

Article

Synthesis and Characterization of Nano-Particles of Niobium Pentoxide with Orthorhombic Symmetry

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Abstract: In this work, a set of nanoparticles of Nb₂O₅ nanoparticles were grown by both the Pechini and the sol-gel methods. The amorphous materials were calcined at 650 °C or at 750 °C. X-ray diffraction, scanning electron microscopy, luminescence and Raman spectroscopy were used in order to characterize the materials. From the study, it is possible to state that the method of production of nanoparticles, beyond the temperature of synthesis, has a great influence on whether the phase produced is hexagonal or orthorhombic. Additionally, compared to de Sol-gel method, the Pechini method produced samples with smaller particle sizes. The photoluminescence spectra of niobium pentoxide nanostructure materials show that the emission peaks are positioned between 334 to 809 nm and there is a change of intensity which varies depending on the synthesis route used. High pressure Raman spectra at room temperature were obtained from two samples grown by the sol-gel method. Up to 6 GPa, where it is possible to observe the Raman bands, no modification other than the increase of disorder was observed, and this can be associated with a change of phase.

Keywords: nanoparticles; sol-gel; photoluminescence; Raman; pressure

1. Introduction

Niobium pentoxide is an important oxide with potential applications in several fields, including Electrochromism and Catalysis [1,2]. It is considered as a catalyst material, being used to prepare some crystals with technological applications such as KNbO₃ and NaNbO₃ [3]. The Nb₂O₅ is not a toxic compound so it can be used as a water decontaminator. This oxide has advantages in its photocatalytic performance because, during the synthesis process, it is possible to control variables such as structure and morphology. From the technological point of view, the niobium pentoxide is of remarkable importance because it presents energy absorption in the ultraviolet region, whereby this semiconductor can be used to protect materials from that radiation. Nb₂O₅ presents a series of structural phases (trigonal, hexagonal, monoclinic or orthorhombic) [4] and consequently, it can present different physical characteristics such as a semiconductor or as a dielectric material, depending on the symmetry. Regarding these phases, many studies have demonstrated how it is possible to obtain a certain phase from a previous one. For instance, it is known that the trigonal L-Nb₂O₅Nb phase turns into a monoclinic high-temperature phase H-Nb₂O₅ close to 900 °C [4]. Also, by heating niobium pentoxide at constant pressure, the sequence of phase transitions H-Nb₂O₅ → B-Nb₂O₅ → T-Nb₂O₅ is observed [5] and, at a constant temperature,

it was demonstrated that B-Nb₂O₅ and T-Nb₂O₅ constitute high pressure polymorphs of Nb₂O₅ [6]. Interestingly, it is believed that many of the existent phases should be metastable or, at least, stabilized by impurities [5]. A suitable combination of chemical, electronic and optical properties make this oxide useful in various applications [7–10]. However, this result is further needed in order to investigate the photoluminescence (PL) because the optical measurements provide important information about the electronic structure of niobium pentoxide [11–13].

Among several physical properties, photoluminescence is important because it allows us to characterize a variety of material parameters. The PL emission produces information on the lifetime of the excited states, the identification of the surface interface and the impurity levels. It can also provide simultaneous information on intrinsic and extrinsic defects [14,15]. The niobate luminescence has been studied in crystalline materials and is strongly dependent upon the crystal structure [16]. The most efficient luminescence occurs in niobyl groups as in the Nb-O group with a short bond distance, of approximately 0.17 nm [17]. Structurally isolated NbO₆ octahedra are not efficient luminescent centers [18], whereas isolated distorted niobate groups, such as in LaNbO₄, where the Nb(V) has a 4 + 2 coordination, provide very efficient centers. The closer the Nb-O-Nb angles are to 180 the more pronounced the effects of the NbO₆ condensation become [16,17,19–21].

In this paper, we study the synthesis of the T-form of Nb₂O₅ through both the sol-gel and the Pechini methods, and analyze some aspects of the materials such as their morphology through scanning electron microscopy (SEM), photoluminescence (PL) and the behavior of samples under high pressure conditions.

