Effect of lanthanum replacement by strontium in lanthanum nickelate crystals synthetized using gelatin as organic precursor

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La1−xSrNiO3 (0 ≤ x ≤ 0.8) nanopowders were successfully synthesized using gelatin as a polymerization agent. Powders were calcined for 4 h at 700 and 900 °C and characterized using thermal analysis, X-ray diffraction and scanning electron microscopy. Perovskite phase formation was achieved at 700 °C, with an increase in crystallinity and secondary phases forming in powders calcined at 900 °C. The structure of the lanthanum nickelate was confirmed as rhombohedral and transition to tetragonal structure occurred by partially substituting lanthanum with strontium.

1. Introduction

LaNiO3 perovskite oxides have been studied extensively owing to their catalytic, optical and electronic properties, among others. The production of high-performance ceramics with these properties has led to new powder synthesis routes aimed at obtaining homogeneous nanoparticle materials that require low temperatures to reach the desired phase. RE-NiO3 perovskites (RE = rare earth) can be produced using several methods. These include conventional ceramic powder technology, sol gel processing, powder coprecipitation, nitrate decomposition, hydrothermal synthesis and the Pechini process, among others [1–3]. Most of these techniques need high temperatures, oxygen flow and extended calcination periods to obtain monophasic homogeneous materials. Lanthanum nickelate is a perovskite-type ternary oxide with a rhombohedral structure. The nickel assumes its highest valence state, which is stabilized at relatively low temperatures. The material must therefore be synthesized by a route that leads to perovskite phase formation at lower temperatures than conventional synthesis methods such as solid state synthesis [4].

In this study, oxides with the general formula La1−xSrNiO3 (0 ≤ x ≤ 0.8) were synthesized by using gelatin as organic precursor. Gelatin has several protein chains composed of aminoacids. These can form larger chains that bind with metals through their coordinate sites. This process is a new alternative to obtain nanoparticles. Nogueira et al (2007) [5] also used gelatin to prepare nanoparticles, but the route was different from the one used in this study. Structural analysis and morphology of the oxides was carried out to evaluate the performance of the synthesis method in obtaining the materials. The impact of adding strontium to the structural parameters of the LaNiO3 perovskite was also assessed.

2. Experimental procedure

Systems were synthesized using metallic nitrates as starting materials and gelatin powder (GELITA®) as organic precursor. Gelatin was added to a beaker containing deionized water and stirred for 30 minutes at 50 °C. Ni(NO3)2.6H2O (99.9% - SIGMA-ALDRICH) and La(NO3)3.6H2O (99.9% - SIGMA ALDRICH ) were added to the solution at 70 °C for several minutes. Sr(NO3) P.A. (≤ 99% - SIGMA-ALDRICH) was added for a further 30 minutes. The temperature was slowly increased to 90 °C and the solution was stirred on a hot plate until a gel formed. The gel was then calcined at 350 °C for 2 hours with a heating rate of 5 °C min−1. This resulted in a precursor powder, which was calcined at 700 and 900 °C for 4 hours and characterized by several techniques. Thermogravimetric curves were recorded using a Shimadzu TGA/DTA-60H thermal analyzer under air atmosphere. Temperature range was between 25 and 800 °C with a heating rate of 5 °C min−1. X-ray patterns were obtained from samples calcined at different temperatures. Measurements were recorded on a Shimadzu XRD-6000 diffractometer with monochromatic radiation of CuK (λ = 1.5406 Å). A 2θ angular range was used between 10 and 90° with a scan rate of 2° min−1 and step of 0.02 °. Crystalline phases were identified using the International Center for Diffraction Data (ICDD) database. Crystallite sizes were obtained with the Scherrer’s equation [7]. The FEG-SEM
images of the powders were examined in a Dual-FIB Quanta 3D microscopy. The specific surface area was measured by nitrogen adsorption on NOVA2000 BET system and the pore size was measured by the BJH method.

3. Results and discussion

Thermogravimetric curves of the natural gelatin and precursor powders are shown in Fig. 1. Loss of mass in these materials varied from 16% to 45%. The curves indicate that gelatin decomposition occurs in three distinct stages. In the first stage, a reduction of 12.254% is related to moisture (water of hydration). In the second, approximately 44.397% is due to the elimination of aminoacid fragments, usually proline, which is thermodynamically susceptible to thermal degradation in an oxidant atmosphere [6]. A loss of around 41.379% in the final stage can be attributed to glycine degradation. Although the precursor curves are similar to the pure gelatin curves, decomposition occurs at higher temperatures. This is due to the interaction of glycine through carboxyl groups and amine with metallic ions. Then, chelates are formed, giving more structural stability and avoiding oxidation of the high glycine content [6].

Figs. 2a, b show the diffractions of the La$_{1-x}$Sr$_x$NiO$_3$ ($0 \leq x \leq 0.8$) powders calcined at 700 and 900 °C, respectively. Crystalline phases were identified using the JCPDS data bank. The X-ray diffraction of LaNiO$_3$ at calcined 700 and 900 °C at indicated the formation of crystalline monophase material with a perovskite-type rhombohedral structure (JCPDS 33-0711).

