Color-center generation in silicate glasses exposed to infrared femtosecond pulses

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The optical properties of silicate glasses under high-power, 850-nm femtosecond laser irradiation have been studied. Photoinduced processes occurred at irradiances well below the threshold for laser-induce damage. Laser spectral line broadening leading to supercontinuum generation in the visible and UV spectral regions was observed in all the glasses studied. Color-center generation and intrinsic luminescence were found in boro-silicate and alkali silicate glasses. It is believed that these processes result from linear and two-photon absorption of the short-wavelength component of the supercontinuum, causing ionization of the glass matrix. No color-center absorption in the visible region was observed in fused silica at irradiances up to the laser-damage threshold. © 1998 Optical Society of America [S0740-3224(97)05311-3]

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1. INTRODUCTION

The transmission of ultrashort, high-intensity laser light through transparent solid media is today a serious topic of study. As femtosecond lasers are developed with ever-decreasing pulse durations, applications that require high laser powers will increase. Small laboratory-scale femtosecond lasers that have powers of several tens of terawatts have now been developed,[1] and peak powers 1 or 2 orders of magnitude higher than this are obtainable in the near future.

The design of applications that use the output of these systems will be strongly influenced by the damage thresholds of the transparent media through which the pulses are propagated. Recent studies of the damage thresholds for femtosecond laser pulses indicated damage thresholds of $\sim 1.5 \times 10^{14}$ W/cm^2 (Refs. 2–5) for fused silica and several crystals. A theoretical model of laser interaction with dielectrics based on multiphoton ionization, joule heating, and avalanche ionization has been developed to explain these results. As a consequence of conducting a similar study of the optical damage characteristics of transparent media with intense femtosecond laser pulses,[6] we recently observed a separate phenomenon that can limit the peak power transmission in optical materials.

This phenomenon, color-center formation, occurs at intensities as low as $\sim 10^{12}$ W/cm^2, well below the optical damage threshold, and appears to have no sharp onset intensity. We have observed this effect in optical borosilicate crown glasses and in high-purity alkali silicate glasses. Whereas optical damage in these media is characterized by the formation of a plasma and irreversible structural dislocations, the color-center formation that we observe takes the form of a uniform slight discoloration of the medium through which the beam has passed. This discoloration is reversible. Annealing of the material above 150 °C causes the color centers to disappear, returning the material to its original transparent state. This is the first time to our knowledge that color-center formation in vitreous media has been observed with IR light.

Color-center formation (solarization) in optical glasses after exposure to sunlight has been well known since the previous century.[7] It was mentioned in Ref. 7 that coloration of alkali silicate glasses can be caused by exposure to UV radiation in the region of 200–230 nm. Later it was proved[8] that the location and the shape of the color-center generation spectrum (the dependence of the optical density of the color centers on the exciting photons' energy) are related to the photoinduced excitation of electrons from the valence band of alkali silicate glass to the levels situated above the electron mobility threshold. This UV irradiation causes the excitation of intrinsic luminescence centers that either can emit radiation and re-

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lax back to the ground state or can release electrons to the conduction band.[9] In the latter case, electron and hole trapping by intrinsic defects or extrinsic additives produces color centers in the medium that can absorb in near IR, visible, and UV spectral regions. Ionization of the intrinsic luminescence centers in alkali silicate glasses cannot be produced by photons with an energy less than 5.4 eV, i.e., under irradiation with wavelengths longer than 230 nm. However, in addition to this single-photon effect, photoinduced processes can be produced in glasses exposed to nanosecond pulses of visible and long-wavelength UV radiation as a result of two- and three-photon absorption.[10–13] In this case the color-center formation changes both the absorption coefficient[10–12] and the refractive index[13] of medium, leading to the formation of optical inhomogeneities. It was revealed recently[6] that discoloration of silicate glass can be produced by femtosecond IR pulses, but the mechanisms responsible for this phenomenon were not discussed in detail.

