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Mn-modification effects on Nb₂O₅ structural, optical and vibrational properties

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Abstract. In this study Mn-modification (at 1%, 2.5%, 5% and 10%) on Nb₂O₅ was carried out through the Pechini method; the annealing temperatures: 400°C, 500°C, 600°C and 700°C, were used to study the thermal stability of the system and the crystalline growth. The crystallization at high temperatures has been investigated because low annealing temperature cannot improve the crystallization and the effect of Mn-modification concentration is worthy of a further investigation. Before annealing the samples were analysed by TGA. The structural analysis through XRD is carried out to study a possible increase of the crystallite size (L) by increasing the Mn concentration; for the samples at 700°C and 1% and 2.5% concentrations, L is increased from 39.81 to 46.45nm while L changes from 32.67 to 35.63 with 5% and 10%, respectively. After Mn-modification the evolution of (100) and (180) peaks Nb₂O₅ was observed suggesting that they were well defined only until 2.5%. IR and Raman spectroscopies allowed to analyse vibrational modes present in the samples: the IR spectrums for the samples at 400°C, 500°C and 600°C showed a band around 1100cm⁻¹ which can be associated to C-C(v_{C-C}) and C-O(v_{C-O}) vibrations; at 700°C the shoulder was distinguished around 750cm⁻¹ characteristics of the Nb₂O₅ orthorhombic structure. Vibration modes associated with Nb₂O₅ were found with the Raman spectroscopy; these become less intense after Mn-modification. The band gap energy was obtained through UV-Vis spectrophotometry which revealed a slight increase at 700°C.

1. Introduction

Photocatalysis is a process based on the excitation of a semiconductor using radiation of adequate energy. The search for efficient highly processes in heterogeneous photocatalysis, which is a promising alternative of decontamination processes and it has directed the investigation to the optimization of existing photocatalysts and to the search of materials that may overcome the TiO₂ in its photocatalytic properties.

Niobium oxide is a p-type semiconductor with a wide band gap of about 3.4eV and has been proposed for a wide variety of applications, such as sensing materials [1-2], to support catalytic processes [3-6] and it has also attracted considerable interest as a raising material for electrochromic devices. All technological applications of oxide are determined by its structures and properties. In catalysis it can be correlated the catalytic activity with the crystalline phase; it has also been demonstrated that the Nb₂O₅ orthorhombic phase presents the greater catalytic activity. [7-8]

Choi *et. al.* [9] analysed the TiO₂ nanoparticles doping effect with 21 metals. There, in some cases, the TiO₂ oxidative capacity was improved of the and in others its reductive capacity. This effect leads



to think in alternative materials that can overcome the TiO_2 properties when they are modified with transition metals.

Here, we report the synthesis of Mn-modification effects on Nb_2O_5 using a simple procedure involving the Pechini method. The value of Nb_2O_5 gap energy was reduced, which could increase its sensitivity introducing little manganese.

2. Materials and methods

$\text{Nb}_{2-x}\text{Mn}_x\text{O}_5$ ($x=0.02, 0.05, 0.1, 0.2$) samples were prepared by the polymeric precursor method - Pechini method. For this, Niobium Chlorure (NbCl_5 99% Sigma-Aldrich) and Manganese Nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ Merck) were used as starting precursors in a concentration previously established; distilled water the solvent employed. Hydrated Citric Acid (Panreac 99.5%) was used as a chelating and Ethylene glycol (Panreac 99.8%) as a polymerizing agent. The chelate was polyesterified shaping a resin; the resin decomposition was done in a pre-calcination at 300°C for 4 hours. The material obtained was grounded in Agate mortar and to study the thermal stability, the powders obtained were subjected to thermal annealing at 400°C , 500°C , 600°C and 700°C for 2 hours.

Thermogravimetric Analysis (TGA) was used in order to detect the physical and chemical changes of the oxides depending on the temperature; for this, the DSC/TGA SDTQ600 equipment was used, applying a heating rate of $10^\circ\text{C}/\text{min}$. These spectres were analysed with the TA Instruments Universal Analysis 2000 analysis software. X ray diffraction (XRD) was done through an Xpert PANalytical Empyrean Series II Alpha 1 employing radiation $\text{Cu K}\alpha_2$ ($\lambda=1.54442\text{\AA}$) operating at 40 mA and varying 2θ between 5° and 80° . Infrared spectroscopy and Raman spectroscopy were used to analyse the vibrational behaviour of the samples; for this, a Prestige-21 Shimadzu IR spectrometer was used with a resolution of 8cm^{-1} and 8 shifted and a TG4000 Jobin Yvon micro-Raman commercial with line of Raman excitation $\lambda=532\text{nm}$. Shimadzu UV-Vis Cary 5000 spectrophotometer was used to obtain reflectance spectra of the samples.

