Structural study of thin films prepared from tungstate glass matrix by Raman and X-ray absorption spectroscopy

http://www.producao.usp.br/handle/BDPI/49322

Downloaded from: Biblioteca Digital da Produção Intelectual - BDPI, Universidade de São Paulo
Structural study of thin films prepared from tungstate glass matrix by Raman and X-ray absorption spectroscopy

Bianca Montanari a, Anne J. Barbosa a, Sidney J.L. Ribeiro a, Younes Messaddeq a, Gaël Poirier b,*, Máximo S. Li c

a Departamento de Química Geral e Inorgânica, Instituto de Química, UNESP, CP 355, CEP 14800-900 Araraquara, SP, Brazil
b Departamento de Ciências Exatas, UNIFAL-MG, CEP 37130-000 Alfenas, MG, Brazil
c Instituto de Física, USP, CP 369, CEP 13560-970 São Carlos, SP, Brazil

1. Introduction

Tungsten oxide thin films present several interesting optical properties. For example, electrochromic [1–5], photochromic [4–6] and thermochromic [7,8] properties are known as a color change by the action of an electric field, electromagnetic radiation and heat, respectively. These properties have been widely studied and were attributed to the action of tungsten atoms to adopt various oxidation states (W⁶⁺, W⁵⁺, and W⁴⁺). Electrochromic and photoelectric properties in tungsten-based films obtained by thermal evaporation have been investigated by Deb since 1966 [9,10]. Therefore, several applications appeared for such films including sensors of gases and of humidity, electronic information in displays, photoelectric sensors or smart windows [11].

On the other hand, tungstate fluorophosphate glasses are promising materials because of their particular chemical, physical and optical properties. Poirier et al. reported elsewhere their optical properties such as upconversion phenomena when doped with Tm³⁺ or two-photon non-linear absorption for the most WO₃ concentrated glasses [12,13]. Moreover, these glasses exhibit an unusual volumetric photochromic effect under visible laser exposure [14–16]. These properties are very promising for applications in integrated optics if these materials could be miniaturized and obtained in the form of thin films. Such films prepared from WO₃-based glass precursors were already obtained from electron beam evaporation and present good optical quality and resistance against atmospheric moisture [17].

However, the structure of WO₃-based glasses and films and specially the coordination state of tungsten atoms is not well understood. Indeed, a majority of authors agree that tungsten oxide units are present in the glass network as WO₄ tetrahedra and WO₆ octahedra whereas a few of them suggest that only sixfold coordinated tungsten atoms are present in the glass [18–25]. The goal of the present work is to investigate the structure of films obtained in the ternary system NaPO₃–BaF₂–WO₃ and the binary system NaPO₃–WO₃ by X-ray Absorption Near Edge Spectroscopy (XANES) at the tungsten L_I and L_III absorption edges. In addition, Raman spectroscopy allowed identifying a break in the linear phosphate chains as the amount of WO₃ increases and the formation of P–O–W bonds in the films network indicating the intermediary behavior of WO₆ octahedra in the film network. Based on XANES data, we suggested a new attribution of several Raman absorption bands which allowed identifying the presence of W–O–P and W=O terminal bonds and a progressive apparition of W–O–W bridging bonds for the most WO₃ concentrated samples (above 40% molar) attributed to the formation of WO₆ clusters.
2. Experimental details

2.1. Preparation of glass samples

Glass samples were prepared in the (NaPO₃)ₓ−BaF₂–WO₃ ternary and (NaPO₃)ₓ–WO₃ binary systems. In the ternary system, several samples with various WO₃ concentrations were prepared according to the following composition in mol%: (80–0.8x) NaPO₃–(20–0.2x) BaF₂–xWO₃, with x = 50 (sample NBW50) and x = 60 (sample NBW60). In the binary system, a sample containing 60% molar WO₃ (sample NW60) was prepared for comparison. Glass samples were synthesized using the conventional melting–quenching method [11,18]. The powdered starting materials were: tungsten oxide WO₃ from Aldrich (99.9% pure); sodium polyphosphate NaPO₃ from Acros (99.8% pure) and barium fluoride BaF₂ from Aldrich (99.8% pure). These glasses present high thermal stability against crystallization, large chemical and mechanical resistance and good optical quality. These glass samples (~3 g) have been used as a target to prepare thin films.

