Glasses in the SbPO_4–WO_3 system

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Abstract

Glasses in the binary system (100–x)SbPO_4–xWO_3 (20 < x < 60, x in mol%) have been prepared and characterized. Differential thermal analysis (DTA) shows that the glass transition temperature, T_g, increases from 412 °C for samples containing 20 mol% of WO_3 to 481 °C observed for glass containing 60 mol%. Sample containing 40 mol% in WO_3 were observed to be the most stable against devitrification. The structural organization of the glasses has been studied by using Fourier transform infra-red (FTIR), Raman, ^31P Magic angle spinning (MAS) and spin echo nuclear magnetic resonance (NMR) spectroscopies. Results suggest two distinct networks comprising the glass structure, one with high SbPO_4 content and the other characteristic of the highest WO_3 content samples. The glasses present photochromic properties. Colour changes are observed for samples after exposure to ultraviolet or visible laser light. XANES, at L_1 absorption edge of tungsten, suggests partial reduction from W_6+ to W_5+ species during the laser irradiation. The photochromic effects and the colour changes, promoted by laser excitation, are reversible and easily removed by heat for during 1 h at 150 °C. Subsequent ‘write/erase’ cycles can be done without degradation of the glasses.

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1. Introduction

Antimony compounds have been used in a large variety of optical materials including thin films [1,2] and glasses [3,4]. Glasses containing Sb present high refractive index and non-linear properties. These characteristics can be used to prepare optical limiters [5] and non-linear optical devices [6]. Depending on the composition, they can be used as photosensitive materials [7,8] as well. Due to the glass former characteristics, as predicted earlier by Zachariasen [9], the oxide is the most common antimony compound employed for glass preparation. Recently, some interesting properties of Sb_2O_3–SbPO_4 glasses were demonstrated [7]. It was shown that those glasses present good thermal properties and that large bulk samples could be obtained. The high stability of the glasses was attributed to the presence of antimony orthophosphate. In the present study, we report the substitution of antimony oxide by tungsten oxide. The new glasses were characterized using differential thermal analysis (DTA), Fourier transform infra-red (FTIR) and Raman spectroscopies, ^31P magic angle spinning (MAS) and spin echo NMR, UV–Vis, absorption spectroscopy, and X-ray absorption near edge structure (XANES) recorded at the W–L_3 edge and M-Lines. Colour changes were observed under laser irradiation. These changes are reversible by heat treatment and the preliminary photochromic results are discussed.

2. Experimental

2.1. Glass synthesis

WO_3 (99.9% pure grade, Aldrich) and SbPO_4, prepared as described before earlier [3], were mixed and melted in a
Pt crucible at 1400 °C for 30 min. Annealing was performed for 2 h at temperatures 10 °C below the glass transition temperature.

2.2. Glass characterization

Differential thermal analysis (DTA) was performed using TA 2910 equipment. Powdered samples were heated at 10 °C/min in platinum pans under N2 atmosphere in the range of 100–1200 °C. Characteristic temperatures of the glasses (Tg for transition temperature, Tx for onset of crystallization and Tp for maximum of crystallization peak) have been determined. The estimated errors are 2°C for Tg and Tx temperatures and 1 °C for Tp. Infrac-red absorption spectra were obtained using a Perkin Elmer FT-IR Spectrum 2000 from powdered glasses dispersed in KBr pallets, in the range between 400 to 4000 cm⁻¹. Raman scattering spectra, in the 200–1300 cm⁻¹ range were obtained from the powdered glasses using a Micro-Raman Renishaw equipped with a microscope under He/Ne laser excitation (632.5 nm) with 30 mW CW power and a spot size around 5 μm. 31P MAS-NMR spectra were recorded for powdered samples in zirconia tubes with an INOVA Varian-300 spectrometer working at 121.442 MHz (31P), with spinning frequency of 6000 Hz, at pulse length of π/2 and a repetition time between each acquisitions of 100 s. Reference at 0 ppm was taken with H3PO4 at 85%, 31P dipolar spin echo decays were measured on non-spinning samples placed in a 5 mm solenoidal probe, using the 90–90–180° Hahn spin echo sequence. The 180° pulse length was 7.9 μs. Absorption spectra of glasses from 200 to 2000 nm were obtained with a Varian, Cary 500 scan spectrophotometer. Refractive indexes were obtained at two wavelengths (543.5 and 632.8 nm in TE mode) by the prism coupling technique with a Metricon-2010 instrument.

