

LaNiO₃ nanopowder prepared by an ‘amorphous citrate’ route

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Available online 8 August 2005

Abstract

Aqueous solution techniques are simple and easy to use technological methods for preparing single-phase ceramic powders with controlled and homogeneous grain size. This study presents the preparation of ferroelectric LaNiO₃ ceramic samples by a gel-method using low sintering temperatures and the evolution of the amorphous complex and LaNiO₃ nanocrystallites with temperature.

Ferroelectric LaNiO₃ powders were prepared using an ‘amorphous citrate’ route. X-ray diffraction, Raman scattering and electron microscopy techniques were used to characterize the obtained products after thermal treatments at between 550 and 750 °C and revealed the formation of LaNiO₃ nanocrystallites of perovskite structure with homogeneous grain size after thermal treatment at 650, 700 and 750 °C, with particle sizes of ~30, 42 and 65 nm, respectively. Raman spectra exhibit the characteristic band of the LaNiO₃ perovskite-phase at 392 cm⁻¹ and decreasing band width with temperature, an effect associated to the observed change in grain size.

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Keyword: LaNiO₃

1. Introduction

From the point of view of both applications and basic research, perovskitic ABO₃ materials are of worldwide interest because of their very interesting properties, such as ferroelectric, magnetic, optical and colossal magnetoresistance,¹ high-Tc superconductivity,² non-volatile memory effects,³ etc, many of them found out during the last two decades. LaNiO₃ belongs to this group of materials and it is known as a good electrically conducting oxide applied as electrode material in electronic devices such as FERAM.⁴

For the synthesis of perovskite-type oxides, gel routes have demonstrated to be very useful, obtaining well crystallized powders with excellent stoichiometric control,⁵ homogeneous composition and microstructure, and large surface areas, using relatively low temperatures for the synthesis. It is well known that a small crystallite size, below a few ten nanometers, could lead to new properties different from those of conventional grain-sized materials. From this point of view

the availability of single-phase powders of good sinterability, with homogeneous microstructure, small grain size and good crystallinity, is desirable.

The aim of this work is the synthesis of LaNiO₃, which has generated considerable interest as metallic conductivity perovskite ceramic using a gel technique, modified from the Pechini method, the ‘amorphous’ citrate route. This synthesis process involves the formation of a polymeric resin, using citric acid and ethylene glycol.⁶ We present the preparation of LaNiO₃ powders by the citrate technique at different temperatures up to 750 °C. The structures of the samples were characterized by Raman scattering, X-ray diffraction, and scanning electron microscopy (SEM). The particle sizes were estimated by transmission electron microscopy (TEM). The effects of thermal annealing on the structure and the particle size of the samples were investigated.

2. Experimental procedure

A given amount of La₂O₃ was dissolved in concentrated nitric acid. Ni(NO₃)₂·4H₂O was added to the solution. Water

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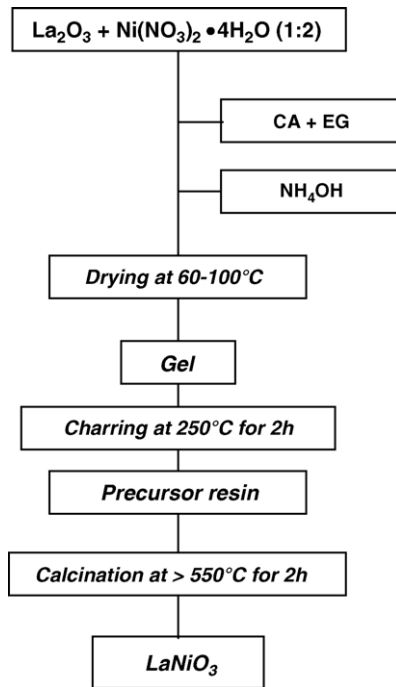


Fig. 1. Flowchart for the preparation of LaNiO_3 through the amorphous citrate complex route.

