Optical absorption and ionization of silicate glasses

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ABSTRACT

Intrinsic, extrinsic (transition metals and hydroxyl), and induced (color centers) absorption of multicomponent silicate glasses in UV, visible and near IR spectral regions are described. Parasitic effects influencing absorption measurements are discussed. Excitation to the intrinsic absorption band results in intrinsic luminescence and ionization followed by color center generation and phosphorescence. The thresholds of electron and hole mobility in glass network are found in the far UV region. The hole-centers generation as a criterion of substance ionization is proposed. A number of nonlinear mechanisms of glass ionization are discussed. Two-photon ionization was detected in alkaline-silicate glasses exposed to high-power laser radiation in nano- and picosecond regimes. . Three-photon ionization was detected in lead-silicate glasses. No reliable data on multiphoton ionization (with number of photons more than 3) of glasses are found. Two- and three-photon cooperative self-multiplication of color centers was found in CuCl-doped glasses. Glass matrix ionization by spectral broadening of femtosecond IR pulses is described. Thermal and surface ionization of glass under intense irradiation by pulsed lasers is described.

1. INTRODUCTION

An extensive use of powerful laser radiation in such areas as military and civilian optical communication and data storage, laser processing of different materials, photolithography, etc. attracts more and more attention to the problem of stability of optical materials under intensive optical illumination. Silicate glasses are still the main components of the most of optical devices and therefore their durability is of high importance for the mentioned applications. The problem of 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. This paper is directed to the survey of publications dealing with linear and nonlinear intrinsic photoionization of silicate glasses as the ultimate mechanisms providing the upper limit of durability of glasses used under intense optical illumination. The main part of discussed results was performed by research teams at Vavilov State Optical Institute at St. Petersburg, Russia, Solid State Physics Institute at the State University of Latvia (Riga, Latvia), and Center for Research and Education in Optics and Laser at the University of Central Florida, Orlando, Florida, the USA.

The problem of interaction of optical radiation with light is usually considered in the frame of excitation of different electronic states in a condensed matter in according with energy zone diagram. The traditional approach is based on consideration of electron states in valence and conduction bands along with localized states of impurities and defects in crystalline lattice. Excitation of electrons from valence band or ground states of impurities or defects creates mobile electrons in the conduction band. Electron and hole migration followed by trapping or recombination is the basis for the most part of photoinduced processes. It is important to note that chemical bonding in glasses is very similar to that one in crystals of the same composition. This is why positions and structure of the main absorption bands are very similar in crystalline and vitreous modifications of each material. The most important difference for glasses is the significantly lower mobility of charge carriers. This difference is caused by a number of localized levels in the range of the bottom of conduction band in glasses which is shown in Fig. 1 for the dielectric vitreous matter. This theoretical background started with Mott's works at 60's [1], is the powerful approach for the analysis of optical properties and photo-stimulated phenomena in glasses. It is important to emphasize that localized states in a bandgap of vitreous matter cover only the small area close to the bottom of the conduction band but do not spread out far to the bandgap (e.g. this is why water is transparent).
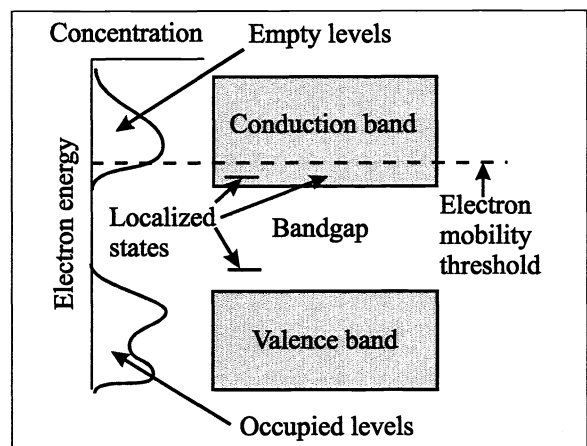

Fig. 1. Energy diagram of electron states in glass

The discussion will be concentrated at the consequent consideration of features of optical absorption, linear photoionization, different mechanisms of nonlinear photoionization. We will try to separate the roles of different types of impurities in the total process of photoionization and emphasize the intrinsic mechanisms. 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 OF SILICATE GLASSES

In oxide glasses, the main components absorbing in the IR, visible, and UV spectral regions are iron and water. Their spectral properties in different glasses are well known from fifties and were described in many articles and classic books [2,3]. 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. One of the important problems which impedes the analysis, is a strong overlapping of absorption spectra of different species. Two recent publications [4,5] have shown a new approach for the overlapped spectra separation and revealed spectral shapes of ferrous ion in the ranges with strong overlapping with ferric, hydroxyl and intrinsic absorption. It was found in Ref. [4,5], that absorption spectra of Na_2O-CaO-MgO-SiO_2 glasses could be described as a sum of tabulated absorption spectra of L-centers (intrinsic UV edge), Fe^{3+} (UV and visible ranges), Fe^{2+} (UV, visible, and IR ranges), and OH^- (IR range). However, no data were published on the properties of intrinsic absorption edge depending on glass composition and melting conditions, and on absorption in the middle IR range where the strong overlapping of ferrous, hydroxyl, and intrinsic vibrational spectra occur. The most recent publication [6] shows the more detailed model of absorption spectra of silicate glasses.