3. Results and discussion

In Figure 1, the results of Thermogravimetric Analysis are presented showing an outstanding region of weight loss, between 320°C and 500°C , being associated to the temperatures of beginning and ending of decomposition of certain species in the samples, then the temperature chosen for the precalcination of the materials was adequate. The sample most thermally stable is the one synthesized at 1% Mn content and the least stable is the one synthesized at 10% Mn content.

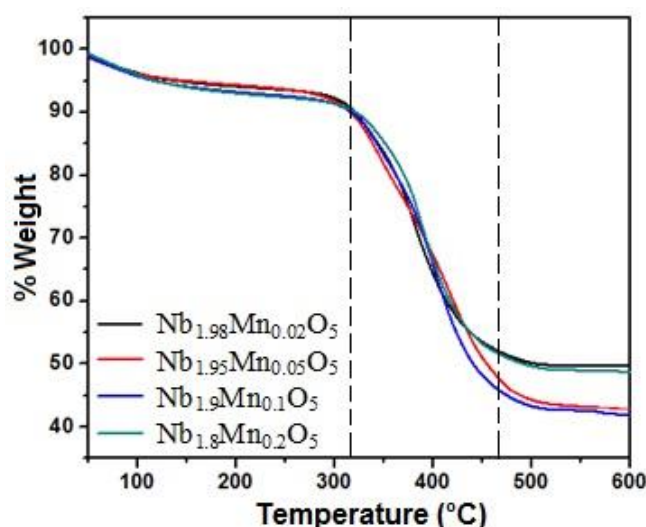


Figure 1. Weight percent graphs as a function of temperature for only precalcined $\text{Nb}_{2-x}\text{Mn}_x\text{O}_5$ samples.

X-ray diffraction patterns presented in Figure 2 show the presence of one phase for $x=0.02$ and $x=0.05$; structure orthorhombic with space group $Pbam$, corresponding to Niobium Pentoxide (this contrasts our results with the stored ones in Power Diffraction File). No reflections related to any secondary phase are detected in the XRD patterns, so for these x values the Niobium Pentoxide structure is not disturbed on substitution. Increasing the Mn concentration arises also peaks of low intensity. For $x=0.1$ and $x=0.2$ was found the structure orthorhombic [10] with space group $Pbcn$, corresponding to Manganese Niobium Oxide; it is believing that the Mn ions enter to Niobium pentoxide matrix occupying substitutional sites. Additional reflections consistent with Mn_3O_4 phase were observed, whose intensity depend on the annealing temperature. The small peak located around 36° for the sample modified with 10% of Mn is related to the cubic phase Mn_3O_4 .