was added until the salts were completely dissolved. An aqueous solution of citric acid and ethylene glycol was also added to the mixed nitrate solution. The molar ratio of lanthanum and nickel was 1:1, whereas the citric acid/metal molar ratio was set to 1.8 and the citric acid/ethylene glycol ratio was set at 60/40 (mass). NH_4OH was again added to the solution, a drop at a time, and stirred continuously until the pH reached 7–8. The temperature was raised to 60–100 °C as the mixed solution turned into a gel. No visible precipitation was observed during this heating process. The gel was heated to 250 °C for 2 h, and a solidified dark black spongy

resin was obtained. The obtained resin is called upon here the ‘precursor’ material. A flow chart including all the sample preparation steps to obtain the lanthanum nickelate precursor is given in Fig. 1. After preparation, the precursor was heat-treated at 550, 650, 700 and 750 °C for 2 h at a rate of 5 °C/min.

The crystalline structure and phase purity of the obtained samples were characterized by X-ray powder diffraction (XRD), using a Siemens D5000 diffractometer with $\text{Cu K}\alpha$ radiation. The XRD patterns were collected with an angle step of 0.01 for all measurements.

Raman spectra of all the samples were recorded at room temperature on a Jobin Yvon micro-Raman spectrometer.

Samples were observed in a JEOL SEM after Pt–Pd coating.

The particle size was evaluated by TEM on a Hitachi apparatus using 200 keV as accelerating voltage. Samples were prepared by dispersing the sample with ethanol in an ultrasonic bath and evaporating a drop of the solution in a carbon microgrid before observation.

3. Results and discussion

3.1. XRD

Fig. 2 presents the evolution of the XRD patterns for LaNiO_3 (LNO) samples heat-treated at different temperatures, 550, 650, 700, 750 °C. It can be observed that the sample annealed at 550 °C is still amorphous, containing NiO phase. The features of LaNiO_3 perovskite-type phase with rhombohedral symmetry appear in the XRD spectra when the annealing temperature is raised to 650 °C. Strong characteristic peaks of the LNO crystallites can be observed in the XRD pattern of all the samples annealed at temperatures equal or higher than 650 °C, in all cases the amorphous precursor