Glass composition for the following absorption spectra is similar to the standard float glass used in the glass industry, mol.%: $13Na_2O$-$10CaO$-$6MgO$-$71SiO_2$. Fe_2O_3 was added in amounts ranging from 0.001 to 0.9 wt.%. Purified raw materials with the sum of transition and heavy metals less then 10^{-4} wt. % were used. Glasses were melted in an electric furnace in fused silica crucibles. Silica and carbonates of sodium, magnesium, and calcium were used to produce a neutral glass. To produce oxidizing melting conditions, part of sodium oxide was introduced as sodium nitrate or oxygen was bubbled through the liquid glass in the furnace. Absorption spectra were measured using double beam spectrophotometers (Cary 500, Perkin-Elmer Lambda 9, and Perkin-Elmer FTIR) in the spectral region from 200 to 10000 nm (50000-1000 cm^{-1}). Optical density (D) was measured on 2 to 4 polished samples of each type with thickness (l) from 0.1 mm to 10 mm. A series of measurements for samples with different thickness at different spectrophotometers were used to calculate an absorption coefficient in the whole spectral region. The root mean square deviation for different measurements of the same samples did not exceed ±5% for the entire spectrum.
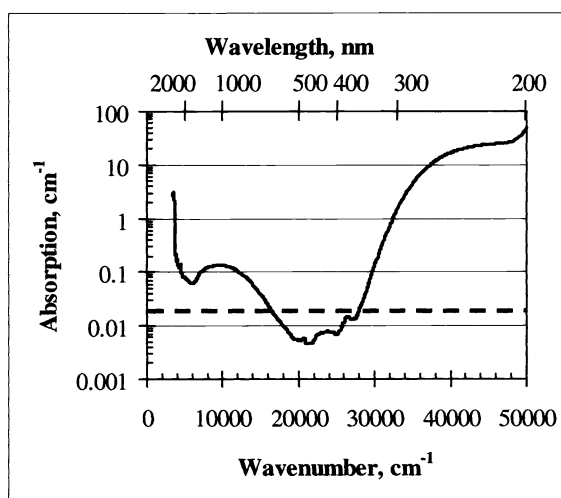

Fig. 2. Absorption spectrum of typical silicate glass. Dashed line shows the level of reliable measurements by commercial spectrophotometer for sample thickness below 1 cm.

The absorption spectrum of silicate glass with iron concentration corresponding to typical contamination in commercial manufacturing process (0.01 Wt.%) in the range from 200 to 10000 nm (50000 – 1000 cm^{-1}) is shown in Fig. 2. It was found in Ref. [4-6] that it contains five main components, which are caused by L-centers of the glass, Fe^{3+}, Fe^{2+}, hydroxyl groups, and intrinsic glass network vibrations. It allows us to assume that experimental absorption spectrum of silicate glass is the sum of individual absorption spectra of these species:

$$A_{rec,k}(N) = A_L(N) + A_v(N) + c_{Fe3,k}A_{Fe3}(N) + c_{Fe2,k}A_{Fe2}(N) + c_{OH,k}A_{OH}(N) \quad (1)$$

where $A_{rec,k}$ is the recorded absorption coefficient of the glass sample #k, A_L is the absorption spectrum of intrinsic glass centers (L-centers) [5], A_v is a glass matrix vibrational absorption spectrum, A_{Fe3}, A_{Fe2} and A_{OH} are specific absorption spectra of

ferric, ferrous and hydroxyl ions, respectively, $c_{Fe3,k}$, $c_{Fe2,k}$ and $c_{OH,k}$ are the concentrations of ferric, ferrous and hydroxyl ions in the glass #k, respectively, and N is a wavenumber.

It is important in the beginning to discuss real accuracy of absorption spectra measurements. The use of commercial spectrophotometers available on the market provides photometric accuracy of optical density measurement ±0.001 or even better which creates an illusion of high accuracy of absorption coefficient measurement. However, fluctuations of repeated measurements of optical density at the same sample are almost an order of magnitude higher then photometric accuracy and approach the value of ±0.005 (±1% of transmission) [7]. This uncertainty is caused by fluctuations of reflection from the surfaces of the sample because of variations of the properties of impurity layers deposited on the surface of the samples. Usually, actual reflection from the glass surface is less than Fresnel reflection. This is why those fluctuations are usually responsible for negative data observed after subtracting of Fresnel reflection in the case of high purity materials with low level of absorption (Fig. 3). Total concentration of iron in Na_2O-CaO-MgO-SiO_2 glass that was used for measurement depicted in Fig. 3, was about 0.00015 Wt.%. In glasses with normal commercial level of

Fig. 3. Absorption spectrum measured in high-purity Na_2O-CaO-MgO-SiO_2 glass 1 mm thick. Fresnel reflection calculated from refractive index dispersion.

contaminations, no negative data are usually occur but values of absorption coefficients calculated with the use of Fresnel reflection for samples with thickness ranged from 1 to 5 mm, are not reliable in the range below 0.02 cm^{-1} (dashed line in Fig. 2). In contrary to the visible region, calculation of surface losses in the far UV region shows significant surface absorption (up to 0.01) which is additional to Fresnel reflection. Properties of the layers precipitated on the surfaces are responsible for a number of photoinduced phenomena, such as intensive luminescence, surface ionization and even triggering the laser-induced breakdown. Those layers can be eliminated by several types of chemical or optical treatments but they are restored after several seconds of exposure to standard lab atmosphere. An exact chemical composition of the layers is unknown, however, the role of hydro-carbonates deposited on the surface of glass (and other materials) is essential.