Along with the perovskite phase, diffractions of the La$_{1-x}$Sr$_x$NiO$_3$ ($x=0.2; 0.4; 0.6$ and 0.8) powders doped with strontium and calcined at 700 and 900 °C also show diffraction peaks of La$_2$O$_3$ (JCPDS 74-1144) and NiO (JCPDS 47-1049) phases. In samples calcinated at 900 °C with higher strontium amounts (La$_{1-x}$Sr$_x$NiO$_3$; $x = 0.6$ and 0.8) were identified SrNiO$_3$ phase (JCPDS 33-1347). According to JCPDS file number 81-2085, all the doped perovskites have a tetragonal phase. Table 1 shows that the crystallites have sizes in the range of 13 nm to 40 nm. The specific surface area, and pore volume, which are also listed in Table 1, shows that the values increased with the temperature. This is probably due to strong interaction between metallic ions and gelatin that in the compounds is completely removed in temperature above 800 °C, as can be seen in the Fig. 1.

It is well known that substituting a trivalent metal ion at site A for a bivalent or tetravalent metallic cation (A') in perovskite-type oxides is accompanied by modification of the oxidation state of metallic cation at site B. However, this process is also accompanied by structural defects. Perovskites containing cobalt suffer from oxygen defects while those containing manganese have excess oxygen [8]. Iron and nickel based perovskites exhibit intermediate behavior [9,10]. In the
compounds studied in this work, results of XRD analyses show that substituting La$^{3+}$ by Sr$^{2+}$ created larger quantities of La$_2$O$_3$, NiO, and SrNiO$_3$. This is because the low solubility of Sr means it can no longer be inserted into the perovskite structure when Sr content increases. One part was therefore segregated and interfered in the formation rate of the perovskite phase. This caused a reduction in crystallite size when the calcination temperature was increased, as seen in materials with strontium substitution starting at 40%.

<table>
<thead>
<tr>
<th>Powders</th>
<th>Crystallite Size (nm)</th>
<th>Specific Surface Area (m$^2$/g)</th>
<th>Average pore diameter (Å)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNiO$_3$ - 700 °C</td>
<td>13.69</td>
<td>8.812</td>
<td>37.510</td>
<td>0.00826</td>
</tr>
<tr>
<td>LaNiO$_3$ - 900 °C</td>
<td>16.28</td>
<td>16.743</td>
<td>41.760</td>
<td>0.01748</td>
</tr>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$NiO$_3$ - 700 °C</td>
<td>14.14</td>
<td>6.336</td>
<td>35.103</td>
<td>0.00651</td>
</tr>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$NiO$_3$ - 900 °C</td>
<td>25.14</td>
<td>12.543</td>
<td>41.103</td>
<td>0.01151</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$NiO$_3$ - 700 °C</td>
<td>32.78</td>
<td>8.430</td>
<td>36.291</td>
<td>0.00789</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$NiO$_3$ - 900 °C</td>
<td>27.52</td>
<td>11.703</td>
<td>51.380</td>
<td>0.01667</td>
</tr>
<tr>
<td>La$<em>{0.4}$Sr$</em>{0.6}$NiO$_3$ - 700 °C</td>
<td>35.84</td>
<td>8.270</td>
<td>35.450</td>
<td>0.00858</td>
</tr>
<tr>
<td>La$<em>{0.4}$Sr$</em>{0.6}$NiO$_3$ - 900 °C</td>
<td>20.08</td>
<td>12.560</td>
<td>49.870</td>
<td>0.01588</td>
</tr>
<tr>
<td>La$<em>{0.2}$Sr$</em>{0.8}$NiO$_3$ - 700 °C</td>
<td>40.57</td>
<td>7.161</td>
<td>31.742</td>
<td>0.00864</td>
</tr>
<tr>
<td>La$<em>{0.2}$Sr$</em>{0.8}$NiO$_3$ - 900 °C</td>
<td>18.19</td>
<td>20.312</td>
<td>48.267</td>
<td>0.01612</td>
</tr>
</tbody>
</table>

The micrographs obtained by FEG-SEM for the LaNiO$_3$ and La$_{0.8}$Sr$_{0.2}$NiO$_3$ samples calcined at 900 °C are shown in Fig. 3. As can be seen, the particles have a round shape, good crystallinity, uniform distribution and do not show noticeable agglomeration. The small particle size (~100 nm) creates high surface tension, which provides a driving force for particle agglomeration. This results in soft agglomeration (easily deagglomerated, composed of Van der Waals forces). The porous surface of the material is caused by the evolution of high
gas content during synthesis and powder production. The gelatin provides to the system a large amount of organic matter, which is removed during calcination and favors the appearance of pores in the material.

4. Conclusions

The powder preparation methods in this study use gelatin, which is a low-cost, non-toxic organic precursor, making it a promising alternative to the usual synthesis methods. The route used in the present study produced satisfactory results and was faster and easier than that used by the others authors [5,11]. Powders produced using this method were nanometric, homogeneous and porous. These are important characteristics for technological application such as catalysts. In the systems studied, perovskite formation was achieved at low temperatures. The lanthanum nickelate presented a rhombohedral structure and transition to tetragonal structure occurred when lanthanum was partially substituted with strontium. The presence of secondary phases rose with the increased amount of strontium in the system.

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