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Bleaching and Darkening Effect in Photochromic Glasses under Irradiation with Femtosecond Laser Pulses

K. Jamshidi-Ghaleh*
Department of Physics, Azarbaijan University of Tarbiat Moallem, Tabriz, Iran

In this paper, the photochromic oxide glass sample under interaction of 200 fs laser pulses at 800 nm wavelength is studied. Two types of laser-induced modifications, bleaching and darkening, are observed. The induced darkening is observed inside the bleached volume. The effect of incident laser shot number and pulse energy on the bleached and darkened area are investigated. The pulse energy accumulation model is applied to investigation of both bleached and darkened area sizes. The bleaching and darkening modification fluence threshold are determined for single and multi-shot laser pulses.

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1. Introduction

Recently the advantages of ultrashort laser pulses (USLP) are being exploited to induce small volume changes inside glasses [1–5]. In most cases, the modifications are related to density changes in the glass matrix. Other type of modifications which appear as color centers induces well below densification threshold. The interaction of USLP in the infrared region with the glass matrix is guided by the generally accepted mechanism for the excitation of dielectrics: the initiating excitation is due to multiphoton absorption, either via morphological or structural defect states in the band gap or by interband transitions, which causes electron heating and additional ionization due to electron impact [6, 7]. This is followed by an energy transfer from the "hot" electronic system into the lattice by electron–phonon coupling [8]. The energy transfer channels and rate can differ depending on the material and the initial conditions. In most cases a noticeable modification inside the material results from subsequent heating during and after the energy transfer is completed. However, other (non-thermal) relaxation channels are viable, which may yield completely different results.

This study reports on laser-induced modifications inside special glasses, originally incorporated with semiconductive nanoparticles to define the special optical properties. This can include the dynamic response to UV light as for photochromic glasses, or the adjustment of the cut-off wavelength in transmittance as for the D6526 super brown glass filter series by Schott, Germany. The laser interaction with these nanoparticles introduces changes in the optical properties which are attributed to alteration in the size, shape and perhaps even in the complete conversion or destruction of these nanoparticles without visible signs of stress related artefacts originating from the surrounding glass matrix [9, 10].

* e-mail: k-jamshidi@azaruniv.edu

2. Experiment

The experimental studies were performed with a femtosecond laser system (Spectra Physics/Quantronix) that generates laser pulses with 200 fs at a repetition rate of 1 kHz and a central wavelength of 800 nm. The available maximum single pulse energy for the study was 450 μJ. A shutter and an attenuator are used to control the number of laser shots and the single pulse energy, measured with an energy monitor device located in front of the sample surface. The laser beam diameter was reduced by a single quartz lens with a focal length of 500 mm. The measured circular $1/e^2$ diameter at the glass samples equal to 320 μm enhanced the laser fluence. The glass samples were fixed on a XY positioning stage for vertical and horizontal translation. The glass type is the photochromic glass "D6526 super brown" from Schott, Germany, which is utilized to fabricate self-adjusting sun-glasses. The photochromic oxide glasses (alkali-alumo-boro-silicate) are doped with silver halides. The presence of silver and halogen ions (Cl- and Br-) in the order of 0.1 to 1% and copper ions in order of several 1/100% by the mass in the matrix, is necessary to provide for photochromism.

3. Results and discussions

The laser fluence and shot number dependence of induced bleaching and darkening are illustrated by generating several dot fields in arrays in 2 mm thick D6526 super brown glass sample. Figure 1 shows the optical microscope image of dotes at different incident laser fluences (columns) and shot numbers (rows). The first laser pulses (depends on incident pulse energy) induce a first irreversible modification inside the sample, which is called "bleaching" in this paper. The bleached areas by the laser pulses are difficult to visualize unless the photo-chromic glass is held several minutes in the sun-light or similar UV light source. As it is shown clearly from Fig. 1, at higher shot numbers, within the laser bleached areas a smaller region of darkening becomes visible, too.

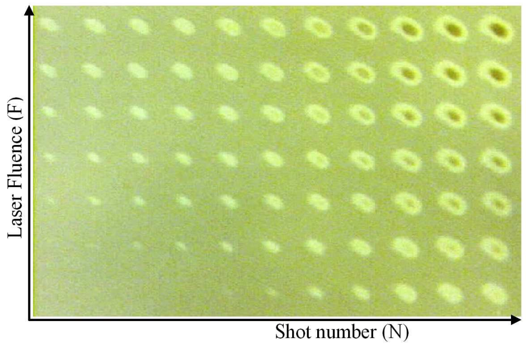

Fig. 1. Optical microscope image(s) of laser induced modification on photochromic glass sample (2 mm thick). Each column was generated at different laser fluence ranged up to down as: $F = 0.412$, 0.331, 0.263, 0.195, 0.132, 0.075 and 0.045 J cm^{-2}, whereas the number of laser pulse (rows) range from left to right as: $N = 1$, 2, 3, 5, 10, 20, 50, 100, 200, 500, and 1000.

