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Characterization of the reversible photoinduced optical changes in Sb-based glasses

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Abstract

Changes occurring in absorption coefficients when glasses in the $SbPO_4$–WO_3 binary system were irradiated by light, at the edge of the absorption band, were measured in real time. These glasses present good thermal and optical properties and photoinduced changes in the absorption coefficients are reversible by heat treatment around 150 °C. Subsequent recording/erasing cycles could be made without sample degradation. The sensitivity of the induced optical changes was studied for different wavelengths, light powers and energy of light dose exposures, and for different compositions of the glasses. The changes in the absorption coefficients of the glass samples were accompanied by a color change from yellow to blue, and were also characterized by visible spectroscopy. The color changes occurred through the entire volume of the glass (~2 mm thickness) for the Ar-ion laser lines at the edge of the absorption band.

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Keywords: Photochromic glasses; Optical constants measurements; Antimony

1. Introduction

Photosensitive materials have attracted great interest due to their application for bi- [1,2] or tri-dimensional data storage [3]. Extensive attention also has been paid to photosensitive thin films based mainly in both amorphous and crystalline WO_3 and MoO_3 [4–7]. These materials can exhibit changes of color after exposure to UV laser light. One of the hypotheses for this behavior is that upon bandgap irradiation, electron–hole pairs may be generated [5]. In the case of tungsten oxide-based materials, the photon-generated free electrons and holes take part in the formation of substoichiometric WO_3 (containing both W^{+6} and W^{+5} oxidation states) leading to color changes. The bandgap of W-based films ranges from 480 to 365 nm [5] depending on the preparation conditions. As discussed above, electron–hole pairs need to be present for the observation of color changes, and their formation is typically achieved by, for example, exposing the films to a 308 nm XeCl excimer pulsed laser (with an energy density of about 3.9×10^6 W cm^{-2}) [4] or to a pulsed 355-nm Nd–YAG laser [6]. Due to the important absorption coefficients of the films at these wavelengths, the color change occurs only on the surface of the film affecting, just a few nanometers. Few papers in the previous literature can be found describing the photosensitivity of tungsten-containing *glasses*. Recently, this research group reported new photochromic materials based in antimony and tungsten based glasses [8,9].

In this paper, the photosensitive properties of the glasses in the $SbPO_4$–WO_3 binary system were studied. Changes in the absorption coefficients were measured in real time using different wavelengths from an Ar-ion laser, and the potential of these materials for 3D optical storage is discussed.

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2. Experimental procedures

The raw material $SbPO_4$, prepared and characterized as previously reported [10], and commercial WO_3 (Aldrich grad purity) were used to make the glasses. The photosensitive glasses were prepared in the 1-$x$$SbPO_4$–$x$$WO_3$ (with $x = 0.4$ and $x = 0.5$ in mol%) binary system by using the conventional casting process [11]. Special attention was paid in polishing the samples in order to minimize loses by scattering. The glasses were exposed to different wavelengths (458, 488 and 541 nm) from an Ar-ion laser. The photosensitive properties were also studied by changing the power of the laser and the time of irradiation. The power of the laser ranged from 35 to 90 mW. The same laser light used to expose the sample was used to measure the transmission of the glass in real time. The measurement was performed using a simple experimental setup as has been previously reported [12]. The laser was expanded and collimated in order to obtain a homogeneous light irradiance in a delimited area (around 5 mm^2) on the incident surface of the glass sample. Behind the sample marked area, a photodetector (also with area around 5 mm^2), connected to a lock-in amplifier measured the transmitted light. The absolute incident irradiances on the first surface of the glass samples were measured using a Newport Radiometer, model 1830C. The signal of the photodetector divided by the signal of the same detector without a sample gave a measurement of transmittance. From these measurements it is possible to obtain the absorption coefficient of the glasses as a function of the time of exposure. Thicknesses of the samples were measured using a micrometer.

The absorbance of the glasses were measured before and after a homogeneous exposure of a fixed energy dose of laser light by using Varian equipment Carry 500 scan UV–Vis–NIR, in the wavelength range of 2000–400 nm.

