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Abstract. Niobium pentoxide (Nb_2O_5) nanoparticles were prepared by the polymeric precursor method using citric acid as a chelating agent and ethylene glycol as a polymerizing agent. The powders obtained were characterized by X-ray diffraction and scanning electron microscopy. The results showed that the presence of HNO_3, HCl or NH_4OH in the employed aqueous solution favour the solubility of the used precursor salt, as well as also inside the oxide phase formation. The initial Nb_2O_5 powders were amorphous. The amorphous powders heated at 500$^\circ C$ contained Nb_2O_5 TT-phase, whereas at 650$^\circ C$ the Nb_2O_5 T-phase was obtained. In this way an increase in the synthesis temperature is related to the increase of the crystallinity, according to the values of the crystallite sizes that were estimated using the Scherrer method.

1. Introduction

The polymeric precursor method –Pechini method– is a chemistry synthesis method in which the general idea is to distribute the atomic cations through all polymeric structures [1]. Chelate formation takes place in an aqueous solution between cations and a carboxylic acid. Once this solution is mixed with a polyhydroxylated alcohol, the chelate is polyesterificated forming a resin. The decomposition of the amorphous resin is done by heating to temperatures below 350$^\circ C$ and then the material obtained is macerated. Powders are heated at temperatures between 500$^\circ C$ and 1100$^\circ C$ where the oxides with fine particles and suitable chemical composition are obtained, depending on the interest phase [2]. This method was chosen because it allows controlling factors such as porosity, surface area, particle size and shape which affect the microstructure, the reactivity and the final form of the oxide.

The oxide chosen is the Niobium pentoxide (Nb_2O_5). This is a n-type semiconductor with a band gap of about 3.4eV and is the most well-known and studied oxide material amongst all those reported oxides [3,4]. Many Nb_2O_5 polymorphs can be obtained depending on the temperature at which amorphous Nb_2O_5 is crystallized. The amorphous Nb_2O_5 begins to crystallize in the TT form (pseudohexagonal) around 500$^\circ C$. At higher temperatures T-, M- (orthorhombic) and H- (monoclinic) Nb_2O_5 forms are obtained [5]. The Nb_2O_5 crystalline behaviour also is influenced by the starting materials used, impurities that may be present and any interactions with other components.

Due to the excellent properties of the Nb_2O_5 (micro-textural, high refractive index, stability and corrosion resistance), this material has remarkable applications in optics, construction of ionic lithium batteries, electrochromic mechanisms and photovoltaic cells. The Nb_2O_5, particularly the T phase, is a promissory material since it provides good stability in aqueous medium for acid-catalysed reactions [6]. The Nb_2O_5 have significant advantages in catalytic performance because the nanochemical synthesis helps to control its structure and morphology [7].

In this work there will be an analysis the Pechini synthesis method of preparation for Nb_2O_5 nanostructures and its crystalline phase evolution.

2. Materials and methods

Nb_2O_5 nanoparticles were prepared by the polymeric precursor method -Pechini method. For this hydrated citric acid (Panreac 99.5%) was used as a chelating agent of niobium cations from $NbCl_5$ (Sigma-Aldrich 99%) and ethylene glycol (Panreac 99.8%) as a polymerizing agent. The employed solvent was distilled water (for the A samples) and solutions that contained HNO_3 (Panreac 65%), HCl (Panreac 37%) or NH_4OH (Panreac 30%) (B, C and D samples, respectively) where the objective was to dissolve better the niobium salt (see Table 1). The chelate was polyesterificated forming a resin. The resin decomposition was realized in a pre-calcination at 300°*C* for 4 hours. The material obtained was macerated and the obtained powders were calcined at temperatures between 500°*C* and 750°*C* obtaining oxides with fine particles and of adequate chemical composition, which was controlled precisely during the process.

The characterization of the samples obtained was realized by X ray diffraction (XRD) with the objective being to determine the crystalline phases. For this an XPERT-PRO Panalytical was employed with radiation Co $K_{\alpha 1}$ (λ=1.78901*Å*) operating at 40*mA*, at a velocity of 0.0133°/*min* and varying 2θ between 10° and 90°. A scanning electron microscope (SEM) FEI QUANTA 200 operating at 5*kV* was used for analysing the morphology of the synthesized materials.