It was shown in Ref. [5] that intrinsic absorption of the studied glass (Fig. 4) has exponential dependence on wavenumber in accordance with the modified Urbach's rule[5]:

$$A_L(N) = \exp\frac{N - N_0}{\Delta_e}, \qquad (2)$$

where N_0 is position of the intrinsic absorption edge at the absorption coefficient value of 1 cm^{-1} and Δ_e is the spectral range in which absorption coefficient increases by e=2.718 times. For the measured samples, N_0=47000 cm^{-1} and Δ_e=870 cm^{-1}. The slope of intrinsic absorption in this glass is almost equal to that of Na_2O-$3SiO_2$ glass but the position of intrinsic edge is shifted to the short wavelength region by about of 1000 cm^{-1} (4 nm). It is important to emphasize that intrinsic absorption edge of standard silicate glass is placed at 47000 cm^{-1} (**213 nm, 5.8 eV**). Positions of the intrinsic absorption edges of most silicate and borosilicate optical glasses are in the same region with deviations of several nanometers only. Numerous data reporting the multicomponent silicate glasses have absorption edge in the near UV region (e.g. Ref. [8, 9]) were based on

Fig. 4. UV absorption spectra of Na_2O-CaO-MgO-SiO_2 glass. Dotted line – experimental spectrum of high purity glass. Strait line – exponential intrinsic absorption.

the measurements of extrinsic absorption (described below) in glasses with significant level of impurities which screen intrinsic absorption (see explanation for Fig. 6 below). In early publications (see survey in Ref. [10]) an intrinsic absorption edge was considered as completely determined by glass composition. However, it was found recently that Na_2O-CaO-MgO-SiO_2 samples with the same composition but melted in different redox conditions, show shift of N_0 up to 400 cm^{-1} (less than

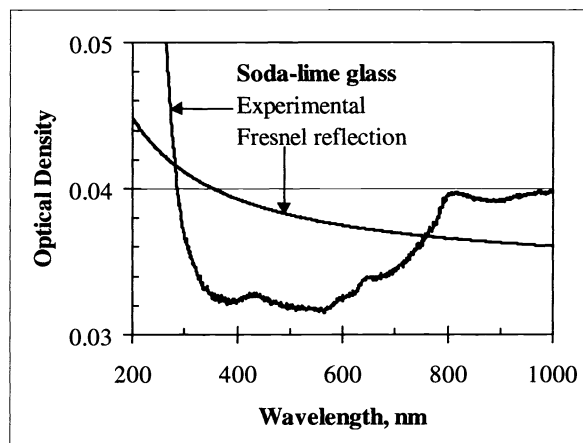2 nm) and variations of the slope in the range of 10 %. Partial substitution of oxygen (5 mol.% Na_2O) with fluorine (10 mol.% NaF) results in the shift of the intrinsic edge to the short wavelength region for about 700 cm^{-1}. It signifies that fluorine substitutes the most weekly bonded non-bridging oxygen ions which are responsible for the utmost part of the absorption edge. It should be noted that this shift is rather small, only about 3 nm and cannot change in general the value of intrinsic absorption edge which is placed in multicomponent silicate glasses at approximately 200 nm (6 eV). Intrinsic absorption edge of lead silicate glasses shifted to the long wavelength side about 30000 cm^{-1} (**310 nm, 4 eV**).

Methods of separation of completely overlapped spectra are described in details in Ref. [4, 5] and we will discuss only the results of those methods application for spectral analysis of doped silicate glasses. It is known [2, 3] that main agent responsible for near IR absorption in silicate glasses is ferrous ion (Fe^{2+}) with its absorption band in the range of 1000 nm. More recent research shows a more complex picture illustrated in Fig. 5. One can see the whole specific absorption spectrum of Fe^{2+}. It was defined as $A_{Fe2}(N)$ in formula (1). Concentration of iron is shown in Wt. % of iron but not in the traditional units of iron oxide. This was made to avoid recalculations between different molar weights of different oxides in the case of variations of redox state of iron resulted from chemical or photoinduced reactions. No special efforts were made do ascribe different part of ferrous absorption to any specific transitions in this ion. Specific absorption spectrum was analyzed with a number of Gaussian bands for mathematical modeling only. Positions and magnitudes of Gaussian bands were fitted to the retrieved specific absorption spectrum to provide accuracy of description about 5 % which corresponds normal accuracy of absorption coefficient measurements (taking into account the problem of surface layers discussed above). It is clear from Fig. 5 that the most known IR

Fig. 5. Specific absorption spectrum of ferrous ion (Fe^{2+}) in Na_2O-CaO-MgO-SiO_2 glass and its Gaussian components

absorption band with maximum value at 1075 nm is a complex one and cannot be described by less than three Gaussian components. Two smaller bands are seen in Fig. 5 at approximately 2000 nm and 3000 nm. They are responsible for absorption in the spectral range usually attributed to hydroxyl ions only and therefore can affect determination of hydroxyl content in glasses. One can see in Fig. 5 that ferrous ion has significant absorption in the whole UV region which reaches several hundreds of cm^{-1}/Wt.% Fe^{2+}. This means that not only ferric (Fe^{3+}) ions are responsible for short wavelength absorption in glass [2, 3] but also ferrous ions can contribute even in glasses with comparable amount of both valent forms of iron. It was mentioned in Ref. [5] that absorption spectra of iron in glasses melted under strong reducing conditions show evidences of existence of some new ferrous centers with distinguished properties but their identification requires an additional research.

