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Synthesis and characterization of the ceramic system $La_xNd_{1-x}NiO_{3-\delta}$ $(0 \leqslant x \leqslant 0.5)$

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Abstract

Lanthanum and neodymium nickelate ($La_xNd_{1-x}NiO_{3-\delta}$) with x equal to 1.0, 0.9, 0.7 and 0.5 were prepared with molar ratios of 1:1.5 and 1:3. The resins were heated at 300°C for 2 h and then calcinated at 800°C for 12 h. The resulting powders were analyzed by thermogravimetry, infrared spectroscopy and X-ray powder diffraction. Chemical analysis of the powders showed that the oxygen vacancy number (δ) becomes higher with the substitution of lanthanum by neodymium for both molar ratios. X-ray patterns showed the formation of perovskite in all samples analyzed. Nevertheless, a small amount of a secondary phase was observed when neodymium content increases in the oxides. This phase was attributed to NiO.

Keywords: $La_{1-x}Nd_xNiO_3$; Perovskite; Oxygen deficiency

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1. Introduction

The development of adequate synthetic methods for the preparation of nanometric ceramic powders at low temperatures and atmospheric pressure is a task of great interest. The preparation of such materials may vary in different methods and conditions [1,2]. The production of materials can be applied to high-tech electro-electronic technologies, where ceramic powders of elevated purity, reproducible chemical composition, atomic homogeneity and controlled particle dimensions are very important [3]. Chemical methods are most efficient, since they permit a better control of stoichiometry, high reactivity, good synterability, controlled dimensions and nanoparticles.

Synthesis of ceramic materials with the above characteristics has utilized several techniques, such as: sol–gel [2,4,5] copreciptation [2], hydrothermal [1] and polymeric complexes [3,6], among others. The advantage of the chemical techniques is the promotion of large cation dispersions in the precursor solutions. The mechanism favors the synthesis of powders with the desired properties.

RE perovskites have been synthesized using the ceramic method [2,7] and chemical routes. The difficulties encountered in the synthesis of such materials are inherent to the Ni^{3+} stabilizations which became highly important for the small RE cations [8,9]. Takagashi et al. [10] showed that nickel ions in $LaNiO_3$, synthesized by the ceramic method, presented oxygen vacancies attributed to the +2 and +3 oxidation states of nickel. The literature reports that $NdNiO_3$ prepared at low temperatures is oxygen deficient [11]. Using the same route of Vassiliou et al. [12], Mahesk et al. [13] synthesized $NdNiO_{3-\delta}$ with $\delta = 0.12$ in which after 48 h of electrochemical oxidation the oxygen vacancy number goes up to 0.05.

Compounds with stoichiometries $La_{1-x}A_xNiO_{3-\delta}$ and $Nd_{1-x}A_xNiO_{3-\delta}$ (A = rare earth metal or alkaline earth metal) were prepared by several synthetic routes in the last years [5,11] using an oxygen atmosphere. Elemental analyses indicate the presence of Ni^{2+} and Ni^{3+} ions promoting oxygen vacancies.

The objective of this article is the evaluation of the metal/citric acid (M/Ac) molar ratio in the preparation

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of rare earth ceramic powders by the Pechini method [3]. Lanthanum and neodymium nickelates ($La_xNd_{1-x}NiO_{3-\delta}$) with $x = 1.0$, 0.9, 0.7, 0.5 were prepared with molar ratios 1:1.5 and 1:3. The resins were heated at 300°C for 2 h and then calcinated at 800°C for 12 h. The resulting powders were characterized by thermogravimetry (TG) analyses, infrared absorption spectroscopy (FTIR) and X-ray powder diffraction (XRD).