2. Materials and Methods

The samples were obtained through both the sol-gel and the Pechini methods. The starting precursors were niobium (V) ethoxide, (Nb(OC₂H₅)₅ 99.999% Alfa Aesar) and niobium chloride (NbCl₅ 99% Sigma-Aldrich). The niobium pentoxide nanostructure materials obtained were calcined at 500 °C, 650 °C and 750 °C for 2 h [19,20].

On one hand, the XRD patterns of the samples synthesized through the Pechini method were obtained using an Xpert-PRO Panalytical diffractometer (Co K α ₁ radiation, λ = 1.78901 Å, UPTC, Tunja, Colombia), operating at 40 mA. A step of 0.0133° in 1 min, in the 2 θ angle range of 10–90° was used. On the other hand, the XRD patterns of the samples synthesized by the sol-gel method were obtained using The Panalytical PW3373 equipment (Cu K α ₁ radiation, λ = 1.540558 Å, Universidad de Antioquia, Medellin, Colombia), operating at 40 mA with a step of 0.05° in 50 s, in the 2 θ angle range of 5–80° was used. A field emission gun-scanning electron microscope (FEG-SEM JOEOL JSM 6701F, Universidad Nacional de Colombia, Bogota, Colombia) operating at 5.0 kV was used to verify the material morphology.

The PL measurements were performed with a monospec 27 monochromator (Thermal Jarrel AS, Franklin, MA, USA) coupled to a R446 photomultiplier (Hamamatsu photonics, Shizuoka, Japan). A Krypton ion laser (Coherent Innova 90 K, Silicon Valley, CA, USA) (λ = 350 nm) was used as excitation source. Raman scattering spectra were obtained in the backscattering geometry with a Jobin-Yvon-T64000 spectrometer, coupled to a N₂ cooled CCD device, using as excitation the 532 nm laser line of a Verdi laser, operating at 160 mW. In order for the Raman to reach a high pressure a National Bureau of Standards diamond anvil cell was used, having as compression medium an ethanol-methanol mixture (1:4) with a stainless steel gasket with 210 μ m thickness preindented to approximately 70 μ m for both samples investigated. The pressure was calibrated through the luminescence of ruby (Al₂O₃:Cr³⁺) through the R₁ and R₂ lines.

The X-ray diffractograms of Figure 1 were recorded from solids obtained through the Pechini method submitted to three different thermal treatments: 500 °C, 650 °C and 750 °C. The (a) and (b) XRD patterns indicate that for the 500 °C and 650 °C treatments, the solids crystallize in a hexagonal structure with resolved peaks at: 2 θ = 22.6°, 28.5°, 36.7°, 46.2° and 56.1°, as reported in JCPDF028-0317. In the case (c), where the sample was heated up to 750 °C, it is found that

the solid crystallizes in an orthorhombic structure with resolved peaks at: $2\theta = 22.6^\circ, 28.8^\circ, 37.1^\circ, 46.0^\circ, 50.9^\circ$ and 56.3° , according to JCPDF027-1313. The orthorhombic structure, which we are particularly interested in due to its potential application, is composed by Nb atoms surrounded by oxygen atoms forming distorted octahedra or pentagonal bipyramids. Figure 2 shows the XRD patterns of Nb₂O₅ obtained through the sol-gel method at (a) 650 °C and (b) 750 °C where the 2θ peaks are compatible with orthorhombic structures. In other words, the diffractogram peaks from the samples obtained by sol-gel method are similar to those samples obtained by the Pechini method at 750 °C. In the synthesis of the two mentioned routes, Ammonia (NH₄OH) was used in the process of obtaining the samples.

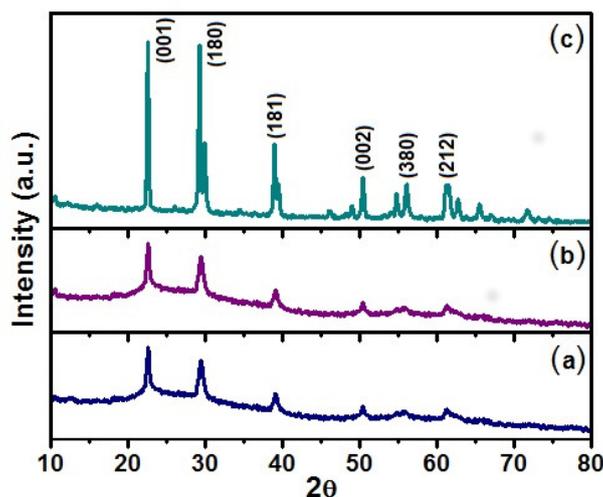


Figure 1. XRD pattern of Nb₂O₅ solids obtained through Pechini method at (a) 500 °C, (b) 650 °C and (c) 750 °C, adding NH₄OH in the sample preparation. The Co K α_1 radiation was used in the experiments.