Specific absorption spectrum of ferric ion (Fe^{3+}) is shown in Fig. 6. It was defined as $A_{Fe3}(N)$ in formula (1). The main absorption bands placed at 225 nm, 380 nm, and 410-440 nm are known for Fe^{3+} (see Ref. [11-13]) but were not shown in the same scale. One can see in Fig. 6 the real ratios between magnitudes of the absorption bands and see some new small bands in the visible region. Let us consider effect of ferric absorption on the positioning of absorption edge of silicate glass. The maximum reliable value of optical density measured in UV region with commercial spectrophotometer is about 2 (high level of scattered light). Consequently, the maximum absorption coefficient for sample of 1 cm thick is approximately 2 cm^{-1}. This means that the detectable absorption edge for glass with 0.02 Wt.% Fe^{3+} (normal contamination for technical glass) is placed at 360 nm and for glass with 0.002 Wt.% Fe^{3+} (normal contamination for optical glass) – at 280 nm. It is important that those values published for silicate optical glasses were used in Ref. [8] for determination of their intrinsic absorption edge. However, it is clear from Fig. 6 that those absorption edges are caused by extrinsic
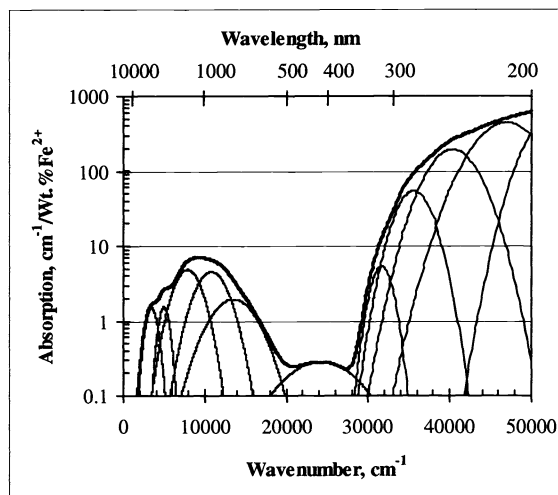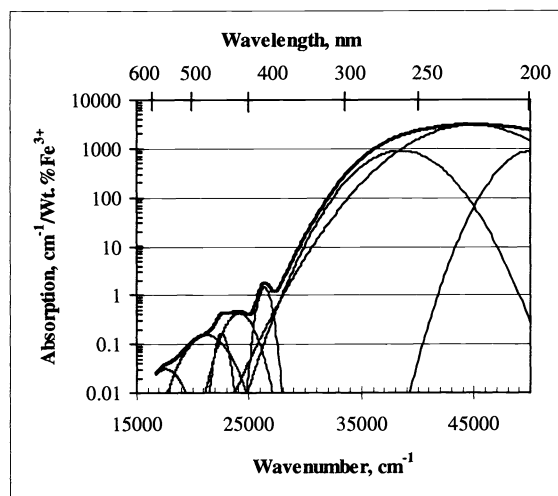

Fig. 6. Specific absorption spectrum of ferric ion (Fe^{3+}) in Na_2O-CaO-MgO-SiO_2 glass and its Gaussian components

absorption of ferric ions. It is clear from Fig. 6 that no significant absorption of ferric ions was detected in the long wavelength region. Special measurements of IR absorption of iron in oxidized silicate glasses performed with very sensitive calorimetric method [14] have shown the absence of ferric absorption at 1060 nm above 0.0005 cm^{-1}/Wt.% Fe^{3+}.

Absorption spectrum of water extracted from experimental spectra (Fig. 7) contains well-known [3] absorption bands at 4350, 3570 and 2860 nm (2300, 2800, and 3500 cm^{-1}) and multiphonon combinations in the short wavelength region. This spectrum was defined as $A_{OH}(N)$ in formula (1). It is interesting that the most known short wavelength absorption band of water placed at 2860 nm (if measured with high accuracy) cannot be described by a singe Gaussian band and it is necessary to place at least 4 Gaussian bands in this spectral region to fit calculation with experimental spectrum. It was found that position and spectral shape of water absorption edge near 2700 nm is very sensitive to glass composition and melting conditions and can be different for glasses with the same other parameters. Usual concentration of hydroxyl in glasses is in the range of several hundredths of percent. Consequently, usual water absorption for wavelengths above 2700 nm is in the range of several cm^{-1}. This absorption is comparable with ferrous absorption with iron concentration in the range of 0.1 %. Hydroxyl absorption for wavelengths below 1500 nm is below 0.001 cm^{-1}. It cannot be detected in commercial glasses, however, one can see small evidences of multiphonon hydroxyl bands in Fig. 3 for high-purity glass. Absorption of hydroxyl in the long wavelength side of spectrum is overlapped with multiphonon absorption of glass matrix defined as $A_v(N)$ in formula (1). It is clear in general that the vibrational edge of silicate glass matrix is placed somewhere above 4000 nm but exact separation between vibrational bands of hydroxyl and glass matrix requires an additional research.
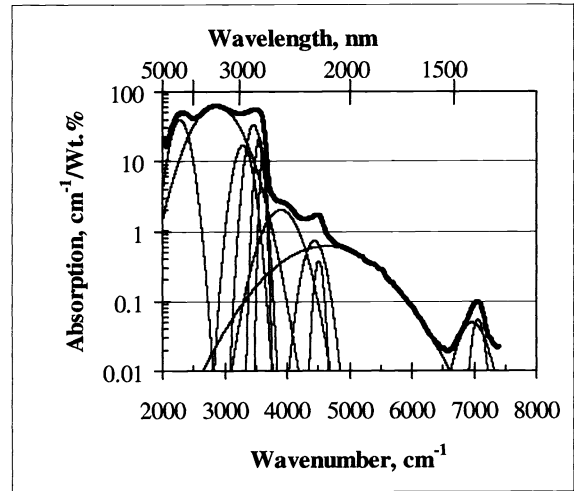

Fig. 7. Specific absorption spectrum of hydroxyl ion (OH⁻) in Na_2O-CaO-MgO-SiO_2 glass and it Gaussian components

Thus, absorption spectra of most of undoped silicate glasses can be described with high accuracy on the basis of formula (1) taking into account absorption spectra of the intrinsic L-centers along with extrinsic ferric, ferrous, and hydroxyl ions always presenting in glass as impurities. An algorithm of such modeling is described in Ref. [5, 6]. It allows determination of impurities contents in glass and describing of experimental spectra for glasses fabricated in different melting conditions with accuracy about 5 %.