In the current experiments the color centers were created by femtosecond pulses from a 100-fs Cr:LiSAF laser system operating at 850 nm (see Section 2). Spectroscopic measurements of the transmitted laser light indicate extensive white-light generation in the media by the laser. White-light generation is generally considered to result from the variation of the refractive indices of condensed media induced by high-power picosecond and femtosecond laser pulses and the consequent changes in the amplitude, phase, and frequency of an exciting beam. These effects induce substantial spectral broadening of the transmitted beam in both the long-wavelength and the short-wavelength regions of the spectrum (white-light generation) owing to self-phase modulation, induced phase modulation, or cross-phase modulation (see Refs. 14 and 15 and references therein). The first research on white-light generation in crystals and glasses of which we are aware was performed in 1970.[16,17] It was found that five to ten small-scale filaments occurred under picosecond pulse excitation at 530 nm. The irradiance in these filaments could achieve powers of 10^{13} W/cm^2. In this case, intense radiation in a wide spectral range from 400 to 700 nm was observed. Similar phenomena were obtained under excitation with other wavelengths.[18,19] Induced spectral broadening of a weak picosecond pulse in glass was also demonstrated,[20] and the variation of the temporal shape of the laser pulse was explained.[21] A description and an explanation of the main mechanisms of this process were presented in Refs. 14 and 15. The phenomenon of white-light supercontinuum generation with femtosecond laser pulses has been used in a number of applications in different areas: generation of ultrashort pulses,[22] time-resolved absorption spectroscopy,[23] and optical fiber diagnostics,[24] for example.

It is well known that optical glass is the principal optical medium for laser applications that include femto second and picosecond devices. It is therefore important to know the stability of the optical parameters of glasses under these conditions. To the best of our knowledge, no experimental evidence has been published of the formation of residual photoinduced optical effects in glasses irradiated with high-power femtosecond IR laser light. In this paper we postulate that the short-wavelength edge of the white-light supercontinuum generated in glass by optical phase modulation is responsible for the formation of color centers at laser pulse intensities well below the threshold for self-focusing and laser-induced damage. This process has important implications for the design of high-intensity lasers, in that it limits still further the peak intensities that can safely be transmitted through optical glass.

2. EXPERIMENT

We studied samples of commonly used optical glasses: fused silica, commercial borosilicate glasses K8 (Russia) and BK7 (USA), and a high-purity silicate glass, $22Na_2O–3CaO–75SiO_2$, synthesized of high-purity materials in a laboratory method[25] that limits the concentration of absorbing impurities to less than 1 part in 10^6. The samples were 2 cm × 2 cm × 0.6 cm in size. All sides of the glass samples were polished so photoinduced coloration and luminescence could be observed in different directions.

The laser used for this investigation was a 100-fs Cr:LiSAF system operating at a wavelength of 850 nm.[26] The laser consisted of a Kerr-lens mode-locked Ti:sapphire laser followed by several stages of flash-lamp-pumped Cr:LiSAF amplifiers in a chirped-pulse-amplification architecture. For these experiments the single-pulse output of the first-stage regenerative amplifier was compressed to a pulse width 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 in 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 a specific distance in front of the sample. The spectrum of the light transmitted through the sample was monitored with a 25-cm grating spectrometer that had a resolution of ~10 nm, as illustrated in Fig. 1. The output of the monochromator was detected by a photomultiplier tube with a sensitivity that spanned the visible–UV regions of the spectrum. The signal from the photomultiplier was recorded by a Tektronix TDS 640 digital oscilloscope.

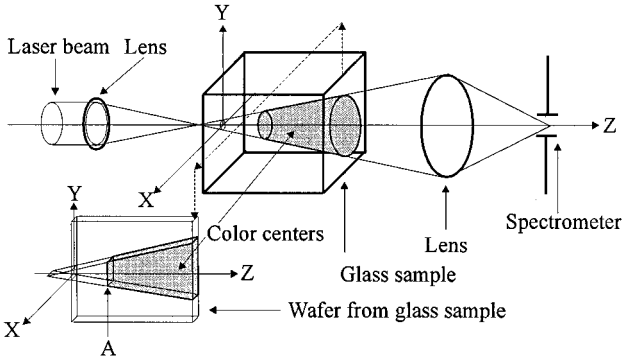

Fig. 1. Experimental setup for exposure of glass samples to IR femtosecond laser pulses, measurement of spectra and spatial distribution of photoinduced absorption, and measurement of spectra of emitted radiation.

