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Low-temperature synthesis of single-phase crystalline LaNiO_3 perovskite via Pechini method

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Abstract

LaNiO_3 powders were prepared from polymeric precursors. The material was calcinated either under flowing oxygen or in air at temperatures ranging from 300 to 800 °C. The formation of new phases upon calcination was investigated using X-ray diffraction, thermal gravimetric analysis, Fourier-transform infrared spectroscopy and CHN analysis. The results revealed the formation of a single-phase powder having the perovskite structure at temperatures as low as 600 °C. The atmosphere did not significantly affect the final product. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: LaNiO_3 ; Rare earth; Perovskite; Pechini method

1. Introduction

Perovskite mixed oxides with general formula ABO_3 and containing both rare earth elements and 3d transition metals in the +3 state can be considered strategic materials due to their electronic, magnetic, optic and catalytic properties, among others [1–4]. The production of high-performance ceramics, which display such properties, has driven forward the elaboration of new powder synthesis routes. RE-NiO_3 (RE = rare earth element) can be produced using a number of methods including conventional

ceramic powder technology, sol–gel processing, powder coprecipitation and nitrate decomposition, to name a few [5–7]. Those techniques generally require high temperatures, flowing oxygen and long calcination periods (usually in excess of 16 h) in order to obtain homogeneous materials.

LaNiO_3 is a typical rare earth metal oxide that has been extensively investigated as a case study among rare earth perovskites containing Ni^{+3} [5]. In the present study, LaNiO_3 was synthesized following the Pechini process [8]. This technique allows for superior stoichiometric control, reproducibility and homogeneity, as compared to physical methods. The effect of the preparation procedure and calcination parameters on the formation of LaNiO_3 was investigated. These are relevant aspects which play an

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important role in determining the overall electronic, magnetic, optic and catalytic properties of this kind of material.

2. Experimental procedure

2.1. Synthesis

Lanthanum nickelate was prepared from highly pure polymeric precursors using the method proposed by Pechini [8]. Lanthanum nitrate and nickel citrate (citric acid to Ni 2.5:1) 1.0-M solutions were prepared using deionized water. The solutions were mixed and homogenized resulting in a La to Ni ratio of 1:1. The mixture was heated up to 90 °C at which point ethyleneglycol was added in a ratio 40:60 with respect to citric acid. The temperature was maintained constant during 2 h resulting in a resin, which was polymerized at 300 °C. The resulting polymer was calcinated in air at different temperatures, i.e., 500, 600 or 800 °C during 4 h. The heating rate was set up to 5 °C min⁻¹. Alternatively, the material was calcinated under in flowing oxygen at 600 or 800 °C during 4 h. A black crystalline ceramic powder was obtained thereafter.

2.2. Characterization

2.2.1. Elemental analysis

The contents of Ni⁺² and La⁺³ in the precursor solutions were determined by atomic absorption us-

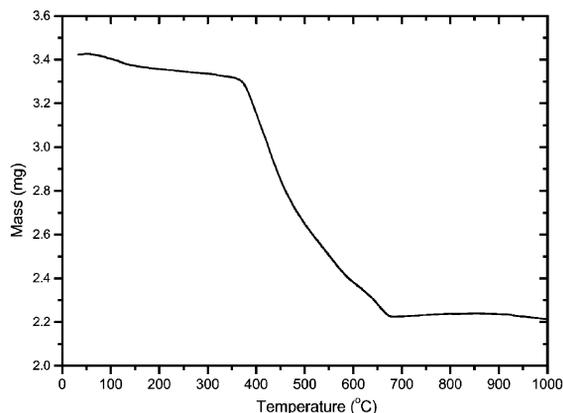


Fig. 1. Thermal gravimetric plot of resin polymerized at 300 °C.