It is well known that some additional absorption can be generated in glass by ionizing radiation (γ-rays, X-rays, UV, etc.). This absorption is caused by electrons and holes generated by ionizing radiation and trapped in different defects of glass matrix or crystalline lattice. Those trapped electrons and holes are called color centers[8, 10, 13]. 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.[10] is shown in Fig. 8. It was found that absorption induced at low temperatures has strong IR component caused by electron centers which are unstable at room temperatures. It is very important for the further consideration that at room temperature induced absorption in visible region is caused by hole centers with absorption maxima at 620, 450 and 310 nm while electron centers with absorption maximum at 240 nm are responsible for UV absorption. This feature of induced absorption spectra gives an opportunity to use the presence of hole bands as an evidence of glass matrix ionization while electron bands can be a result of ionization of different impurities.
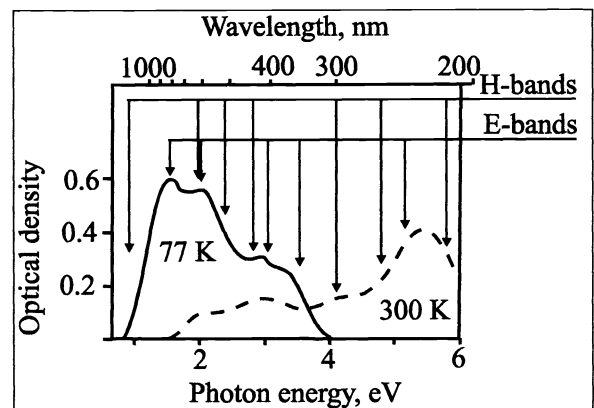

Fig. 8. Absorption spectra of intrinsic color centers in Na_2O-SiO_2 glass. Arrows show positions of maxima of electron and hole absorption bands

3. PHOTOIONIZATION OF SILICATE GLASSES

Photoinduced coloration of glass exposed to sunshine was described first time in a scientific publication almost two centuries ago [15]. However, it was the long way to reveal the features and understand the mechanism of this process. It was found [16] in 1938 that the spectral region of optical radiation causing coloration is ranged from 200 to 230 nm and it was 1971 when the first model of intrinsic color center generation was proposed in Ref. [17]. Detailed study of the features of optical ionization of silicate glass matrix was undertaken in Ref. [18] and summarized in book [10]. This study has confirmed that in high-purity silicate glasses a dependence of induced absorption on the wavelength of exciting radiation (color center generation spectrum) represents the narrow band placed in the far UV region (curve 1 in Fig. 9). Measurements of photoconductivity in the same glasses have shown that effective generation of charge carriers occurs under excitation by vacuum UV radiation only (curve 2 in Fig. 9). Photoconductivity under excitation in the region of color center generation spectrum was detected at the level of gage sensitivity of 10^{-16}A. This result means that no generation of free carriers with high mobility occurs in silicate glass under optical excitation. However, it was found that both electron and hole centers were generated by UV radiation. It was supposed in Ref. [17] that color center generation spectrum

Fig. 9. Dependence of induced absorption (1), photoconductivity (2) and original absorption of sodium-silicate glass on wavelength

corresponds to absorption band of excitons which expected in the range of 200 nm. However, no specific absorption bands were found in the mentioned spectral region. The whole of color center generation spectrum was placed (see Ref. [19, 20]) within the long wavelength tale (curve 3 in Fig. 9) of the first absorption band of alkaline-silicate glass with maximum at 165 nm (7.5 eV).

It was found in Ref. [18], that position and shape of color center generation was not stable but 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. 10). One can see in Fig. 10 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 then this value and no additional energy is consumed if photon energy if higher then 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, electron mobility threshold is shifted for about 0.1 eV to the short wavelength side compare to the intrinsic absorption edge (Fig. 4). This shift is the result of inhomogeneous distribution of bonding energy in glass matrix compare to the crystal lattice. Thus, spatial fluctuations of electron energy in glass matrix[1] are responsible for the difference in positions of the intrinsic absorption edge and low mobility of carriers resulting in very low photoconductivity in glasses under UV excitation (Fig. 9).