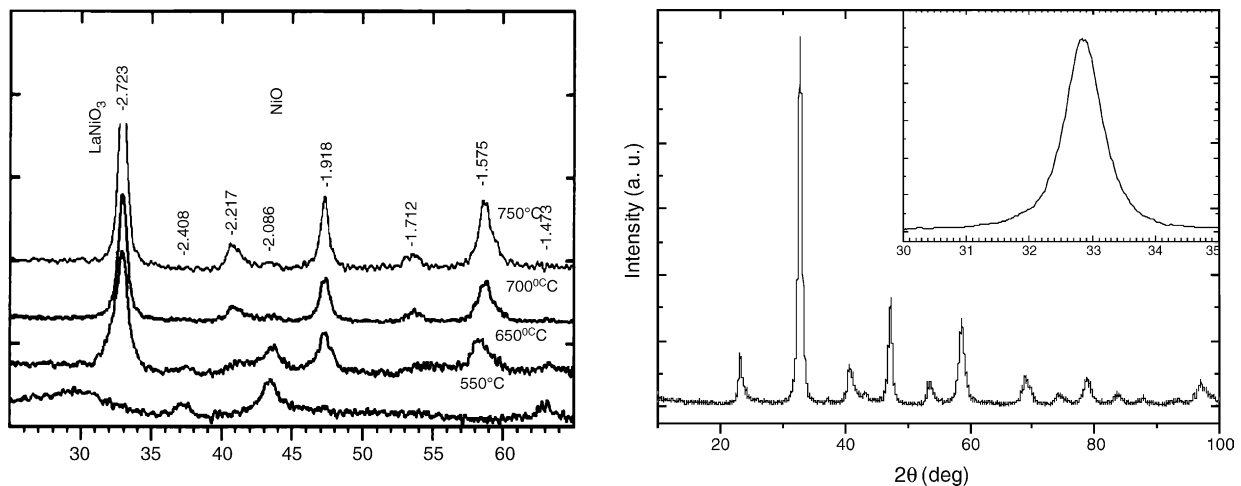


Fig. 2. (Left) X-ray diffraction patterns of the powders calcined for 2 h at different temperatures, from below: 550, 650, 700, and 750 °C. (Right) Pattern at 700 °C with an enlarged view of the main LaNiO_3 X-ray peak at $2\theta \sim 33^\circ$.

sor crystallized in the LNO phase. Increasing the annealing temperature, the NiO/LNO ratio decreases gradually, and the NiO phase nearly disappeared when the annealing temperature increased to 750 °C.

The patterns have broad diffraction peaks, attributed to the small size of the LaNiO_3 nanocrystallites. The half-width decreases gradually with increasing annealing temperature. It implies that the lattice distortion in the crystalline grains decreases, which probably is related to an increasing particle size. The crystallite sizes were calculated using the Scherrer equation, $L = 0.9\lambda/\beta \cos \theta$, where L is the mean crystallite size, β the full-width at half-maximum and λ is the used radiation wavelength (1.54183 Å). Calculated values were 10.5,

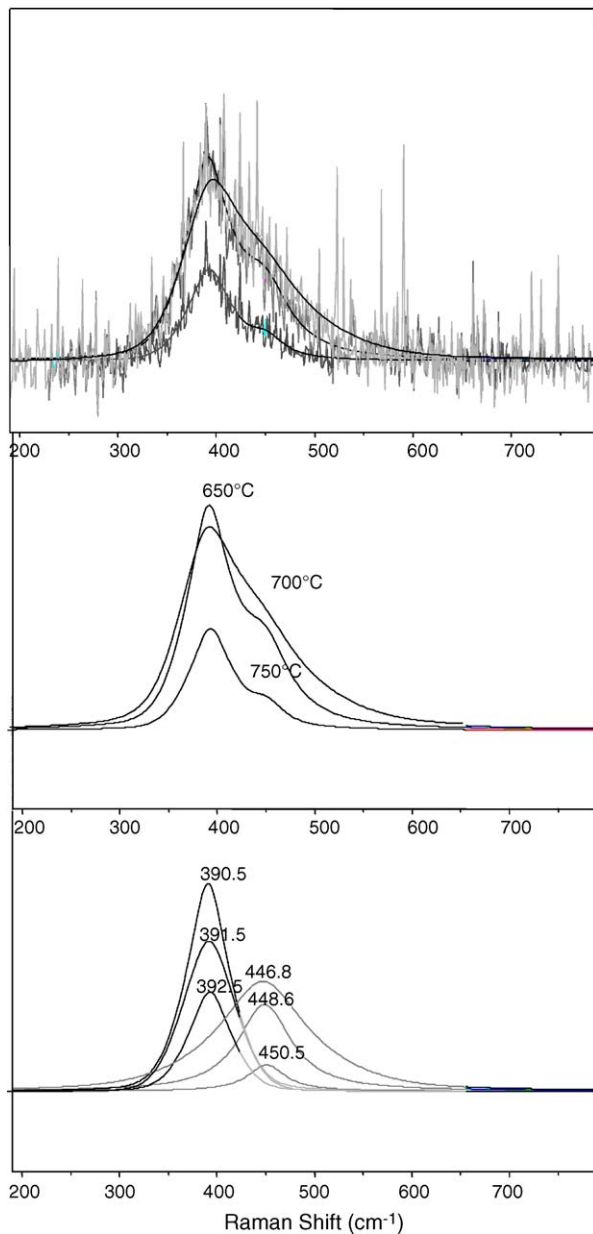


Fig. 3. (Top) Raman spectra of the LaNiO_3 samples annealed at different temperatures. (Below) Deconvolution of Raman spectra.