The following observations were made. First, the laser beam was focused by a 100-cm lens and the sample was located at the beam waist. In this case the sample was irradiated with a quasi-parallel beam of ~40-μm diameter and an intensity as great as 2×10^{15} W/cm^2. At high irradiances ($\sim 1.5 \times 10^{14}$ W/cm^2) laser-induced breakdown was produced in all the glass samples. One could see radiation of laser-induced plasma emitted at the moment of breakdown and damage sites and coloration in the sample after exposure. These damage sites were as large as several hundred micrometers, depending on the irradiance. They were prolonged in the direction of the laser beam. It is clear that self-focusing participates in the process of femtosecond laser-induced damage of glasses, at least for the large-focal-length lens used in this experiment.

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 the 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 bulk glass was generated in the form of a cylinder or a cone with a shape similar to that of the laser beam (shaded areas in Fig. 1); i.e., the size of colored region was several tens of micrometers to approximately a nanometer. This dark track was directed along the direction of laser-beam propagation.

The absorption spectra of the original and the irradiated glasses were measured with a Perkin-Elmer 330 spectrophotometer. The transverse square of the light beam in this spectrophotometer is ~1 cm^2, which means that the absorption spectrum of the fraction of the glass sample that was colored by a single laser beam of $\sim 10^{-4}$-cm^2 area cannot be measured in the usual way. Therefore, to measure a spectrum of photoinduced absorption in the glasses, we exposed an approximately 1 cm $\times$ 1 cm fraction of the sample with a transverse size approximately 2 cm $\times$ 2 cm to laser radiation. The sample was placed after the focal plane to prevent self-focusing, and laser damage and was slowly scanned perpendicular to the direction of the propagation of laser beam (in the $X-Y$ plane in Fig. 1) with multiple lasers shots to produce a colored region of a size large enough to be used in the spectrophotometer.

The distribution of color centers in the direction of the laser-beam propagation in each glass sample was estimated by the following technique. The laser beam was focused with an f = 100 cm lens to produce a beam almost parallel to the focal plane. The sample was scanned in the $X-Y$ plane (Fig. 1) to produce a colored section of a few 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 (Fig. 1). This small wafer was then polished and analyzed along the Z axis 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 was equal to the distance from the front surface of the original sample in the Z direction). The spatial resolution of this method was ~0.1 mm. This approach provided a value for color-center absorption averaged over the visible spectrum.

3. RESULTS AND DISCUSSION

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. No sharp onset with intensity or threshold was detected. 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. In addition, the white-light distribution drifted during prolonged irradiation of the same site by multiple laser shots.

Glasses such as K8, BK7, and alkali silicate exhibited a bright blue luminescence and a dark track in the direction of laser-beam propagation. These dark tracks appeared after the first exposure to a laser pulse. The photoinduced coloration increased with the number of exposures. Both the luminescence intensity and the induced optical density were homogeneously distributed across the laser-beam diameter. No thin threads (as would be expected if self-focusing were occurring) were observed inside the area exposed to the laser beam. We could make the photoinduced coloration disappear by heating the samples to 150 °C for several minutes. No visible damage was observed after such heat treatment. No coloration in the visible region was observed in fused silica.

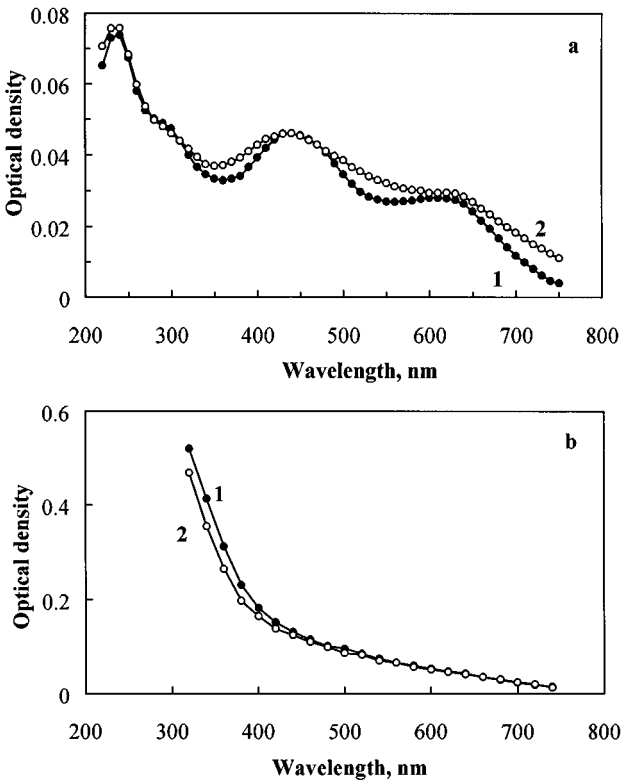

Fig. 2. Spectra of additional absorption of a, high-purity alkali silicate glass and b, K8 borosilicate glass exposed to 1, γ radiation or 2, femtosecond laser radiation at 850 nm. The thickness of both samples was 6 mm.

