

L.B. Glebov

School of Optics/CREOL, University of Central Florida, P.O. Box 162700 Orlando, FL, 32816-2700 USA

1. Introduction

An extensive use of powerful laser radiation in such areas as optical communication and data storage, laser processing, photolithography, etc. attracts more and more attention to the problems of both stability and photo-controlled transformations of optical materials under intensive optical illumination. Interaction between intensive optical radiation and matter is usually connected with different thermal effects and different types of photoionization. The history of the research in this direction is rather long and counts hundreds of publications dedicated to features of optical absorption, photoinduced phenomena, and laser-induced damage of silicate glasses. The discussion will be concentrated at the consequent consideration of features of optical absorption, linear photoionization, and different mechanisms of nonlinear photoionization. The glasses for consideration are the main types of glasses used in optical devices, such as alkaline-silicate, sodium-calcium-silicate, borosilicate, and lead-silicate glasses. This survey does not provide the whole list of references (it is huge) but shows a number of publications which include necessary references.

2. Absorption Spectra

The spectral properties of different glasses are well known and were described in many articles and classic books [1-2]. In undoped oxide glasses, the main components absorbing in the IR, visible, and UV spectral regions are impurities of iron and water. However, the problems of comprehensive description of the absorption spectrum of silicate glasses and determination of absolute concentrations of ferric, ferrous, and hydroxyl ions are not solved up to now. An important problem, which impedes the analysis, is a strong overlapping of absorption spectra of different species. A new approach was found in Ref. [3-5], which allowed separating of overlapped spectra and describing of absorption spectra of silicate glasses as a sum of absorption spectra of L-centers (intrinsic UV edge), Fe³⁺ (UV and visible ranges), Fe²⁺ (UV, visible, and IR ranges), and OH⁻ (IR range). It was shown in Ref. [6] that the coefficient of intrinsic absorption of silicate glass (Fig. 1) has an exponential dependence on wavenumber. For the typical silicate and borosilicate glasses, intrinsic absorption edge is placed in the range of 46000 - 48000 cm⁻¹ (213 nm, 5.8 eV) the absorption coefficient tripling each 1000 cm⁻¹. Intrinsic absorption edge of lead silicate is placed at about 30000 cm⁻¹ (310 nm, 4 eV).

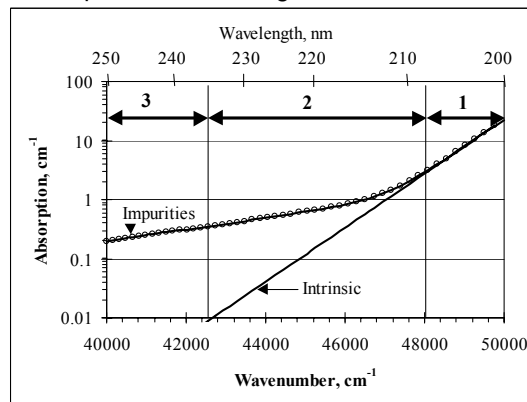


Fig. 1. Spectral regions of different types of electronic excitations generated by optical irradiation.

- Circles- absorption spectrum of Na₂O-CaO-MgO-SiO₂ glass having about 1 ppm iron.
- 1 – excitation to intrinsic delocalized states and direct generation of electrons and holes.
- 2 – excitation to intrinsic localized states and thermoinduced generation of electrons and holes.
- 3 – excitation to the levels of impurities.

3. Intrinsic Photoionization

The spectral region of optical radiation causing coloration of silicate glasses is ranged from 200 to 230 nm [1] It was found [7] that position and shape of color center generation depended on thickness of the sample and temperature of irradiation. These features allowed calculating of activation energy of the process of color center generation (Fig. 2). One can see in Fig. 2 that activation energy increases with decreasing of photon energy of exciting radiation (increasing of wavelength) and drops to zero level at approximately 48000 cm^{-1} (208 nm, 5.9 eV). This value signifies a position of the electron mobility threshold because it is necessary to get additional energy for color center generation (electron and hole migration) if photon energy is less than this value and no additional energy is consumed if photon energy is higher than this value. Actually, this is a definition of the bottom of a conduction band in crystal which corresponds to the intrinsic absorption edge. For alkaline-silicate glasses, a position of an electron mobility threshold corresponds to intrinsic absorption coefficient of about 1 cm^{-1} .