Photochromic properties were studied using a glass sample, with dimension 40 × 20 × 3 mm. The non-exposed sample is labelled (wsbp5NI) and the sample irradiated under a 458 nm line of an Ar laser is labelled (wsbp5IR). Laser power outputs of 200 mW and irradiation time of 2 h were used for achieve the photosensitive changes. To ‘erase’ the changes promoted by the laser irradiation, a heat treatment at 150 °C for 2 h was performed. X-ray absorption near edge structure (XANES) measurements were done in order to determine the electronic changes promoted by the laser. Measurements at the tungsten LIII (10207 eV) edge were performed on the XAS beam line at LNLS (Campinas-Brazil) working with an electron energy of 1.37 GeV and a maximum electron current of 250 mA. A double crystal Si (111) monochromator was used to obtain the monochromatic X-ray incident beam was first calibrated using a metallic tungsten foil. Data were collected at room temperature in total electron yield (TEY) mode in grazing incidence (∼10°) in order to collect electronic and structural information on the surface of the glasses. Energy calibration was checked by using a Tungsten foil (10207 eV) recorded between each sample. W–L3 spectra were collected over 80 eV with an energy step of 0.5 eV and counting time of 3 s. For each sample several scans were recorded to improve the signal-to-noise ratio. WO3 (W6+) and W2O5 (W5+) powdered samples deposited onto Millipore membranes were recorded in TEY as reference compounds. The absorption background was subtracted from the rough XANES spectra using a linear function. Then, the spectra were normalized far from the edge (10235 eV).

3. Results

Homogenous yellow glasses up to 20 mm thick were obtained. The typical amorphous halo was observed in X-ray diffraction for all compositions. In Table 1 are shown, together with glass compositions, the characteristic temperatures and the thermal stability parameter (Tx−Tg), commonly used to estimate the thermal stability of the glasses [10]. Increasing the WO3 content Tg increases. Tx and Tp increase from wsbp2 to wsbp5 composition and decrease for higher WO3 contents.

FTIR spectra of the glasses are presented in Fig. 1. Absorption bands of higher energy, assigned to asymmetric and symmetric stretching of PO4 species in the range of 1250–850 cm⁻¹, became larger and exhibit an intensity with increasing WO3 content. The band observed in the region from 850 to 650 cm⁻¹ present the same behavior as described above. The respective infra-red and Raman assignments for crystalline compounds and glasses are contained in Table 2.

In Fig. 2 are shown the Raman spectra of the glasses and reference compounds. Monoclinic WO3 is constituted of distorted WO6 octahedra where all the corners are shared building up a tridimensional crystalline network. This structural unit presents two bands at 810 cm⁻¹ and 720 cm⁻¹ assigned to asymmetric and symmetric stretch vibrations of W–O–W linkages respectively and two weak shoulders at 330 cm⁻¹. The Raman spectrum of crystalline WO3 presents a sharp peak at 1051 cm⁻¹ and a broad peak at 974 cm⁻¹.