2. Experimental

The polycrystalline powders, $La_xNd_{1-x}NiO_{3-\delta}$ were prepared by the polymeric precursors method described by Fernandes et al. [6] with molar ratios 1:1.5 and 1:3, respectively. The powders obtained at 300°C were characterized by FTIR measurements on a Perkin-Elmer 16PC equipment, using KBr pellets from 4000 to 500 cm^{-1}. The thermal behavior of the precursors was studied using a Shimadzu TGA-50 H thermobalance, between 30°C and 1000°C in dynamic air atmosphere of 50 mL min^{-1} flow, using a 3.5 mg sample in a platinum crucible with a heating rate of 5°C min^{-1}. The oxygen concentrations for the powders heated at 800°C at room pressure were determined by iodometric titration assuming that RE is (3+) and O (2−) [16]. The crystalline phases were identified by powder diffraction patterns, using a Shimadzu XRD-6000 diffractometer, with Cu$K\alpha$ radiation ($\lambda = 1.5406$ Å), with $20° < \theta < 80°$, pass 0.02° and 0.6 at each step.

3. Results and discussion

3.1. FTIR spectroscopy

IR spectra of precursor powders prepared using M/Ac 1:1.5 are shown in Fig. 1 They showed a broad band at 3300–3400 cm^{-1} due to O–H stretching of the citrates and water adsorbed from the atmosphere.

Nakamoto [14] considers the differences $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ ($\Delta\nu = \nu_{as} - \nu_s$) to determine the type of bonding in such a class of compounds. These values are found between 1630–1550 and 1540–1450 cm^{-1}, respectively for free carboxylate ions [15]. Higher values for those frequencies indicate the existence of monodentate carboxylate. Low $\Delta\nu$ values indicate a bidentate coordination. Values close to those of the free ions [14] are indicative of the existence of bridge bonds. $\nu_{as}(COO^-)$ between 1630 and 1400 cm^{-1} and $\nu_s(COO^-)$ between 1401 and 1362 cm^{-1} suggest a monodentate coordination of the carboxilates to nickel, since $\Delta\nu$ varies between 144 and 129 cm^{-1} for all the series prepared. The bands at about 840 cm^{-1} were attributed to $\pi(COO^-)$ vibration modes. The precursors calcinated at 800°C during 12 h do not present citrate bands, indicating the total decomposition of the organic phase. The FTIR spectra of the nickelates using different molar ratios are identical (Figs. 1 and 2).

3.2. Decomposition temperatures of $La_xNd_{1-x}NiO_{3-\delta}$

TG curves of the 1:1.5 (Fig. 3) and 1:3 (Fig. 4) of precursors showed that the total mass losses for all

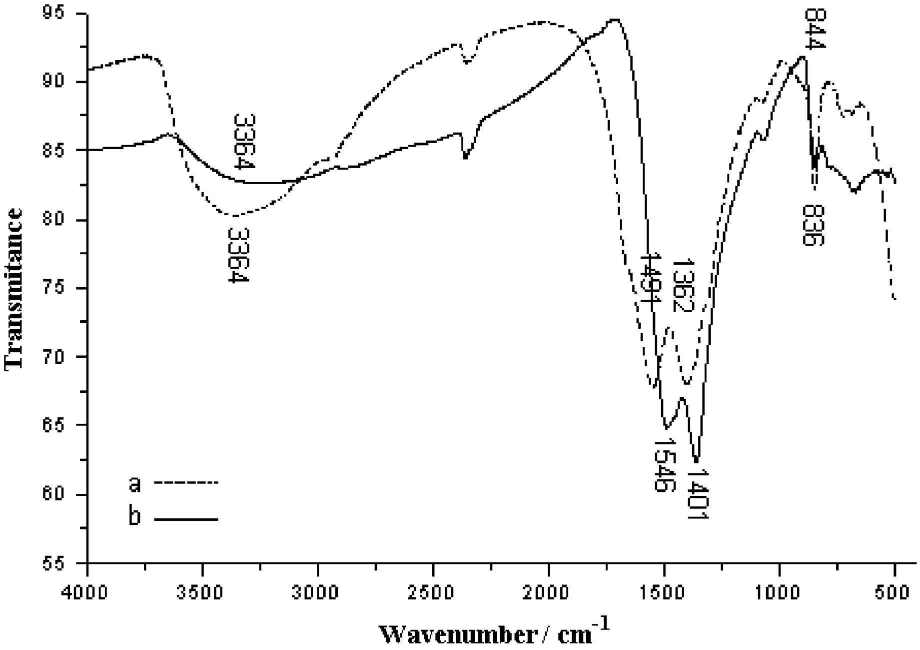

Fig. 1. FTIR pattern of powder precursors prepared using M/Ac 1:1.5: (a) $LaNiO_{3-\delta}$ and (b) $La_{0.5}Nd_{0.5}O_{3-\delta}$.

