PHOTO-INDUCED PROCESSES in SILICATE GLASSES EXPOSED to IR FEMTOSECOND PULSES

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ABSTRACT

The optical properties variation in silicate glasses (fused silica, boro-silicate crowns K8 (Russia) and BK7 (USA), and high purity alkali-silicate glass) after exposure to high-power femtosecond laser radiation at 0.85 μm have been studied. The laser spectral line broadening leading to the supercontinuum generation in visible and UV spectral regions was observed in all studied glasses. Color center generation and intrinsic luminescence were found in boro- and alkali-silicate glasses. It is believed that these processes result from linear and/or two-photon absorption of the short-wavelength part of this supercontinuum which causes glass matrix ionization. No color center absorption in the visible region was observed in fused silica at irradiances up to the laser damage threshold. It was concluded that there is no significant ionization of fused silica under exposure to IR femtosecond laser pulses with irradiance below laser induced damage threshold.

1. INTRODUCTION

It is well known that a refractive index variation of condensed media induced under high-power pico- and femtosecond laser pulses results in changes of the amplitude, phase and frequency an exciting beam. These effects induce substantial spectral broadening of the transmitted beam both in the long-wavelength and in the short-wavelength regions ("white" light generation) due to self-phase modulation, induced-phase modulation, or cross-phase modulation (e.g. [1, 2] and references therein). The first works on white light generation in crystals and glasses were performed in 1970 [3, 4]. It was found that from five to ten small-scale filaments occurred under picosecond pulse excitation at 0.53 μm. The irradiance in these filaments could achieve 10^{13} W/cm^2. In this case, intense radiation in a wide spectral range from 0.4 to 0.7 μm was observed. Similar phenomena were obtained in works [5, 6] for other wavelengths. The induced spectral broadening of a weak picosecond pulse in glass was also demonstrated in [7]. The variation of the temporal shape of a laser pulse was explained in [8]. Description and explanation of the main mechanisms of this process were presented in [1,2].

The phenomenon of generation of the white light supercontinuum has been used in a number of applications in different areas: ultrashort pulses generation [9], time-resolved absorption spectroscopy [10], optical fiber diagnostics [11]. It is clear that photoinduced nonlinear processes can restrict the

usage of this phenomenon. There are the papers devoted to the investigation of laser-induced damage of crystals and glasses, in which an multiphoton excitation of these materials under femtosecond IR laser irradiation is considered as a mechanism of initial free electron generation for avalanche ionization [12-14]. However, to the best of our knowledge, there is no experimental evidence of photoinduced optical properties variation in glasses under high power IR irradiation. It should be noted, that photoinduced processes can be obtained in glasses exposed to nanosecond pulses of visible and long wavelength UV radiation as a result of two- and three photon absorption [15-18]. In this case the color center formation changes both an absorption coefficient [15-17] and a refractive index [18] of medium, which leads to the optical inhomogeneity formation.

Thus, the investigation of photoinduced processes in glasses under femtosecond IR irradiation is important both for applications of the white light generation and for the understanding of the mechanisms of laser damage in these materials. In this connection, the present work goal is to study the optical phenomena arising in silicate glasses under high-power femtosecond laser radiation.

2. EXPERIMENTAL

The following samples of silicate glasses were studied: fused silica, commercial boro-silicate glasses K8 (Russia) and BK7 (USA), and high purity alkali-silicate glass. The last one was specially synthesized of high purity materials using the laboratory method [19] which limits the absorbing impurities concentration to less than 10^{-4} %. Nonlinear absorption and coloration of such alkali-silicate glasses exposed to nanosecond laser pulses, were studied and described earlier in [15,16]. It was shown that two-photon ionization of the intrinsic states of vitreous media occurs under laser irradiation of glasses with photon energies ranging from $E_g/2 < h\nu < E_g$ (band gap E_g is about 6 eV for alkali-silicate glasses). Electron and hole trapping and recombination lead to color center formation and fundamental luminescence, correspondingly. It should be emphasized that in this case the color center generation was clearly observed at the irradiance $I = 10^{-3}I_0$ (where I_0 is laser-induced damage threshold of glass). An intrinsic luminescence was recorded at an intensity $I = 10^{-4}I_0$ [20]. When glasses were exposed to radiation with $h\nu < E_g/2$, these phenomena were not observed even at $I = 0.98I_0$. This means that the three- and the higher order processes of photo-ionization were not revealed in these glasses. All sides of the glass samples were polished in order to observe photoinduced coloration and luminescence in different directions.

