Photoionization of glasses by IR femtosecond laser pulses

O. M. Efimov*, L. B. Glebov, S. Grantham, M. Richardson

Center for Research and Education in Optics and Lasers, University of Central Florida, Orlando, FL 32826, USA

* SC Vavilov State Optical Institute, Sosnovy Bor, St. Petersburg region, 188537, Russia

ABSTRACT

Photoionization of silicate glasses under high-power, 850 nm, femtosecond laser has been studied. It was found that color centers formation and intrinsic luminescence of boro- and alkali-silicate glasses occurred at irradiances well below the threshold for laser-induced damage. Simultaneously a supercontinuum generation in the visible and UV spectral regions was observed in all the glasses studied. From these studies it was deduced that photoionization of glass matrix results from linear and two-photon absorption of the short-wavelength component of the supercontinuum. No color center absorption in the visible region was observed in fused silica at irradiances up to the laser damage threshold.

Keywords: femtosecond radiation, silicate glasses, supercontinuum generation, photoionization, color centers.

1. INTRODUCTION

The spectroscopic characteristics and photo-chemical processes mechanisms in alkali-silicate glasses under low-intensity UV light exposure were studied a long time ago [1-3]. Absolute values of the specific absorption of the various iron forms, the charge states of matrix color centers, fundamental luminescence spectrum and the boundaries of fundamental absorption, external photoeffect and photoconductivity were determined. It was shown that under photoexcitation in the fundamental absorption region edge of the glasses mentioned an ionization of intrinsic centers of the glass matrix takes place. This causes the photoluminescence [1,2], the photoconduction[2], and the formation of stable [1,2] and unstable [3] color centers due to localization of the charge carriers on the glass structure defects. The exposure of glasses by X-ray or by γ-radiation leads to the same phenomena. It was established that an edge of the fundamental absorption region of the glasses is formed by levels of the local intrinsic centers of matrix, concerned with $\equiv Si - O^- \ldots Na^+$ (or other alkali ion) structural fragments (L - centers). The long-wave carriers mobility boundary E_i (minimal energy at which there occurs generation of electron - hole pairs) coincides with the fundamental absorption edge E_g and is approximately 6 eV for alkali-silicate glasses. It should be underlined that radiation exposure of glasses with quantum energy, insufficient for fundamental absorption region excitation, does not lead to matrix ionization and relative photochemical processes.

Further, it was shown [4,5], that glass exposure sufficiently powerful laser radiation with $E_i/2 < h\nu < E_i$ causes intensive luminescence and appearance into glass bulk color centers. It should be emphasized that radiation wavelengths causing these effects were beyond color centers formation

spectra in these glasses. The studies were done which allow to draw a conclusion that in the crown glasses under laser irradiation with $E_i/2 < h\nu < E_i$ the same color centers are formed as under the excitation in fundamental absorption range. The spectral-temporal characteristics of laser-induced luminescence completely conformed to the measurements done under low-intensity light exposure [2]. Thermal discoloration of irradiated glasses was similar to thermal decay of color centers. Thus, at laser radiation exposure of crown glasses with $E_i/2 < h\nu < E_i$ the two-photon glass matrix ionization occurs leading to color centers formation and fundamental luminescence. It is important that in this case the color centers formation effect is definitely registered at $q = 10^{-3} \cdot q_0$ (q_0 is the optical breakdown threshold of glass), while fundamental luminescence is registered at $q = 10^{-4} \cdot q_0$ [6]. At radiation exposure of glasses with $h\nu < E_i/2$ these effects were not found even at $q = 0.98 \cdot q_0$, i.e. it is impossible to register three- and more quantum processes in alkali-silicate glasses.

However, the processes of photoexcitation, luminescence, and color centers formation in lead-silicate glasses are more complicated because their energy structure is sufficiently complex. It was shown that the long-wave boundary of carrier mobility of these glasses is placed considerably higher then the fundamental absorption edge of the material matrix [7]. For this reason the detection of linear formation of color centers in the lead silicate glasses is not possible. Their coloration arises only from the multi-photon matrix ionization and the excitation occurs through virtual states that are located in the fundamental absorption region. Namely the last condition leads to the significant increase of multiphoton excitation probability and therefore it is possible to observe in lead-silicate glasses not only two-, but three-photon absorption too. To the best of our knowledge there are not other experimental evidences of existence of three- and more-photon absorption in silicate glasses before the present.

Nevertheless it was shown recently [8] that it is possible to observe a coloration of silicate glasses under powerful femtosecond pulses and the likely mechanisms of this phenomenon were discussed. Here we present the experimental evidences of existence of new type of transparent media ionization under short time laser pulses.

