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## Bulk photochromism in a tungstate-phosphate glass: A new optical memory material?

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In this work, we present a new photochromic tungstate based glass which have both absorption coefficient and refractive index modified under laser exposure. The photosensitive effect is superficial under ultraviolet (UV) irradiation but occurs in the entire volume of the glass under visible irradiation. The effect can be obtained in any specific point inside the volume using an infrared femtosecond laser. In addition, the photosensitive phenomenon can be erased by specific heat treatment. This glass can be useful to substitute actual data storage supports and is a promising material for 3-dimensional (3D) and holographic optical storage. © 2006 American Institute of Physics. [DOI: 10.1063/1.2364476]

Glasses have revolutionized human life for more than 7 000 years. Far from the limit of its applications, these amazing and versatile materials are present in our daily life from the most simple kitchen tool to the high-tech photonic crystal fibers employed to reach very high speeds in telecom. Recently, glasses have shown to be promising supports for optical data storage and optical memories.<sup>1</sup> Nowadays, the storage technology comprises mainly the uses of chalcogenides glassy thin films for CD's and DVD's manufacture.<sup>2-4</sup>

However, the development of cheaper, more efficient and less toxic materials make it necessary to provide the enormous development of data processing in all human activities, such as advanced research as well as daily life, with the use of memory with higher data storage capacities. In this way, a new goal of research is the obtainment of tridimensional optical memories which can store data throughout the entire volume of the material and thus considerably enhance the storage capacity.<sup>5-9</sup>

Tungsten oxide based materials are well-known for their electrochromic and photochromic properties and were intensively studied because of the resulting wide range of practical applications like smart windows, display devices, or sensors.<sup>10-13</sup> Up to now, these particular chromic properties were only observed on amorphous and microcrystalline WO<sub>3</sub> thin films or on WO<sub>3</sub> nanocrystalline particules.<sup>14-16</sup> In the case of photochromic amorphous WO<sub>3</sub> thin films, an ultraviolet (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.<sup>14</sup> This photochromic phenomenon can be usually erased by thermal treatment under

air atmosphere.<sup>17</sup> The color change was identified to be due to the reduction of W<sup>6+</sup> atoms in W<sup>5+</sup> and/or W<sup>4+</sup> and subsequent formation of the so-called tungsten bronzes H<sub>x</sub>WO<sub>3</sub>.<sup>18-20</sup> It is important to note that amorphous WO<sub>3</sub> films can show a photochromic behavior under visible light by insertion of specific elements from a non-aqueous electrolyte<sup>21</sup> or when in contact with a thin layer of specific material like CdS.<sup>22</sup>

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 for the absorption in the visible.<sup>23</sup> In this way, the color of the final glass is determined by the composition and size of the nanocrystals. One fundamental limitation of this photochromic phenomenon in glass is that it is nonreversible 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.<sup>24,25</sup> 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.

In this work, we have synthesized a new tungstate fluorophosphate glass which is photochromic in a wide range of wavelengths. The glass was synthesized in the NaPO<sub>3</sub>-BaF<sub>2</sub>-WO<sub>3</sub> ternary system and must contain a high amount of WO<sub>3</sub> to exhibit good mechanical and optical properties and to be photochromic. However, glasses with high concentrations of WO<sub>3</sub> are known to be dark blue or black colored because of reduced tungsten species (W<sup>5+</sup>) in the vitreous network. For that reason, it was necessary to use small quan-

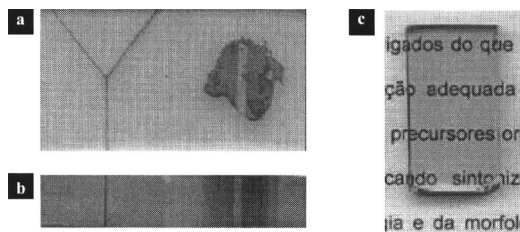


FIG. 1. Photochromic phenomenon in a tungstate fluorophosphate glass by 514 nm laser illumination. In (a), it can be seen that different features like a Y or the Einstein face can be written in the glass. In (b), the side of the written sample is presented and show that the photochromic effect occurs in the entire volume of the glass.

