Synthesis, characterization and photocatalytic activity of titanophosphate glasses

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Abstract: Photocatalytic activity of (50-x)/2Na2O-xTiO2-(50-x)/P2O5 glasses (0 ≤ x ≤ 10 mol%) has been studied with an increase in the TiO2 content using UV-Visible spectrophotometry. Thermal properties were carried out from DTA measurement, and the variation of glass structure was investigated by Fourier Transform Infrared (FT-IR).

The first addition of the TiO2 up to 3 mol% entrained depolymerization of the phosphate skeleton (PO4)6−
chains in the binary 50Na2O-50P2O5 glass, resulting in poor cross-linking, which in turn the glass network becomes less rigid and the glass transition temperature (Tg) was decreased. Beyond this value, FT-IR reveals the formation of P−O−Ti bonds, which increases the cross-link density in the glass network and therefore increases Tg of the glasses. The photocatalytic activity results showed that these glasses ensure the discoloration of Rhodamine B by a removal efficiency of about 94% after 4h of irradiation.

Keywords: Titanium phosphate glasses, Fourier Transform Infrared Spectroscopy (FTIR), Photocatalysis.

Introduction

Like silica, phosphorus pentoxide “P2O5” is an excellent glass former with a structural entity PO4 tetrahedron, P2O5 has a much less rigid structure than SiO2 since at maximum, three oxygens are bridging, one less than in silica. This will lead to a significant difference in physicochemical properties such as poor chemical durability which limits their applications 3.

Phosphate glasses can be described as a regular tetrahedral network based of [PO4] groups; their structure is presented using Qn terminology, where n is the number of bridging oxygens per tetrahedron. Depending on the [O]/[P] ratio as set by glass composition, the phosphate glasses can be described by different structures: rich P2O5 network; polymer-like metaphosphate chains of Q3 tetrahedra; ‘invert’ glasses based on small pyro (Q1) and orthophosphate (Q0) species.

Phosphate glasses find an ever-increasing and a wide variety of applications in optoelectronic devices, laser host materials, as solid electrolytes, solid state ionic devices, waveguides, bio-implants, optical switches and fibres or power limiters 5, 6, as well as vitrification of radioactive waste 6-8, photonics 9, fast ion conductor 10, and glass-to-metal seals 11. These glasses could also be environmentally applicable as they can purify air and water since they can destroy and degrade different organic pollutants 12.

The additions of TiO2 into oxide glass-forming systems, usually contribute to the stabilization of their structure 13-15 and the improvement of their properties 16, 17, e.g. chemical durability, mechanical properties, electrical conductivity, etc. However, when TiO2 is added to those glasses, the phosphate chains are depolymerized while Ti-O-P bonds are formed 18. In this sense, C. Rousselot et al. 19 have prepared glasses in the system (NaPO3)1-x-y(TiO2)x where the TiO2 content can be up to 40%. FTIR spectroscopy reveals the depolymerization of the phosphate glass network by systematic conversion of metaphosphate chains into pyrophosphate groups and then orthophosphate groups in the richest TiO2 glass. Titanium generally exhibits two valencies in the oxide glasses, namely purple trivalent Ti3+ ion

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which occupies the octahedral sites and the colourless tetravalent Ti$^{4+}$ ion which occupies tetrahedral sites. The probability of the occurrence of Ti$^{3+}$ or Ti$^{4+}$ ion depends on the melting process used for the preparation of glass samples. Synthesized perfectly stable glasses with TiO$_2$ contents of up to 35%. Most of the work cited above worked on glasses with TiO$_2$ contents exceeding 10 mol%.

Rhodamine B is one of the most important dyes belonging to the xanthene group. Its simple structure is C$_{22}$H$_{14}$ClN$_2$O$_4$. It is currently used in the textile industry and the production of laser dyes, which are used for their long wavelengths. It was also, the object of many studies of its photocatalytic degradation in the presence of photocatalysts particles in aqueous media.

The UV-Visible absorption spectrum of an aqueous solution of Rhodamine B shows three bands of absorbance. Two bands are located in the ultraviolet range, and one is visible. In the visible region, the maximum band is located at 554 nm. The other two bands are located at 260 nm and 356 nm in the ultraviolet region.

Our interest, in this work, was to obtain using infrared spectroscopy valuable information concerning the structure of the glasses with the general composition (50-x/2)Na$_2$O-xTiO$_2$-(50-x/2)P$_2$O$_5$ where the TiO$_2$ content does not exceed 10 mol%. Furthermore, the influence of this substitution on the evolution of glass transition temperature, density, molar volume and on the photocatalytic degradation of RhB as a model pollutant is also discussed.