A Kerr lens modelocked Ti: sapphire laser was used as the femtosecond pulse source. The output pulses from this laser were expanded in an anti-parallel grating-pair pulse stretcher and injected into a Cr:LiSAF regenerative amplifier. Pulse slicers were used before and after the regenerative amplifier to select a single pulse out of the input and output pulse trains. The single pulse was compressed using a parallel grating pair pulse compressor. The output beam diameter was about 25 mm and the energy output reached 1 mJ. Laser system was operated at 6 Hz repetition rate. The laser beam was focused into the samples using singlet lenses with a wide variety of focal lengths (10-100 cm). The glass samples were exposed to laser radiation at a wavelength of 0.85 μm with pulse halfwidth about of 100 fs.

A mirror monochromator with a concave grating was used to measure the spectrum of supercontinuum generated in the samples. The intensity of output of the monochromator was detected by the photomultiplier tube with 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.

Finally to measure an photoinduced absorption spectrum in the glasses after the exposure to laser radiation, a fraction of the sample volume with cross section about 1 cm×1 cm was colored by scanning of the sample. Then the absorption spectrum of this section of the sample was measured by Perkin-Elmer 330 spectrophotometer. The color centers' distribution in the volume of the glass was measured using the wafer with thickness about 1 mm that was cut from the exposed sample in the direction of laser beam axis. This wafer was polished and the dependence of optical density on the distance from the wafer edge (the distance from the front surface of the original sample) was determined by scanning microphotometer. Spatial resolution of this method was about 0.3 mm. An induced absorption was integrated over the visible region.

3. RESULTS AND DISCUSSION

The performed experiments showed that white light generation occurred in all studied glasses at irradiance more than 10^{12} W/cm^2. This white light was propagated collinear to the exciting laser beam. Such glasses as K8, BK7 and alkali-silicate exhibited a bright blue luminescence and the dark track in the direction of laser beam propagation. No coloration in visible region was observed in fused silica. The absorption spectra induced by femtosecond irradiation both for commercial and tentative glasses were similar to the absorption spectra of these glasses after exposure to gamma or X-rays (Figure 1, [15, 21]). Thermal bleaching of photoinduced absorption in studied glasses was similar to thermal bleaching of color centers generated by ionizing radiation. The obtained data allowed to conclusion that the same color centers are formed in the multicomponent silicate glasses exposed both to IR femtosecond laser pulses and to short wavelength ionizing radiation.

It is known that for color center generation the photon energy should be no less that the band gap (6 eV in the case of studied glasses). Therefore, the process of color centers formation under the excitation at 0.85 μm can be associated either with the four-photon absorption of laser radiation (1.46 eV) or with linear or two-photon absorption of the short wavelength fraction of supercontinuum. However, as it has already been noted, three- and higher order processes have not been observed earlier in the glasses investigated. Moreover, it was found that the color centers and intrinsic luminescence starts only at some distance from the front surface of the sample (Figure 2). The absence of the photoinduced coloration under the front surface, in the region of the maximum intensity of the laser beam, brings about the conclusion that coloration and luminescence of the glasses cannot be ascribed to multiphoton absorption of laser radiation at 0.85 μm. Then one can suppose that these processes are caused by spectral broadening of exciting radiation in the glass bulk, followed by linear or two-photon excitation of the glass matrix with the short wavelength portion of the continuum generated. It is known (see, for example, [1]) that the value of spectral broadening is proportional to the length of interaction between exciting radiation and media. Then some distance of interaction is necessary to induce enough broadening for single or two photon excitation of the glass intrinsic states. To verify this assumption a dependence of the distance between the front surface and colored region (point A in Figure 2) on the irradiance was measured. One can see in Figure 3 that this distance is really in inverse proportion to the irradiance of incident laser beam. This result allows the supposition that the ionization of glass is due to two-step nonlinear process. The first step is a spectral broadening of transmitting laser radiation, and the second one is a linear or two-photon absorption of short wavelength part of this broadened supercontinuum.