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition (mol%)</th>
<th>Characteristic temperatures (°C)</th>
<th>Tg−Tx (°C)</th>
</tr>
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<tbody>
<tr>
<td>wsbp2</td>
<td>80/20</td>
<td>Tg (±2 °C)</td>
<td>Tp (±1 °C)</td>
</tr>
<tr>
<td>wsbp3</td>
<td>70/30</td>
<td>412</td>
<td>503</td>
</tr>
<tr>
<td>wsbp4</td>
<td>60/40</td>
<td>421</td>
<td>530</td>
</tr>
<tr>
<td>wsbp5</td>
<td>50/50</td>
<td>447</td>
<td>591</td>
</tr>
<tr>
<td>wsbp6</td>
<td>40/60</td>
<td>467</td>
<td>599</td>
</tr>
</tbody>
</table>
(934 cm\(^{-1}\)) modes of the \(\text{PO}_4\) units. Middle range vibrations (622, 581 cm\(^{-1}\)) are assigned to asymmetric bending modes of the \(\text{PO}_4\) group while the band at 475 cm\(^{-1}\) is attributed to a symmetric bending mode. All of these modes are probably coupled with Sb–O–P stretching modes. At 544 cm\(^{-1}\), a symmetric bending vibration of the \(\text{SbO}_4\) group (E representing a lone pair) is observed while the lowest Raman shifts (353 and 213 cm\(^{-1}\)) vibrations are attributed to group modes.

Glass curves are characterized by a large absorption bands centred at 910 and 820 cm\(^{-1}\), that became larger by increasing \(\text{WO}_3\) content. The higher energy bands, at approximately 980 and 1080 cm\(^{-1}\), can be assigned to \(\nu_{as}\) of \(\text{PO}_4\) units. Also, phosphate lower energy bands are observed in the range from 650 to 450 cm\(^{-1}\). The band centred at 300 cm\(^{-1}\) envelops both \(\text{PO}_4\) and \(\text{WO}_6\) group vibrations.

Representative \(^{31}\text{P}\) MAS-NMR spectra are shown in Fig. 3. Nearly symmetric peaks are observed and the isotropic chemical shifts are consistent with fully polymerized phosphate groups (\(Q^4\) units), which are tetrahedrally surrounded by antimony. Weak spinning sidebands are observed indicating rather small chemical shift anisotropies. The chemical shift values observed for glasses are listed in Table 3. On this basis we can rule out both the presence of significant amounts of P–O–P linkages, as well as the presence of O=PO\(_{3/2}\) units, since both types of bonding would produce significant \(^{31}\text{P}\) chemical shift anisotropies. Fig. 4(a) shows the typical \(^{31}\text{P}\) spin echo decay curves for glasses. Over a wide range of dipolar evolution times, the decays are nearly Gaussian [4]. The average magnitude, \(M_2\), of the \(^{31}\text{P}–^{31}\text{P}\) magnetic dipole–dipole interactions could be obtained by analyzing these decay curves (Fig. 4(b)) and the results can be seen in Table 3. Supporting the MAS results, the dipolar data suggest a homogeneous distribution of the orthophosphate units through the glass structure.

Absorption spectra of the glasses, in the UV–Vis range, are shown in Fig. 6. The addition of \(\text{WO}_3\) shifts the band gap to lower energy values (420–520 nm from wsbp2 to wsbp6).

Refraction index values \(n\) were measured for three compositions (wsbp4, wsbp5 and wsbp6) and the results shows

<table>
<thead>
<tr>
<th>Table 2</th>
<th>FTIR and Raman assignments for reference compounds and glasses</th>
</tr>
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<tr>
<td>(\text{SbPO}_4)</td>
<td>(\text{WO}_3)</td>
</tr>
<tr>
<td>FTIR</td>
<td>Raman</td>
</tr>
<tr>
<td>1140 (\nu_{as}) (\text{PO}_4)</td>
<td>1051 (\nu_{as}) (\text{PO}_4)</td>
</tr>
<tr>
<td>1068 (\nu_{as}) (\text{PO}_4)</td>
<td>974 (\nu_{as}) (\text{PO}_4)</td>
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<td>1035 (\nu_{as}) (\text{PO}_4)</td>
<td>934 (\nu_{as}) (\text{PO}_4)</td>
</tr>
<tr>
<td>990 (\nu_{as}) (\text{PO}_4)</td>
<td>622 (\delta_{as}) (\text{PO}_4)</td>
</tr>
<tr>
<td>643 (\delta_{as}) (\text{SbPO}_4)</td>
<td>581 (\delta_{as}) (\text{PO}_4)</td>
</tr>
<tr>
<td>593 (\nu_{as}) (\text{Sb–O}^\text{–})</td>
<td>544 (\delta) (\text{SbO}_3)</td>
</tr>
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<td>473 (\delta_{as}) (\text{PO}_4)</td>
<td>475 (\delta_{as}) (\text{PO}_4)</td>
</tr>
<tr>
<td>440 (\delta_{as}) (\text{Sb–O}^\text{–})</td>
<td>353 group</td>
</tr>
</tbody>
</table>
that increasing WO$_3$ content increases $n$ from 1.94 to 2.04 at 543 nm while at 632 nm, $n$ increases from 1.92 to 2.01. These refractive index changes are better shown in Fig. 7.

