Synthesis of LaNiO$_3$ perovskite by the proteic gel modified method using collagen

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As perovsquitas são materiais estratégicos devido as suas propriedades catalíticas, eletrônicas e magnéticas. Estas propriedades são influenciadas pelas condições de síntese e calcinação. Este trabalho apresenta um estudo da síntese de perovsquitas LaNiO$_3$ via método do gel protéico modificado variando o teor de colágeno. Os óxidos perovsquitas com a composição LaNiO$_3$ foram sintetizados usando nitrato de níquel, nitrato de lantânio e colágeno como materiais de partida. Os pós obtidos foram caracterizados por termogravimetria, espectroscopia na região do infravermelho e difratometria de raios X. As curvas de TG e espectros FTIR foram particularmente uteis no estabelecimento da temperatura de calcinação ideal dos pós precursores. Os padrões de difração de raios X revelaram a formação da estrutura perovsquita em todas as amostras preparadas pelo método de síntese variando o teor de colágeno e após calcinações a 700 °C/2h. Na otimização do teor de colágeno, a melhor proporção mássica de metal (Ni^{2+})/colágeno usada foi 1,0/1,0, em que foi possível obter a perovsquita monofásica.

Palavras-chave: perovsquita LaNiO$_3$; colágeno; método gel protéico modificado

The perovskite oxides are strategic materials due its catalytic, electronic and magnetic properties. These properties are influenced by the calcinations and synthesis conditions. This work describes a study on the synthesis of LaNiO$_3$ perovskites via modified proteic gel method varying the content of collagen. Perovskites oxides with the composition LaNiO$_3$ were synthesized by modified proteic gel method using nickel nitrate, lanthanum nitrate and collagen as starting source. The obtained powders were characterized by thermogravimetric analysis (TGA), infrared spectroscopy (FTIR) and X-ray diffraction. TGA curves and FTIR spectra were particularly useful in establishing of the optimal calcination temperature of the precursor powders. X-ray diffraction patterns revealed the formation of the perovskite structure in all samples prepared by synthesis method varying the content of collagen and after calcinations at 700 °C four 2 hours. In the optimization of the collagen content, the bester bulk proportion of metal (Ni^{2+})/collagen used was 1.0:1.0, where it was possible to obtain monophasic perovskite.

Keywords: LaNiO$_3$ perovskites; collagen; modified proteic gel method

1. INTRODUCTION

Perovskite mixed oxides are ceramic materials that combine metal elements with non-metallic, usually oxygen, with general formula ABO$_3$, where A represents a lanthanide or alkaline earth ion and B a transition metal ion trivalent [1-3]. These materials are considered strategic due of its electronic, magnetic, optical and catalytic properties, among others [4-6].

The perovskite containing a lanthanide in position A and a transition metal in position B have been known as good catalysts for various reactions. Important applications of these materials are in the catalytic combustion devices with high heat transfer, such as gas turbines or industrial burners. The relatively high oxidation activity of transition metal oxides combined with the thermal stability of rare earth oxides provides to perovskite the essential properties for applications in the high temperatures [7].

In recent decades many routes have been used for the preparation of mixed oxides with perovskite structure, such as sol-gel, polymeric precursors, chelating precursors, the proteic sol-gel process, combustion synthesis, among others [3-6, 9-10]. In general, these methods aim to obtain a material with high homogeneity, low amount of impurities, particle size and surface area suitable for different applications [4].

The modified proteic gel method is a new alternative for synthesis of the perovskite oxides. This method consists in the formation of a metal-chelating complex system, including a chelating agent and metal precursor, replacing for ethylene glycol and citric acid or EDTA as the organic precursor by collagen. The choice of this method is justified by the possibility to obtain materials with high purity and good control of stoichiometry.

In this study, $LaNiO_3$ perovskite-type oxide was synthesized via modified proteic gel method using collagen as the organic precursor aim to optimize the content of complexing agent used during synthesis.