3. Results

Two glass compositions were chosen: 60$SbPO_4$–40WO_3 and 50$SbPO_4$–50WO_3, hereafter wsbp4 and wsbp5, respectively. The thicknesses of the samples were 2.28 mm (wsbp4) and 2.20 mm (wsbp5). In Fig. 1, the spectral transmittance curves for both glasses (carried out in the Varian spectrophotometer) are shown. The increase of WO_3 content shifts the bandgap energy to lower values, and this behavior can be attributed to the formation of a more covalent glass network and is explained by the nephelauxetic effect [13]. Also in Fig. 1, the wavelengths of the laser used in the present study are shown, which are on the edge of the absorption band. The glasses were yellow colored. After being exposed to the laser, the irradiated region became blue throughout the whole volume of the glass. More intense color changes could be achieved by increasing density powers (higher than 90 mW). Moreover, the higher the incident laser energy, the more intense and more superficial the photochromic effect is.

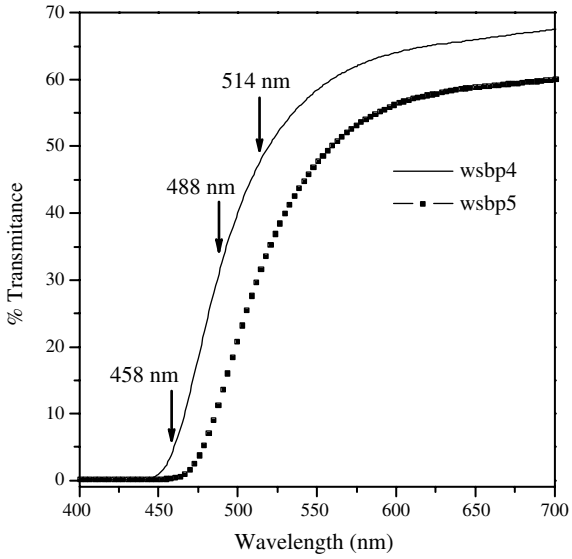

Fig. 1. Visible transmission spectra for the two studied glass compositions (wsbp4 and wsbp5).

The absorption-coefficient variation ($\Delta\alpha$) can be obtained from the voltages measured by the lock-in amplifier by using the equation

$$\Delta\alpha = -\frac{1}{d}\ln\left(\frac{V_t}{V_0}\right) \quad (1)$$

with d being the thickness of the glass sample (in mm), V_t the voltage measured by the photodetector behind the sample after an exposure time t, and V_0 the initial voltage measured by the same photodetector at the same place at $t = 0$.

Fig. 2(a) and (b) show the real-time evolution of the absorption-coefficient variation ($\Delta\alpha$) for the two glass samples: wsbp4 and wsbp5, respectively. Each Fig. shows the evolution of the absorption-coefficient variation for the same absolute light incident irradiance on the sample in W/m^2, but for three different wavelengths (514, 488 and 458 nm). Note that in Fig. 2(a), the $\Delta\alpha$ reaches a maximum value of 0.005 mm^{-1} (for 514 nm), of 0.02 mm^{-1} (for 488 nm) and 0.065 mm^{-1} (for 458 nm). This means a 13-fold increase in the $\Delta\alpha$ value for the same dose of energy when the wavelength of exposure was changed from 514 to 458 nm. About the same factor of increase in $\Delta\alpha$ with the same wavelengths is observed in Fig. 2(b) for the sample wsbp5. For this sample, with higher content of WO_3, higher absolute variations of absorption coefficient were observed. The maximum value of $\Delta\alpha$, for the same irradiance, wavelength and exposure time, reaches about twice the corresponding values for the sample wsb4. For the wavelength of 458 nm, $\Delta\alpha$ reaches 0.13 mm^{-1}. This fact suggests that the observed effect is proportional to the concentration of tungsten. In the same way, more important changes are observed for higher irradiance energies; i.e., for energies for which the absorption of the material is higher.