To verify this assumption measurement of the spectrum of the output radiation from samples,

exposed to IR femtosecond laser pulses, was made. It was found for the samples of K8 and BK7 that if an incident radiation is a narrow line at 850 nm, the output radiation is a continuum from the IR out to 220 nm. It should be noted, that these glasses are opaque for wavelength less than 350 nm. This means that in each point of the glass volume exciting radiation generates UV radiation that is absorbed by the glass itself. Only the thin layer near the back surface generates short wavelength radiation that can be detected out of the glass bulk. The observation of the transmitted radiation up to 220 nm indicates that an effective transformation of IR radiation occurred inside the samples out to the far UV region. It should be noted, that the intrinsic absorption boundary (at the level of ~1 cm^{-1}) of alkali-silicate and boro-silicate glasses is in the region of 200-210 nm. The maximum of color center generation spectrum in silicate glasses is placed near the intrinsic absorption boundary and it extends to long wavelength side out to 230-240 nm. Hence, the excitation of intrinsic states of glasses can be connected with both a linear absorption of radiation in the region 220-240 nm and a nonlinear absorption in the region 250-400 nm. To clarify the relative role of these processes in the glass matrix excitation the additional experiments are necessary.

As was mentioned above, the mechanism of subthreshold excitation of fused silica at femtosecond IR laser irradiation was supposed for initial free electron generation to trigger avalanche ionization leading to damage [12-14]. However, it is well known that any ionizing irradiation of fused silica leads to an intrinsic luminescence and an appearance of color center absorption [22]. The absence of these effects under multiple irradiation by femtosecond laser pulses at 850 nm with irradiance up to damage shows that there is no significant ionization of fused silica under such conditions, and the mechanisms of laser-induced damage of this material under femtosecond radiation demand the further investigations.

4. CONCLUSION

Incident radiation spectral broadening out to 220 nm, color center formation and intrinsic luminescence in multicomponent silicate glasses were observed under exposure to high-power femtosecond laser pulses at 850 nm. Coloration and luminescence were absent in the layer near the front surface of glass and appear at the distance from surface that increases at decreasing the irradiance. These processes are caused by linear and/or two-photon absorption of the short-wavelength part of supercontinuum that is generated in the volume of glass. Fused silica exhibits spectral broadening too but color center formation under multiple irradiation by femtosecond laser pulses at 850 nm with irradiance up to the laser damage threshold did not occur.