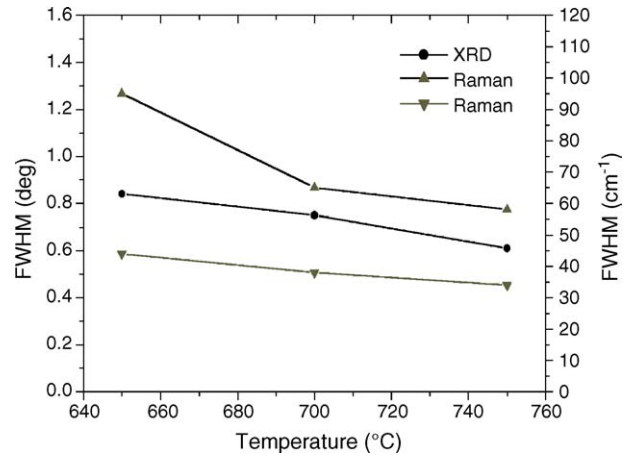


Fig. 4. Evolution with annealing temperature of the full-width at half-maximum for the deconvoluted Raman peaks and for the main XRD peak.

11.7 and 14.5 nm for samples treated at 550, 650 and 750 °C, respectively.

3.2. Raman

As known LNO belongs to the ABO_3 perovskite group of materials, it has the rhombohedral unit cell, so its Raman spectra could exhibit a high number of active modes. The Raman measurements showed that the LaNiO_3 perovskite-type phase with rhombohedral symmetry is not present after thermal treatment at 550 °C, in agreement with XRD results. The Raman spectra of LNO samples treated at temperatures of 650, 700, and 750 °C are shown in Fig. 3. The spectra exhibit a wide peak at 392 cm^{-1} , one characteristic Raman line of LaNiO_3 . The small crystallite size of the samples, indicated by XRD results, lead to a significant reduction of the number of Raman peaks compared to those observed in a non-distorted crystalline lattice, so the study of the Raman spectra of these homogeneous powder with very small crystalline size

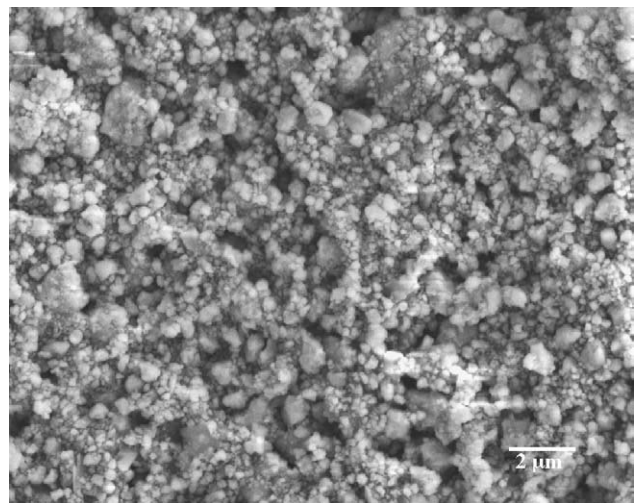


Fig. 5. SEM micrograph showing the LaNiO_3 amorphous precursor after thermal treatment at 550 °C.

