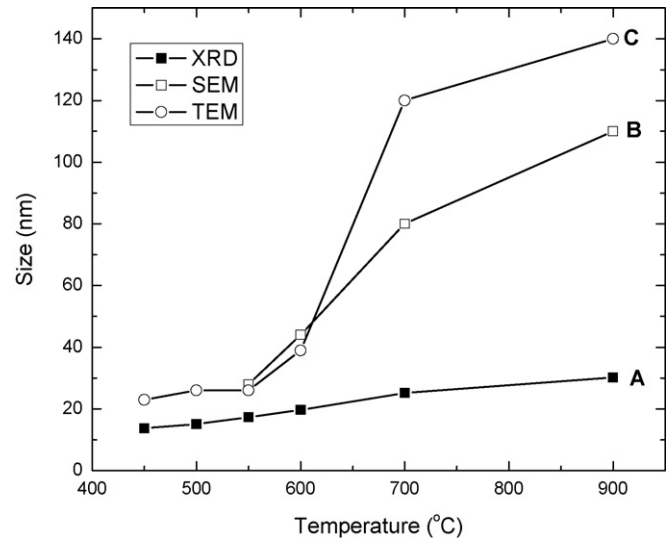


Fig. 9. Evolution with temperature of the crystalline domain size (A) and of the average particle size, measured from SEM (B) and TEM (C) micrographs.

surements by Scherrer's method. Direct nucleation of LaCoO₃ nanocrystallites by combustion of the organic part in the amorphous precursor matrix occurs between 400 and 450 °C; grain sizes after calcinations at temperatures between 450 and 550 °C are ~20–25 nm, in good agreement with single crystalline domain sizes, ~15–20 nm. After 1 h at 600, 700 and 900 °C, the average grain size grows to ~40, ~90 and ~130 nm. In spite of the significant particle growth, crystalline domain sizes grow much less, to ~30 nm at 900 °C. The curves in Fig. 9 indicate that, at temperatures close to 600 °C, the formation of polycrystalline aggregates composed of several crystalline grains or domains is thermally activated. The ratio particle size/particle domain, constant between 450 and 550 °C, grows slightly at 600 °C, and becomes three times bigger at 700 °C, remaining around this value at 900 °C. Results indicate that it is possible to obtain dense ceramics with homogeneous equiaxed grain size by sintering at temperatures around 600 °C. We have indeed obtained a dense ceramic pellet by pressureless sintering at 600 °C after cold isostatic pressing. The polished surface of the

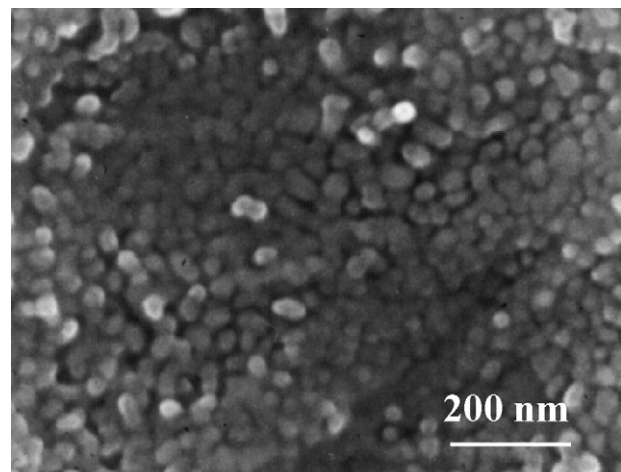


Fig. 10. SEM micrograph of a dense ceramic pellet after sintering at 600 °C.

pellet is shown in Fig. 10 showing that the particle size has remained around 40 nm, after sintering.

4. Conclusions

The method using citric acid as chelating agent and water as solvent provides very homogeneous, single-phase LaCoO₃ powders. Equiaxed nanopowders of LaCoO₃ with crystal size of 20–25 nm and free of polycrystalline aggregates were obtained at 550 °C.

LaCoO₃ demonstrates a strong tendency to multiple isolated nucleation of nanocrystals in the amorphous precursor. The carbon content in the polymeric precursor is completely eliminated by thermal combustion at 550 °C, without the formation of agglomerates or inhomogeneities in grain size; LaCoO₃ crystallites with an average particle size ~20–25 nm without organic or carbon contamination are obtained at this temperature. Formation of grain boundaries, sintering and grain growth begins at about 600 °C. High-resolution electron microscopy measurements show that the nanopowder is composed of single crystalline grains at 550 °C while dislocations networks and other domain boundary-related features are clearly observed after treatments at 700 and 900 °C; at these temperatures crystalline size measured by XRD is several times smaller than the particle size observed by SEM and TEM. The average particle size reaches ~130 nm after successive thermal treatments of 1 h at 600, 700 and 900 °C. The results indicate that dense homogeneous LaCoO₃ ceramics with an average grain size of ~40 nm can be obtained by sintering at 600 °C.

The results observed during the thermal evolution of the LaCoO₃ amorphous precursor can find application in the production of different pure single-phase homogeneous nanopowders of LaCoO₃-based ceramics, including LaM_xCo_{1-x}O₃ solid solutions with other transition metals and group II metals (M=Fe, Mn), perovskites which are of great interest due to their electronic and magnetic properties.

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