**Experimental**

**Preparation of glasses**

The preparation of the glasses was carried out by direct melting of sodium polyphosphate (NaPO$_3$ - extra pure, Riedel- de Hȧën) and titanium oxide (TiO$_2$ – Sigma Aldrich, 99.99% rutile) reagents mixed in stoichiometric proportions with compositions (100-x) NaPO$_3$-xTiO$_2$ (0 ≤ x ≤ 10 % mol). The amount of each product was calculated to obtain 12 g of phosphate glasses. The weighed materials were thoroughly mixed and pulverized in an agate mortar and then were placed in a porcelain crucible. A first thermal stage at 300 °C for 2 hours was achieved and then a second stage at 700 °C for a duration of one hour to minimize the evaporation of P$_2$O$_5$. The melting temperature of the most refractory composition (1100 °C) is used as the preparation temperature of the entire composition series of this system. Finally, after heating for half an hour at the desired temperature, the glasses were poured into the air on a stainless-steel plate.

**Characterizations**

**X-ray diffraction**

The X-ray diffraction patterns were collected on finely ground powder at room temperature using a Siemens D5000 diffractometer with CuK$_\alpha$ radiation ($\lambda_{K\alpha} = 1.5418$ Å) in the 2θ ranges from 10° to 60° with a scanning speed of 2° per minute.

**Infra-red spectrometry**

The Fourier transformation infrared spectroscopy (FT-IR) was recorded in a Jasco FT/IR 4600 spectrometer equipped with a Jasco ATR PRO ONE module with a resolution of 4 cm$^{-1}$ and over 400–4000 cm$^{-1}$ range. For this, the samples glass were crushed to fine powder. A small amount of this powder was mixed and ground with a relatively large quantity of KBr (3%) which is transparent to IR radiation. Discs for IR absorption spectra measurement were formed by pressing it under 10–15 tons of pressure for a few minutes.

**Thermal behavior**

The glass transition temperature $T_g$ was measured by a differential thermal analyzes (SHIMADZU DTG device) at the range 25–800 °C with 10 °C min$^{-1}$ of heating rate and under a Nitrogen atmosphere. The samples are introduced into alumina crucibles, and the results were corrected by using an empty cell to provide the baseline. The temperatures values are given with about ±5 °C of estimated accuracy.

**Density and molar volume**

The density of the glasses was determined at room temperature using the Archimedes method with diethylorthophthalate as the immersion fluid. The mass glasses used deprived of bubbles. The following relation made it possible to determine the density values:

$$\rho = \frac{M_{air}}{M_{air} - M_{imm}} \rho_{ortho}$$

With:

- $\rho_{ortho}$: Density of diethylorthophthalate at T °C (g/cm$^3$),
- $M_{air}$: Sample mass in the air (g),
- $M_{imm}$: Sample mass immersed in water (g).

The average uncertainty in the measured density was found as ±0.03 g/cm$^3$. The molar volume ($V_m$) was calculated from the experimentally determined density ($\rho$) according to the relation:

$$V_m = \frac{M}{\rho}$$

Where M is the molar weight of the glass.

**Photocatalytic experiments**

The photocatalytic activities of the prepared powders were evaluated by the degradation of rhodamine B in an aqueous medium. Five
Commercial Puritek lamps (7 W lamp) were used as a UV light source. Each powder (mass of 100 mg) was suspended in 100 mL of RhB solution (5 mg/L). Before the irradiation, the solution was vigorously stirred for 1 hour in the dark in order to establish the adsorption-desorption equilibrium between the catalyst and RhB. The light was then turned on to initiate the photocatalysis process. About 5 mL sample was taken each 20 min. The concentration of RhB was determined as a function of irradiation time using a UV–visible spectrophotometer (UV-2300). The photocatalytic efficiencies were determined from the variation of the concentrations resulting from these intensities:

\[ I(\%) = \frac{C_0 - C}{C_0} \times 100 \]  

Where \( C_0 \) and \( C \) are the concentrations of the solutions before and after UV irradiation, respectively.

**Results and discussion**

**X-Ray analysis**

Fig. 1 shows the XRD patterns of the five glass samples taken at room temperature. No diffraction peaks on the recorded diffractograms of our synthesized glass samples are observed, but they all show diffuse and broad peaks characteristic of the vitreous state confirming the amorphous structure of our samples.

![Figure 1. X-ray diffractograms of xTiO_2-(100-x)NaPO_3 glasses (0 ≤ x ≤ 10 mol% TiO_2).](image)

**Infra-red spectra**

The infrared spectra of the glass system \((50-x/2)Na_2O-xTiO_2-(50-x/2)P_2O_5\) \((0 ≤ x ≤ 10 \%\) mol TiO_2) in the frequency region 400-1400 cm\(^{-1}\) are represented on Fig.2. The various spectra are composed of fairly wide lines which are typical of amorphous systems.