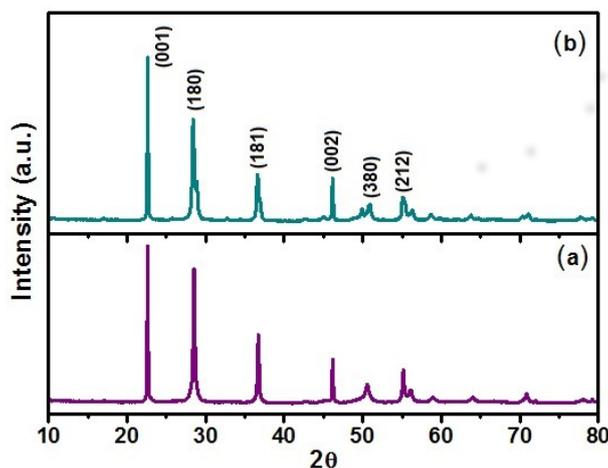


Figure 2. XRD pattern of Nb₂O₅ solids obtained through sol-gel method at (a) 650 °C and (b) 750 °C, adding NH₄OH in the sample preparation. The Cu K α_1 radiation was used to obtain the two diffractograms.

3. Results and Discussion

Figure 3 shows the SEM images of niobium pentoxide synthesized at $T = 650^\circ\text{C}$ using NH₄OH through (a) sol-gel and (b) Pechini methods. The bar in Figure 3a represents 1 μm , while the bar in Figure 3b represents 100 nm. We observe that the grains in the two figures have these dimensions

as their characteristics. So, it is evident that the use of the Pechini method allows to synthesize samples with smaller particle sizes. In order to compare the materials synthesized at 650 °C and at 750 °C. Figure 4 shows the SEM images of samples of Nb₂O₅ produced by different conditions at $T = 750$ °C: (a) sol-gel, (b) Pechini (NH₄OH), (c) Pechini (HCl—hydrochloric acid) and (d) Pechini (HNO₃—nitric acid). From these images, the morphology of the particles can be observed. In Figure 4, all the samples belong to the T-polymorph of niobium pentoxide. Again, the bar in Figure 4a represents 1 μm, while the bars in Figure 4b–d represent 100 nm. Clearly the samples produced by the sol-gel method (NH₄OH) have higher particle sizes than those synthesized by the Pechini method for both temperatures (650 °C and 750 °C).

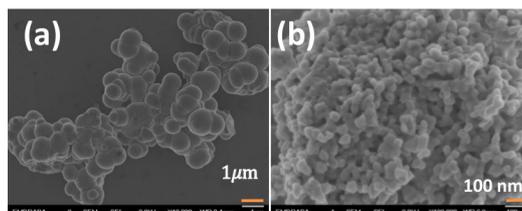


Figure 3. SEM micrographs of Nb₂O₅ with NH₄OH in obtaining samples: (a) Sol-gel, Nb₂O₅—650 °C for a resolution of 1 μm; (b) Pechini, Nb₂O₅—650 °C for a resolution of 100 nm.

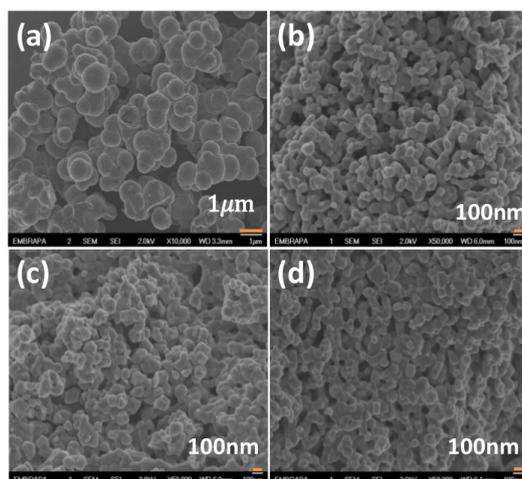


Figure 4. SEM micrographs of Nb₂O₅: (a) Sol-gel (NH₄OH) Nb₂O₅—750 °C for a resolution of 1 μm; (b) Pechini (NH₄OH) Nb₂O₅—750 °C for a resolution of 100 nm; (c) Pechini (HCl) Nb₂O₅—750 °C for a resolution of 100 nm; and (d) pechini (HNO₃), Nb₂O₅—750 °C for a resolution of 100 nm.