The glass sample, irradiated under 458 nm line of the Ar laser, has its colour changed from yellow to blue. Both, yellow and blue parts of the sample were analyzed by XANES in order to determine electronic changes promoted by light. W–L$_2$ absorption spectra, obtained for both irradiated and non-irradiated parts of the glass, are shown in Fig. 8. The white line energy position is an indication of the oxidation state of the element (W). The results were compared with the reference compounds WO$_3$ and W$_2$O$_5$8 that are known to exhibit W$^{6+}$ and W$^{5+}$ species respectively [11]. Due to the energies proximity between W$^{6+}$ and W$^{5+}$ species, the comparison is better viewed taking the differential of the absorption curve (Fig. 9). Notice that the irradiated part presents the maximum of the white line at 10211.8 eV while for the non-irradiated it is centred at 10213.1 eV. These results match with the reference compounds suggesting that the irradiation process induce the reduction of the W$^{6+}$ in W$^{5+}$ species.

4. Discussion

By comparing with the previous study reported in [4], the new SbPO$_4$–WO$_3$ glasses were observed to be thermally more stable. Thermal analysis shows that the addition of WO$_3$ to SbPO$_4$ increases $T_g$ values while $T_x$–$T_g$ increases until the sample containing 40 mol% of tungsten oxide. For higher WO$_3$ content $T_x$–$T_g$ is observed to decrease. For samples containing low WO$_3$ content, the basic structure of the glasses can be idealized as a random orthophosphate network. For this situation, it is likely that WO$_6$ octahedra are inserted along all glass network. It implies that some oxygen atoms, at the corners of these octahedral, are not bonded and consequently W–O terminal bonds may be appended. In fact, these bonds are observed in both FTIR and Raman spectra, Figs. 1 and 2. The shoulder at 940 cm$^{-1}$ observed in the infra-red spectra and the intense peak at 910 cm$^{-1}$ present in Raman are attributed to W–O terminal bonds. This last assignment was taken based on the observation of this band in the Raman spectrum of Na$_2$WO$_4$ [11]. W–O terminal bonds are not observed for

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta_{uu}$ ($^{31}$P) (ppm)</th>
<th>$M_2d$ ($10^6$ s$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbPO$_4$</td>
<td>18.1</td>
<td>7.1</td>
</tr>
<tr>
<td>wsbp2</td>
<td>16.9</td>
<td>6.3</td>
</tr>
<tr>
<td>wsbp3</td>
<td>15.9</td>
<td>5.2</td>
</tr>
<tr>
<td>wsbp4</td>
<td>14.3</td>
<td>4.4</td>
</tr>
<tr>
<td>wsbp5</td>
<td>13.5</td>
<td>3.6</td>
</tr>
<tr>
<td>wsbp6</td>
<td>12.6</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Fig. 3. Representative $^{31}$P MAS-NMR spectra for glasses.