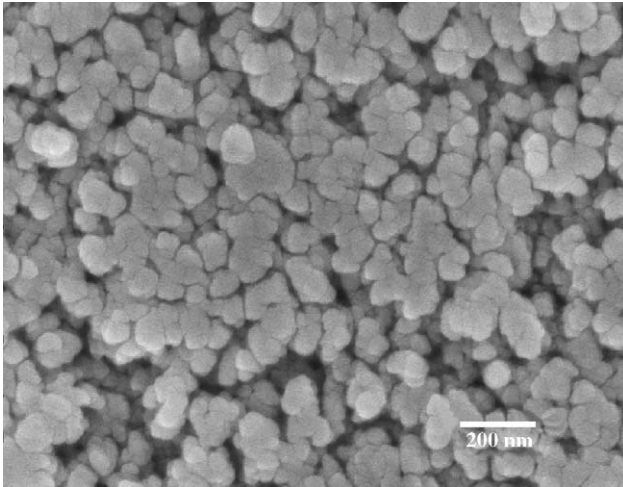


Fig. 6. SEM micrograph showing the LaNiO_3 nanoparticles formed after thermal treatment at 700°C .

is of interest. A detailed study of the Raman spectra will be carried out elsewhere, here we can note that the wide band at $\sim 391\text{ cm}^{-1}$ seems to be formed by at least two peaks. By using an Spectral Analysis Program we deconvoluted the Raman band into two separated Gaussian–Lorentzian peaks, shown also in Fig. 3. From the results of the peak separation process the half-widths of the separated peaks were estimated and are presented in Fig. 4. The half-width of the Raman peaks clearly decreases with increasing annealing temperature, an effect that we associate to the formation of a less-distorted lattice due to particle growth, similarly to what we concluded from XRD results.

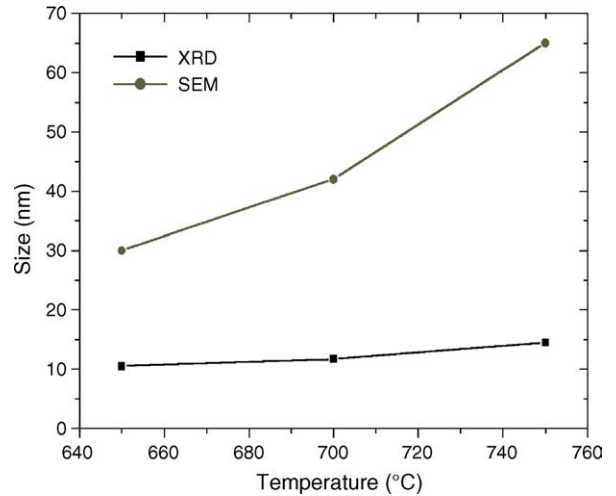


Fig. 7. Evolution with annealing temperature of the particle size measured by SEM and the crystallite size given by XRD.

3.3. SEM

Fig. 5 is a SEM micrograph of the LNO precursor calcined at 550°C . It can be observed the presence of flake-like particles of irregular shape with typical sizes from hundreds of nanometers to a few microns, many of which appear covered by numerous smaller rounded agglomerate-like structures. At this temperature, at the early stages of LaNiO_3 crystallization in a still mostly amorphous matrix, XRD measurements did not detect the presence of LaNiO_3 crystallites. A typical microstructure with nanocrystalline nuclei embedded in the amorphous matrix has been reported in high-resolution

