Oxide Glasses for Holographic Data Storage

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Abstract: Novel photochromic oxide glasses are presented in this section. These glasses are based on phosphate formers containing both tungsten and antimony atoms. Exposure to visible continuous or pulsed laser beam results in an intense photochromic effect witch is shown to occur in the volume of the glass and results in a broad absorption band in the visible and near infrared. This effect was not identified to be related with a structural change and is assumed to be entirely electronic. A change in the absorption coefficient is observed in function of tungsten content, exposure time and increases with beam power. These glasses have been investigated regarding the possibility of holographic data storage using visible lasers sources. Changes in both refractive index and the absorption coefficient were measured using a holographic setup. The modulation of the optical constants is reversible by heat treatment.

1. Introduction

Recently, glasses have shown to be promising supports for optical data storage and optical memories[1]. Nowadays, the storage technology comprises mainly the uses of chalcogenides glassy thin films for CD's and DVD's manufacture[2]. However, the development of cheaper, more efficient and less toxic materials is necessary to supply the enormous development of data processing in all human activities like advanced research as well as daily life that always requires the use of memories with higher data storage capacities. In this way, a new goal of research is the obtention of tridimensional optical memories witch can store data throught the entire volume of the material and then considerably enhance the storage capacity[3]. Tungsten oxide based materials are well-known for their electrochromic and photochromic properties and where intensively studied because of the resulting wide range of practical applications like smart windows, display devices or sensors[4-5]. Up to now, these particular chromic properties were only observed on amorphous and microcrystalline WO_3 thin films or on WO_3 nanocrystalline particules[6]. In the case of photochromic amorphous WO_3 thin films, a UV laser exposure of the transparent as-prepared film results in the apparition of an intense blue or brown coloration characterized by an intense absorption band in the visible and near infrared region. This photochromic phenomenon can be usually erased by thermal treatment under air atmosphere[7]. The color change was identified to be due to the reduction of W^{6+} atoms in W^{5+} and/or W^{4+} and subsequent formation of the so-called tungsten bronzes H_xWO_3[8]. It is important to note that amorphous WO_3 films can show a photochromic behavior under visible light by insertion of specific elements from a non-aqueous electolyte or when in contact with a thin layer of specific material like CdS[9]. On the other hand, the photochromic effect is well-known and of technological importance in several glasses. In this case, the phenomenon is due to a precipitation of nanocrystals inside the glass bulk under UV illumination. These nanoparticles are generally noble metals (Au, Ag) or halide compounds (NaF, CuCl, AgBr) and are responsible of the absorption in the visible[10]. In this way, the color of the final glass is determined by the composition and size of the nanocrystals. One fondamental limitation of this photochromic phenomenon in glass is that it is non reversible and can't be erased. Another way to obtain a photochromic glass is to incorporate the photochromic oxide on the surface of a porous glass[11]. In all cases, it can be seen that the photochromic effect using glasses matrix arises from the crystalline particle and not directly from the vitreous network.

New phosphate-based glasses containing both tungsten and antimony were developped and exhibit efficient 3D photochromic properties under visible exposure. Both absorption coefficient and refractive index varie with light irradiation and make possible the use of these materials for holographic 3D storage.

2. Experiments

Photochromic glasses are based on phosphate glass formers containing both tungsten and antimony cations in the vitreous network. These glasses can be for example prepared in the systems $NaPO_3$-WO_3-Sb_2O_3 or $SbPO_4$-WO_3. A high WO_3 concentration (>30%molar) is requiered to obtain the photochromic effect. Results are shown for a glass composition $50SbPO_4$-$50WO_3$ named sbpw5. Samples sbpw5 were prepared using the conventional melting/quenching method and subsequent annealing below Tg. Special attention was paid in polishing the samples in order to minimize optical losses by scattering. Glasses are yellow coloured. The glasses were exposed to different wavelengths (458, 488 and 541 nm) of an Ar-ion laser. The photosensitive properties were also studied by changing the time of exposure. The same laser light used to expose the sample is used to measure the transmission of the glass in real time. The measurement was performed using a simple experimental setup as shown elsewhere[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 measures the transmitted light. The absolute incident irradiances at 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 sample gives us 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, if the thickness of the sample is known. The thicknesses of the samples were measured using a micrometer. The absorbance of the glasses were measured before and after an homogeneous exposure of fixed energy dose of laser light by using a Varian equipment Carry 500 scan UV-Vis-NIR in the wavelength range of 2000 to 400 nm. Real time photoinduced changes in the optical constants of the glasses were measured using a holographic setup (Fig. 1), and a phase sensitive technique[13]. When the fringe pattern is projected into the photosensitive material, the changes in the material optical constants, induced by light, generate a phase and an amplitude grating that self diffracts the interfering beams. By measuring the interference between the transmitted and the diffracted beams it is possible to identify the presence of both gratings and simultaneously to measure separately their diffraction efficiency[13]. The experiment was performed using an Ar laser and irradiances on the glass samples of about 50 mW/cm^2 in each of the interfering beams. The diffraction signals were measured through a single photodetector and two lock-in amplifiers, switched respectively into the first and second harmonic of a reference signal[13]. The measured voltage signals (V_ω and $V_{2\omega}$) are proportional to the square root of the diffraction efficiencies of the phase and amplitude grating respectively[13]. For small modulations, these signals are directly proportional to the refractive index modulation Δn and to the absorption coefficient modulation $\Delta\alpha$ respectively.