Fig. 10. Dependence of activation energy of intrinsic color center generation in Na$_2$O-SiO$_2$ glass on wavelength of exciting radiation

It is well known that color centers can be bleached by thermal treatment or by optical radiation [10, 13] because of recombination between mobile electrons and holes. In silicate glasses this recombination is followed by intrinsic luminescence with maximum at 365 nm which was studied in Ref. [19-21]. This luminescence shows fast (about 1 μs) 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 which results in restoring of neutral
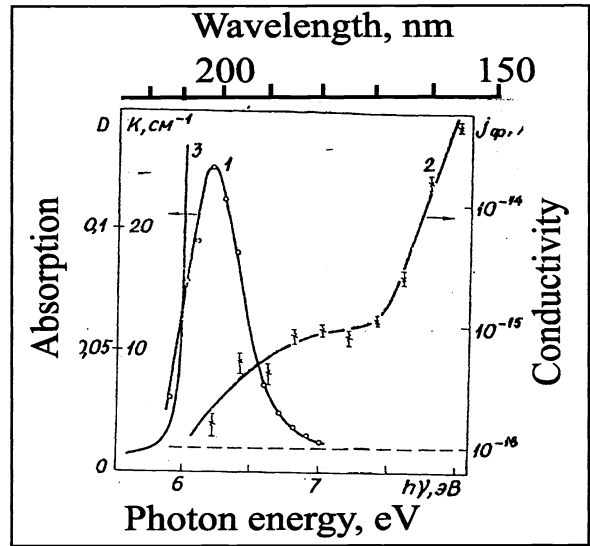
L-center at excited level. Relaxation to the ground state produces luminescence with the same spectrum. An excitation spectrum of luminescence coincides with the color center generation spectrum. This means that these luminescence centers form the intrinsic absorption edge (this is why intrinsic absorption in formula (1) is defined as $A_L(N)$). It is important that in the case of excitation by polarized light, luminescence is polarized. Polarization of luminescence disappears at elevated temperatures above 300 K and if exciting photon energy is above 7.5 eV (wavelength below 165 nm). This means that alkaline-silicate glass is homogeneous and isotropic in macro-scale but possesses strong anisotropy at atomic micro-scale because only anisotropic centers can absorb selectively polarized light and emit polarized luminescence. Moreover, it is an evidence that holes are immobile under mentioned conditions because ionized hole must conserve its orientation to emit a photon of luminescence polarized in the same direction as the exciting photon.

Chemical interpretation of the luminescence center (L-center) is a quasi-molecular group consisting of non-bridging oxygen and alkaline ions. Photoionization of silicate glass means electron release from L-center and creation of ionized L^+-center as a hole center and a movable electron which is trapped by different defects in glass network. Finally one can divide absorption spectrum of glass in three regions depicted in Fig. 11. The first region in the short wavelength side of spectrum (N>48000 cm^{-1}, λ<208 nm) is represented mostly by intrinsic absorption of L-centers which are excited to delocalized states releasing electrons and transforming to L^+-centers. The second region (42000 cm^{-1}<N<48000 cm^{-1}, 235 nm>λ>208 nm) is the area of mixed absorption of L-centers and impurities introduced into glass structure with raw materials and technological setup. Excitation of L-centers causes intra-center luminescence and thermo-stimulated electron and hole color center generation. The third region placed in the long wavelength side (**N<42000 cm^{-1}, hv<5.2 eV, λ>235 nm**) is represented by impurities absorption only. Excitation of impurities can result in extrinsic luminescence or ionization. However, the only hole centers generating in such process are photo-oxidized ions of impurities. 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.
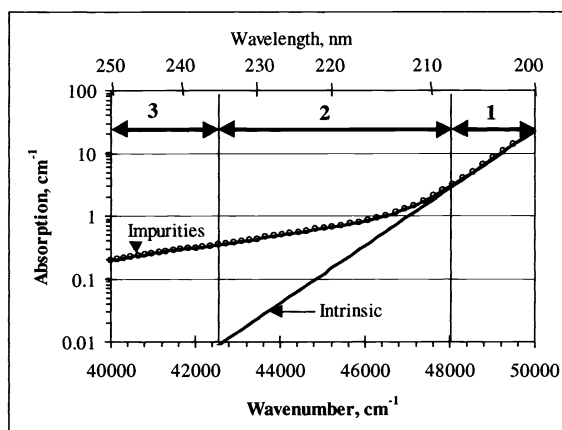

Fig. 11. Spectral regions of different types of electronic excitations generated by optical irradiation.
1 – excitation to intrinsic delocalized states and direct generation of electrons and holes.
2 – excitation to intrinsic localized states and thermoinduced generation of electrons and holes.
3 – excitation to the levels of impurities resulted in electron generation and impurities valence transformations.

Thus, there is an opportunity to generate intrinsic electron color centers when photon energy of exciting radiation is not enough for ionization of the intrinsic states of glass. Extrinsic ionization was obtained, if donors' excited level being placed above the threshold of charge carriers mobility. In this case, a mobile electron can be trapped either by glass matrix defect, with intrinsic electron center formation, or by another dopant, i. e. to recharge the activators. It was shown in Ref. [22-25] that dopant ion was ionized if it was excited to the upper level placed above the mobility threshold. The result was that dopant ion was oxidized and the released electron has created one of intrinsic electron centers or reduced another dopant ion. The depth of dopant ground level in 25Na$_2$O-75SiO$_2$ glass are 5.2 eV (240 nm) for Fe^{2+}, 5.0 eV (250 nm) for Tb^{3+}, and 3.6 eV (345 nm) for Ce^{3+}. The comparison of these values for ferrous ion with Fig. 5 shows that the ionization threshold of **Fe^{2+}** corresponds to the long wavelength edge of the peak with maximum at 6.5 eV (191 nm).

It was found in Ref. [22-25] that dopant ionization could occur not only when the excited upper level was placed above the mobility threshold but as well by tunnel transitions. Tunnel ionization can be observed with efficiency about 1-2 orders of value lower than that of over barrier ionization. The thresholds of the tunnel ionization of dopants in the same glass are 3.5 eV (350 nm) for Fe^{2+}, 3.1 eV (400 nm) for Tb^{3+}, and 3.1 eV (400 nm) for Ce^{3+}. Referring this to Fig. 5 one can see that the tunnel ionization of Fe^{2+} is obtained at excitation to the long wavelength bands with peaks at 5.1 and 4.4 eV (243 and 282 nm). Unlike the case of intrinsic ionization that inevitably produces electron and hole centers, at the excitation to dopant absorption bands, the only hole center generated is the same (but oxidized) dopant ion. All newly created centers are electron ones (either intrinsic or extrinsic).

