



Generation and bleaching of intrinsic color centers in photo-thermo-refractive glass matrix

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ABSTRACT

Photo-thermo-refractive (PTR) glass is a photosensitive multicomponent silicate glass that imparts refractive index change after exposure to ionizing radiation and thermal treatment. The origin of this photosensitivity is explained by thermal precipitation of sodium fluoride crystals controlled by atomic silver nucleation centers. These centers are produced by photo-reduction of silver ions resulted from photoionization (photo-oxidizing) of cerium ions. This feature of PTR glass is successfully used for high efficiency phase hologram recording. However, the mechanism of electric charge exchange (transfer) between these ions is not known and the role of intrinsic electron and hole centers was not studied. To elucidate this problem, pure PTR glass matrix with no dopants was prepared and the subsequent absorption spectra of color centers were studied after excitation of the intrinsic absorption edge of glass matrix. Color centers were bleached by thermal treatment and by optical excitation of induced absorption bands. The analysis of the structure of absorption spectra at different stages of coloration and bleaching led to the deconvolution of complex spectra to Gaussian components. Based on this analysis and comparison with simple silicate glasses, induced absorption bands were assigned to different intrinsic electron and hole centers. Interconversion of different centers is also studied.

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1. Introduction

Photo-thermo-induced crystallization in multicomponent silicate glasses doped with Ce, Ag, and F was discovered in 1949 by Stookey [1]. Based on this effect, photo-thermo-induced precipitation of metallic Ag allowed producing black coloration while the precipitation of NaF crystals in UV-exposed areas allowed producing white coloration of a glass plate. These two effects paved a way for black-and-white photography in the bulk of silicate glass. However, despite these very promising results, no real applications were found. Thirty years later, it was demonstrated [2] that additional UV exposure and thermal development of a similar glass resulted in a precipitation of metallic Ag particles on the surface of NaF crystals. These particles produced different colors depending on UV dosage. These new results laid the groundwork for full color image recording. But once more, no useful applications were found. It is only after 35 years of study and development of this class of glasses, that refractive index variation due to NaF microcrystals precipitation was revealed but evaluated as insufficient for practical applications [3]. A few years later, this effect was re-investigated and refractive index variation was re-discovered and applied to the recording of the first hologram using the photo-thermo-refractive (PTR) phenomenon [4]. This was the starting point

for a large number of improvements in this class of glasses that resulted in the recording of the first holograms in PTR-like glasses with high relative diffraction efficiency [5] and then the first high efficiency volume Bragg grating in PTR glass [6,7]. Today's technology allows the fabrication of holograms in PTR glasses with diffraction efficiency up to 99.9%, absorption in near IR between 1 and $2 \times 10^{-4} \text{ cm}^{-1}$, scattering down to $5 \times 10^{-3} \text{ cm}^{-1}$, aperture up to $50 \times 50 \text{ mm}^2$ which enabled dramatic increase of brightness and power of solid state, fiber and semiconductor lasers [8]. The actual level of PTR glass technology allows the production of PTR glass with absorption in near IR region of $5 \times 10^{-5} \text{ cm}^{-1}$, refractive index fluctuations 10^{-5} , and apertures up to $100 \times 100 \text{ mm}^2$.

The basic mechanisms of photo-thermo-induced structural transformations in PTR glass can be stated as follow: UV exposure within the absorption band of Ce^{3+} triggers the photoionization of Ce^{3+} into Ce^{3++} and one electron; the latter is trapped by an ionic silver to yield an atomic silver [9]. At this stage of the process, photoionization caused the generation of additional absorption and a refractive index increment of about 10^{-6} . Moreover, exposure of UV-exposed glass to high power visible radiation causes bleaching of pre-nucleation centers [10]. The second stage occurs when heating up to $490 \text{ }^\circ\text{C}$ and consists in the creation of nucleation centers which include Ag and Br [11]. Then subsequent heating up to $520 \text{ }^\circ\text{C}$ results in precipitation of cubic NaF [12]. Cooling of the glass sample down to the room temperature induces stresses caused by difference in coefficients of thermal expansion of NaF and PTR glass which induce refractive index

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decrement of about 10^{-3} through the photoelastic properties of the glass [13]. Despite this very broad knowledge about photo-induced processes in PTR glass, some of the basic mechanisms are still unknown. Among the unknowns are: the fraction of Ce^{3+} responsible for photosensitivity, the centers created by UV exposure and what centers are those bleached by high power visible radiation. The goal of this work therefore consists in determining spectra and identifying the centers responsible for initial photoionization and induced coloration in PTR glass. In this paper we first analyze the structure of the absorption in PTR glass matrix before and after exposure to ionizing radiation. Then we study the induced absorption spectra by deconvolution into Gaussian functions and use this decomposition to study the mechanisms of thermal bleaching of color centers. Finally, we study the ability of UV and visible radiation to optically bleach color centers.

2. Experimental

2.1. Glass preparation

A fluorinated multicomponent silicate glass (photo-thermo-refractive (PTR) glass) was used in this study. The batch composition for the PTR glass was: $70SiO_2-15Na_2O-5ZnO-4Al_2O_3-5NaF-1KBr$ (wt. %). No dopant was added to the glass in order to produce only the glass matrix. High purity raw materials were melted in air using Pt crucibles at $1500\text{ }^\circ\text{C}$ for 5 h. Stirring was applied to homogenize the melt. The glasses were rapidly cooled down to about $460\text{ }^\circ\text{C}$, then annealed for 1 h at $460\text{ }^\circ\text{C}$ and finally slowly cooled down to room temperature at $0.1\text{ }^\circ\text{C}/\text{min}$. Lastly glasses were cut and polished into $25\times 25\text{ mm}^2$ samples with thickness from 0.5 to 5 mm. All samples used in this study had homogeneity better than 50 ppm peak-to-valley over the aperture and flatness better than 1 wave at 633 nm. Those characteristics allowed performing accurate optical transmission measurements.