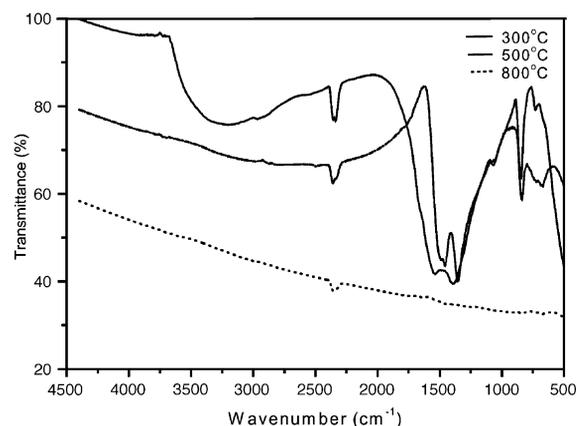


Fig. 2. FTIR pattern of powders calcinated at 800, 500 or 300 °C during 4 h in air.

ing a Varian equipment. Carbon, hydrogen and nitrogen microanalyses were also carried out in a Perkin-Elmer CHN analyzer in order to ascertain the presence of residues after the thermal decomposition of the polymer.

2.2.2. X-ray diffraction

The calcinated material was evaluated by X-ray diffraction using CuK α radiation in a Siemens D5000 apparatus. The diffraction angle (2θ) range between 5° and 75° was scanned.

2.2.3. Infrared spectroscopy (FTIR)

Both the precursor materials and the organic matter remaining after each calcination were analyzed by Infrared Spectroscopy using KBr pellets in a Perkin-Elmer 16 PC instrument.

2.2.4. Thermal analysis

Thermal gravimetric analyses were carried out in a TGA-7 Perkin-Elmer balance under an air flow of 50 ml min⁻¹. The maximum temperature was set to 900 °C and the heating rate to 2 °C min⁻¹.

3. Results and discussion

Fig. 1 shows the thermal gravimetric plot corresponding to the decomposition of the material polymerized at 300 °C. The decomposition reaction took place in two steps, stabilizing at 660 °C. The mass

loss between 300 and 660 °C accounted for the decomposition of organic matter.

The results from infrared spectroscopy carried out at 300 °C in air are depicted in Fig. 2. A wide band was observed at 3700–3000 cm^{-1} and could be attributed to the O–H stretching of the citrate. Vibrations at 1538–1394 cm^{-1} were related to the coordination of the Ni^{3+} cation by the carboxylic group in

the form of a bidentated complex. Upon calcination at 500 °C, a shift of the 1538–1394 cm^{-1} bands to 1458–1356 cm^{-1} suggested the formation of an intermediate carbonate-rich phase. The existence of such phase was later confirmed by X-ray diffraction (Fig. 3b). The presence of carbonates is rather common in the synthesis of alkaline titanates from polymeric precursors [9]. The presence of either absorbed