tities of the oxidizing couple  $\text{Sb}_2\text{O}_3/\text{NaNO}_3$  to obtain a glass with a good transparency in the visible. In addition, it was found that the presence of  $\text{Sb}_2\text{O}_3$  in the vitreous network is required to obtain the photochromic effect. The molar composition of the photochromic glass presented in this work is:  $40 \text{ NaPO}_3 - 8,5 \text{ BaF}_2 - 50 \text{ WO}_3 - 1 \text{ Sb}_2\text{O}_3 - 0,5 \text{ Na}_2\text{O}$ . The starting materials were mixed and heated at  $1050^\circ\text{C}$  for 1 hour in a platinum crucible for melting and homogenization. The melt was then cooled in a brass mold preheated below the glass transition temperature  $T_g$  ( $T_g$  of  $20^\circ\text{C}$ ). Annealing was implemented at this temperature for 4 hours in order to minimize mechanical stress resulting from thermal gradients upon cooling. The bulk sample was cut and polished before performing optical characterizations. Thermal analyses performed on this glass sample revealed that the glass transition temperature is around  $490^\circ\text{C}$  and the crystallization temperature is  $680^\circ\text{C}$ .

The photochromism of this glass was first observed when we exposed to a  $488 \text{ nm}$  continuous argon laser beam. We were surprised to observe a dark coloration of the yellow sample throughout the entire thickness of the sample exactly where the glass had been excited by the laser spot. Then, we used a focused  $514 \text{ nm}$  Cu vapour laser controlled by a graphic program to “write” pre-determined pictures or geometric forms like a “Y” or the “Einstein face”. These results are shown in Fig. 1(a) and the volumic photochromic phenomenon can be clearly seen from Fig. 1(b) according to the fact that the sample thickness is  $5 \text{ mm}$ . The glass was then exposed to UV light using a continuous argon laser operating at  $350 \text{ nm}$ . In this case, the effect is observed only at the surface of the sample. Finally, we investigated the possibility of inducing the photochromism of this sample by two-photon absorption. The glass was exposed to a femtosecond laser beam focused inside the bulk. This laser was operating at  $900 \text{ nm}$ ,  $120 \text{ fs}$  laser pulses at a  $1 \text{ KHz}$  repetition rate and with an intensity of  $2 \times 10^{15} \text{ W/cm}^2$ . After a few seconds, the effect could be observed visually and occurs only around the focal point of the beam. The spatial characteristic of the photochromic effect as a function of the incident wavelength is plotted in Fig. 2. Finally, it was found that the written glass can be erased by an appropriate thermal treatment and that a higher treatment temperature results in a higher erasing rate. For example, the effect disappears after a few minutes by thermal treatment around  $250^\circ\text{C}$  as shown by the picture of the erased glass in Fig. 1(c). In addition, it was confirmed that the photochromism in these glasses is due to the appa-

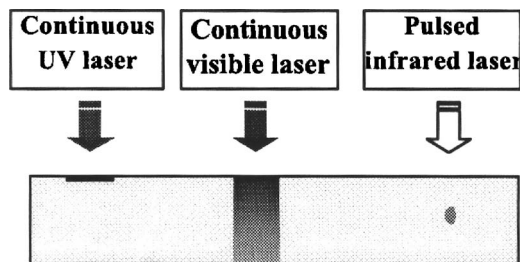


FIG. 2. Schematic representation of the photochromic effect in function of the laser beam characteristics. Exposure to UV laser light results in the apparition of the effect at the surface of the glass sample whereas exposure to visible light allows to obtain the effect in the whole volume of the glass. Irradiation by a femtosecond infrared laser focused inside the glass volume results in the photochromic effect at the focusing point.

rition of a large absorption band in the visible and near infrared centered around  $900 \text{ nm}$  and Fig. 3 shows that the intensity of this absorption band is function of the irradiation time.