However, not only impurities introduced into the glass structure can affect the photoionization but also different types of glass surface modifications can be responsible for some photoinduced processes [19-21]. Strong luminescence of surface layers under UV excitation requires special tricks to separate intrinsic luminescence discussed above. Intensity of surface

luminescence can be decreased by burning with powerful UV radiation but it is restored after exposure to atmosphere. Surface chemical reactions (including leaching) modify composition of glass layers next to the surface and dramatically change measured reflection coefficient, color center generation and both intrinsic and extrinsic luminescence of silicate glass. Detected photoconductivity of glass samples increases by several orders of magnitude if no special protection of the surface is applied in the measurements. Thus, a number of parasitic surface phenomena, such as glass composition change, emission and absorption of deposited layers, emission of charged particles, etc. should be eliminated to get reliable data on photoinduced phenomena in glasses because strong intrinsic absorption results in small thickness of glass volume obtainable for this study. It should be noted that no intrinsic hole color centers and intrinsic luminescence can be generated by surface phenomena, contrary to excitation of glass matrix itself.

It is important to emphasize that impurity ionization of silicate glasses can be observed at relatively long wavelength radiation (almost visible region) while intrinsic ionization requires high photon energies corresponding far UV radiation. The main evidence of intrinsic ionization is detection of intrinsic hole centers or intrinsic luminescence described above. At the same time all our attempts to reveal intrinsic ionization of lead-silicate glasses were not successful. No evidences of photoionization and color center generation were observed[26] in these glasses but only intensive luminescence of lead. However, it is well known that X- and γ-rays generate color centers in lead silicate glass with high efficiency. These results can be explained with supposition that in lead silicate glasses gap between intrinsic absorption edge and electron mobility threshold (~2 eV) is significantly more than in alkaline-silicate glasses (0.1 eV). In this case, color center generation spectrum should be placed in the region of intrinsic absorption with high absorption coefficients and, consequently, the thickness of colored layer should be too thin for induced absorption detection. Additional study is necessary to solve the problem.

4. NONLINEAR PHOTOIONIZATION OF SILICATE GLASSES

It was shown in Chapter 3 that no linear intrinsic ionization occurs in silicate glasses at exciting radiation photon energies below 5.2 eV (λ>235 nm) and no extrinsic ionization of dopants occurs at hν<3.1 eV (λ>400 nm). However, there are a great number of works reporting nonlinear photoionization of different types of glasses at lower exciting photon energies. Nonlinear ionization is usually considered as a result of multiphoton absorption of optical radiation with photon energy below threshold of intrinsic or extrinsic ionization. One of the first publications reporting multiphoton ionization of glass was Ref.[27]. Photoconductivity induced by nanosecond Nd-laser at 1.17 eV (1.06 μm) was detected in fused silica and silicate glasses and ascribed to multiphoton ionization of those materials. One can see from Chapter 3, that this should be five-photon process even for multicomponent silicate glasses. No evidences of glass matrix ionization were observed in Ref.[27]. In Ref.[28], thermoluminescence induced by similar laser was ascribed to multiphoton ionization of impurities. However, at least four-photon absorption is necessary for ionization of iron which is the most impurity in glass, but no evidences of such excitation were published. In later works[29,30], an observation of additional absorption was reported under exposure to visible nanosecond pulses and ascribed to two-photon absorption of glass. However, at least three photons are necessary to produce excitation of silicate and borosilicate glasses (but not impurities in those glasses). Thus, let us summarize data on laser-induced glass ionization where different types of nonlinear excitation of glass matrix or specific dopants were experimentally justified.

4.1. Two-photon ionization of silicate and borosilicate glasses.

High-purity sodium-silicate glass with contamination level of 1 ppm was exposed to radiation of four harmonics of Nd:YAG laser with photon energies 1.17 eV (1064 nm), 2.34 eV (532 nm), 3.51 eV (355 nm), and 4.68 eV (266 nm) which was focused into the volume of glass specimen[31,32]. It was found that after exposure to radiation of third and fourth harmonics 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. 12). This means that **glass matrix was ionized by laser radiation** even photon energy in laser radiation was not enough for linear color center generation. Efficiency of

3 - exposure to the UV lamp at λ<220 nm
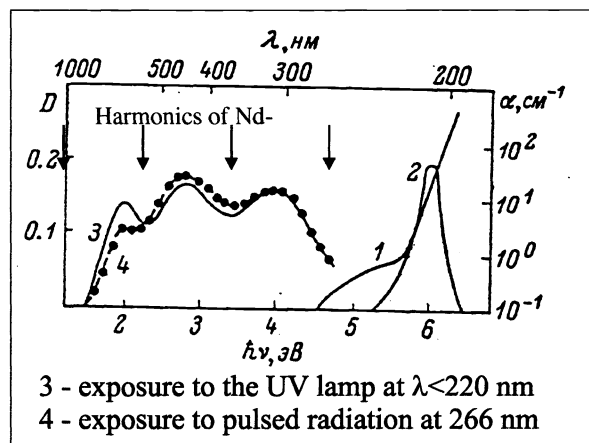4 - exposure to pulsed radiation at 266 nm