2. EXPERIMENTAL

The $LaNiO_3$ perovskite type oxides were synthesized by the modified proteic gel method using lanthanum (J.T. Baker, 99.9%) and nickel (Vetec, 97.0%) nitrates as starting and collagen powder as chelating agent. Firstly, was prepared aqueous solutions of metal nitrates by dissolution of nickel nitrate in 100 ml of distilled water at 30 ° C for 30 minutes under agitation and after that the lanthanum nitrate added to the system under the same conditions of agitation time and temperature. Then the solution was heated up to 70 ° C, and collagen was added under stirring. The temperature of system was kept constant for 1 h until the formation of a gel. This gel was heated treated at 350 ° C for 2 hours with a heating rate of 10 ° C min^{-1}. The precursor powder was calcined at 700 ° C for 2 hours. The mass ratio of metal (Ni^{2+}) used for the collagen were of 1.0:5.0, 1.0:2.0, 1.0:1.0 and 1.0:0.5. The obtained powders were characterized by thermogravimetric analysis, infrared spectroscopy and X-ray diffraction.

The samples heated treated were analyzed by Infrared Spectroscopy using the technique of Attenuated Total Reflectance (ATR) in a Varian spectrophotometer, model 640-IR. The thermal decomposition process of samples was investigated by thermogravimetric thermal analysis (TGA) using a TA Instruments equipment SDT-2960 thermal analyzer under nitrogen atmosphere, in the temperature range between 30 and 900°C, with heating rate of 10 °C min^{-1}. X-ray diffraction (XRD) measurements of samples calcined were performed on a Rigaku DMAX100 diffractometer using CuKα ($\lambda = 1.5406$) radiation. The diffraction angle (2θ) range was used between 10 to 60° with step of 0.020°. The identification of crystalline phases was performed using data from the cards of JCPDS - International Center for Diffraction Data.

3. RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of the $LaNiO_3$ precursor powders synthesized by the modified proteic gel method varying the bulk proportion metal (Ni^{2+})/collagen and heated treated at 350 ° C for 2 hours. The spectra of samples with ratio metal (Ni^{2+})/collagen of 1.0/5.0, 1.0/2.0, 1.0/1.0 and 1.0/0.5, can be seen in this figure. All samples showed broad bands in the region between 3600-3000 cm^{-1}, which can be attributed to asymmetric stretching vibrations of the O-H group of reticular water - remaining organic matter [11].
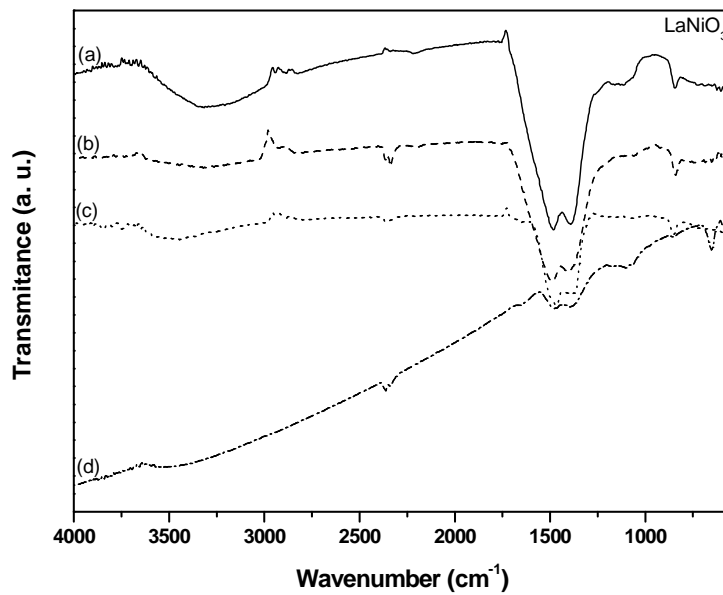
Figure 1: FTIR spectra for LaNiO₃ precursor powders with ratio metal (Ni^{2+})/collagen: (a) 1.0:5.0, (b) 1.0:2.0, (c) 1.0:1.0 and (d) 1.0:0.5.