3. Results and discussion

Figure 1 presents the XRD patterns of the B samples as a function of the temperature. For all samples the Nb_2O_5 was identified using data contained in the Power Diffraction File, cards No. 28-0317 for the pseudohexagonal TT-phase (a=b=3,607*Å*, c=3.925*Å*) and cards No. 30-0873 for the orthorhombic T-phase, (a=6,175*Å*, b=29,175*Å*, c=3,930*Å*). The crystallite sizes were estimated using the Scherrer method (see Table 1).

Table 1. Results of XRD analysis at room temperature[a].

Sample	Heating temperature (°C)	Solvent	Phase composition	Crystallite size (nm)
B-Nb500	500	H_2O - HNO_3	Nb_2O_5 (TT)	34 (9)
C-Nb500	500	H_2O – HCl	Nb_2O_5 (TT)	18 (6)
D-Nb500	500	H_2O - NH_4OH	Nb_2O_5 (TT)	45 (17)
B-Nb650	650	H_2O - HNO_3	Nb_2O_5 (T)	37 (5)
C-Nb650	650	H_2O – HCl	Nb_2O_5 (T)	39 (7)
D-Nb650	650	H_2O - NH_4OH	Nb_2O_5 (T)	35 (1)
B-Nb750	750	H_2O - HNO_3	Nb_2O_5 (T)	42 (2)
C-Nb750	750	H_2O – HCl	Nb_2O_5 (T)	41 (3)
D-Nb750	750	H_2O - NH_4OH	Nb_2O_5 (T)	44 (4)

[a] The heating time was 2 hours.

TT = low-temperature pseudohexagonal phase. T = orthorhombic phase.

The samples heated at 500°*C* corresponded to Nb_2O_5 (TT) and showed broad diffraction lines. Nb_2O_5 (T) formed upon the heating of samples A, B, C and D at 650°*C* and exhibited rather sharp diffraction lines. The single diffraction lines of the TT-phase were well resolved in the T-phase as seen in Figure 1. The analysis of these patterns indicates that an increase in the synthesis temperature leads to materials with higher crystallinity. In the Figure 2 another trend was observed at the oxide

orthorhombic formation when the synthesis routes B and D are utilized. This is an indication that the HNO_3 and the NH_4OH produced the same crystalline structure (homogeneous Nb_2O_5 orthorhombic).

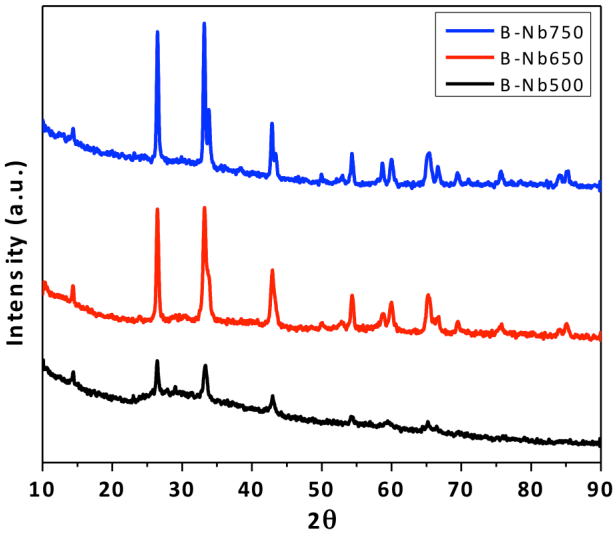

Figure 1. XRD patterns of the B samples as a function of the temperature.

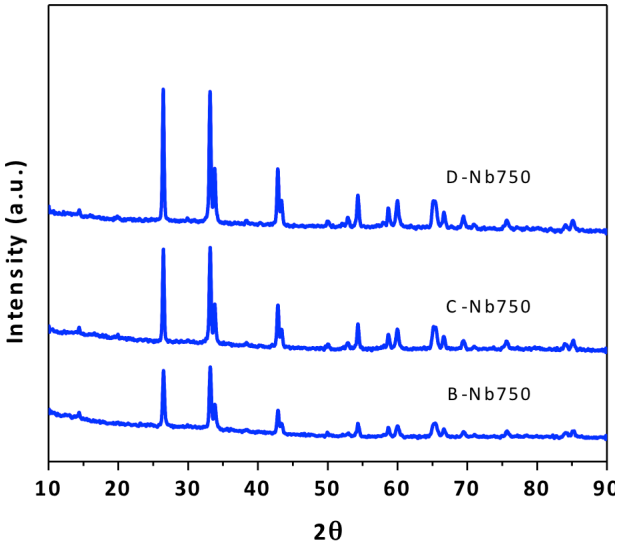

Figure 2. XRD patterns of the samples heated at 750℃.