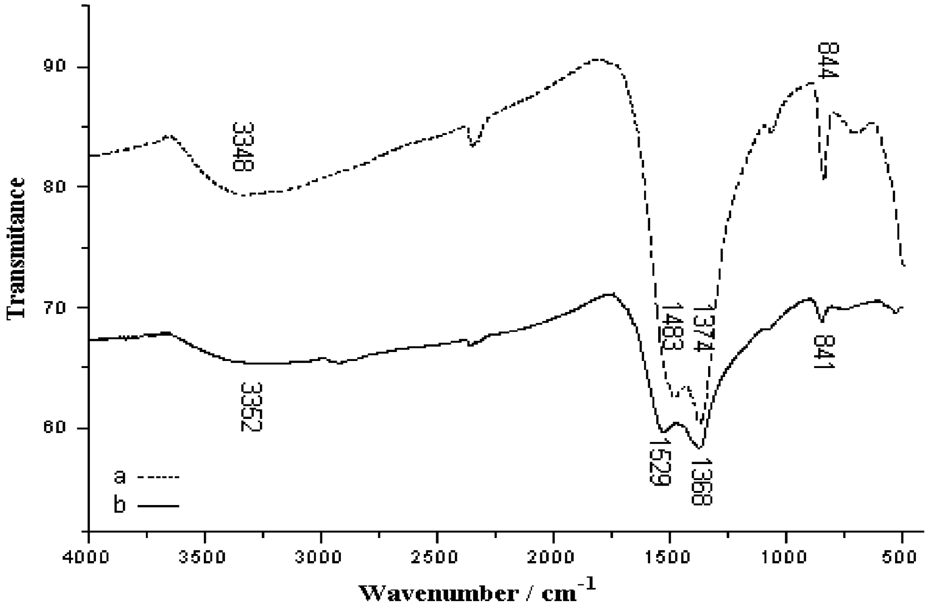

Fig. 2. FTIR pattern of powder precursors prepared using M/Ac 1:3: (a) $LaNiO_{3-\delta}$ and (b) $La_{0.5}Nd_{0.5}O_{3-\delta}$.

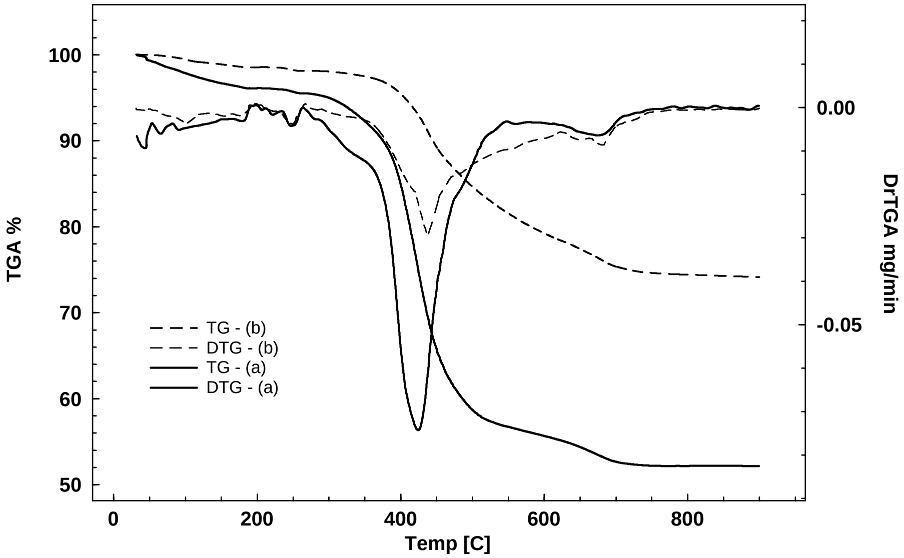

Fig. 3. TG/DTG plot of resin polymerized at 300°C prepared using M/Ac 1:1.5: (a) $La_{0.9}Nd_{0.1}NiO_{3-\delta}$ and (b) $La_{0.5}Nd_{0.5}O_{3-\delta}$.