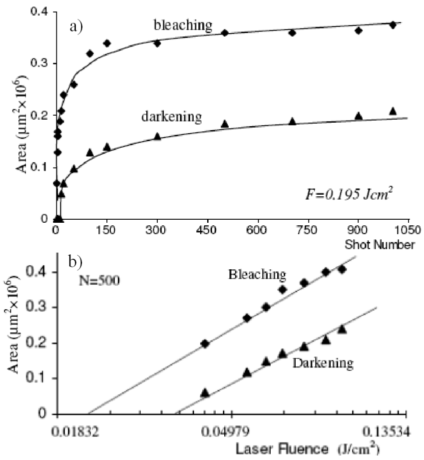

Fig. 2. (a) The variation of bleached and darkened areas over shot numbers at 0.195 J/cm^2 incident laser fluence. Linear curves show the theoretical prediction. (b) Half-logarithmic plot of the laser bleached and darkened area versus the laser fluence for $N = 500$ shots.

For any incident laser shot and laser fluence, the darkened volumes are smaller than the bleached one and centered on the bleached zone. With increasing incident laser fluence and shot numbers the size of both, bleached and darkened areas increase, too. In addition, bleaching and darkening thresholds varies at different number of shots. At higher shot number both types of modifications, bleaching and darkening, sizes remains constant, in other expression, the modifications saturate.

We have measured the diameters of bleached and darkened areas under optical microscope with 2 μm acuracy. Figure 2a shows, for example, the variations of bleached and darkened areas at different shot numbers for 0.195 J/cm^2 incident laser fluence. The same behavior was observed at other incident laser fluences. The curves in Fig. 2 present the theoretical results. The half--logarithmic plot of the bleached and darkened areas over the incident laser fluence at any number of laser pulses N yields in first approximation a linear dependence with identical slopes. Figure 2b shows for $N = 500$ shot number as an instance. This linear dependence is reported in studies involving e.g. the surface damage threshold of transparent materials, where USLP with a Gaussian spatial energy distribution were used [11, 12]. The slope in the linear fit is indicative for the laser spot size acting in the interaction. Due to possibly non-linear excitation it does not necessarily need to directly reflecting the actual physical spot size.

Increasing of bleaching and darkening diameter with incident laser shots indicates a pulse energy accumulation effect [13]. If one considers the Gaussian shaped intensity profile, illustrated in Fig. 3, it becomes clear that the lower intensity outer edges of the beam caused no effective modification at low shot numbers for incident laser fluence, but did cause darkening after high number of shots. It seems this is due to the pulse energy accumulation in the outer regions of the irradiated area. From schematic presentation of modified area (Fig. 3), a simple relationship can be derived between the diameter of a modified area, D, and the modified threshold fluence, F_{th}, at given shot number and the applied laser peak fluence, F_0:

$$D = \omega\sqrt{2\ln\left(\frac{F_0}{F_{\text{th}}(1)N^{s-1}}\right)}. \quad (1)$$

According to the laser energy accumulation model for metal surfaces by Jee et al., the laser fluence at N-shot surface damage threshold is given by $F_{\text{th}}(N) = F_{\text{th}}(1)N^{s-1}$ [13]. The evaluation based on Eq. (1) backs the assumption presented in a recent study [9], that the laser-induced bleaching in photochromic glass is based on direct laser–nanoparticle interaction via two-photon excitation. The electron system in the glass matrix surrounding the silver halide takes only a very minor part in the energy transfer mechanism leading to the bleaching effect. The strong involvement of the nanoparticles in the absorption of USLP could also explain the high efficiency and low (multiple) shot threshold of only a few mJ/cm^2 during the accumulative laser-induced bleaching inside photochromic glass. Figure 3 shows these phenomena graphically.