2.2. Preparation of thin films from the vitreous samples

Thin films containing WO₃ were prepared by physical vapour deposition (PVD) using an electron beam evaporation method. This technique allows to obtain high purity films. This evaporation technique is the most widely used to produce tungsten oxide films which exhibit good optical switching capacity. A tantalum crucible was utilized. The soda–lime glass substrates (1.5 cm × 2.5 cm) were previously cleaned with sulfochromic solution during 45 min and washed several times with deionized water. The vacuum in the evaporation chamber was maintained under 10⁻⁵ Torr. The voltage used was of 6.00 kV. Many studies were undertaken starting from preliminary tests and some parameters such as the electric current, the power of the electron beam and the evaporation rate were adjusted to obtain films with a high WO₃ concentration. This was achieved by applying a high electric current (~42 mA) providing a high-power (270 W) electron beam and consequently a high evaporation rate. The soda–lime glass substrates were maintained at 300 °C during the evaporation process to improve the film adherence. The improvement of all these experimental parameters finally allowed to obtain blue–colored stable films with a high WO₃ concentration.

2.3. Characterizations of as-prepared glasses

X-ray diffraction (XRD) measurements indicated that the samples are non-crystalline and differential scanning calorimetry (DSC TA Instruments) analyses identified a vitreous transition in every sample. These results confirm the vitreous state of the prepared samples.

2.4. Analyses of prepared films

The composition of the glass precursors and films was estimated using an energy-dispersive X-ray analysis (EDS) system coupled to the SEM system. The thickness and surface morphology of the deposited films were analyzed with a Taylor Hobson Precision profilometer. Film thicknesses ranged from 1.2 to 4.0 µm and the error estimation is around 20 nm.

Tungsten L₁ (12.100 eV) and L₃ (10.207 eV) X-ray absorption near edge structure (XANES) measurements 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 (1 1 1) monochromator used to obtain the monochromatic X-ray incident beam was first calibrated using a metallic tungsten foil at the W-L₃ absorption edge. The energy steps and counting times were adjusted to improve the resolution. Data were collected at room temperature in fluorescence mode. Experimental spectra were treated with the following procedure: the absorption background was subtracted using a linear extrapolation, E₀ was determined at the inflection point of the absorption edge and the spectra then normalized by taking an energy point around 50 eV above the edge.

Raman scattering spectra were recorded at room temperature in the wave number range from 1300 to 150 cm⁻¹ using a Renishaw RM 200 microprobe spectrometer with a single monochromator and a filter. The excitation was provided by a He–Ne laser at 632.8 nm and the monochromator was operating with a resolution of about 2 cm⁻¹.

3. Results and discussion

The chemical compositions (at.%) of glasses and resulting films were estimated by X-ray energy dispersion spectroscopy and are presented in Table 1 for compositions NBW50, NBW60 and NW60. The error estimation is around 10%. From a general observation of these results, it can be seen that the chemical compositions of the films and starting glasses are only slightly different as is usual after evaporation because the pressure vapor of each compound is different. First, the EDS analysis performed on glasses prepared in the ternary system NaPO₃–BaF₂–WO₃ identify barium elements but fluorine was not detected. It can be inferred that fluorine is lost during the melting step but not by sublimation of BaF₂ (the F₂ may be liberated as gas and the Ba remains). Whereas a consistent concentration of barium was found in film NW60, this element could not be detected in film NBW50 within the sensitive range of the EDS experiments. This behavior can be due to a reduced ability of barium to be efficiently evaporated depending on its concentration in the sample and the evaporation parameters. All of these different evaporation abilities may be responsible for the deviation observed between the glass and film compositions. In fact, film NW60 prepared from the binary system NaPO₃–WO₃ and used for comparison exhibits a chemical composition, which is close to the composition of glass NBW60. These results suggest that elements P, O and W are more efficiently evaporated on the substrate than Ba is. Despite these small differences in the glasses and film composition, the phosphorus, oxygen and tungsten concentrations are similar in both compounds.