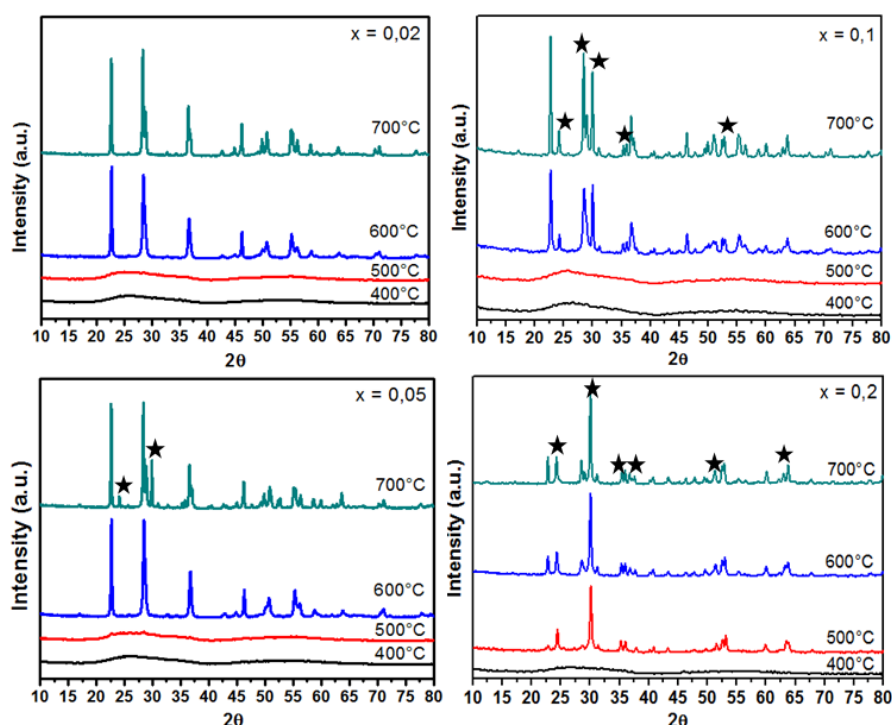


Figure 2. Comparison between XRD patterns of Mn-modified Nb_2O_5 at 1%, 2.5%, 5% and 10%. The star-type convention is used to highlight peaks that appear with the inclusion of metal.

Table 1 shows the crystallite size values (L) obtained through the Scherrer equation for the samples submitted at $700^\circ C$. It seems to have a slight tendency to increase as a concentration of the ion content increase too, only in the case when x pass from 0.02 to 0.05 or when x pass from 0.1 to 0.2, taking into account that two different phases were obtained. The width of the reflections increases with increasing Mn content, indicating decreasing in the particle size. In the same table, the respective lattice parameters are presented. An increase is expected in those as the Mn concentration is increased, due to the ionic radius of Mn^{2+} (0.80\AA) is larger than the ionic radius of Nb^{+5} (0.75\AA).

Figure 3(a) shows the evolution with the temperature of the infrared spectra of $Nb_{1.95}Mn_{0.05}O_5$ sample. Similar bands are found in the spectra rest at others Mn content. At $400^\circ C$, bands around 1600cm^{-1} are associated with the presence of residual organic components. At $500^\circ C$ the spectra show a shoulder at about 350cm^{-1} , attributed to the amorphous phase of niobium pentoxide. A shoulder located around 1100cm^{-1} is distinguished for samples subjected to $400^\circ C$, $500^\circ C$ and $600^\circ C$; this can correspond to the elongation type vibrations of the $C-C(v_{C-C})$ and $C-O(v_{C-O})$ groups, which are due to methoxy bridge species or may also be due to solvents, products and by-products of synthesis reaction of material. At $600^\circ C$, the small band at about 500cm^{-1} can be attributed to vibration ν_3 (Nb-O). At

700°C, the shoulder around 750 cm^{-1} is characterized of the orthorhombic structure [11]. Figure 3(b) shows the Raman spectra varying Mn concentration for the samples submitted at 600°C. Raman modes for the calcination temperature of 400°C could not be observed. At 600°C and 700°C, bands correspond to vibrations of cations occupying centres of octahedrons and tetrahedrons are found in the 150-400 cm^{-1} range. Bands in the 400-800 cm^{-1} region are assigned to the symmetric and antisymmetric stretching mode of the Nb-O-Nb linkage [12].

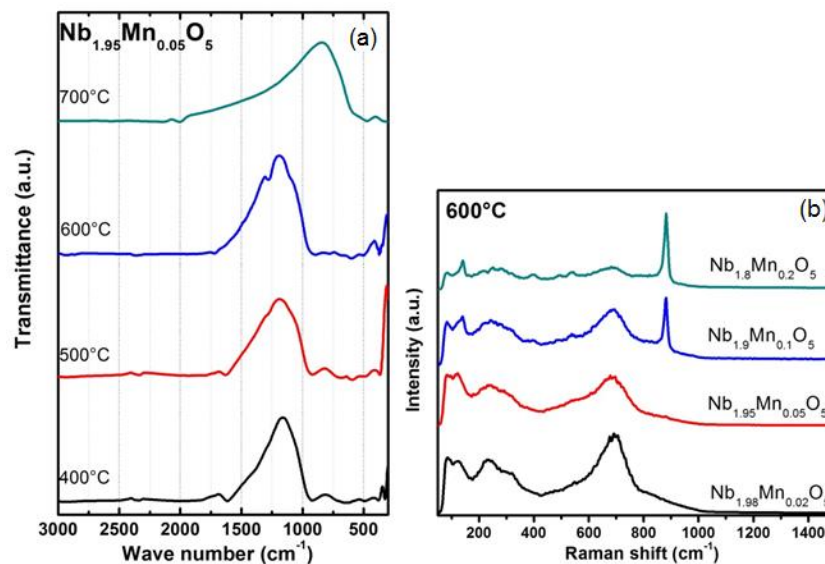


Figure 3. (a) Evolution with the temperature of the infrared spectra of $\text{Nb}_{1.95}\text{Mn}_{0.05}\text{O}_5$ sample. (b) Raman spectra varying Mn-content of the sample submitted at 600°C.