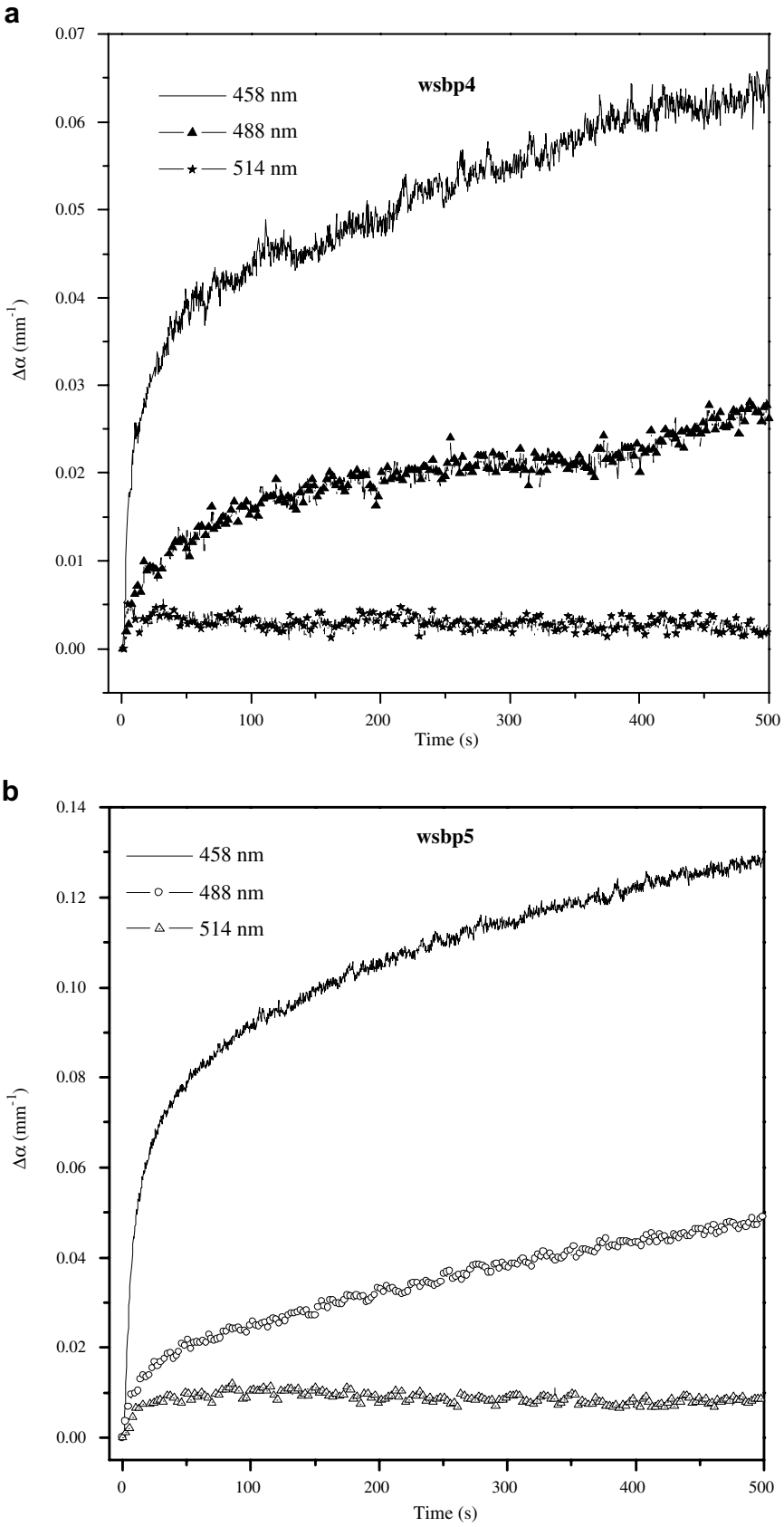

Fig. 2. Time evolution of the variation of absorption coefficient ($\Delta\alpha$), for the same absolute irradiance incident (W/cm^2) on the surface of the glass samples, for three wavelengths from an Ar laser (514, 488 and 458 nm). (a) Sample wsbp4 and (b) sample wsbp5.