From the fit in Fig. 2b one can estimate the modification threshold for the different number of laser shots $F_{\text{th}}(N)$ by extrapolation of the linear fit with the zero area cross-over. The half-logarithmic behavior demonstrates a strong decrease in the bleaching threshold starting from over 400 mJ/cm^2 for $N = 1$ down to a few mJ/cm^2 at multiple laser shots $N > 1000$. By extrapolating of D^2 back to zero, a value for the bleached and darkened threshold fluence, $F_{\text{th}}(N)$, can be obtained at given shot number. The threshold fluences have been obtained for incident laser shots of 1, 3, 5, 10, 20, 50, 100, 500, and 1000. By fitting of experimental data with

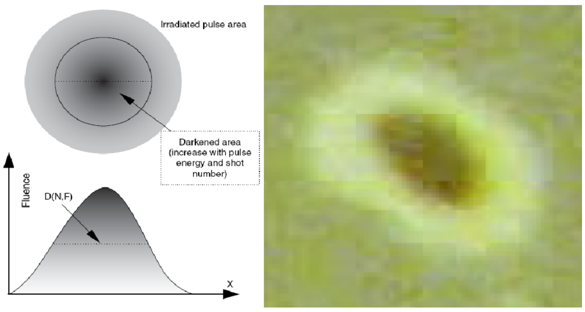

Fig. 3. For a given pulse energy, F, the diameter of bleached and darkened site increases with increasing incident laser shot number, N.

results of pulse energy accumulation model (not inputed here graphically), the values of single pulse modification threshold and modification factor are obtained as respectively: $F_{\mathrm{th}}^{\mathrm{dar}}(1) = 0.45$ J/cm^2, $F_{\mathrm{th}}^{\mathrm{ble}}(1) = 0.13$ J/cm^2 and $S^{\mathrm{dar}} = 0.55$, $S^{\mathrm{ble}} = 0.75$.

To determine the optical changes in transmission spectroscopically, a 2 mm thick photochromic sample was scanned at areas of 4×4 mm^2 with USLP (200 fs) at different fluence levels. The scanning was conducted by a zigzag movement of the sample with a grating distance of 25 μm, which is more than 12 times smaller than the beam diameter at the sample of 320 μm. The translation velocity was set to 5 mm/s. This leads to an average number of laser shots for laser scanned areas of $N_{\mathrm{ave}} = 820$ (repetition rate of 1 kHz). The optical transmission of each USLP modified area was determined spectroscopically in a wavelength range from 300 to 850 nm and then compared to the original tranmission curve of the photochromic sample. The difference in transmission between the original state (in "normal" laboratory environment without additional UV excitation) and the laser-modified regions is depicted in Fig. 4. A negative change characterizes an enhancement in transmission, as observed in the bleached area after illumination with USLP of a laser fluence 145 mJ/cm^2, which is about a factor 3 above the bleaching threshold. Indeed, with the naked eye a slight impression of bleaching can be recognized even without additional UV light illumination and photochromic darkening. Increasing the laser fluence to 220 mJ/cm^2, a striking change to darkening can be observed, verified in the spectroscopic analysis as depicted in Fig. 4. A further increase in laser fluence enhances the changes in transmittance with a wide and strong peak established around 500 nm.

4. Conclusion

Two types of laser-induced modifications: bleaching and darkening are observed on photochromic oxide glass samples under interaction with 200 fs laser pulses and wavelength of 800 nm. The darkening will be induced inside the bleaching volumes at incident pulse energies that depend on the number of shot. For high incident pulse

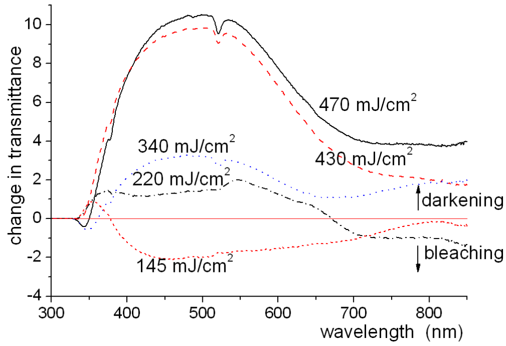

Fig. 4. Absolute change of optical transmittance in a 2 mm thick photochromic sample after USLP radiation (200 fs, 800 nm, 1 kHz, $N_{\mathrm{ave}} = 820$) at different fluence levels: 145, 220, 340, 430, and 470 mJ/cm^2 [15].

energies only few shot numbers is needed for inducing the darkening. But on low incident pulse energies more shot number is needed. The effect of incident laser shot number and pulse energy on the bleached and darkened area are investigated. The pulse energy accumulation model is applied to analyses of both types of modified area sizes. The bleaching and darkening modification fluence threshold determined for single and multishot laser pulses.

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