2. EXPERIMENTAL

In this work we studied samples of commonly used optical glasses: fused silica, commercial boro-silicate glasses K8 (Russia) and BK7 (USA), as well as a high purity silicate glass $22Na_2O$-$3CaO$-$75SiO_2$. The samples were of 2 cm×2 cm×0.6 cm in size. All sides of the glass samples were polished in order to observe photoinduced coloration and luminescence in different directions.

The laser used for this investigation was a 100 fs, Cr:LiSAF system operating at a wavelength of 850 nm [9]. The laser consists of a Kerr lens modelocked Ti: sapphire laser followed by several stages of flashlamp-pumped Cr:LiSAF amplifiers in chirped pulse amplification architecture. For these experiments the single pulse output of the first stage regenerative amplifier was compressed to a pulsewidth of ~100 fs. Pulse energies of 2 - 3 mJ were used for these experiments. The size of the beam entering the compression gratings was ~ 25 mm diameter. Each compressed pulse was bandwidth-limited with a Gaussian (FWHM) spectral width of 11 nm. The laser operated at a frequency of 6 Hz. The output of the laser beam (Fig. 1) was focused in air by a lens (either 10 or 100 cm focal length) to a point located at specific distance in front of the sample. The spectrum of the light transmitted through the sample was monitored with a 25 cm grating spectrophotometer having a

resolution of ~10 nm, as illustrated in Fig. 1. The output of the monochromator was detected by a photomultiplier tube with a sensitivity which spanned from the visible to the UV region of the spectrum. The signal from photomultiplier was recorded by a Tektronix TDS 640 digital oscilloscope.

When the laser was operated at irradiances lower the thresholds of self-focusing and laser-induced breakdown white light emission in the same direction as laser beam occurred and coloration of the exposed region was observed. In these experiments focusing lenses with a range of focal lengths were used and the focal point was in front of the sample as in Fig. 1. The coloration in the glass bulk was generated in the form of the cylinder or cone with a shape similar to the laser beam one (gray area in Fig. 1). This dark track was directed along the laser beam propagation.

The distribution of color centers in the direction of the laser beam propagation in each glass sample was estimated by following technique. The laser beam was focused with the F=100 cm lens to produce an almost parallel beam near the focal plane. The sample was scanned in the X-Y plane (Fig. 1) to produce a colored section about of few of millimeters. A small wafer, ~1 mm thick was then cut from the exposed sample in the plane of propagation of the laser beam that produced the color centers as it is shown in Fig. 1. This small wafer was then polished and analyzed along the axis Z (Fig. 1) with a scanning microphotometer that measured the local absorption of white light. The photoinduced optical density in the visible region was then measured as a function of the distance from the small wafer edge (this distance is equal to the distance from the front surface of the original sample in Z direction). The spatial resolution of this method was about 0.1 mm. This approach provided a value for the color centers absorption averaged over the visible spectrum.

3. RESULTS AND DISCUSSION

It is well known that under high-power pico- and femtosecond laser pulses white light generation occurs as a result of variation of the refractive index of condensed media and the consequential changes of the amplitude, phase and frequency an exciting beam (e.g. [10, 11] and references therein). White light generation occurred in all the glasses studied when the femtosecond IR pulses had an irradiance of more than 10^{12} W/cm^2. This white light was observed to propagate approximately collinearly with the laser beam but its intensity distribution differed significantly from the distribution of the laser beam.

Glasses such as K8, BK7 and alkali-silicate exhibited a bright blue luminescence and the dark track in the direction of laser beam propagation. These dark tracks appeared after the first exposure to laser pulse. The photoinduced coloration increased with the number of multiple exposures. No coloration in the visible region was observed in fused silica.

The absorption induced in these samples by femtosecond laser pulses for both commercial and experimental glasses were measured. It was shown that the absorption spectra of color centers produced in the same glasses by γ radiation from a Co^{60} radioactive source and by IR laser pulses are very similar. Thermal bleaching of the photoinduced absorption in the glasses studied was similar to thermal bleaching of color centers generated by ionizing radiation. These data allow us to conclude that the darkening of the exposed to femtosecond IR laser pulses fraction of the glass samples is caused by the color center generation. No laser induced damage sites or threads were found in colored tracks.