The as-prepared films exhibited a deep blue coloration which is known to be due to reduced tungsten species W⁵⁺ and W⁴⁺ [26,27]. This reduction can be easily understood if we consider the evaporation method used in this work. In fact, W⁶⁺ species are evaporated from the glass using a high power electron beam which can easily reduce oxidized species. Since W⁶⁺ is partially replaced by W⁵⁺ in the final film, the electric charge can be maintained by formation of oxygen vacancies in the film structure (loss of O²⁻). Anyway, transparent colorless thin films are required for applications in integrated optics such as non-linear devices or waveguides in the visible. For that reason, we realized thermal treatments of

<table>
<thead>
<tr>
<th>Samples</th>
<th>Film (at.%)</th>
<th>Precursor (glass) (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O  W  P  Na  Ba</td>
<td>F  O  W  P  Na  Ba</td>
</tr>
<tr>
<td>NBW50</td>
<td>60  18  15  8.0  –</td>
<td>–  62  19  9.1  7.9  2.6  –</td>
</tr>
<tr>
<td>NBW60</td>
<td>57  22  12  6.9  2.4</td>
<td>–  58  22  9.4  8.0  2.9  –</td>
</tr>
<tr>
<td>NW60</td>
<td>60  25  10  5.7  x</td>
<td>x  55  25  12  7.0  x  x</td>
</tr>
</tbody>
</table>
the thin films in air atmosphere (oxidizing atmosphere) at 370 °C with the attempt to oxidize reduced tungsten species with O₂. The following redox reaction is expected:

4W⁵⁺ + O₂ → 4W⁶⁺ + 2O²⁻

In fact, the annealing at this temperature for 1 h resulted in bleached samples for all the compositions whereas a similar treatment in N₂ atmosphere did not change the film coloration. The Raman scattering spectra of references (NaPO₃, γ-WO₃, and Na₂WO₄) and film samples NBW50, NBW60 and NW60, are shown in Fig. 1.

Sodium polyphosphate NaPO₃ is built up of linear PO₄ chains, thus each tetrahedron possesses two bridging oxygen (P–O–P) and two terminal oxygen (P=O and P–O⁻) which are equivalent by resonance. NaPO₃ Raman spectrum, shown in Fig. 1, presents two intense bands centered around 700 and 1160 cm⁻¹ assigned to symmetric stretching vibrations of P–O–P linkages [28–31] and symmetric stretching vibrations of terminal P–O bonds in Q² tetrahedra, respectively [32] and three weak bands centered around 330, 1010 and 1270 cm⁻¹ assigned to the bending vibrations PO₄ tetrahedra, symmetric stretching vibrations of terminal P–O bonds in Q² tetrahedra and asymmetric stretching vibrations of terminal P–O bonds in Q¹ tetrahedra [33]. In sodium polyphosphate, Q¹ tetrahedra are located at the end of the linear chains of PO₄ entities.

Monoclinic tungsten oxide γ-WO₃, with P₂₁/n space group [34], is constituted of distorted WO₆ octahedra where all the corners are shared with another octahedron building up a three-dimensional crystalline network. Consequently, γ-WO₃ does not possess any terminal W–O bonds (W=O or W–O⁻) but only W–O–W bridging bonds. Its Raman spectrum, shown in Fig. 1, presents two bands at 810 and 720 cm⁻¹ assigned to symmetric and asymmetric stretching vibrations of W–O–W linkages, respectively, and two weak shoulders at 330 and 280 cm⁻¹ assigned to bending vibrations of WO₆ octahedra [20].