phases are between 30°C and 755°C. The first step occurs between 30°C and 286°C, attributed to the loss of adsorbed water. The decomposition of the organic material occurs between 286°C and 680°C in two or three consecutive steps. The number of steps decreases when the amount of Nd increases in the mixed oxide. Between 497°C and 755°C the mass losses are attributed to the decomposition of carbonates and/or oxicarbonates, as intermediates of the desired phases. The beginning of perovskite crystals formation occurs between 690°C and 750°C. The residues at ~800°C are: (a) $La_{0.9}Nd_{0.1}NiO_{3-\delta}$, and (b) $La_{0.5}Nd_{0.5}NiO_{3-\delta}$ with 42.65% and 23.54%, respectively.

TG curves of the phases prepared with the molar ratio 1:3 (Fig. 4) show the loss of adsorbed water between 30°C and 170°C. For such systems, the decomposition of organic material, occurred in one or two consecutive steps, between 170°C and 505°C is characteristic of pirolysis. The mass losses due to organic material were 19.13%, 38.76%, 51.98% and 34.01% for the phases $LaNiO_{3-\delta}$, $La_{0.9}Nd_{0.1}NiO_{3-\delta}$, $La_{0.7}Nd_{0.3}NiO_{3-\delta}$ and $La_{0.5}Nd_{0.5}NiO_{3-\delta}$, respectively. The mass losses of 4.47%, 5.74%, 4.55% and 4.11% in the temperature range between 446°C and 739°C correspond to decompositions of carbonates and/or oxicarbonates, followed by the formation of the respective mixed oxides. Above

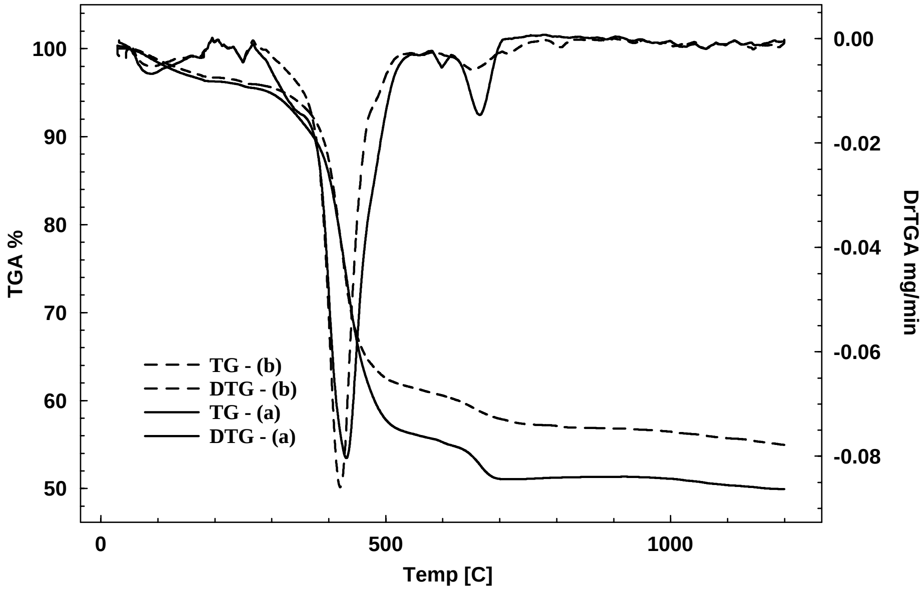

Fig. 4. TG/DTG plot of resin polymerized at 300°C prepared using M/Ac 1:3: (a) $La_{0.9}Nd_{0.1}NiO_{3-\delta}$ and (b) $La_{0.5}Nd_{0.5}O_{3-\delta}$.