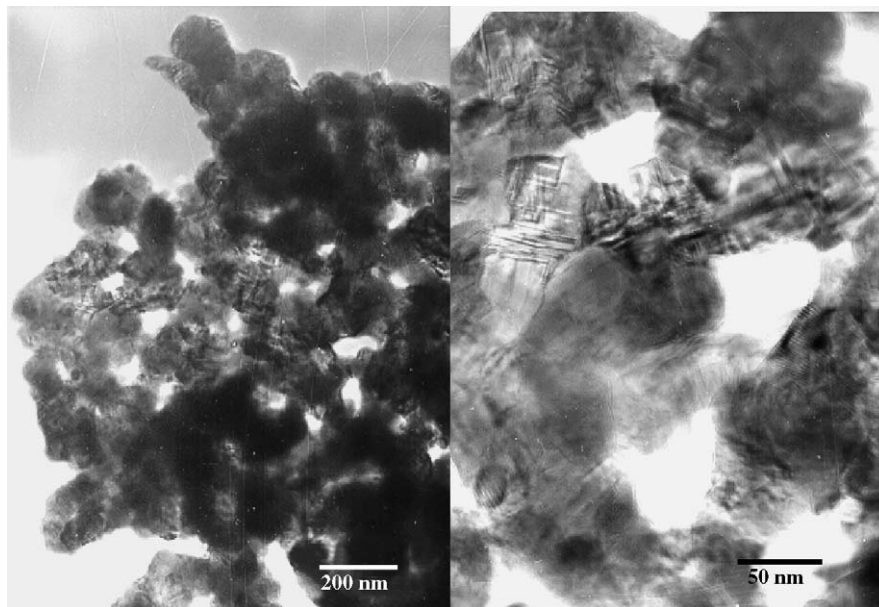


Fig. 8. TEM micrographs of the sample annealed at 700°C . The higher magnification micrograph (right) shows clearly the internal features inside the rounded nanoparticles. The LaNiO_3 nanoparticles consist of a number of different crystalline domains of smaller size.

TEM studies on the evolution of the amorphous calcined gel for amorphous citrate precursors of other perovskitic materials, such as LiNbO_3 ,⁷ at the early stages of crystallization, around this temperature. After thermal treatment at 550 °C, the combustion of the organic part of the precursor must be almost complete; the change in appearance, from flakes to agglomerated particle-like structure, indicates that the formation of nuclei from which LNO particles will crystallize might have already occurred at this temperature. At 650 °C the combustion of the organic part of the amorphous precursor is complete, as shown by previous studies on the evolution with temperature of amorphous citrate complexes. The change in the microstructure at the nanoscale is evident, it is observed the formation of nanoparticles with homogeneous particle size around 40 nm, while the amorphous agglomerates have disappeared. Fig. 6 shows a SEM micrograph of the obtained LaNiO_3 particles. The size of the nanocrystallites determined by the Scherer equation from XRD measurements is smaller than the particle size values measured from SEM micrographs (Fig. 7). This can be explained by the existence of different crystalline domains in the nanoparticles. Thus the particle sizes measured in SEM corresponds to polycrystalline grains and is bigger than the crystallite size given by XRD.

3.4. TEM

We carried out further characterisation by TEM in order to observe the LaNiO_3 nanocrystallites in the nanoparticles observed by SEM. Fig. 8 shows a TEM micrograph of the sample annealed at 700 °C. The particle size is similar to that observed in SEM micrographs and we can note inside the grains what seem to be grain boundaries or typical contrast effects associated to the existence of crystalline domains with different orientation. The higher magnification micrograph in Fig. 8 allows us to see clearly the presence of internal features inside the rounded nanoparticles. These observations explain the discrepancy between the observed particle size observed by SEM and crystalline size measured by XRD and confirms that the LaNiO_3 nanoparticles are made up of a number of different crystalline domains of smaller size (~12 nm at this temperature). The small crystalline sizes are in agreement with the observed Raman features.

4. Conclusions

The ‘amorphous citrate’ gel method is a simple and easy to use technological method that allows the preparation of single-phase ceramic powders of LaNiO_3 with controlled grain size by thermal annealing. We obtained single-phase LaNiO_3 nanopowders at 650 °C with particle sizes from 30 to 65 nm at annealing temperatures from 650 to 750 °C, while the crystalline size, given by XRD measurements, varied from 10 to 15 nm.

The main observed Raman feature of the small LaNiO_3 crystallites was a wide peak at 392 cm^{-1} , with decreasing half-width at increasing temperatures, an effect that we attribute to the increase in the grain size as the temperature of thermal treatment increases.

Acknowledgments

The study was carried out with financial support from the National Fundamental Research Program for Natural Science, a Grant from NCST of Vietnam D.C. was funded by CICYT, grant MAT2004-01214, and Generalitat de Catalunya grant 2001-SGR-00190.

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