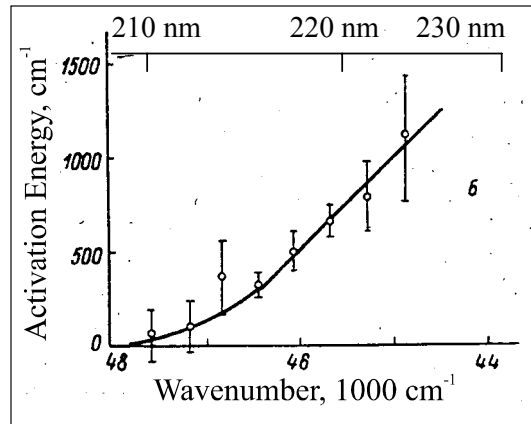


Fig. 2. Dependence of activation energy of intrinsic color center generation in $\text{Na}_2\text{O}-3\text{SiO}_2$ glass on wavelength of exciting radiation

One can distinguish three different regions in an absorption spectrum of glass depicted in Fig. 1. The first region in the short wavelength side of spectrum ($N > 48000\text{ cm}^{-1}$, $\lambda < 208\text{ nm}$) is represented mostly by the levels of the intrinsic absorption centers which are excited to the delocalized states releasing electrons and holes. Displacement of electrons and further generation of intrinsic radiation defects occur with no additional energy consumption. The second region ($42000\text{ cm}^{-1} < N < 48000\text{ cm}^{-1}$, $235\text{ nm} > \lambda > 208\text{ nm}$) corresponds to the excitation of those centers to localized states placed below an electron mobility threshold. In this case, a displacement of electrons occurs by thermo-induced hopping. The third region placed in the long wavelength side ($N < 42000\text{ cm}^{-1}$, $h\nu < 5.2\text{ eV}$, $\lambda > 235\text{ nm}$) is represented by impurities absorption only. Excitation of impurities results in their luminescence or ionization. No intrinsic hole centers can be generated in this process and no intrinsic luminescence can occur as the result of recombination of electrons with ionized impurities.

4. Phenomena Caused by Photoionization

Excitation of intrinsic centers of glass results in a number of processes. The first one is an intrinsic luminescence with maximum at 365 nm (Fig. 3) [7]. This luminescence shows fast (about $1\text{ }\mu\text{s}$) and slow (up to several days at low temperature) components. The fast one is a result of radiative transition of electron from excited to ground state in the luminescence center. The second one is the result of recombination of electron with hole. An excitation spectrum of luminescence coincides with the color center generation spectrum. This means that these luminescence centers form the intrinsic absorption edge. Chemical interpretation of the luminescence center (L-center) is a quasi-molecular group consisting of non-bridging oxygen and alkaline ion. Photoionization of silicate glass means an electron release from L-center and creation of ionized L^+ -center as an intrinsic hole center and a movable electron which is trapped by different defects in glass network. It was found that intrinsic luminescence is polarized under excitation by polarized light. This means that alkaline-silicate glass is homogeneous and isotropic in a macro-

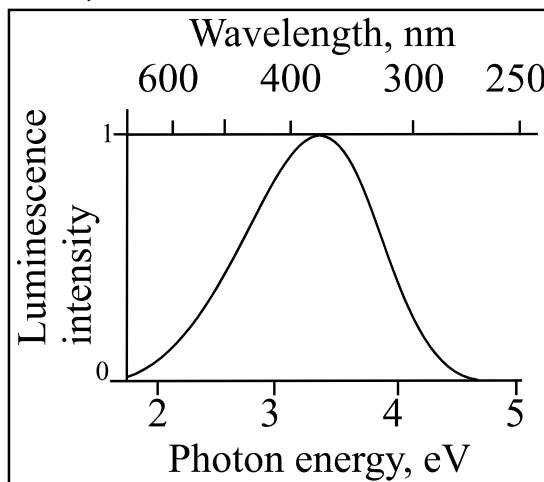


Fig. 3. Spectrum of intrinsic luminescence of $\text{Na}_2\text{O}-3\text{SiO}_2$ glass

scale but possesses a strong anisotropy at atomic micro-scale. Moreover, it is evidence that holes are immobile under mentioned conditions because an ionized hole must conserve its orientation to emit a photon of luminescence polarized in the same direction as the exciting photon.