880°C the $LaNiO_{3-\delta}$ and $La_{0.9}Nd_{0.1}NiO_{3-\delta}$ systems showed a weight gain of 0.91% and 0.87%, respectively, attributed to the residues formed by the oxidative furnace atmosphere.

3.3. *Oxygen concentration and oxidation state of nickel*

It has been observed that the RE volume has an influence on the number of oxygen vacancies (δ) in the prepared phases and that the M/Ac molar ratio does not have a significant influence on oxygen vacancies of the powders. The δ factor increases when La^{3+} is substituted by Nd^{3+}. The vacancies are directly associated with the Ni amount, stabilized by the respective nickelates. The stabilization under high oxygen pressures and temperatures is related to the increase in the covalent character of the Ni–O bond. Two factors may contribute to that increase: a smaller deviation of the Ni–O–Ni angle ($180^{o}-\phi$) in the octahedral NiO_6 of the ideal perovskite structure; favoring the overlap between the 3d ($t_{2}g^{6}\ eg^{1}$) of Ni^{3+} and the 2p orbitals of O^{2-}, increasing the Ni^{3+} formal charge and the higher polarizability associated to the higher electropositive character of the RE ions (La^{3+}, Pr^{3+} and Nd^{3+}), resulting in ionic bonds RE–O with higher covalent character, with oxygen presenting a decrease in its negative character [8,9,17]. The proposed stoichiometries for the compounds described are in accordance with the literature [5,18–20,23,24], see (Table 1).

3.4. *XRD analysis*

The precursor powders obtained from the resins at 300°C for 2 h are amorphous. Fig. 5 shows the XRD patterns of the products obtained at 800°C for 12 h.

Table 1
Oxygen vacancy number rates for $La_xNd_{1-x}NiO_{3-\delta}$ prepared by different synthetic routes

Amostras	$3\pm\delta^a$	$3\pm\delta^b$	$3\pm\delta^c$	$3\pm\delta^d$
$LaNiO_{3-\delta}$	2.99	3.00	2.95	2.96
$La_{0.9}Nd_{0.1}Ni\ O_{3-\delta}$	2.98	3.00	3.03	3.02
$La_{0.7}Nd_{0.3}Ni\ O_{3-\delta}$	2.98	2.98	2.99	2.99
$La_{0.5}Nd_{0.5}Ni\ O_{3-\delta}$	2.92	2.95	2.92	2.93

[a] Data from Ref. [24].
[b] Data from Ref. [5].
[c] Data from this work, using M/Ac 1:1.5.
[d] Data from this work, using M/Ac 1:3.

After 12 h (800°C) heating these compounds have a perovskite crystalline structure. The oxides $LaNiO_{3-\delta}$ and $La_{0.9}Nd_{0.1}NiO_{3-\delta}$ are monophasic (Fig. 5a). The diffraction peaks are wide as compared to samples prepared by the ceramic method under high oxygen pressures [21]. The broadening of these peaks may be attributed to the formation of tiny crystals small oxide stoichiometry differences and crystalline defects associated to oxygen vacancies favored by the synthesis conditions employed as for instance: low oxygen pressure, small 800°C calcination time. Samples with $0.3\geqslant x<0.5$ prepared using 1:1.5 and 1:3 molar ratios present a small of amount NiO impurity which increases with increasing x values, as shown in Fig. 5b. It is evident that the powders are composed of two crystallographic phases: the lanthanun and neodymium nickelate and NiO. The presence of these phases may lead to the existence of other phases as: La_2O_3, Nd_2O_3 and $La_{1-x}Nd_xNi_{1-y}O_{3-\delta}$ whose Bragg reflections are absent due to the formation of small amounts of them and the randon distribution along the whole sample, again due to the preparation method. The crystallite size of the