One can suppose that the process of color center formation under the excitation at 850 nm is associated either with the four-photon absorption of laser radiation (1.46 eV) or with the linear or with two-photon absorption of the short wavelength fraction of supercontinuum. However, it was found that the color centers and intrinsic luminescence starts only at some distance from the front surface of the sample (Fig. 2). This phenomenon was observed even when the sample was placed immediately

adjacent the focal plane of the lens F=10 cm and the laser beam was diverging into the bulk of the sample (Fig. 1). The absence of the photoinduced coloration close to the front surface, in the region of the maximum intensity of the laser beam, suggests that this coloration and luminescence in these glasses cannot be ascribed to multiphoton absorption of laser radiation at 850 nm.

This then leads us to suggest that color center generation is caused by spectral broadening of exciting radiation in the bulk glass, followed by linear or two-photon excitation of the glass matrix by the short wavelength portion of the continuum that is generated. It is known (see, for example, [14]) that the degree of spectral broadening is proportional to the length of the interaction between the exciting radiation and the media. In this case an intrinsic interaction distance is necessary to induce sufficient broadening for either single or two photon excitation of the glass matrix. To investigate this further the dependence of the distance between the front surface and colored region (point A in Fig. 1 and 2) on the irradiance was measured. One can see in Fig. 3 that this distance is really inversely proportion to the irradiance of incident laser beam.

Further, the measurements were made of the spectrum of the output radiation from the samples investigated. It was found for the samples of K8 and BK7 that the output radiation is a continuum spreading from the IR out to 220 nm. This result is surprising since it well known that these glasses are opaque for wavelength less than 330 nm. The only explanation for the observation of the UV light as short as 220 nm in the transmitted spectra, is that this radiation is generated at each point of the glass volume.

The results depicted above suggest the need for a new model to describe the processes that occur in multicomponent silicate glasses when irradiated by femtosecond IR laser pulses. This model takes into account these processes that occur at intensities much less than the threshold for self-focusing and laser breakdown. The model is illustrated in Fig. 4. Originally all the electrons in dielectric glass are located in the valence band and the energy levels of the conduction band and of the impurities are empty (Fig. 4a). The bandgap in silicate glasses is ~4 times greater that the energy of incident photons (1.46 eV) as can be seen from comparison Fig. 4a and left part of Fig. 4b. It was found that no photoinduced coloration is occurred due to four photon ionization. Therefore no coloration one can see near the front surface of the sample (left part of Fig. 4c). The spectral width of the laser beam is broadened in the process of the pulse transmission through the glass sample in the direction of the Z axis (Fig. 4b). At the distance from the front surface ("A" in Fig. 1, and 2) that corresponds to the position along Z axis where the broadening has increased such that the energy of photons at the UV edge of the supercontinuum reaches half the bandgap (E_g), two photon ionization of glass matrix occurs if the intensity is more than 10^6 W/cm^2 [4]. Coloration of the glass bulk then results from electrons and holes trapping in the region Z>A (Fig. 4c). The process of single photon ionization of glass matrix begins at Z>B (Fig. 4) that corresponds the distance from the front surface that is required for the UV edge of supercontinuum to reach a maximum photon energy equal to the energy of the glass bandgap. In this case color center generation occurs with high quantum efficiency, independently on irradiance. It should be noted that glass is opaque for these photons and only a thin layer near the back surface of the sample can emit this radiation outside of the glass. This is why the intensity of the short part of the UV radiation measured outside of the glass sample, is very low.

The absence of the visible coloration in fused silica under multiple irradiation by femtosecond laser pulses at 850 nm with irradiance up to the damage threshold can be a result of two possible causes. Firstly, the band gap energy in fused silica is much greater than in multicomponent glasses and therefore its intrinsic absorption begins only in the vacuum UV region [30]. The conversion of IR radiation to supercontinuum radiation in this short wavelength UV region is consequently mach lower

and no significant ionization of fused silica occurs. Secondly, color centers produces in high purity fused silica have low absorption in the visible region, and may not be seen [12].

4. CONCLUSION

Coloration of multicomponent silicate glasses has been observed for the first time under exposure to infrared femtosecond laser pulses at irradiances well below the threshold of self-focusing and laser induced damage. This coloration is caused by color center formation as a result of glass matrix photo-ionization and the consequent trapping of electrons and holes. The photo-ionization results from absorption of the short-wavelength component of the supercontinuum that is generated in the volume of glass as a result of the femtosecond laser pulses spectral broadening. The supercontinuum extends up to the short wavelength UV region even if the glass is opaque in this region. Fused silica exhibits the same spectral broadening too but color center formation in the visible did not occur at irradiance up to the laser damage threshold.