Based on the fact that photochromic effects in glasses are always caused by small crystallites dissolved in the vitreous network, we first thought that the laser exposure had induced a crystallization of micrometric or nanometric crystals. However, x-ray diffraction and transmission electronic microscopy did not identify any crystalline phase into the glass. A  $\text{WO}_3$  concentration higher than  $40\%$  molar and the presence of antimony oxide, even in small quantities ( $<0.5\%$  molar) are required to observe the photochromic effect. Structural characterizations of the glass were performed before and after laser irradiation by Raman and infrared (IR) spectroscopies and by x-ray absorption spectroscopy but did not reveal any structural change in the glass network.

To our knowledge, this is the first report of a photochromic effect in a  $\text{WO}_3$ -based bulk glass and beyond this it is the first report of a photochromic effect in a totally amorphous glass, i.e., a glass without any crystalline phase. In this material the photochromic phenomenon seems to be similar to that observed in  $\text{WO}_3$  amorphous films. Indeed, a large absorption band is observed in the visible and near infrared

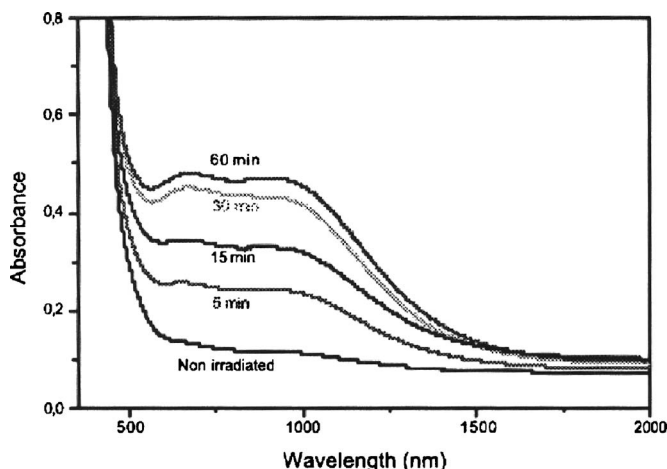


FIG. 3. Absorption spectra of the glass in function of the irradiation time. The intensity of the absorption band observed in the visible and near infrared by visible light exposure appears after only a few minutes of irradiation and increases with the irradiation time.

under laser exposure and a large concentration of  $\text{WO}_3$  is required to induce the effect in the material.

Previous structural works on these tungstate fluorophosphate glasses show that glasses containing more than 40% molar in  $\text{WO}_3$  exhibit W–O–W bonds related to the formation of  $\text{WO}_6$  clusters in the vitreous network.<sup>26</sup> The photochromism phenomenon in  $\text{WO}_3$  and  $\text{MoO}_3$  amorphous materials is known to be a “dimensional property”.<sup>25</sup> It means that the effect can only occur in tungsten or molybdenum oxide clusters but not in its isolated form like  $(\text{WO}_4)^{2-}$  or  $(\text{MoO}_4)^{2-}$ . Moreover, it was found that the presence of the oxidizing agent is necessary for the photochromic effect to occur. For that reason, the exact mechanisms responsible of the photochromism in these  $\text{WO}_3$ -based glasses are not yet well understood up to now and are under intensive investigations.

We would like to emphasize that it is the first time that such photochromic effect is reported in a tungstate-based glass and more generally we report the first photochromic effect in a glass without any crystalline phase. This phenomenon, well-known under UV exposure in amorphous  $\text{WO}_3$  films, can occur at the surface, throughout the entire thickness or at a desired point inside the material depending on the incident laser conditions. For that reason, beyond the scientific and academic interest to understand the mechanisms involved in the photochromism of this glass, its specific behavior under laser illumination allows this material to be multifunctional for optical applications. Our opinion is that this new photochromic glass is a very promising material for classical, 3D, and holographic optical storage. In this way, this work is described and protected by a recent Brazilian patent.<sup>27</sup>

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