Electrons and holes generated by ionizing radiation are trapped in different defects of glass matrix or crystalline lattice. Those trapped electrons and holes cause an additional absorption of an ionized material and they are usually called color centers [1, 7]. Absorption spectra of color centers in silicate glasses were studied in hundreds of works and summarized in a number of surveys. An illustration of such spectra from Ref. [7] is shown in Fig. 4. Seven hole and five electron color centers were found in sodium-silicate glass. An absorption induced at low temperatures has strong IR component caused by electron centers which are unstable at room temperatures. The presence of hole bands in an induced absorption spectrum as an evidence of glass matrix ionization while electron bands can be a result of ionization of different impurities.

Trapping of electrons and holes at defects causes atomic relaxation in those sites. This atomic relaxation results the dramatic increase of volume of those centers and, therefore, in an expansion of the ionized area, stress generation in a surrounding glass matrix (birefringence), and in a refractive index variation [8, 9]. Bleaching of color centers results in the shrinking of the bleached area. Refractive index increment of silicate glass caused by photoionization of cerium is shown in Fig. 5. One can see that the typical value of photoinduced refraction is in the range of several ppm. This effect disappears after thermal bleaching of radiation defects. It was found that additional energy introduced in glass by photoionization is cumulated in elastic deformation of glass matrix surrounding an exposed area.

It was found [10] that generation of radiation defects by UV illumination resulted in variations of the etching rate of silicate glasses in hydrofluoric acid. Both increase and decrease of the etching rate up to 50 % was found depending on glass composition and UV illumination conditions. Photoinduced etching was observed for a variety of commercial and experimental glasses. As an example, a surface profile of borosilicate glass BK-7 after exposure to UV radiation of Xe-lamp and etching in HF is shown in Fig. 6. One can see the almost vertical walls of the exposed area. It is remarkable that the roughness of the etched surface is less for the exposed area than for the unexposed one. Thus, photoionization of silicate glass matrix causes electron and hole mobility following by intrinsic luminescence, color centers generation, a refractive index increment, expansion of an exposed area, and change in rate of chemical etching. All these phenomena can be used for photoinduced processing, such as data storage,

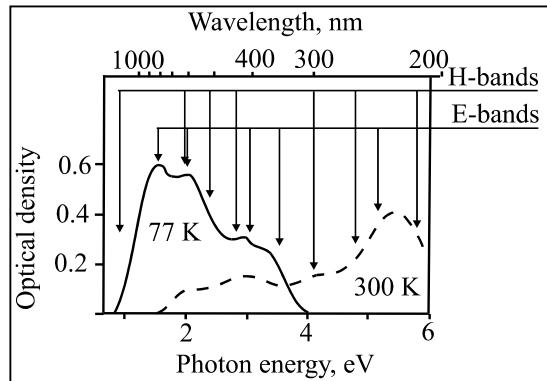


Fig. 4. Absorption spectra of intrinsic color centers in $\text{Na}_2\text{O}-3\text{SiO}_2$ glass

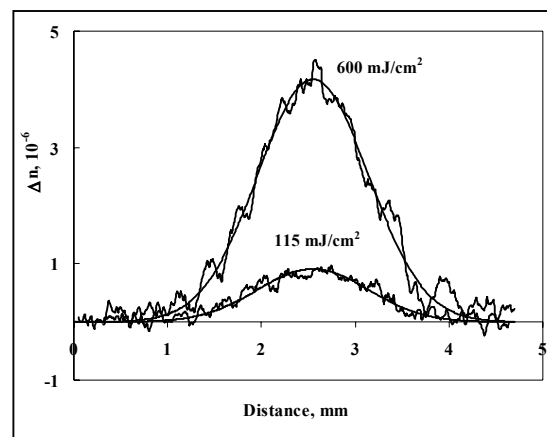


Fig. 5. Profile of induced refractive index in $\text{Na}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass exposed to UV radiation