Sodium tungstate Na₂WO₄ is built up with isolated WO₄²⁻ tetrahdra where all the W–O bonds are terminal (two W=O and two W–O⁻ bonds equivalent by resonance). Its spectrum shows two bands centered at 930 and 810 cm⁻¹. Several works attributed these Raman bands to stretching vibrations of W–O terminal bonds in WO₄ [35–37] based on the fact that they are present in the Raman spectra of crystalline tetrahedral references M₆WO₄ (M = Li, Na, Ca, etc.) but not on the spectrum of γ-WO₃ (octahedral configuration). In other words, these works suggested that this Raman band can only be observed when tungsten atoms are in tetrahedral configuration. However, recent structural investigations were performed on Li₂W₂O₇ by Raman scattering [38] and apparently contradict these Raman bands assumptions. In fact, this compound is built up with LiO₄ tetrahedra and much distorted WO₆ octahedra sharing their edges to form anionic (WO₄)₂⁻ chains. LiO₄ tetrahedra connect these chains by sharing their corners with WO₆ octahedra. Thus, this compound possesses both bridging W–O–W bonds linking WO₆ octahedra in the plane and terminal W–O bonds between the WO₆ planes but all the tungsten atoms are sixfold coordinated. In fact, its Raman spectrum exhibits two bands at 810 and 720 cm⁻¹ due to W–O–W bridging bonds but also another one at 930 cm⁻¹ like for tetrahedral compounds. Consequently, the bands observed at 930 and 810 cm⁻¹ are obviously due to symmetric and asymmetric stretching vibrations of isolated WO₄⁻⁻ [20,39] but can be observed in Li₂W₂O₇ and are then attributed to symmetric and asymmetric stretching vibrations of W–O terminal bonds in WO₆/₂O₄ octahedra.
Shekiya et al. suggested that the position of these bands is independent of the tungsten coordination number and thus, does not allow identifying the tungsten environment [20].

Fig. 1 compares Raman spectra of as-prepared blue films and crystalline references. The films present broad bands in relation with the references. The broad bands located in the higher frequency range could be deconvoluted into three bands at 730, 790 and 950 cm\(^{-1}\) for NBW50 film and four bands at 700, 810, 960 and 1060 cm\(^{-1}\) for NBW60 and NW60 films (Fig. 2). Based on Raman spectrum of \(\gamma\)-WO\(_3\), the bands at 700 and 730 cm\(^{-1}\) corresponds to asymmetric stretching vibrations of W–O–W linkages and the bands at 790 and 810 cm\(^{-1}\) are assigned to symmetric stretching vibrations of W–O–W linkages. These bands indicate that WO\(_n\) polyhedra (\(n = 4\) or 6) are progressively linked together. The band observed at 950 cm\(^{-1}\) is attributed to stretching vibrations of W–O terminal bonds (W–O\(_-\) or W=O) in WO\(_n\) polyhedra.

Based on Raman bands observed at 330 and 280 cm\(^{-1}\) for crystalline WO\(_3\), the broad band observed at 240 cm\(^{-1}\) for the samples can be due to bending vibrations of WO\(_6\) octahedra and suggest a sixfold coordination of tungsten atoms [40]. However, Raman investigations were not able to clearly determine the coordination number of tungsten and further experiments were realized by X-ray absorption to identify the neighborhood of tungsten atoms.