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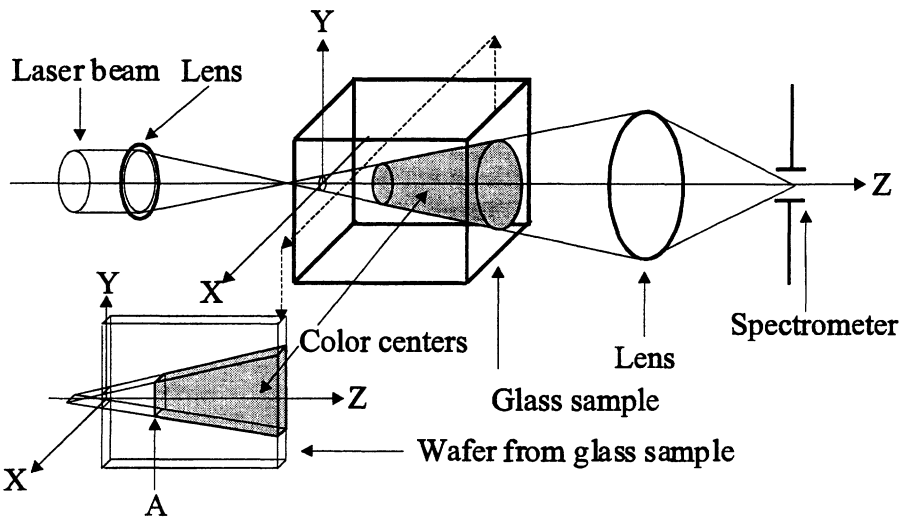

Fig. 1. Experimental setup for glass samples exposure to IR femtosecond laser pulses, measurement of spectra and spatial distribution of photo-induced absorption, and spectra of emitted radiation.

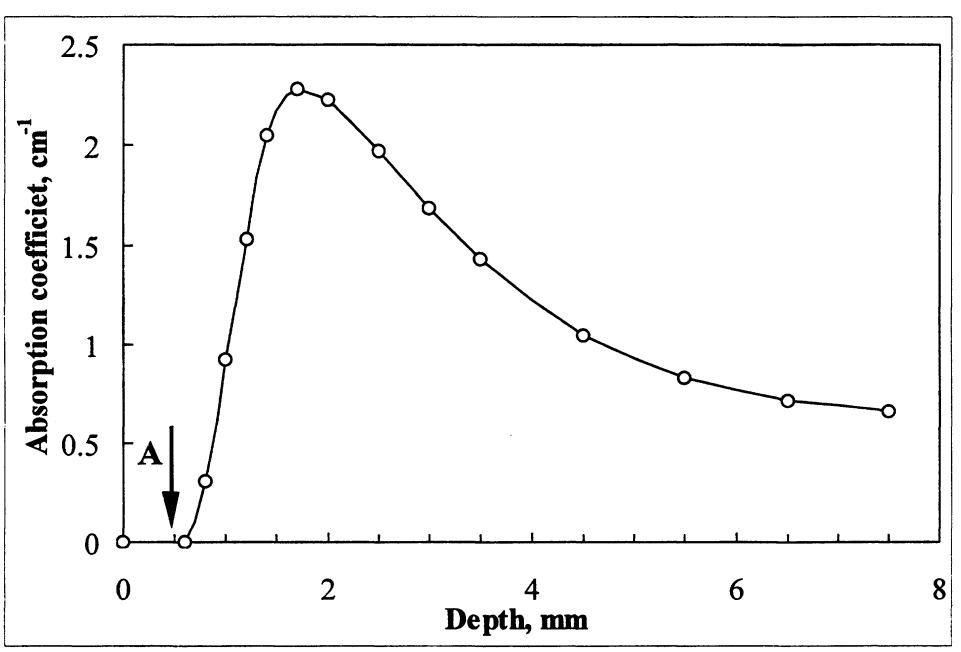

Fig. 2. The dependence of additional absorption coefficient on distance from the front surface of K8 glass (depth, axis Z in Fig. 1) irradiated by femtosecond laser radiation at 850 nm. Lens focal length is 100 cm, sample thickness was 2 cm.