The absorption spectra induced in these samples by femtosecond laser pulses for both commercial and experimental glasses are shown in Fig. 2. In addition, Fig. 2 shows the absorption of color centers produced in the same glasses by γ radiation from a ^{60}Co radioactive source. Curve 1 of Fig. 2(a) shows the four maxima of the intrinsic color centers in the visible and UV regions that are well known for sodium silicate glass.[27,28] The same maxima can be observed in the femtosecond laser-induced spectra of alkali silicate glass in both the visible and the UV regions [Fig. 2(a), curve 2]. One can see the same shape of induced absorption in commercial borosilicate glass K8 (BK7) samples exposed to both γ rays and IR laser pulses. 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 fraction of the glass samples exposed to femtosecond IR laser pulses is caused by the color-center generation. The same color centers were formed in the glasses exposed both to IR femtosecond laser pulses and to the short-wavelength ionizing radiation. Blue luminescence was caused by excitation of the intrinsic centers of the glass matrix and by electron–hole recombination.[9] No laser-induced damage sites or threads were found in the colored tracks.

It has been shown[10,11] that two-photon ionization of the intrinsic states of vitreous media occurs when glasses are irradiated by laser pulses (the half-width was 10–30 ns) with photon energies of $E_g/2 < h\nu < E_g$, where E_g is the bandgap energy. E_g is ~6 eV for alkali silicate and borosilicate glasses. Electron and hole trapping and recombination lead to color-center formation and intrinsic luminescence, respectively. The photoinduced absorption spectra in the visible and the near UV exhibit the same shapes as those presented in Fig. 2 for the respective glasses. It is interesting to note that in the case of two-photon excitation by nanosecond laser pulses the color-center generation was clearly observed at an irradiance of $I = 10^{-3} I_0$ (where I_0 is the laser-induced damage threshold of glass).[29] An intrinsic luminescence was recorded in this case at intensity of $I = 10^{-4} I_0$. When glasses were exposed to radiation with $h\nu < E_g/2$ these phenomena were not observed, even at $I = 0.98 I_0$. This means that the third- and higher-order processes of photoionization did not occur in these glasses when the glasses were exposed to nanosecond pulses.

It is known[8] that for color-center generation the photon energy should be more than the threshold of the electron mobility (5.4 eV for the glasses used in this study). Therefore one can assume that the process of color-center formation during excitation at 850 nm is associated either with four-photon absorption of laser radiation (1.46 eV) or with linear or two-photon absorption of the short-wavelength fraction of the supercontinuum. However, as has already been noted, third- and higher-order processes were not observed in the same glasses investigated previously with nanosecond pulses. Nonetheless, we measured the color-center distribution in the glass sample to check for the possibility of four-photon ionization of the glass matrix by the femtosecond IR laser pulses. We found that the color centers and the intrinsic luminescence start only at some distance from the front surface of the sample (Fig. 3). This phenomenon was observed even when the sample was placed immediately adjacent to 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 photoinduced coloration close to the front surface in the region of 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 finding then leads us to suggest that color-center generation is caused by spectral broadening of the 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, Ref. 14) that the degree of spectral broadening is proportional to the length of the interaction between the exciting radiation and the medium. 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 interaction further we measured the dependence of the distance between the front surface and the colored region (points A in Figs. 1 and 3) on the irradiance. One can see from Fig. 4 that this distance is inversely proportional to the irradiance of incident laser beam. This result supports the supposition that the ionization of the glass is due to a two-step nonlinear process. The first step is a spectral broadening of transmitting laser radiation, and the second step is linear, or two-photon, absorption of the short-wavelength part of this broadened supercontinuum. As the laser intensity increases, the UV component of the supercontinuum increases and the interaction distance that will yield photons with energy enough for coloration is reduced.