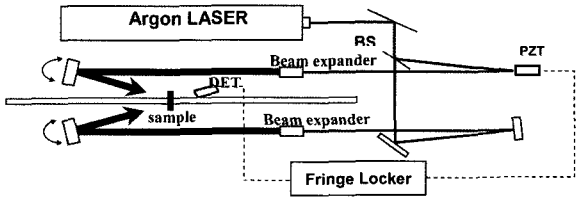
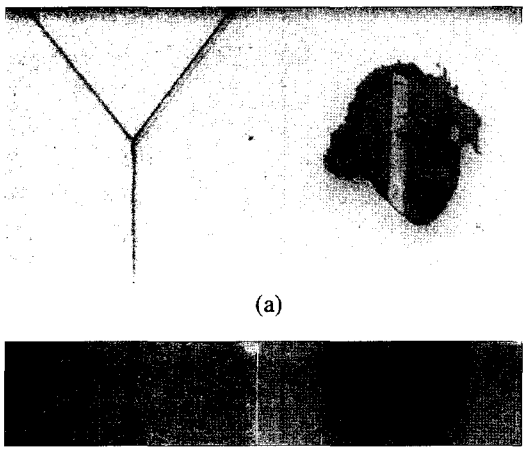


Fig. 1. Holographic setup used in this work.

3. Results and Discussion

Fig. 2 shows an irradiated sample using a 514nm pulsed laser as an illustration of the photochromic effect in antimony-tungsten based phosphate glasses.

One of the first interesting aspects observed for these glasses is the fact that this photochromic effect occurs in the entire volume of the glass (Fig. 2(b)) and can be erased by heat treatment at room atmosphere at around 150°C for 1h. After exposed to the laser, the irradiated region becomes blue throughout the whole volume of the glass. More intense colour changes can be achieved by increasing powers density (higher than



(a)

(b)

Fig. 2. Picture of a glass sample irradiated using a pulsed visible laser.

90mW). Moreover, higher the incident laser energy, more intense and more superficial the photochromic effect is.

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 is the voltage measured by the photodetector behind the sample after a time of exposure t and V_0 is the initial voltage measured by the same photodetector at the same place at $t = 0$.

Fig. 3 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 the $\Delta\alpha$ reaches a maximum value of $0.01mm^{-1}$ (for 514 nm), of $0.05mm^{-1}$ (for 488nm) and $0.13\ mm^{-1}$ (for 458 nm). It means an increase of about 13 times in the $\Delta\alpha$ value for the same dose of the energy when we change the wavelength of exposure from 514 to 458 nm.

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 it was monitored before and after exposition to certify that no changes occured during the irradiation process. As it can be seen, a large absorption band appears after the exposure between 1600 and 500 nm. Two broad peaks are observed around λ = 1000 nm and 800 nm. The same absorption band was observed for the others wavelengths used in this work and is 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 of the absorption edge. This result shows that the material presents an efficient photochromic effect.

Electrochromic and photochromic materials containing

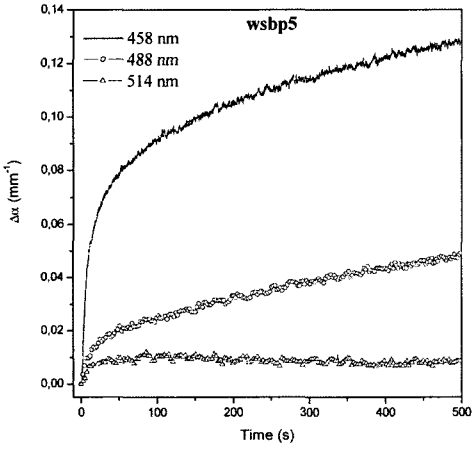


Fig. 3. Time evolution of the variation of absorption coefficient ($\Delta\alpha$), for the same absolute irradiance (W/cm^2) incident on the surface of the glass samples, for three wavelengths of an Ar laser (514 nm, 488 nm and 458 nm).