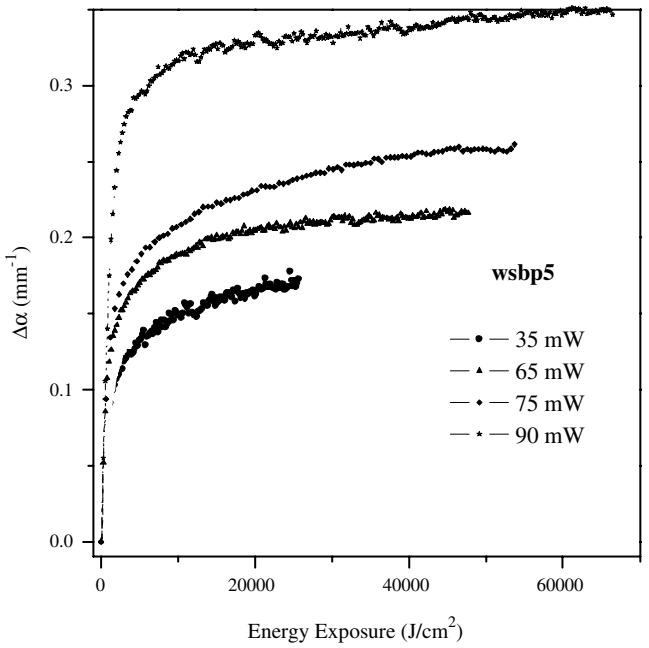

Fig. 3. Variation of the absorption coefficient ($\Delta\alpha$) as a function of the dose of energy exposure (J/cm^2) for different incident irradiances (W/cm^2) on the surface of sample wsbp5 at 458 nm.

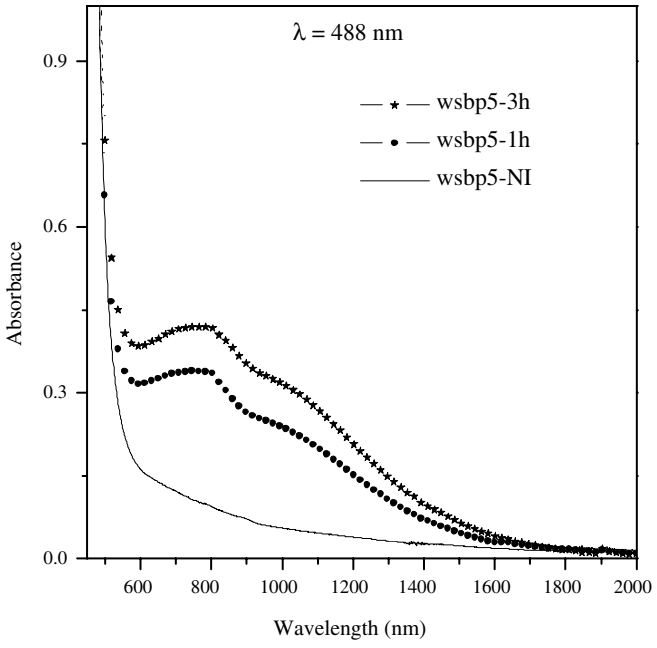

Fig. 4. Absorbance in the UV–Vis–Near IR spectra for non-irradiated and irradiated wsbp5 sample at 488 nm.

Fig. 3 shows the $\Delta\alpha$ curves as a function of the energy dose (light irradiance versus exposure time) for the sample wsbp5 using the same laser wavelength (458 nm) but different absolute irradiances (W/m^2). The irradiances on the glass samples were changed by a factor of about three, and $\Delta\alpha$ was observed to increase for higher laser powers. Therefore, the effect not only depends of the energy of incident light dose, but also on the irradiance in the sample.

Fig. 4 shows the absorbance spectra of the sample wsbp5 without irradiation (NI), and irradiated with the same irradiance but different times (resulting in different energy doses) at the 488 nm laser line. For this experiment, the laser power was locked at 200 mW cm^{-2} and was monitored before and after exposure to certify that no changes occurred during the irradiation process. As can be seen, a large absorption band appears after exposure between 1600 and 500 nm. Two broad peaks are identified around $\lambda = 1000$ nm and 800 nm. The same absorption band was observed for the other irradiance wavelengths used in this study. It was observed to be more pronounced for the lower wavelength (458 nm). This result demonstrates that the increase in the absorption coefficient is caused by the appearance of an absorption band and not by a red shift in the absorption band edge. This fact suggests that the material presents a photochromic effect.