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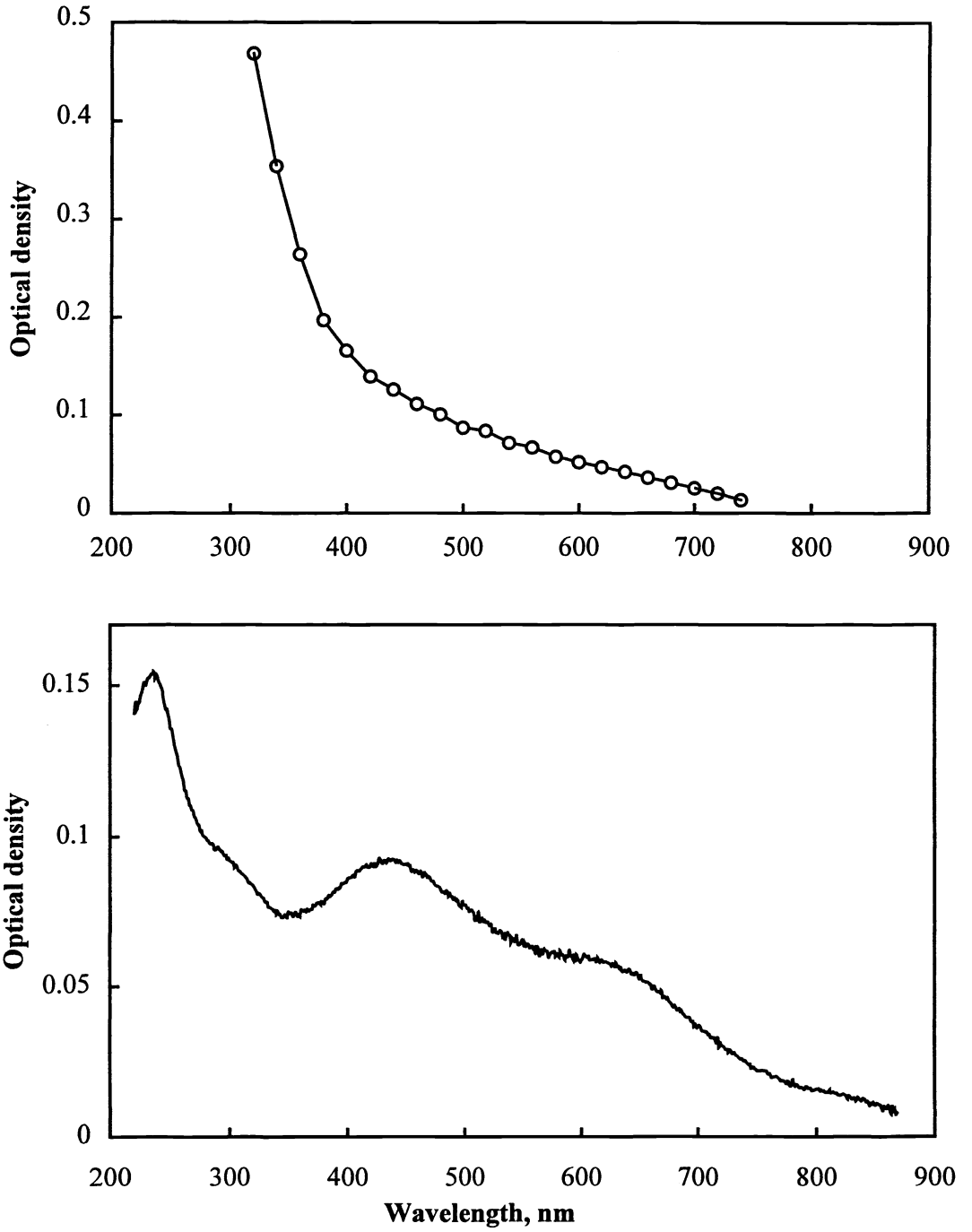

Figure 1. Spectra of additional absorption of K8 boro-silicate glass (a) and high purity alkali-silicate glass (b) irradiated by femtosecond laser radiation at 850 nm. Thickness of the both samples was 6 mm.