Figure 5 presents the number of particles vs. the size of the particles for several samples calcined at 750 °C for 2 h: (a) Sol-gel (NH₄OH) the average size is 733.3 nm and (b) Pechini (HNO₃), (c) Pechini (HCl) and (d) Pechini (NH₄OH). For the Pechini method, the average size was 71.4 nm. This shows that the Pechini method must be used to obtain samples with smaller particle sizes. In the Supplementary Material, we present the number of particles as function of the size of particles for the samples calcined at 650 °C. Again, it is possible to note that the Pechini method produces samples with smaller particle sizes 40 nm, while the sol-gel method produces samples with a size of 733.3 nm. The particle size through the Pechini method is similar to the reported in the work of Yun et al. [21].

In photoluminescence, a change is observed with the increasing calcination temperature of the samples. Figure 6 shows photoluminescence of: (a) sample to 500 °C through the pechini method with addition of NH₄OH. Here the peaks with an energy of 432 nm (2.87 eV), 474 nm (2.61 eV), 529 nm (2.34 eV), 610 nm (2.0 eV) and 819 nm (1.5 eV) are observed. Figure 6b sample to 500 °C

through the Pechini method with addition of HCl, with peaks at around of 432 nm (2.83 eV), 553 nm (2.24 eV) and 621 nm (2.0 eV). Therefore, in Figure 6c for the sol-gel method with temperature at 650 °C, we have peaks at the following positions: 434 nm (2.8 eV), 465 nm (2.67 eV) and 605 nm (2.0 eV). Finally, Figure 6d shows the photoluminescence for the Pechini (HCl) sample at 650 °C. The peak positions are: 440 nm (2.81 eV), 532 nm (2.33 eV) and 624 nm (1.98 eV). According to the work of Xiaofeng et al. [22], the niobium oxides of low valence are oxidized with the annealing temperature, so the content of Nb₂O₅ is increased. In this Figure, the sol-gel method which has the maximum emission is in blue, with the Pechini being the orange, green and blue regions.

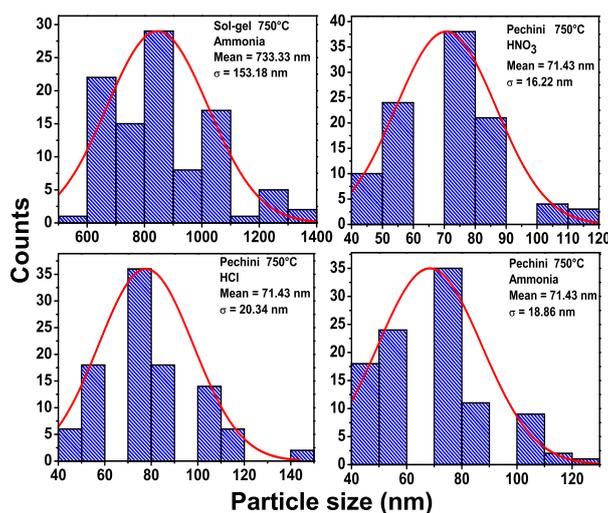


Figure 5. The plot shows the amount of particles vs. size of the particle. In a count of 100 particles, the sample was calcined at 750 °C for 2 h: (a) Sol-gel (NH₄OH) the average size is 733.3 nm and (b) Pechini (HNO₃), (c) Pechini (HCl) and (d) Pechini (NH₄OH) by the Pechini method the average size is 71.43 nm.