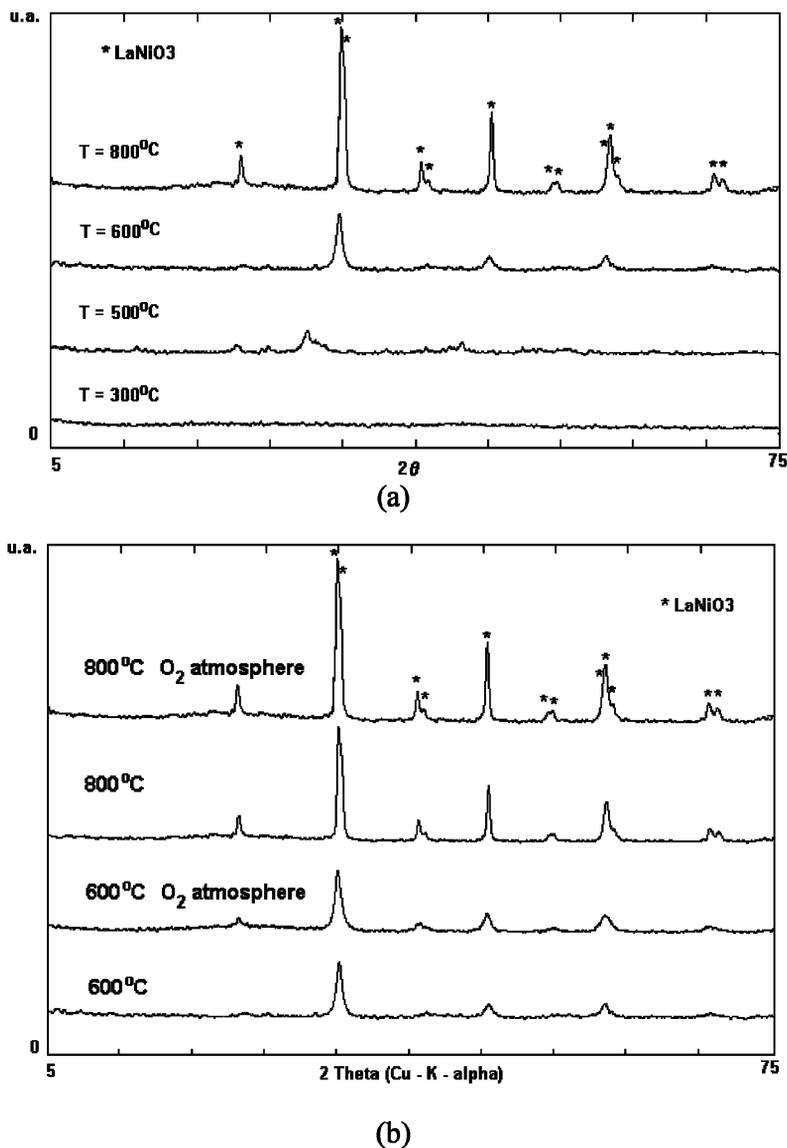


Fig. 3. X-ray diffraction pattern of LaNiO_3 calcinated (a) in air at different temperatures and (b) under O_2 at 600 or 800 °C.

Table 1
Result of CHN elemental analysis

LaNiO ₃ (calcinated in air)			
Temperature (°C)	C (wt.%)	H (wt.%)	N (wt.%)
500	0.35	0.15	0.06
600	0.29	0.13	0.01
800	0.17	0.09	0.01

or atmospheric CO₂ was suggested by the band at 2350 cm⁻¹. The FTIR pattern of the powder calcinated at 800 °C revealed the total decomposition of organic matter. The results from elemental CHN analyses as a function of the calcination temperature are listed in Table 1. After calcination at 500 °C, a small amount of carbon and hydrogen remained. The contents of such elements decreased as the calcination temperature increased, clearly indicating the continuous process of organic matter elimination. No signs of organic residues were observed after calcination at 800 °C, suggesting the high purity of the resulting powders. Fig. 3a shows the X-ray diffraction pattern of the polymeric precursors calcinated at 300, 500, 600 or 800 °C in air. The results revealed the amorphous nature of the material after calcination at 300 °C. At 600 °C, a carbonate phase was formed confirming the FTIR data. X-ray standards calcinated at 600 °C indicated the formation of a poorly crystallized monophase material possibly corresponding to LaNiO₃. Well-resolved X-ray patterns were obtained only from powders calcinated at 800 °C clearly suggesting the formation of a highly crystallized powder. Similar behavior was observed from the powders calcinated under O₂, as suggested from Fig. 3b.

4. Conclusions

The synthesis of LaNiO₃ by the Pechini method resulted in the formation of a monophase material with highly-crystalline particles upon calcination at 800 °C. The study of the thermal decomposition of polymeric precursors revealed that the LaNiO₃ phase nucleated following the full decomposition of organic matter and the formation of an intermediate phase. XRD patterns indicated that calcinating under O₂ did not assist the formation of LaNiO₃.

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