One of the most interesting effects observed for these glasses is the fact that this photochromic effect can be erased by heat treatment at room atmosphere at around 150 °C for 1 h. Blue samples submitted to thermal treatment turned back to their original yellow color with the same absorption coefficient. Heat treatments below 100 °C were observed to not change the color of the sample. This 'write/erase' cycle was performed more than ten times, with the same performance.

4. Discussion

Electrochromic and photochromic materials containing tungsten compounds have been studied in amorphous and crystalline thin films [14,15]. The photochromic changes in such films were promoted by the incidence of pulsed or CW lasers in the UV region of the spectra. Although, electrochromic properties have been reported in a couple of glass systems [16], no evidence can be found about the photochromic effects in such materials. Therefore, as far as is known, this is the first time that the presence of the photochromic effect in a bulk glass material has been reported. The photochromic effect, observed through the entire glass volume, opens up the possibility of using such materials for 3D data storage.

In the previous literature, color changes in WO_3 films, induced either by light or electrical field, are caused by the formation of species such as $[W^{VI}_{1-x}W^{V}_{x}O_3]$ and/or $HW^{+V}O_3$ (called hydrogen–tungsten bronzes). But in both cases, a second ion is required to make up part of the redox system. Usually the reduction of W^{+VI} to W^{+V} or W^{+IV} is accompanied by the oxidation of hydrogen atoms coming from water, present inside and on the surface of the films. The water can be previously photoelectrolysed by laser irradiation or by implantation of Li-based compounds [17–19].

For the glass samples studied here, it is difficult to believe that hydrogen can play the role of the reducing agent for the formation of W^{+V} species. The first reason for this is the fact that the glasses are prepared at

1400 °C and then annealed around 450 °C. Glasses are kept at this temperature for at least 3 h before the furnace is turned off and after this step, it takes around 10 h to reach room temperature. Considering that the color change promoted by laser irradiation has been observed through the entire volume of the glass (4–5 mm) and that the color can be bleached by heat treatment at 150 °C and also that many write/erase cycles can be carried out, it is reasonable to believe that after some cycles, no more hydrogen would be present in the sample and then, no more color changes could be observed.

On the other hand, it is possible that the antimony atoms can play the role of reducing agent. It is known that antimony atoms can display two oxidation states, Sb^{+III} and Sb^{+V}. In pure antimony-based glasses, it has been shown that UV irradiation can induce the oxidation of the antimony atoms [8]. Considering that during the preparation of the glasses, defects can be formed due to the quenching process, oxygen vacancies can be expected to be present inside the glassy structure. Therefore, the same mechanism proposed elsewhere [15] could only be assumed, replacing hydrogen or lithium by antimony, as follows:

$$2W^{+VI}O_3 + Sb^{+III} \underset{\Delta}{\overset{h\nu}{\Longleftrightarrow}} 2(W_x^{+V}W_{1-x}^{+VI}O_3) + Sb^{+V}.$$

There is, however, no sufficient evidence to confirm the above assumptions. In order to elucidate the mechanism responsible for the color changes in these glasses more experiments must be conducted.

5. Conclusion

New photosensitive binary glasses in the $SbPO_4$–WO_3 system were characterized under the irradiation of three wavelengths from an Ar^+ laser.

The increase of WO_3 content in the glass composition increases the photoinduced changes of the absorption coefficient. The effect is more sensitive to the wavelength of 458 nm, which is closer to the absorption band and is reversible by thermal treatment at 150 °C for 1 h. Many write/erase cycles can be carried out without loss of sensitivity of the photochromic effect of the glasses. The increase in the absorption coefficient induced by light is accompanied by the appearance of a broad absorption band in the near infrared spectra that changes the color of the glass samples from yellow to blue. This effect is similar to the photochromic effect presented by WO_3 films.

This photochromic effect was, for the first time, observed through the entire volume of a glass. This discovery may be useful for 3D data storage, and can make such materials potential candidates for the next generation of recording materials.

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