In Figure 4, the Diffuse Reflectance spectra are presented as a function of energy for the sample $\text{Nb}_{1.9}\text{Mn}_{0.1}\text{O}_5$, varying the temperature. Similar spectra were obtained for the samples rest. A decrease in the reflectance intensity is observed with increasing x ; this is explained in terms of the lattice distortion due to the incorporation of the larger Mn^{2+} ions inside the Nb_2O_5 lattice.

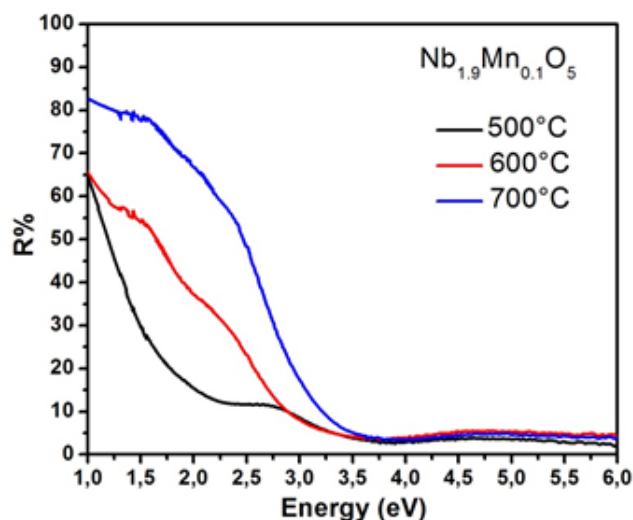


Figure 4. Diffuse reflectance spectra as a function of energy for the $\text{Nb}_{1.9}\text{Mn}_{0.1}\text{O}_5$ sample, varying the temperature.

The evolution of the gap energy values (E_g) with Mn content, at 700°C, is presented in the Table 1. In all cases the E_g value lightly increases at 700°C. In general, optical studies show a decrease in the band gap increasing Mn content, considering two cases separately: 1 and 2.5%, and 5 and 10%. Despite this behaviour, the E_g values obtained are suitable for photocatalytic purposes. The E_g values obtained can be attributed to the spin forbidden transition on Mn^{2+} in a tetrahedral environment.

Table 1. Crystallite size values, lattice parameters and gap energy values for the samples submitted at 700°C.

Sample	L(nm) ^a	JPDF cards No.	Lattice Parameters ^b	E_g (eV)
Nb _{1.98} Mn _{0.02} O ₅	39.81	00-027-1003	a=6.1680Å	3.17
Nb _{1.95} Mn _{0.05} O ₅	46.45		b=29.3120Å c=3.9360Å	
Nb _{1.9} Mn _{0.1} O ₅	32.67	01-075-2159	a=14.4204Å b=5.7566Å c=5.0784Å	3.16
Nb _{1.8} Mn _{0.2} O ₅	35.63	00-025-0543	a=5.0700Å b=5.7500Å c=14.4300Å	

^a The crystallite size values were estimated for the peak of maximum intensity.

^b The lattice parameters were determined contrasting the results with the stored ones in Power Diffraction File.

4. Conclusions

Nb_{2-x}Mn_xO₅ (x=0.02, 0.05, 0.1, 0.2) nanoparticles have been synthesized using a simple Pechini method. With the increasing of Mn content, lattice parameters increase due to the larger ionic radius of Mn. Samples modified with the highest Mn content reveal the formation of small amounts of Mn₃O₄.

In general, the vibrational study shows that an increase of the synthesis temperature causes an increase in the material crystallinity because an increase in the synthesis temperature led to a sharp peak, this fact is verified with the values of the crystallite size.

Optical investigations through Diffuse Reflectance reveal that the presence of Mn^{2+} in tetrahedral coordination, possibly due to the substitution on Mn for Nb in the Nb₂O₅ lattice.

The presence of Mn^{2+} ions in the tetrahedral sites, the increased lattice parameters and the violet shift of the band gap, are some of the indicators of the incorporation on Mn ions inside the Nb₂O₅ lattice.

Acknowledgements

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