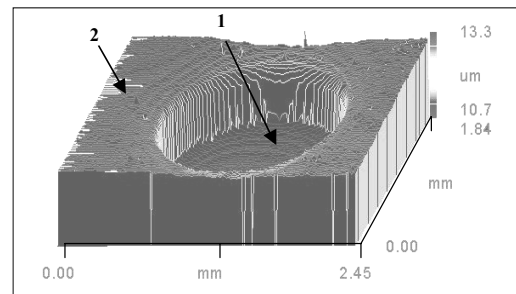


Fig. 6. Profile of the surface of borosilicate glass BK-7 after etching in HF. 1 – area exposed to UV radiation

hologram recording, optical element fabrication, etc.

5. Multiphoton ionization

It was found in Ref. [11] that after exposure to radiation of third and fourth harmonics of Nd-laser a gray cone directed along the laser beam propagation could be observed in vicinity of focal plane of exciting radiation. Absorption spectrum of exposed area shows the same absorption bands of intrinsic hole color centers as were generated by exposure within color center generation spectrum (Fig. 7). The presence of hole color centers means that glass matrix was ionized by laser radiation even photon energy was not enough for linear photoionization. Induced absorption was observed if irradiance exceeded value of 10^6 W/cm^2 . It was found that final concentration of color centers resulted from competition between two-photon ionization of glass matrix and single-photon optical bleaching of color centers by laser radiation. Two-photon color center generation was followed by intrinsic luminescence in all cases. No color center generation and intrinsic luminescence were detected after irradiation by first and second harmonics of Nd-laser at irradiance ranging up to laser-induced damage threshold at 10^{12} W/cm^2 . This means that no detectable multi-photon excitation of glass matrix occurs in silicate and borosilicate glasses. The single exception from this rule was a demonstration of three-photon coloration of lead-silicate glass by the second harmonics at 532 nm in Ref. [12]. To the best of our knowledge, no other evidences of three-photon absorption in silicate glasses were published. Moreover, no evidences of multiphoton ionization of silicate glass matrix were observed for photon number more than 3.

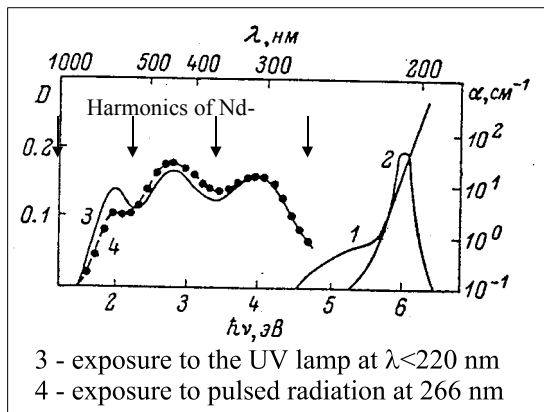


Fig. 7. Additional absorption induced in $\text{Na}_2\text{O}-3\text{SiO}_2$ glass. (1) absorption spectrum, (2) color center generation spectrum, (3) and (4) induced absorption spectra.