The morphological characterization samples are realized through SEM imagery analysis. In Figure 3 the morphological differences are observed into the samples A-Nb500 (a), A-Nb650 (b) and A-Nb750 (c). The sample A-Nb500 presents isotropic morphology and reveals the presence of abundant nanoparticles agglomerate; this agglomeration infers that the calcination temperature used is still low. Figure 3(b) shows a typical SEM image of Nb_2O_5 nanostructured. It can be seen that the nanoparticles surface is well defined. Since these samples were not calculated it was difficult to count the mean particle size since. Figure 3(c) shows a uniform distribution of the nanoparticles; this indicates that the thermal treatment at 750℃ for 2*h* promotes the growth of the particles. These results suggest that the increase in the synthesis temperature allowed significant morphological modifications.

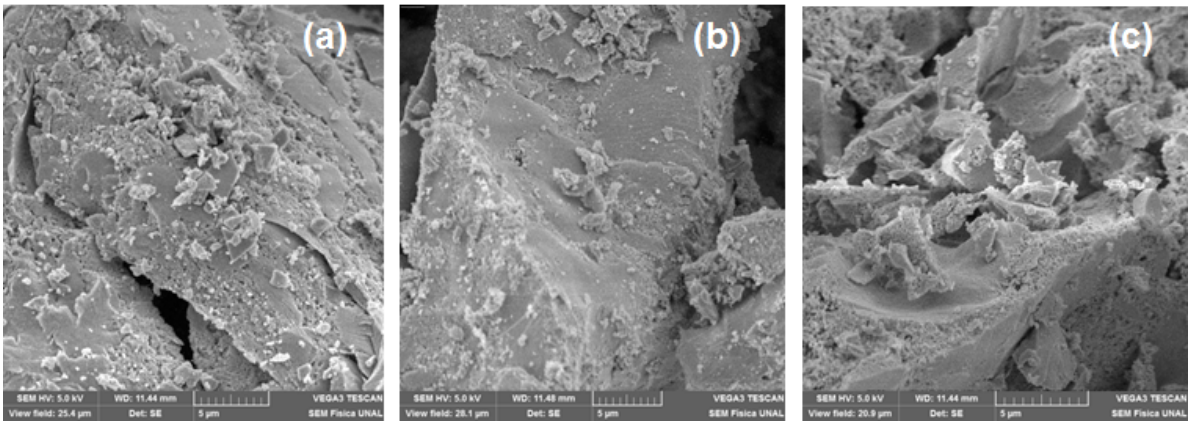

Figure 3. Imagery obtained by SEM for A samples heated at (a) 500, (b) 650 and (c) 750 *°C*.

4. Conclusions

It was verified that the synthesis method is suitable to obtain the desired oxide phase. In the four routes, the Pechini method helps significantly to improve the structural properties studied in this work since the T-phase Nb_2O_5 was accepted, in which an orthorhombic structure was confirmed by XRD. The thermal conditions that best favoured the growing of the particles were obtained to thermal treatment at 750 *°C* for 2 hours. According to the results presented, it can be noted that the best synthesis conditions for the obtaining of the T-phase Nb_2O_5 corresponded to the samples that employed an aqueous solution of HNO_3.

References

[1] Pechini MP 1967 *Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor* (US: Patent No.3.3306.97)
[2] Vargas M A, Franco Y, Ochoa Y, Ortegón Y and Rodriguez J E 2011 *Bol Soc Esp Ceram Vidr* **50** 267
[3] Sreethawong T, Ngamsinlapasathian S, Lim S H and Yoshikawa S 2013 *Chemical Engineering Journal* **215** 322
[4] Lin H Y, Yang H C, Wang W L 2011 *Catalysis Today* **174** 106
[5] Zhao Y, Zhou X, Ye L and Edman Tsang S C 2012 *Nano Reviews* **3** 17631
[6] Prado A G S, Bolzon L B, Pedroso C P, Moura A O and Costa L L 2008 *Applied Catalysis B Environmental* **82** 219
[7] Lopesa O F, Paris E C and Ribeiro C 2014 *Applied Catalysis B Environmental* **144** 800