To verify this assumption we made measurements of the spectrum of the output radiation from the samples investigated. We found for the samples of K8 and BK7 that the output radiation is a continuum spreading from the IR to 220 nm. This result is surprising because it well known that these glasses are opaque for wavelengths less than 330 nm. The only explanation for the observation of the UV light as short as 220 nm in the transmitted

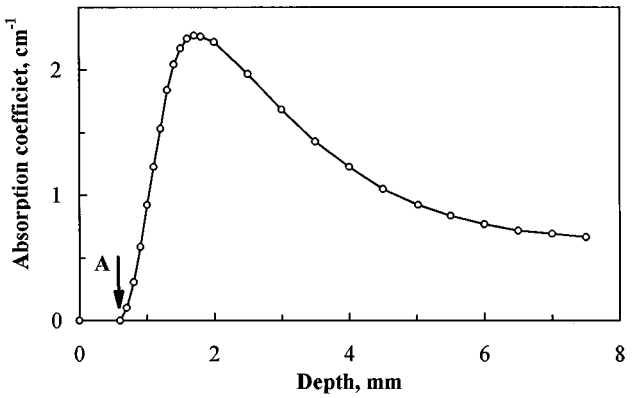

Fig. 3. Dependence of the additional absorption coefficient on the distance from the front surface of K8 glass (depth, axis Z in Fig. 1) irradiated by femtosecond laser radiation at 850 nm. The lens focal length was 100 cm; the sample thickness was 2 cm.

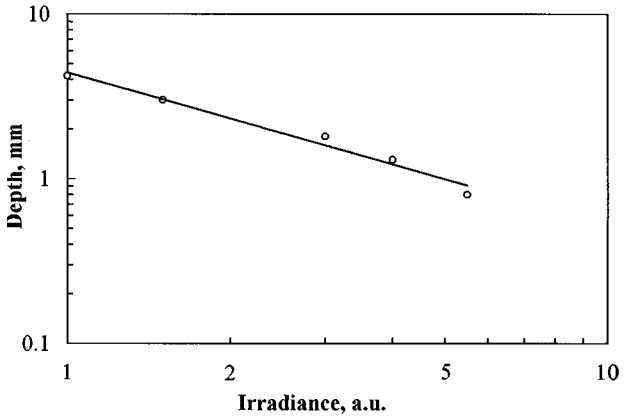

Fig. 4. Dependence of the distance between the front surface of the sample and the colored region (depth, marked A in Figs. 1 and 3) on the irradiance of the incident laser radiation. The solid line is a hyperbolic curve: $y \propto x^{-0.93}$.

spectra is that this radiation is generated at each point of the glass volume. Thus, only the thin layer near the rear surface contributes the short-wavelength radiation (220–330 nm) that can be detected outside the bulk glass. The absence of radiation detected with a wavelength of less than 220 nm can be caused both by a decrease in the efficiency of the supercontinuum emitting in the far UV region and by a sharp increase in the intrinsic absorption of glass at those wavelengths.

The observation of 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 $\sim 1\ \mathrm{cm}^{-1}$) of alkali silicate and borosilicate glasses is in the region of 210–220 nm. The maximum of the color-center generation spectrum in silicate glasses is placed near the intrinsic absorption boundary, and it extends to the long-wavelength side out to 230–240 nm. Hence the presence of such short-wavelength radiation transmitted within the glass sample, in accordance with data obtained in Refs. 8 and 9, proves that color-center generation results from the excitation of the intrinsic states of glasses by the short-wavelength part of the supercontinuum. This excitation can be created both by a linear absorption of radiation in the region 220–240 nm (Ref. 9) and by nonlinear absorption in the region 250–400 nm.[10] To clarify the relative roles of these processes in glass matrix excitation requires additional experiments. One can see some decrease of the induced absorption at long distances from the front surface (Fig. 4). This phenomenon can be caused by several physical mechanisms, and it is necessary to study this process separately.