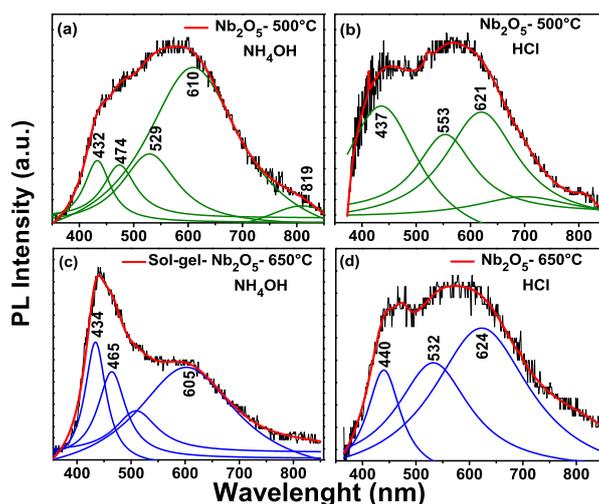


Figure 6. Photoluminescence spectra at room temperature: (a) Pechini (NH₄OH) Nb₂O₅—500 °C; (b) Pechini (HCl) Nb₂O₅—500 °C; (c) Sol-gel (NH₄OH) 650 °C; and (d) Pechini (HCl) 650 °C.

In Figure 7a the photoluminescence for the sol-gel sample is presented, with the positions of peaks at: 435 nm (2.85 eV), 469 nm (2.64 eV) and 621 nm (1.99 eV). In Figure 7b the highest intensity is in the peak position 612 nm (2.0 eV). The sample with an addition of HCl in the synthesis through the Pechini method is shown in Figure 7d, with the highest peak being at 607 nm (2.0 eV). The ultraviolet

emission band is at about 40 nm and some authors [23] have attributed this to the near-bandgap emission from Nb₂O₅. The other intensity band is ascribed to structural defects such as distorted NbO₆ octahedral groups. The differences between the sol-gel and Pechini methods are the peak positions and the intensity of the photoluminescence. For the sol-gel method, the maximum intensity of the peak is related to the near band gap emission; however, for the Pechini method, the highest peak is related to the distortion of the octahedral groups. This can be seen in Figures 6 and 7. In other words, for the sol-gel method, the maximum emission is shown in the violet wavelength (2.85 eV) and the maximum emission of Pechini is shown in orange (2.0 eV).

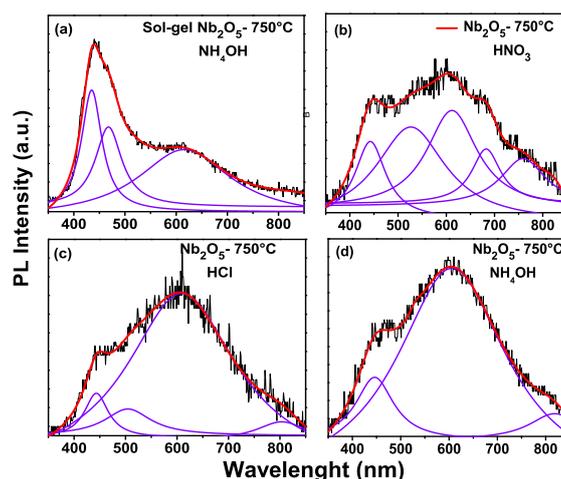


Figure 7. Photoluminescence spectra at room temperature at 750 °C in Nb₂O₅: (a) Sol-gel (NH₄OH); (b) Pechini (HNO₃); (c) Pechini HCl; and (d) Pechini (NH₄OH).

Figure 8 shows the Raman spectra of Nb₂O₅ obtained by the sol-gel method at 650 °C (NH₄OH) at several pressures recorded while at room temperature. All the pressure measurements started at ambient pressure, observing the following bands: Bands observed between 200 and 550 cm⁻¹ are assigned as bending of NbO₆ while the broad band close to 700 cm⁻¹ could be associated with stretching modes of NbO₆ [24]. Moreover, an assignment was done for the H-Nb₂O₅ polymorph, where bands between 204 and 549 cm⁻¹ were assigned as bending vibrations of NbO₆. Bands between 615 and 995 cm⁻¹ were assigned as Nb–O stretching of NbO₆. Although the symmetry of the sample studied in this work, corresponding to the T-polymorph, is different from the symmetry of the work of Reference [24], we can understand that the bending and stretching vibrations in the orthorhombic polymorph must be in the same spectral range.