6. Ionization by cooperative sensitization

It is important to note that multiphoton absorption is not a single mechanism of nonlinear ionization. It can be caused by a number of different mechanisms. One of such mechanisms was discovered in borosilicate glasses doped with CuCl microcrystals [7]. This glass belongs to a group of a photochromic glass. The mechanism of its coloration is illustrated in Fig. 8a. Absorption of UV photon by an exciton in CuCl microcrystal causes its decay with a release of electron and creation of two radiation defects Cu^{2+} and Cu^0 . Colloidal particles of Cu are responsible for additional absorption in the visible range. It was found that illumination of this glass with visible and even IR radiation having photon energy below of the threshold of CuCl photoionization results in color center generation. The mechanism of nonlinear ionization is shown in Fig. 8b,c. Two color centers created by a preliminary UV irradiation (a few seconds of standard laboratory illumination is enough) absorb two low-energy photons and occupy excited states. After that, both centers relax to the ground state and synchronously transfer energy to the next center and create an exciton in a nonradiative process. Then a new color center is created by the mechanism depicted in Fig. 8a. This cycling process enable increasing of a number of color centers up to saturation. Such mechanism of cooperative multiplication of color centers occurs at a very low power density about 1 W/cm^2 for two-center sensitization by visible radiation and

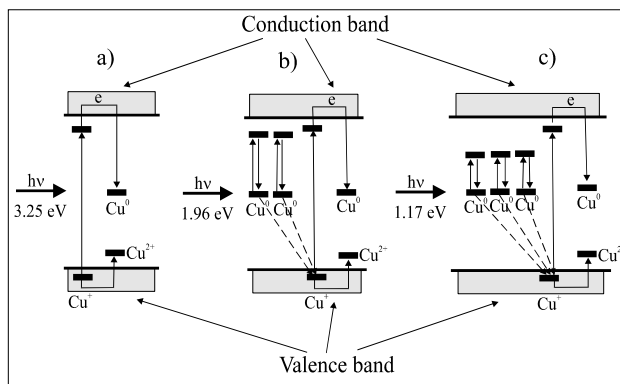


Fig. 8. Energy diagram for color center generation in CuCl-doped glass. a) – single-photon ionization of exciton. b) and c) two- and three-photon cooperative self-multiplication of color centers.

10^6 W/cm^2 for three-center sensitization by IR radiation. Thus, a linear absorption of byproducts of the initial photochemical reaction can be a catalyst for the consequent photoinduced processes.

7. Ionization by spectral broadening of exciting radiation

It was found in Ref. [13] for silicate and borosilicate glasses that exposure to radiation of femtosecond laser pulses with $\lambda=850 \text{ nm}$ (1.5 eV) with power density about 10^{12} W/cm^2 causes generation of intrinsic hole color centers. This means that glass matrix ionization occurs while at least four photons are necessary to overcome the threshold of ionization. It was found that this process could not be ascribed to any type of multiphoton absorption. Measurement of spectrum of transmitted beam has shown that UV radiation up to 220 nm (5.6 eV) was detected. It is remarkable that even for commercial glasses with an extrinsic absorption edge at 330 nm this far UV radiation was detected. The mechanism of photoionization is depicted in Fig. 9. One can see that after some distance of laser beam propagation in the medium, the short wavelength component of the beam has enough photon energy for two-photon ionization and after some additional distance even single-photon ionization occurs. Thus, ionization by spectral broadening (ISB) is the mechanism of color center generation by IR femtosecond pulses. ISB has a remarkable feature to penetrate into the medium which is transparent for IR radiation, and then to show ionization ability similar to X-rays.