The results depicted above suggest the need for a new model to describe the processes that occur in multicomponent silicate glasses when they are irradiated by femtosecond IR laser pulses. This model takes into account those processes that occur at intensities much less than the threshold for self-focusing and laser breakdown. The model is illustrated in Fig. 5. 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. 5(a)]. The bandgap in silicate glasses is ~ 4 times greater than the energy of the incident photons (1.46 eV), as can be seen from a comparison of Fig. 5(a) and the left-hand part of Fig. 5(b). No photoinduced coloration owing to four-photon ionization occurred. Therefore no coloration can be seen near the front surface of the sample [left-hand part of Fig. 5(c)]. The spectral width of the laser beam is broadened in the process of pulse transmission through the glass sample in the direction of the Z axis [Fig. 5(b)]. This broadening is assumed to be linear in this figure in accordance with Ref. 14. At the distance from the front surface (points A in Figs. 1, 3, and 5) 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 of the bandgap (E_g), two-photon ionization of glass matrix occurs if the intensity is more than 10^6 W/cm^2.[10] Coloration of the bulk glass then results from electron and hole trapping in the region $Z > A$ [Fig. 5(c)]. The process of single-photon ionization of the glass matrix begins at $Z > B$ (Fig. 5), which corresponds to 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 of irradiance. It should be noted that glass is opaque for these photons and that only a thin layer near the back surface of the sample can emit this radiation outside the glass. This is why the intensity of the short part of the UV radiation measured outside the glass sample is so low.

The absence of visible coloration in fused silica after multiple irradiation by femtosecond laser pulses at 850

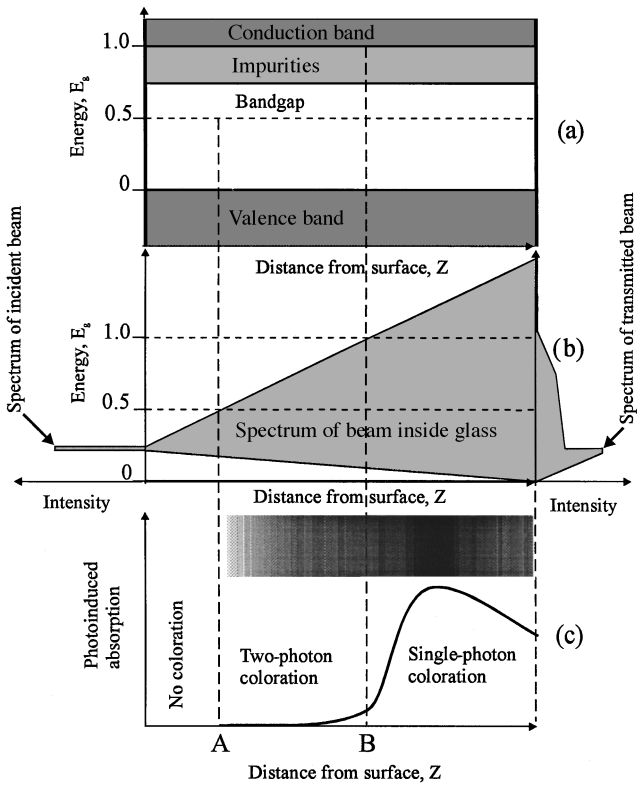

Fig. 5. Photoinduced processes in a dielectric material exposured to femtosecond IR pulses.

nm with irradiance up to the damage threshold can have either of two causes. First, the bandgap 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 amount of IR radiation that is converted into supercontinuum radiation in this short-wavelength UV region is consequently much less, and no significant ionization of fused silica occurs. Second, color centers produced in high-purity fused silica have low absorption in the visible region and may not be seen.[30]

As was mentioned in Section 1, in previous studies of laser-induced damage of crystals and glasses under femtosecond IR laser irradiation, multiphoton absorption of the laser radiation was considered the mechanism of initial free-electron generation for avalanche ionization.[2–5] The results obtained in the present paper show that photoionization of dielectrics with large bandgap energies, such as silicate glasses, is caused by absorption of the short-wavelength part of the supercontinuum that is generated in the all materials and not by multiphoton absorption of the laser radiation. This finding suggests that the mechanisms responsible for laser-induced damage of these materials under femtosecond radiation are connected with the photoinduced processes described above and demand further investigation.

4. CONCLUSION

We have observed, for the first time to our knowledge, coloration of multicomponent silicate glasses following their exposure to IR 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 photoionization and the consequent trapping of electrons and holes. The photoionization results from absorption of the short-wavelength component of the supercontinuum that is generated in the volume of glass as a result of spectral broadening of femtosecond laser pulses. The supercontinuum extends to the short-wavelength UV region even if the glass is opaque in that region. Fused silica exhibits the same spectral broadening, but color-center formation in the visible did not occur at irradiance up to the laser-damage threshold.

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