Fig. 3a presents normalized XANES spectra registered at the tungsten L\(_{1}\) absorption edge (12,100 eV) for the as-prepared (blue) and bleached films NBW60. The crystalline compounds Na\(_2\)WO\(_4\) and \(\gamma\)-WO\(_3\) were used as reference for W coordination number. Sodium tungstate (Na\(_2\)WO\(_4\)) from Aldrich (99+%) is a cubic phase with space group \(Fd\overline{3}m\) [41]. In this compound, the tungsten atom is in a regular tetrahedral coordination WO\(_4\); tungsten oxide (WO\(_3\)) from Alpha (99.8%) is a monoclinic phase with space group \(P2_1/n\) [42]. In this compound, the tungsten atom is in a distorted octahedral coordination WO\(_6\). The intensity of the pre-edge feature labeled A observed for the references and samples depend of the site symmetry of the transition metal ion. In fact, this pre-edge absorption is due to a 2s(W) \(-\rightarrow 5d(W) + 2p(O)\) electronic transition which is dipole forbidden in the case of regular octahedra (inversion center) but allowed for distorted octahedra and tetrahedra [43–45]. The intensity of the pre-edge feature A appears to be the largest for sodium tungstate Na\(_2\)WO\(_4\) where W is tetrahedral but is very weak in the case of monoclinic \(\gamma\)-WO\(_3\) where W is in a distorted octahedral configuration. Fig. 3a shows that the XANES spectra of the as-prepared and bleached films NBW60 and of \(\gamma\)-WO\(_3\) are very similar. A more detailed view is proposed in Fig. 3b in the 10,190–10,220 eV energy range. The intensity of the pre-edge feature A is very similar for films NBW60 and \(\gamma\)-WO\(_3\) but very different from Na\(_2\)WO\(_4\) indicating that tungsten atoms form only distorted octahedra (WO\(_6\)) for all the compositions and that these films are free of WO\(_4\) tetrahedra. In addition, while the intensity of this pre-edge feature A is directly
related to the degree of WO$_6$ distortion, we assumed that the distortion of tungsten octahedra in the films is similar to that of γ-WO$_3$. The glass precursors were studied by Poirier et al. [46] and the results by XANES show that the intensity of the pre-edge is very similar for vitreous samples and γ-WO$_3$, then, the distortion of tungsten octahedra in the films is similar to that of glass precursors [46].

XANES spectra at the tungsten L$_{III}$ edge of the as-prepared and bleached films NBW60 and crystalline reference γ-WO$_3$ are shown in Fig. 4. These spectra differ by the amplitude of the “white line” resonance and by the position in energy of the absorption edge. The white line A is due to the electronic transition 2p$_{1/2}$(W) → 5d(W) + 2p(O) [43,44] and its position in energy is directly related to the local density of d states, thus to the number of unoccupied 5d states. Consequently, the characteristics of the white line depend of the local environment around the tungsten atom. Since the X-ray absorption edge is related with electronic transitions, the position of the absorption edge is strongly related with the oxidation number of the studied element. Lower oxidation numbers are usually observed at lower energies. It can be seen from Fig. 4 that the position in energy of the absorption edge for as-prepared film NBW60 is shifted to lower energies compared with bleached film NBW60 (blue) and γ-WO$_3$. This behavior is consistent with the hypothesis that a large proportion of tungsten atoms are present as reduced W$_6^+$ in the as-prepared film and that the thermal treatment allows oxidation of reduced tungsten atoms to W$_6^{6+}$. Since W$_6^{6+}$ exhibit a d$^8$ electronic configuration, the resulting material does not show any electronic transition in the visible and is transparent.

4. Conclusions

Structural investigations were performed on thin films obtained from electron beam evaporation using glass targets prepared in the ternary system NaPO$_3$–BaF$_2$–WO$_3$ and the binary system NaPO$_3$–WO$_3$. X-ray absorption near edge structure measurements at the tungsten L$_I$-edge allowed to conclude that tungsten atoms are only sixfold coordinated in the films as in the glass precursors and crystalline γ-WO$_3$. XANES investigations at the tungsten L$_{III}$-edge also pointed out that the blue coloration observed in the as-prepared films is due to tungsten reduced species W$_5^{2+}$ and that thermal treatment induces the oxidation of these species to W$_6^{6+}$. Finally, Raman spectra of these thin films indicated that the non-crystalline network is constituted of PO$_4$ tetrahedra and WO$_6$ octahedra linked by P–O–W bonds and the presence of WO$_6$ clusters identified from an intense Raman band attributed to W–O–W. These bleached films can be used in integrated optics for optical limiting or photochromic waveguides.

Acknowledgments

The authors acknowledge the financial support from FAPESP, CNPQ and CAPES.

References