The bands observed in the region of 1550-1338 cm^{-1} in the FTIR spectra can be assigned to the asymmetric stretching vibrations of carboxylic groups of gelatin coordinated to the metal, since these frequencies have been displaced in relation the vibrations of the carboxylic group (in the region between 1637-1523 cm^{-1}) of collagen spectrum (Figure 2). Nevertheless, the spectrum of the sample with lower content of collagen showed a band at 651 cm^{-1} relating to metal-oxygen bond [9], which may indicate the formation of oxide in this material.
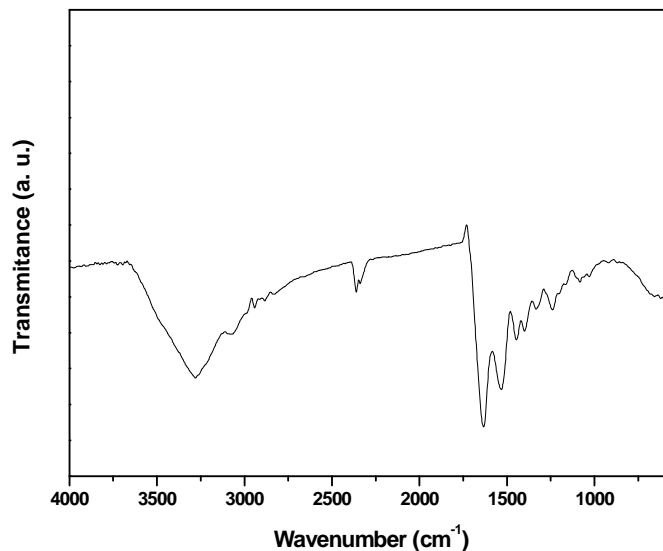

Figure 2: FTIR spectrum of the collagen.

Thermogravimetric curves of the LaNiO₃ perovskite precursor powders heated treated at 350 ° C and prepared by modified proteic gel method are shown in Figure 3. Thermal analysis has

been found to yield information on the decomposition temperatures of the materials obtained during the synthesis as also about its thermal stability [12].
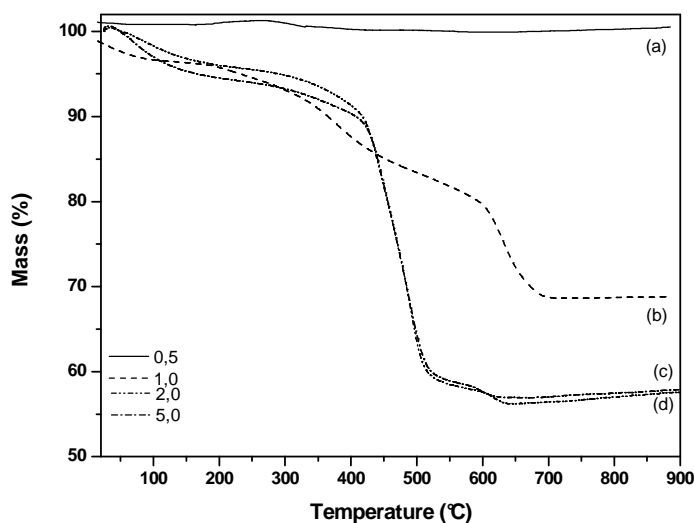

Figure 3: TG curves for LaNiO$_3$ precursor powders with ratio metal (Ni2+)/collagen: (a) 1.0:0.5, (b) 1.0:1.0, (c) 1.0:5.0 and (d) 1.0:2.0.

In general, the curves indicate that decomposition reaction took place in two temperature ranges. Initial mass loss observed in the temperature range of 30-250 °C that is attributed to water loss and initial decomposition of the residual material synthesis process. In the temperature range of 250-700 °C can be observed the greatest loss mass which is due residual organic matter decomposition. On the basis of study previously discussed in the literature, using gelatin as a precursor, it was found that the thermal decomposition of pure gelatin takes place in three distinct stages: the first, associated with loss of water of hydration (moisture), the second attributed to the elimination of fragments of amino acids residues, usually Proline (Pro), which degrades into oxidizing atmosphere and the last loss related to the decomposition of Glycine (Gly) at about 600 °C [13].