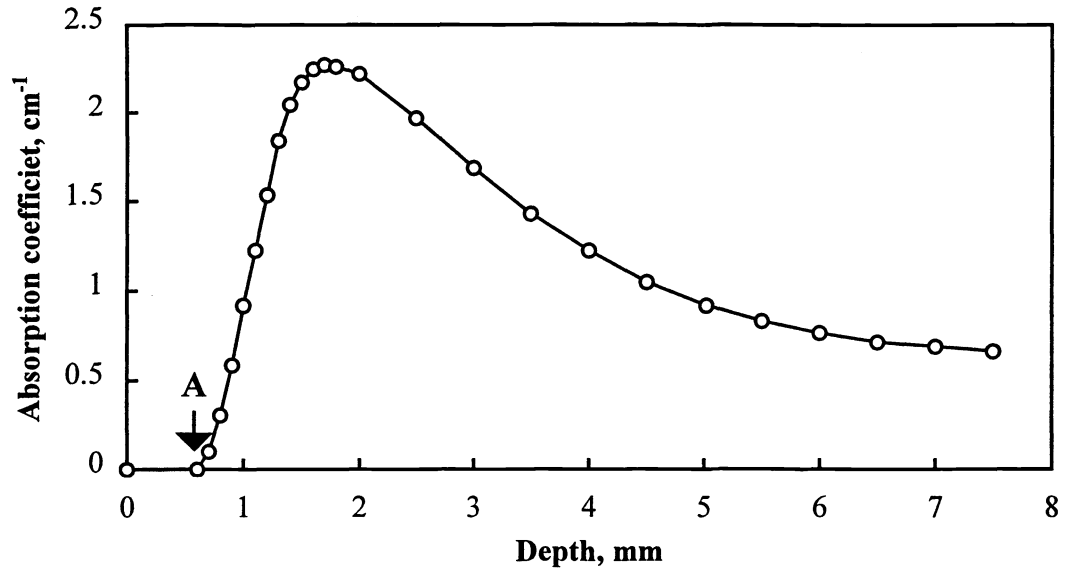

Figure 2. The dependence of additional absorption coefficient on distance from the front surface of K8 glass (depth) irradiated by femtosecond laser radiation at 850 nm.

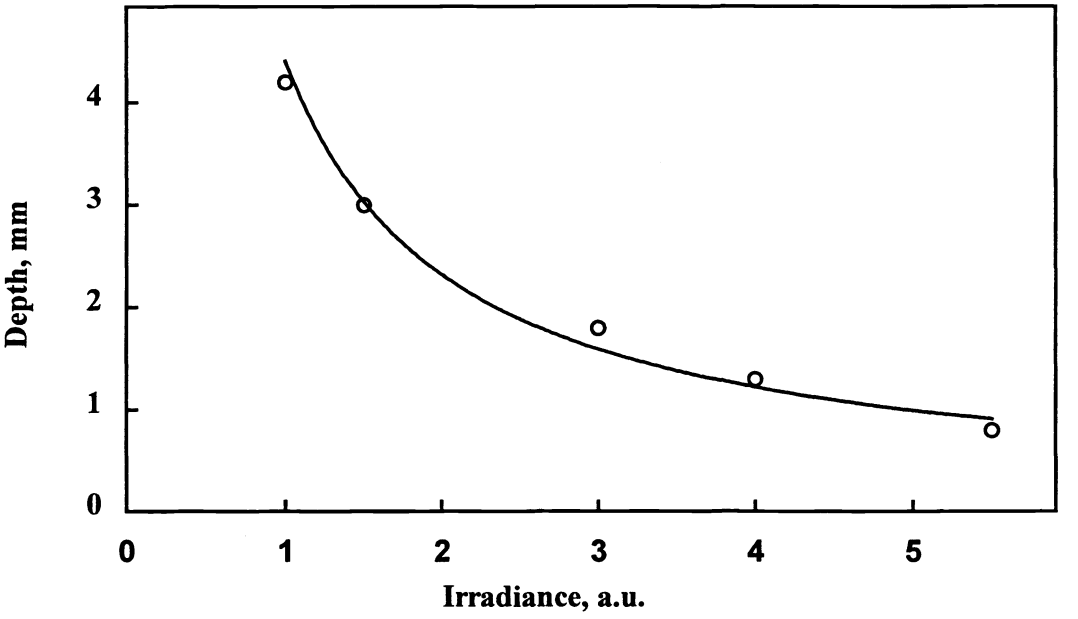

Figure 3. The dependence of the distance between the front surface of the sample and the colored region (depth, marked as A in Figure 2) on irradiance of incident laser radiation. The solid line is the hyperbolic curve: $y \propto x^{-0.93}$.