![Figure 2. FTIR Spectrum of glasses with composition (50-x/2)Na_2O-xTiO_2-(50-x/2)P_2O_5 (0 ≤ x ≤ 10 mol% TiO_2)](image)
The representative curve of sodium metaphosphate 50Na₂O–50P₂O₅ (NaPO₃) (x = 0) is in agreement with data reported in the literature on this type of composition. The antisymmetric and symmetric valance vibrations of the PO₂ groups at 1276 and 1160 cm⁻¹, respectively, are characteristic of highly condensed phosphates. The absorptions at 1090 and 1000 cm⁻¹ correspond respectively to the antisymmetric and symmetric valance vibrations of the PO₃ groups (terminal groups). The bands located around 870 cm⁻¹ and around 750 cm⁻¹ (doublet) are attributed respectively to the antisymmetric and symmetric absorptions of the P-O-P bonds. All the deformation vibrations of the PO₄ tetrahedra are grouped in the zone 530-470 cm⁻¹.

The spectra corresponding to the glasses containing the titanium (x = 3, 5, 7 and 10) have absorption bands typical of the metaphosphate glass NaPO₃. It is noted that the band attributed to the antisymmetric valence vibration of PO₂ (νₐ(P-O₂)) moves from 1276 cm⁻¹ for the NaPO₃ glass to 1214 cm⁻¹ for the composition 45Na₂O–10TiO₂–45P₂O₅. This result was expected since the phosphate chains interact more strongly with titanium than with sodium and consequently, the phosphorus-oxygen bonds linked to titanium ions P=O(−Ti) are longer than those linked to sodium ions P=O(−Na). In addition to the displacement of the νₐ (PO₂) bands, it can be observed that the absorption band intensities corresponding to νₐ (O–P–O) and νₛ (P–O–P) decrease with increasing TiO₂ content. These changes in the spectra of the glasses when the TiO₂ content increases are due to a decrease in the length of the phosphate chains. Depolymerization of NaPO₃ by titanium oxide TiO₂ leads to the formation of short phosphate chains, characterized by the appearance of the νₐ (PO₂) band at 1214 cm⁻¹. This band appears at 1000-1240 cm⁻¹ in tetrapolyporphosphates (P₂O₇)²² and at 1215 cm⁻¹ in sodium triply phosphates (Na₃P₃O₁₀)²⁴.

For all compositions (exempt and containing titanium), the glasses show two bands around 770-720 cm⁻¹ which are attributed to the presence of two P–O–P bridges in the metaphosphate-based chains (P₂O₇)² (Fig. 3)²⁸.

Figure 3. Metaphosphate (P₂O₇)² containing two P-O-P units

**Density and molar volume**

To better understand the effect of TiO₂ content on the properties of the studied glasses, density (ρ) and molar volume (V_m) have been studied. Table 1 shows the changes in both density and molar volume during the addition of TiO₂ to the system (50-x/2)Na₂O–xTiO₂–(50-x/2)P₂O₅. The density increases with the increase in TiO₂ content from 2.51 to 2.63 whereas the molar volume changes in the opposite manner from 40.7 to 38.0. The increase in density may reflect the crosslinking effect of titanium.

As the molar volume is a good structural indicator on the degree of compactness of the vitreous network and the deformation of the oxygen ions, its decrease as a function of the increase in TiO₂ confirms that the titanium ions crosslink the vitreous network. The same phenomenon was observed during the study of the glasses of a similar system (100-x)NaPO₃–xZnO with (100-x)NaPO₃–xCuO.

| Table 1. Density and Molar volume of (50-x/2)Na₂O–xTiO₂–(50-x/2)P₂O₅ glasses (0 ≤ x ≤ 10 mol% TiO₂) |
|-----------------|-----|-----|-----|-----|-----|
| Mol% TiO₂       | 0   | 3   | 5   | 7   | 10 |
| Density (±0.03 g/cm³) | 2.51 | 2.56 | 2.58 | 2.60 | 2.63 |
| Molar volume (cm³/mol) | 40.7 | 39.6 | 39.1 | 38.7 | 38.0 |

**Glass transition temperature**

The glass transition temperature (T_g), which might be a critical thermal property, increased when TiO₂ replaced both Na₂O and P₂O₅ as shown in Fig. 4. The increase in the glass transition temperature implies an increase in the rigidity of the network. Indeed, the titanium connects the short chains thus formed using strong P-O-Ti bonds, which replace the weaker P-O-P bonds. This result is in agreement with the evolution of IR spectra.
Photocatalytic performance

It is well known that titanium, with gap energy of 3.2 eV, presents interesting photocatalytic properties. It has been reported that it can efficiently degrade organic dye molecules under UV illumination. However, in our case, titanium is inserted in an amorphous structure, to identify its photocatalytic properties, a model photocatalytic reaction was carried out by choosing rhodamine B (Rh-B) as a substrate and phosphate glass with different percentages of titanium as a catalyst. The illumination of the catalyst leads to the formation of a positive hole ($h^+$) in the valence band and an electron ($e^-$) in the conduction band (CB). This electron before recombination with the hole reacts with the surface-bound water molecule to produce -OH radicals. These radicals then react with the surface-bound organic molecules to degrade them.