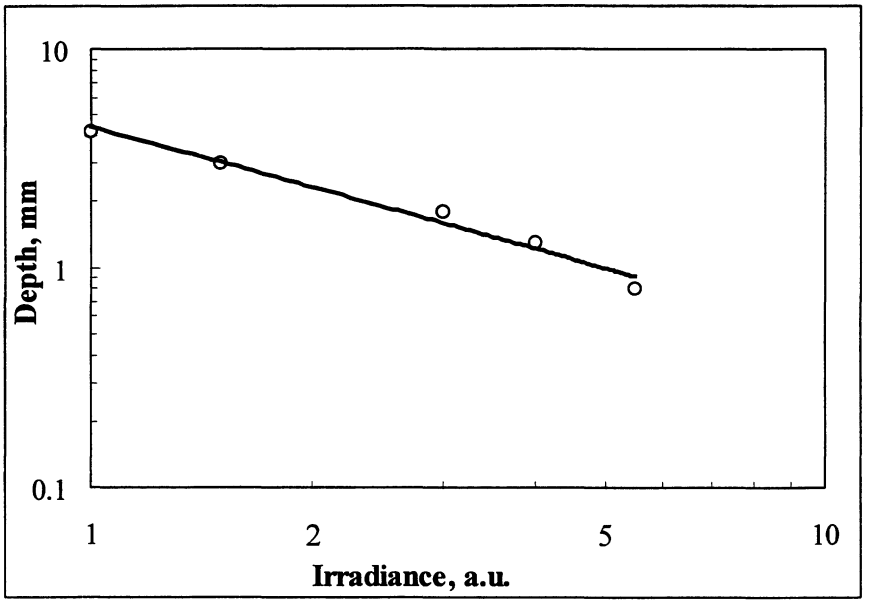

Fig. 3. The dependence of the distance between the front surface of the sample and the colored region) on irradiance of incident laser radiation. The solid line is the hyperbolic curve: $y \propto x^{-0.93}$.

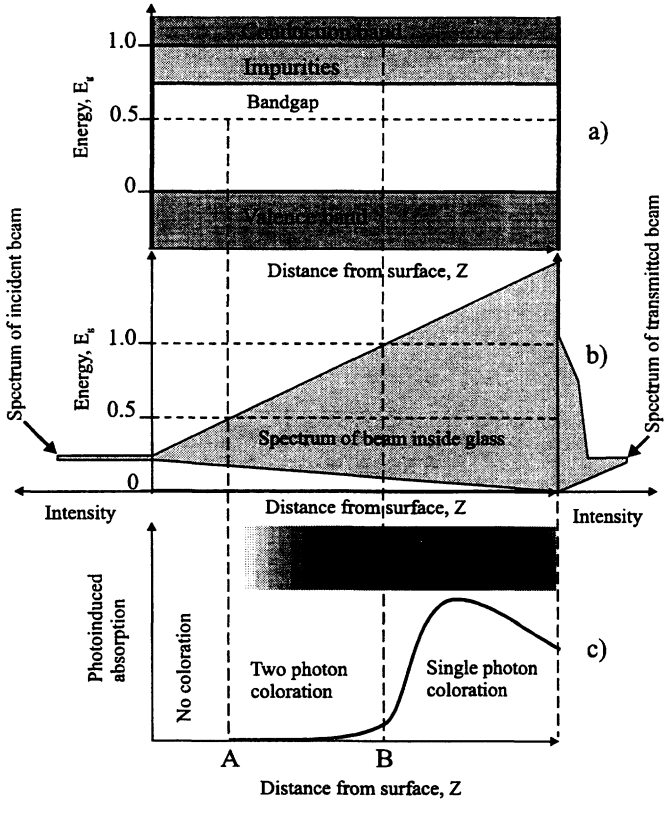

Fig. 4. Diagram of photo-induced processes in a dielectric material under exposure t femtosecond IR pulses.

DISCUSSION

Q. You showed both gamma irradiation and different laser wavelength irradiation were effective at inducing these color centers in glass. Have you looked at annealing of these glasses once the color centers go away to see if there are any residual differences between the different materials?

A. These color centers have several degrees of thermal stability. The outer part of the center disappears at lower temperatures . Some disappear at about 50° C, some at the main part of the center disappear at about 150° C and the rest at about 350° C. All the centers have the same behavior independently of normal ultraviolet gamma x-ray or infra red irradiation. You can find differences between concentration of different types of color centers, but I didn't discuss it because it is not important for this. There is some difference in fine structure organization, but the principle is the same. Holes and electrons produce the same color centers in all cases of exposure.

Q. In the continuum generation that you just showed (120 femto second pulse) what was the intensity of the laser, and what type of pulse length would you have to go to for which this would not be a strong effect any more?

A. You can find discoloration under femto second irradiation, if the radiance is more than 10^{13} Watts per square centimeter.

Q. What about for longer pulses, i.e.: one picosecond?

A. We could not find any coloration using about 100 picosecond pulses, and we did not have pulses in the range of one picosecond, we have no data about this behavior.

Q. A comment, I think cell phase modulation is relatively well understood and it could be calculated, probably with pretty good accuracy; what intensity is needed for what pulse width to produce a spectrum broad enough to see discoloration.