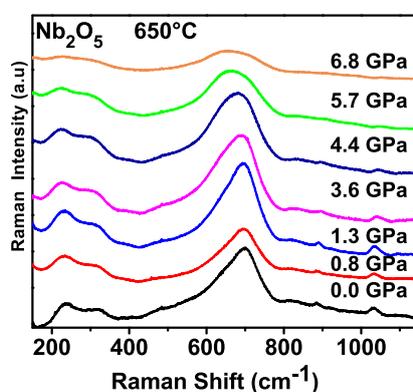


Figure 8. Raman spectra of Nb₂O₅ obtained by the sol-gel method at 650 °C (NH₄OH) as function of the hydrostatic pressure, recorded at room temperature.

With increased pressure, we notice some modifications in the Raman spectrum. For example, the bands observed between 200 and 400 cm^{-1} maintain their intensities up to approximately 4.4 GPa but above this pressure, the intensities decrease. The bands observed between 200 and 400 cm^{-1} , as occurs with the other bands in the Raman spectrum of niobium pentoxide, maintain intensity up to 4.4 GPa. After this pressure, the value of intensity of the bands diminishes in such a way that, in the spectrum recorded at 6.8 GPa, the peaks have very small intensities. The decreasing of intensity of the Raman bands is a point that deserves a brief discussion. Moreover, in general terms, when a material is submitted to compression, its Raman bands decrease in intensity and the linewidth increases. This is understood mainly as a consequence of the disorder introduced by the compression [25,26]. So, we can understand that some disorder is being introduced in the sample due to the compression. Additionally, we observe that the frequency of the stretching mode of Nb–O diminishes in compression, i.e., the energy of this mode presents a red shift. The softening of the stretching vibration Nb–O can be interpreted as a strengthening of interactions between NbO_6 octahedra. We have also obtained the pressure Raman spectra of Nb_2O_5 synthesized by the sol-gel method at 750 °C (NH_4OH); the same behavior of the sample obtained at 650 °C is observed (See Supplementary Material).

Although we observed evidence of disorder produced by the application of pressure, there is no evidence that the material had undergone any kind of phase transition, and we can understand that the orthorhombic phase of the sample is stable, up to the highest pressure reached in our experiments. Note that a transition $\text{H-Nb}_2\text{O}_5 \rightarrow \text{T-Nb}_2\text{O}_5$ was previously observed at 0.5 GPa (although the temperature necessary for the occurrence of this transition is higher than 1000 °C as shown in the work of Reference [5]). To our knowledge, the present study is the first high pressure investigation of the T-polymorph of Nb_2O_5 . Up to the highest pressure at which it was possible to record the Raman spectrum, the material seems to be stable.

4. Conclusions

We have observed in this work that, beyond the temperature of synthesis, the method of production has a great influence on the phase of Nb_2O_5 nanoparticles. If Nb_2O_5 nanoparticles are synthesized using the Pechini method at 650 °C, we obtain samples with hexagonal symmetry, while if the synthesis is done through sol-gel, at the same temperature $T = 650$ °C, we obtained samples with orthorhombic symmetry. Also, independently from the temperature of synthesis 650 °C or 750 °C—the Pechini method produces Nb_2O_5 samples with smaller particle sizes (≈ 71 nm) when compared to the sol-gel method (≈ 733 nm). In relation to PL measurements through the sol-gel method, the maximum intensity is observed in the blue and violet that could be related to "near-bandgap". For the Pechini method, the maximum intensity in the orange region may be related to defects in the distortion of the octahedral NbO_6 . Finally, concerning the high pressure study we were able to observe that two samples prepared through the sol-gel method (at 650 °C and 750 °C), i.e., in the orthorhombic T-phase, are stable up to about 6 GPa, the highest pressure where it was possible to observe Raman bands. As a possibility of future work we suggest the study of the T- Nb_2O_5 submitted to high pressure and high temperature, in order to compare it with results on H- Nb_2O_5 .

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-4701/7/4/142/s1>.

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Author Contributions: Miryam and José conceived and designed the experiments; Angela performed the experiments; Gadelha, Angela and Miryam analyzed the data; José and Paulo contributed reagents/materials/analysis tools; Paulo wrote the paper.

Conflicts of Interest: The authors declare that there is no conflict of interest in regards to the publication of this paper.

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