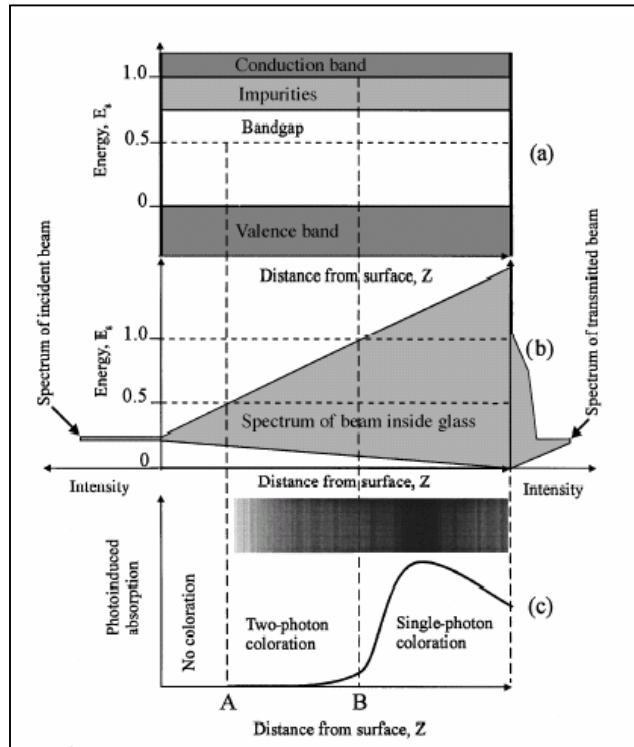


Fig. 9. Diagram of photo-induced processes in a dielectric material under exposure to femtosecond IR pulses. (a) – energy diagram of electron levels, (b) – spectral broadening of propagating laser pulse, single- and two-photon color center generation.

8. Ionization by the third harmonic generated in glass

A series of Bragg gratings in photo-thermo-refractive glass [14] was studied under excitation by radiation of Ti-sapphire laser with pulses of 125 fsec at 775 nm providing power density $\sim 10^{12} \text{ W/cm}^2$ [15]. The experimental geometry is shown in Fig. 10. It was found for PTR glass having a grating phased to satisfy the Bragg conditions for radiation at 775 nm, that two beams at the wavelength of 258 nm, which corresponds the third harmonic of the fundamental wave, appeared. The UV beams were in the same plane and placed between the transmitted and diffracted beams of the fundamental wave. UV beams satisfy Bragg conditions of the recorded grating. The efficiency of THG was $\sim 0.01\%$. This means that UV radiation with photon energy of 4.8 eV and power density about 10^8 W/cm^2 is propagating in the medium. It is clear from Section 5, that this UV radiation can ionize any silicate glass by means of two-photon absorption.

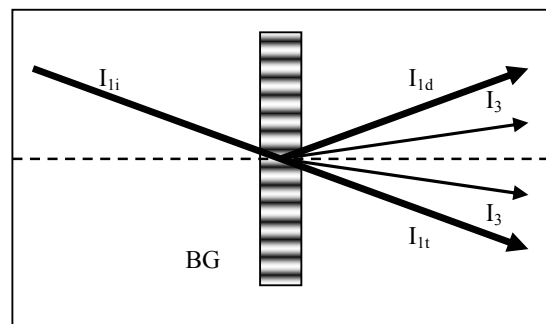


Fig. 10. Geometry of third harmonic generation in a transmitting Bragg grating (BG) recorded in PTR glass, I_{ii} , I_{it} , and I_{id} – incident, transmitted and diffracted beams at 775 nm, I_3 – third harmonic beams at 258 nm

Conclusions

- Absorption spectra of undoped multicomponent silicate and borosilicate glasses consist of such main components as intrinsic electron absorption of L-centers in far UV region (~200 nm), and spectra of ferric (Fe^{3+}), ferrous (Fe^{2+}), and hydroxyl (OH^-) ions. Intrinsic absorption edge for lead silicate glasses is placed at ~300 nm.
- Photoionization of glass matrix occurs under excitation by photons with $h\nu > 5.2$ eV ($\lambda < 235$ nm). Irradiation with $h\nu > 5.9$ eV ($\lambda < 210$ nm) results in electron excitation to delocalized states. Consequent electron and hole trapping by glass matrix defects results in intrinsic color center generation.
- Two-photon ionization of glass matrix occurs at irradiance above 10^6 W/cm² and photon energy above 3 eV (½ of bandgap for silicate and borosilicate glasses). Three-photon ionization was observed at photon energy above 1/3 of bandgap for lead-silicate glass.
- Two- and three-center cooperative ionization by visible and IR radiation followed by color center generation was observed in CuCl-doped glasses which were previously exposed to UV.
- Color center generation under femtosecond IR pulse irradiation with irradiance above 10^{12} W/cm² resulted from glass ionization by spectral broadening (ISB).
- Third harmonic generation in Bragg grating recorded in silicate glass was detected under irradiation with femtosecond IR laser pulses having irradiance of about 10^{12} W/cm².

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