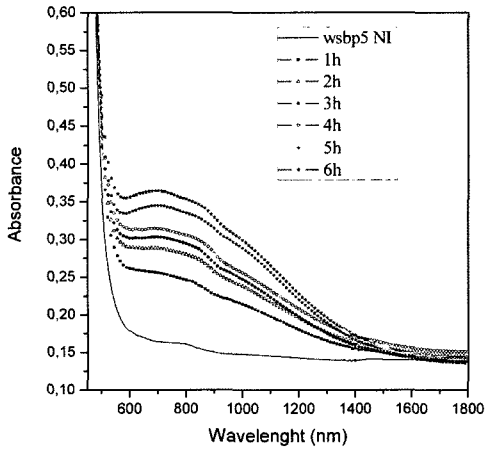


Fig 4. Absorbance in the UV-Vis-Near IR spectra for non-irradiated and irradiated wsbp5 sample at 488 nm.

tungsten compounds have been studied in amorphous and crystalline thin films[14]. The photochromic changes in such films are 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[15], no evidence can be found about the photochromic effects in such materials. In this sense, to our knowledge, it is the first time that the presence of the photochromic effect in a bulk WO_3-based glass material is reported under visible exposure. The photochromic effect, observed along the entire glass volume, brings the possibility of use of such materials for 3D data storage.

It seems an unanimity in the literature that the colour changes in films of WO_3, 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 it requires an ion to make part of the redox system. Usually the reduction of W^{+VI} to W^{+V} or W^{+IV} is done by the oxidation of hydrogen atoms coming from water, present inside and in the surface of the films. The water can be previously photoelectrolysed by laser irradiation or by implantation of Li-based compounds. In our case, it can be sugested that the antimony atoms can play the role of reducing agent. It is known that antimony can present two oxidation states, Sb^{+III} and Sb^{+V}. In pure antimony based glasses it was shown that UV irradiation can induce the oxidation of the antimony atoms[16]. Considering that during the preparation of the glasses, defects can be formed due to the quenching process, oxygen vacancies can be attended inside the glassy structure. In this sense, the same mechanism proposed elsewhere could be assumed only, replacing hydrogen or lithium by antimony, as follow:

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

The real time photoinduced changes in the optical constants of the same samples were investigated by using the holographic setup shown in Fig. 1. By analysing the measured signals (V_ω and $V_{2\omega}$), it was possible to identify the presence of a phase grating, while no absorption coefficient modulation was observed. This occurs probably because although, the holographic measurements might detect refractive index

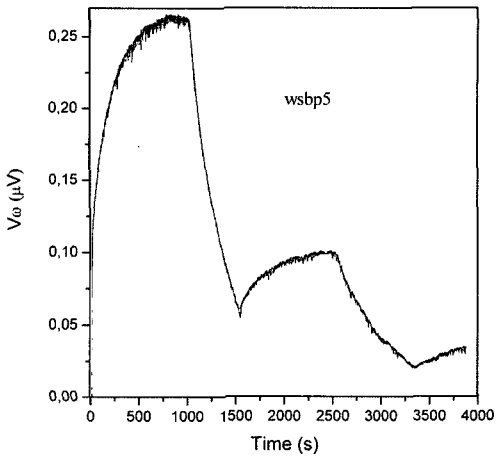


Fig. 5. Real-time photoinduced changes in Sb-W based phosphate glass.

modulations as low as 10^{-5}, it is less sensitive to detect absorption coefficient changes, due to the lower diffraction efficiency of amplitude gratings.

Fig. 5 shows the time evolution of the voltage signal (V_ω), measured during the sample exposure that is proportional to the refractive index modulation Δn of the glass sample. As it can be seen, the index modulation saturates after about 1000 seconds of exposure. If the light pattern is suppressed for some minutes and turn on again, any decay in the refractive the index modulation was observed.

At the time equal to 1015 and 2540 seconds the fringe pattern was shift by 180° inverting the positions between the dark and bright fringes, in order to erase the grating. Note that, during this time interval, the V_ω signal decreases because the dark regions of sample are now exposed, reducing the contrast of the refractive index modulation. At 1548 and 3360 seconds the pattern was inverted again by 180° in order to continue the recording at the first fringe position. Note that the successive write/erase cycles homogenize the refractive index destroying the phase grating.

4. Conclusion

New phosphate-based glasses containing antimony and tungsten cations were obtained and show an efficient photochromic effect under visible laser exposure. This colour change can be erased by thermal treatment at 150°C for few minutes. Such effect is due to a large

absorption band between 1600nm and 400nm after exposure. The kinetics of the mechanism was studied and identified an increase and saturation of the absorption coefficient as a function of time. Preliminary holographic measurements were realized and show that successive write/erase cycles can realized in the volume of the material. These first results suggest that this new phosphate glass can be used for holographic optical data storage.

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