Fig. 4. (a) $^{31}$P spin echo decays of SbPO$_4$–WO$_3$ glasses. (b) Typical Gaussian fit of a spin echo decay data set resulting in a $M_2$ value characterizing the $^{31}$P–$^{31}$P dipole–dipole coupling.
crystalline WO₃ because all units WO₆ are linked together by the corners forming a three-dimensional structure [11,12]. On the other hand, the higher WO₃ content, the higher is the intensity of the peak at 830 cm⁻¹ in the Raman suggesting the formation of W–O–W bonds by linking WO₆ units and consequently forming a second network. For glasses containing more than 50 mol% of WO₃, the formation of W–O–W bonds decreases the stability of the glasses as observed by thermal analysis.

The formation of a second network, composed of WO₃, is supported by ³¹P MAS NMR. It is characterized by changes of the chemical shift towards less negative values from wsbp2 to wsbp6 which implies breaks in the phosphate network resulting in the presence of PO₄ units. Complementary NMR results, spin echo decay curves, suggest a homogeneous distribution of the phosphate units throughout the glass network with increasing WO₃ content. This result is supported by the linear behavior of the M₂ values plotted in Fig. 5.

Fig. 6 shows that the addition of WO₃ in the SbPO₄ based matrix results in a shift of the UV cut-off to higher wavelengths. This behavior can be explained by the fact that the introduction of WO₃ results in a more covalent vitreous network because W–O bonds have a more covalent character than Sb–O bonds. Consequently, the resulting occupied and unoccupied molecular orbitals of this network will exhibit a smaller energy gap when the network is predominantly composed of W–O bonds.

![Graph](image1)

**Fig. 5.** Linear correlation between M₂ and WO₃ content suggesting a homogeneous distribution of the orthophosphate units. The line is a guide for the eyes.

![Graph](image2)

**Fig. 7.** Refractive index measured at 543 nm and 633 nm in function of composition.

![Graph](image3)

**Fig. 6.** UV spectra obtained from bulk glasses in transmission mode.

![Graph](image4)

**Fig. 8.** XANES in the W–L₃ edge for the non-irradiated and irradiated wsbp5 glass.
The increase of refractive index with respect to WO$_3$ concentration can be explained by the fact that WO$_6$ units are more polarizable than SbO$_4$ units. In addition, the increase of WO$_3$ content results in W–O–W linkages as shown above. Therefore, WO$_3$ concentrated samples exhibit large clusters of WO$_6$ similar to that of crystalline WO$_3$. These clusters are much more polarizable than individual WO$_6$ units.

Photosensitivity is observed in these glasses under UV and visible laser exposure. This phenomenon can be understood by the fact that these materials totally or partially absorb these wavelengths and the absorbed energy initiates electronic or structural change in the glass network. XANES measurements gave us the first indication of the changes occurring during irradiation. It is known that colour changes in tungsten oxide thin films are attributed to the formation of bronzes of tungsten, like W$^{5+}$WO$_6$ (X = H, Li or Na) [13–16]. For the SbPO$_4$–WO$_3$ glasses the blue colour is supposed to be due to the formation of electron/hole pairs and/or the formation of antimony–tungsten bronzes. The detailed mechanism of this phenomenon is actually under study. However, for SbPO$_4$–WO$_3$ glasses, the effect is different from that observed in thin films. In this case, once, the photochromic effect can be completely erased by heat treatment at 150 °C for 2 h and a subsequent exposing leads to the blue colour state.

5. Conclusion

New stable glasses have been obtained in the system SbPO$_4$–WO$_3$. These glasses present good thermal stability and high refraction index. Structural results suggest the presence of two distinct glass networks. One consisting of random phosphate chains with WO$_6$ octahedra inserted along the structure. The second one is formed by linking together the WO$_6$ octahedra as the tungsten oxide concentration increases. Spin echo decay curves, suggests a homogeneous distribution of the phosphate units through the glass network with increasing of the WO$_3$ content. Glasses are photosensitive when exposed to visible lasers and the photochromic effect can be erased by heat treatment. XANES data suggests the presence of W$^{5+}$ species in the exposed glasses.

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