2.2. UV exposure and bleaching procedure

In order to study the photoionization of the PTR glass matrix, an unfiltered radiation of a 300-W high pressure xenon lamp was used to expose the samples. The emission spectrum ranges from below 200 nm up to visible/near IR ranges. Hence such an exposure produced simultaneously ionization of the PTR glass matrix and a partial optical bleaching of the created color centers. A homogeneously exposed area was equal to $8\times 8\text{ mm}^2$. Exposure durations ranged from 10 to 180 s and 180 s was used as a standard for all analyses as it produced an induced absorption large enough to be precisely measured. Color centers created by the UV exposure were then thermally bleached by heat-treating the samples at different temperatures between 100 and $400\text{ }^\circ\text{C}$ (i.e. below T_g) to avoid any incipient crystallization. Optical bleaching was also carried out. Collimated beams of the fourth (266 nm) and second (532 nm) harmonics of a Nd:YAG laser (7 ns pulse width, about 1 mJ pulse energy) and of a 1 mW He-Ne (633 nm) laser were used for optical bleaching.

2.3. Optical spectroscopy

Absorption spectra were measured in the 200–800 nm range using a double beam UV–Vis–NIR spectrophotometer (Varian Cary 500). Due to dynamic range of the spectrophotometer, only values corresponding to absorbance (optical density) below 2 were considered in this study. Relative precision of $\sim 0.001\text{ cm}^{-1}$ was obtained in the whole spectrum region. A decimal absorption coefficient was calculated as $A = (D_m - D_F)/t$ where D_m is the measured optical density, D_F is the calculated optical density resulting from Fresnel reflection losses and t is the thickness of the sample in centimeter.

3. Results

3.1. Absorption spectra of virgin PTR glass matrix

The structure of the absorption spectrum of virgin PTR glass matrix was studied in the range from 200 to 800 nm (Fig. 1). One can see that absorption starts to be non negligible at 300 nm and is above 1 cm^{-1} at about 230 nm. Based on an exponential decay of absorption at lowest wavelengths, the intrinsic exponential absorption edge of PTR glass was extracted. It can be shown that it is comparable to one of soda-lime silicate glass [14] and therefore, the absorption edge is in the range of 220 nm.

3.2. Induced absorption spectra of UV-exposed PTR glass matrix

Photoionization of PTR glass matrix was then investigated. The samples were exposed to radiation from a xenon lamp for 10, 20, 40 and 180 s and absorption spectra were measured in the range from 200 to 800 nm (Fig. 2). One can see an induced absorption with the main band at $\sim 350\text{ nm}$. The intensity of the induced absorption increases when dosage is increased. In order to study the structure of this spectrum into more details, we calculated the induced absorption spectrum resulting from the difference between the spectra measured after ionization and before any ionization. The induced absorption spectrum measured after 180 s is shown in Fig. 3. A logarithmic scale was used to allow better analysis of the spectrum. One can see that not only one band appeared, but at least three with maxima at 235, 365 and 665 nm. This behavior is very similar to the one that can be seen in alkali silicate glasses [15], with a slight difference in the positions as compared to the one that can be seen in soda-lime silicate glasses for example [14].

3.3. Thermal bleaching of UV-exposed PTR glass matrix

Thermal bleaching of UV-exposed PTR glass matrix was studied. The procedure consisted in bleaching samples for 1 h at constant temperature. It is well known that color centers generated in soda-lime silicate glasses are very unstable and fade even at room temperature [16]. Moreover, increasing the temperature of bleaching in the range from 150 to $200\text{ }^\circ\text{C}$ allows bleaching color centers in soda-lime silicate glasses after only 1 h heat-treatment. However, it was found that bleaching efficiency of color centers generated in PTR glass matrix is extremely small at such low temperature (Fig. 4), and higher temperatures such as $300\text{--}400\text{ }^\circ\text{C}$ are required to produce an efficient bleaching of color centers generated in PTR glass matrix. Kinetics of bleaching was also investigated at 200 and $300\text{ }^\circ\text{C}$ (Fig. 5a and b). It is seen that the mechanisms of bleaching appear to be complex as non-monotonous evolution of spectra can be observed in the process of bleaching. For example, at $200\text{ }^\circ\text{C}$, while the band at 235 nm appears

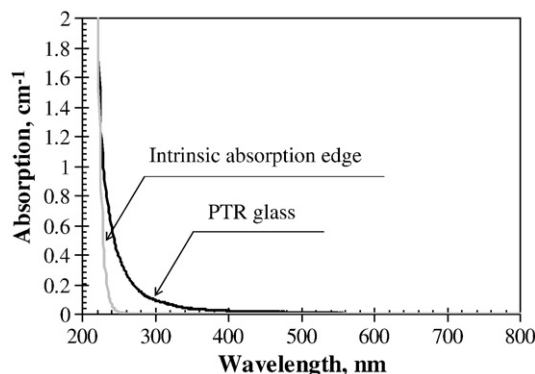


Fig. 1. Absorption spectrum of PTR glass matrix and its calculated intrinsic absorption edge.

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