The thermogravimetric curves showed that the content of the complexing agent (collagen) influenced in the final temperature decomposition of the LaNiO$_3$ perovskite precursor powders. The samples with lowest ratios metal/collagen stabilized at lower temperatures due to the ratio metal/chelating agent (collagen) to influence the thermal stability of the material.

X-ray diffraction patterns of the powders calcined at 700 °C for 2 hours (Figure 4) prepared by modified proteic gel method varying bulk proportion metal/collagen (1.0:5.0, 1.0:2.0, 1.0:1.0 and 1.0:0.5) revealed the formation of crystalline phases. All samples showed the formation of crystalline perovskite phase, in agreement with the diffraction patterns of the LaNiO$_3$ structure, obtained in the literature [14]. Peaks corresponding to secondary phases attributed to NiO (nickel oxide) and La$_2$O$_3$ (lanthanum oxide) were also found.
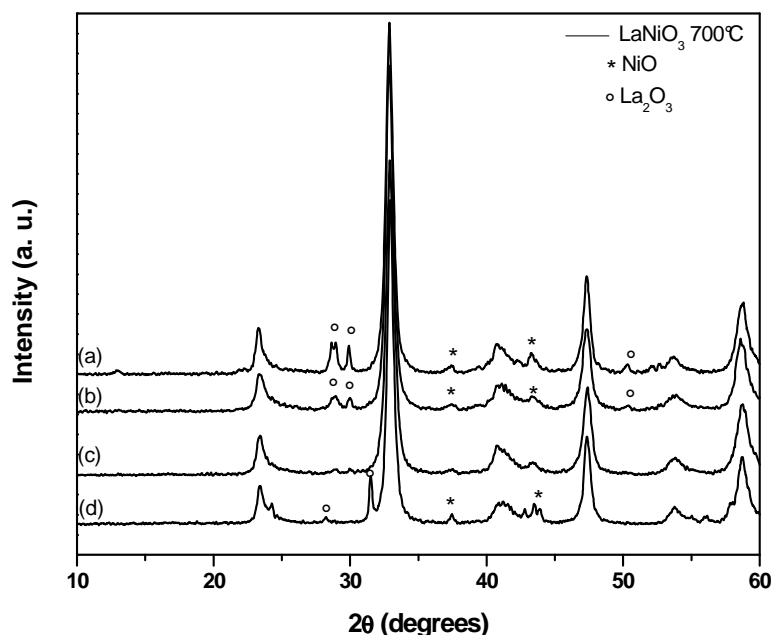
Figure 4: XRD patterns for LaNiO₃ perovskite calcined at 700 ºC with ratio metal (Ni2+)/collagen. (a) 1.0:5.0, (b) 1.0:2.0, (c) 1.0:1.0, (d) 1.0:0.5.

According to diffraction patterns can be observed that the intensities of the peaks of the secondary phase decreased as the content of collagen used in the synthesis, exception of the sample with ratio metal/collagen of 1.0:0.5. Moreover, it is suggested that the ratio metal/collagen of 1.0:1.0 is the best in the formation of the perovskite single phase, whereas the peaks related to secondary phases disappeared. The perovskite structure was characterized by rather intense peaks at 2θ equal to 32.9 °, 47.3 ° and 58.1 °. All perovskite structure peaks were indexed as rhombohedral structure (JCPDS 34-1028).

4. CONCLUSION

This study demonstrated that the oxides with $LaNiO_3$ perovskite-type structure can be obtained using the modified proteic gel at low ratios of metal (Ni^{2+})/collagen. Collagen is inexpensive, non-toxic organic, as very good chelating agent in the formation of perovskite oxides. In accordance with TG curves and FTIR spectra, all organic residual material of the synthesis process decomposed about 700 °C.

X-ray diffraction patterns revealed the formation of the structure perovskite in all samples prepared by this synthesis method and after calcinations at 700 ° C for 2 hours formed the perovskite phase. However, secondary phases attributed to NiO and/or La_2O_3 were observed in the $LaNiO_3$ perovskite prepared by modified proteic gel method, exception of the sample with ratio metal (Ni^{2+})/collagen of 1.0:1.0.

5. ACKNOWLEDGEMENTS

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