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Synthesis of $LnNiO_3$ (Ln = La and Pr) System for Catalytic Applications

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Abstract – In this work, the $LnNiO_3$ (Ln = La e Pr) powders were synthesized by a method similar to Pechini, in which ethylene glycol was replaced by gelatin. The powders were calcinated at 973 K and 1173K submitted to the usual characterization techniques such as XRD, TG, DTA, and TPR. The X-Ray patterns were refined by the Rietveld method. The results showed nanometric powders with perovskite structure for application in catalysis.

Ceramic oxides with perovskite structure, ABO_3 (where A and B are usually metal ions of rare earth and transition metals, respectively) have been used for various types of catalytic reactions and have great appeal to researchers in the field, as they have great stability at high temperatures, high oxygen mobility and stabilization of unusual oxidation states of the cation in the structure. Based on geometrical considerations, were defined tolerable limits to the ions size by a tolerance factor t. The perovskite structure is formed within the range 0.75 <t <1, with values of the tolerance factor between 0.8 and 0.9.

The polymeric precursor's method (Pechini's method) consists of a synthesis that allows to obtain very pure oxides. The main advantage of the Pechini's method is the formation of ceramic materials with low particle sizes and high uniformity [1].Recent work reported the successful of the gelatin use as a polymerization agent in the development of catalyst [2] and this process appears as a new alternative for obtaining oxides with high efficiency and low cost. The advantage of using gelatin is that besides being a chelating agent and polymerizing of metal ions, is a low cost and non-toxic material, making the synthesis easier and faster. The perovskites $LnNiO_3$ (Ln = La e Pr) were synthesized by a route similar to the Pechini's method, using gelatin as the reaction guiding, for catalysis application.

The thermogravimetric curve of the precursors powders show two levels of mass loss. The first stage, between 298 K and 373 K, is associated with hydration water and the second loss (28 to 38%) between 573 K and 873 K can be attributed to the removal of amino acids fragments from gelatin. The gelatin shows three levels of mass loss. The first stage, between 298 K and 373 K, is associated with hydration water, the second loss between 573 K and 673 K can be attributed to the removal of amino acids fragments usually prolyne. The last stage, between 673 K and 873 K, can be attributed to the glycin degradation.

The X-Ray patterns of the calcinated powders at 973 K and 1173K (Figures 1 and 2) present the perovskite phase. Beyond this phase, the diffraction peaks of La_2O_3, PrO and NiO were observed. As expected, the crystallinity increased with calcination temperature increasing, because higher temperatures (greater thermal energy) accelerate the atoms accommodation in the crystal structure. The higher temperature also promotes an increase in the crystallites growth, as shown in Table 1.

Table 1 – Calcination Temperature Influence in the Crystallinity parameters.

Sample	T_{cal} (K)*	D_{DRX} (nm)	<e> (%)*	Crystallinity (%)
$LaNiO_3$	973	13,69	0,007924	47,3473
$LaNiO_3$	1173	16,28	0,005807	56,2816
$PrNiO_3$	973	47,90	0,002556	66,3025
$PrNiO_3$	1173	52,52	0,001819	83,7994

* T_{cal} = Calcination Temperature; <e> = Micro strain

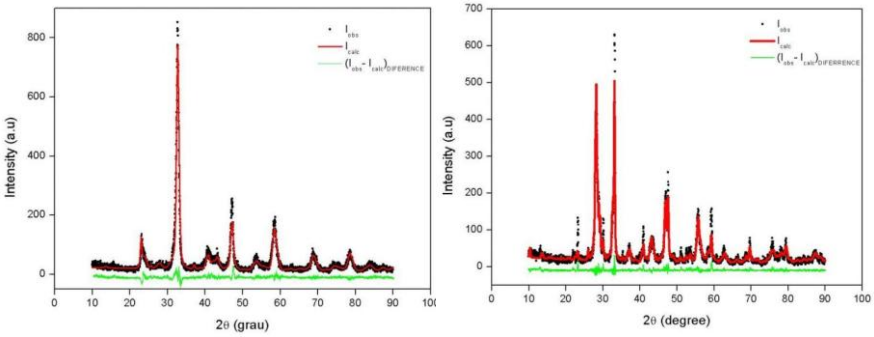

Figure 1 – Rietveld refinement of (a) $LaNiO_3$ and (b) $PrNiO_3$ calcinated at 973K

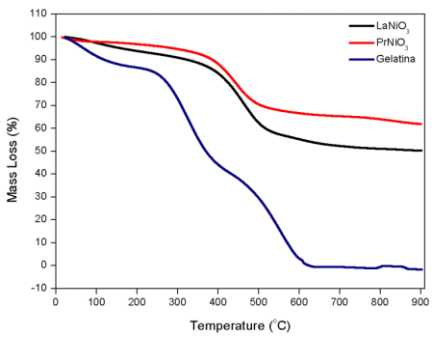

Figure 2 – Thermogravimetric analysis of $LnNiO_3$ (Ln=La and Pr) and gelatin

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2. A.O.G. Maia et al.; Journal of Non-Crystalline Solids 352, 3729–3733, 2006.