Figure 5. Absorption spectrum of photodegradated RhB under UV excitation: (a) without catalyst, (b) with titanium-free glass, (c) with glass containing 5% of titanium, and (d) with glass containing 10% of titanium.
Figures 5b, 5c and 5d show the evolution of the absorption spectrum of RhB as well as the changes (decrease) of the adsorption wavelength at 554 nm for the three phosphate glasses after the UV irradiation. As the figure illustrates, the intensity of the maximum absorption band of RhB decreases with time in the presence of different catalysts; this decrease varies depending on the titanium percentage. After 4 h of reaction time, we have almost a complete disappearance of the absorption band at 554 nm characteristic of the RhB molecule and consequently its quasi-total transformation, which reaches 94%

Figure 6 presents the degradation efficiencies of the three samples (glass with 0, 5 and 10% TiO₂) after 4 hours of irradiation, which are 64%, 75%, and 94%, respectively.

Whereas, in the absence of a photocatalyst (Fig. 7), only a 15% degradation of the RhB is obtained by the phenomenon of photolysis after 4 hours of irradiation under UV light, which signifies that there is not an important degradation of the dye (by photolysis) during the analysis period.

The figure illustrates that the degradation follows a pseudo first order kinetics rate law (Langmuir–Hinshelwood model)

\[ \ln \left( \frac{C_0}{C} \right) = k \cdot t \]

Where \( k \) is the observed first-order rate constant and \([C_0]\) and \([C]\) are the concentration of RhB at any time \( t \) and at a time after the adsorption process in dark nature, respectively.

The different values of the reaction constant are given in the following Table 2. As the percentage of titanium increases in the compositions of the glasses, the constant rate increases, which means that titanium enhances the photodegradation process even in its amorphous structure.

### Table 2. The K values of different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>10 % Ti</th>
<th>5% Ti</th>
<th>0% Ti</th>
<th>Without photocatalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (min⁻¹)</td>
<td>0.012</td>
<td>0.008</td>
<td>0.006</td>
<td>0.001</td>
</tr>
</tbody>
</table>

A possible correlation between the photocatalytic activity and sample properties such as glass transition temperature (\( T_g \)), density (\( \rho \)) and molar volume (\( V_m \)) may exist; as \( T_g \) and \( \rho \) increases (\( V_m \) decreases), the photocatalytic performance gets higher.

On another side, Ohtani et al.\(^{34}\) have reported that photocatalytic activity of amorphous TiO₂ is negligible, whereas the photocatalytic activity of anatase, which is having the same particle size as amorphous TiO₂, is appreciable.

The value obtained for degradation efficiencies of glass free titanium (64%) probably due to the adsorption of Rh-B on it. Addition of TiO₂ increases the degradation efficiency of 47.5Na₂O-5TiO₂-47.5P₂O₅ and 45Na₂O-10Na₂O-45P₂O₅ glasses, indicating that there is a synergistic mechanism for Rh-B degradation by adsorption in NaPO₃ and the photocatalytic activity of TiO₂.
Conclusion

In this work, we have synthesized a series of glass compositions in which we have varied the percentage of titanium (50-x/2)Na2O–xTiO2–(50-x/2)P2O5 (0 ≤ x ≤ 10 mol%). The diffractograms of X-ray diffraction have confirmed the amorphous state of the study of the structure by IR spectroscopy showed that the metaphosphate chains are depolymerized when titanium is added. Once the TiO2 content is sufficient, the structure is cross-linked, and the titanium connects the more formed chains via stronger P-O-Ti bonds than those of P-O-P. This description is in complete agreement with the evolution of Tg, the density, and the molar volume.

The results of our study emphasize that the synthesized materials have good photocatalytic activity in the decolorization of an aqueous solution of RhB dye under UV light irradiation. The decolorization extent of dyes was obviously affected by a synergistic mechanism for Rh-B degradation by adsorption in NaPO3 and the photocatalytic activity of TiO2. Indeed, their presence leads to a quasi-total disappearance of the organic species studied after a time of irradiation of 4 hours.

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