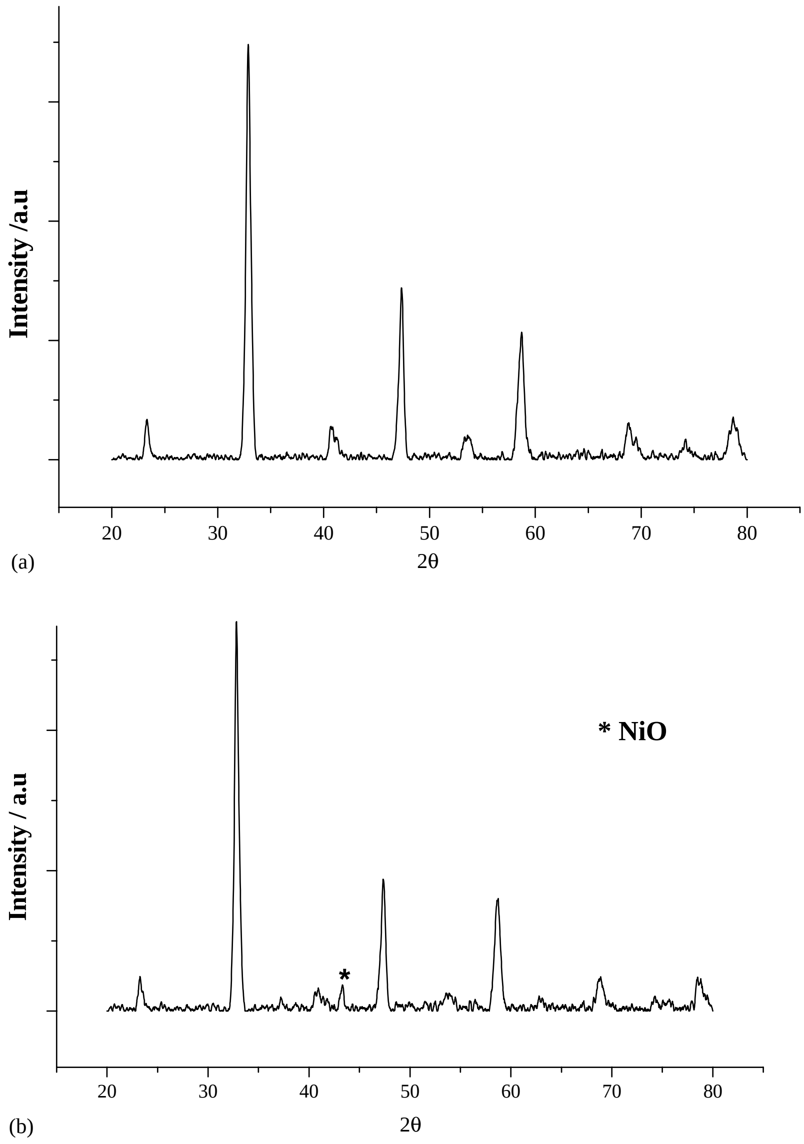

Fig. 5. X-ray pattern of powders prepared with M/Ac 1:3 and calcinated at 800°C for 12 h: (a) $La_{0.9}Nd_{0.1}NiO_{3-\delta}$ and (b) $La_{0.5}Nd_{0.5}NiO_{3-\delta}$.

monophase samples were determined from the full-width at half-maximum width (FWHM) of the XRD peaks using the Scherrer equation [22]. The results indicate dimensions between 15 and 25 nm.

The $La_xNd_{1-x}NiO_3$ with $0.3 \geqslant x < 0.5$ oxides prepared using different Me:citric acid molar ratios by the Pechini method at room pressure and low temperature showed a similar small number of oxygen vacancies. In both preparations, the citrate ions act as monodentate. TG curves for the precursors do not show significant differences in thermal behavior between the several nickelates as indicated by TG curves. It is possible to observe that the increase in citric acid amount leads to a faster organic matter decomposition step. The XRD patterns study indicated that at 800°C the system $La_xNd_{1-x}NiO_3$ form a perovskite-type structure. Systems with $x = 1$ and 0.9 are monophasic whereas systems with $x = 0.3$ and 0.5 present NiO as secondary phase.

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