Fig. 12. Additional absorption induced in sodium-silicate glass with absorption spectrum (1) by UV irradiation within color center generation spectrum (2) or by harmonics of Nd-laser shown by arrows.

color center generation does not depend on presence of additional absorption levels at exciting wavelengths but is driven by actual power density (irradiance) of radiation absorbing by glass matrix. Induced absorption was observed if irradiance exceeded value of 10^6 W/cm^2. Additional absorption in glass depends on exposure (energy density) and represents the curve with saturation. The level of saturation depends on irradiance. 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. A model was created describing this combination of linear and nonlinear photoinduced processes caused by the same radiation [33]. Two-photon color center generation was followed by intrinsic luminescence in all cases. Glass exposure to laser pulses at irradiance below 10^6 W/cm^2 did not generate color centers and only luminescence of iron presenting in glass as contaminant was detected.

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 glasses with photon number exceeding 2 under exposure to nanosecond laser pulses.

All described experiments were conducted with a number of silicate and borosilicate technical and optical (crown) glasses with different level of contaminations. In all cases, color center generation was observed for the third and fourth harmonics with photon energy exceeding a half of photoionization threshold which placed for those glasses in vicinity of 6 eV (200 nm). No coloration was observed for the first and second harmonics. Thus, **silicate and borosilicate glasses can be ionized by nanosecond laser pulses in two-photon process if wavelength of radiation is below 400 nm and irradiance is above 10^6 W/cm^2**. No three-photon ionization was detected in these conditions.

4.2. Three-photon ionization of lead-silicate glasses

Color center generation in lead-silicate glass was discovered in Ref. [34] and ascribed to nonlinear solarization. In this case, the problem is the absence of linear solarization as it was described in Section 3 and therefore the absence of data for comparison. Solution of the problem was found in Ref. [35] where it was proven that threshold of lead silicate matrix ionization is placed in the region between 6 and 6.5 eV similar to other silicate glasses. It is necessary to emphasize that in lead-silicate glasses intrinsic absorption edge at 4 eV is created by lead centers which are responsible for luminescence [26] but no electron release occurs from the excited level. Matrix ionization is possible under excitation with wavelengths below 200 nm where absorption coefficient is above several thousands cm^{-1} and therefore the thickness of excited layer is in the range of few micrometers only. This is why no color centers were recorded in single photon process in these glasses. Two-photon coloration by the third harmonics at 351 nm and three-photon coloration by the second harmonics at 532 nm at irradiances above 10^6 W/cm^2 were

Fig. 13. Transmission of 20 nm laser pulse at 532 nm through lead-silicate glass sample and its components resulted from three-photon absorption of glass matrix and single-photon absorption of color centers

discovered in Ref. [35] because of relatively small coefficients of nonlinear absorption and consequent opportunity to observe coloration in the volume of the sample. It was found that photoinduced absorption is identical to that generated by γ-irradiation. This proves that ionization of glass matrix was produced by exposure to laser radiation. Three-photon absorption was measured in that work (Fig. 13). One can see that attenuation of transmitted radiation resulted mainly from linear absorption by color centers which were generated after three-photon absorption by lead-silicate glass matrix. It should be noted that this is a common situation in nonlinear measurements when linear absorption of species generated in nonlinear process is higher than nonlinear absorption itself. 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. However, it is the goal of this paper to show that not only multiphoton absorption can result in glass matrix ionization but also a number of different mechanisms which can contribute this process.
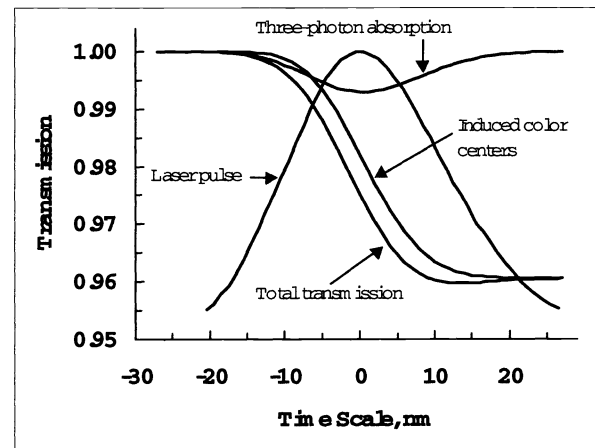
4.3. Cooperative ionization of CuCl doped borosilicate glass

An interesting example [10] of nonlinear ionization at extremely low irradiance is coloration by visible light of borosilicate glasses doped with microcrystals of CuCl. These are commercial photochromic glasses with reversible induced absorption. Mechanism of photosensitivity of this glass is shown in Fig. 14. CuCl exciton absorption band is placed in near UV region at 3.25 eV (380 nm). Absorption of photon causes transition to the excited state. Thermal dissociation of exciton results in electron release and ionized hole center Cu^{2+} creation. Electron is trapped by another copper ion and transforms it to a neutral atom Cu^0. Coagulation of copper atoms produces glass coloration in the visible region. However, it was found that this glass is sensitive to visible radiation (CW 1 mW He-Ne laser at 633 nm) while no significant original absorption was detected in this glass. Detailed study of the process has shown that sensitivity to visible radiation occurs only in glasses that were previously exposed to UV radiation and coloration rate is proportional to squared initial concentration of color centers. Spectral shape of absorption was the same before and after visible irradiation. Coloration rate was proportional to squared irradiance of exciting radiation. Finally, in contradiction with known photoinduced processes, coloration rate increased within exposure.
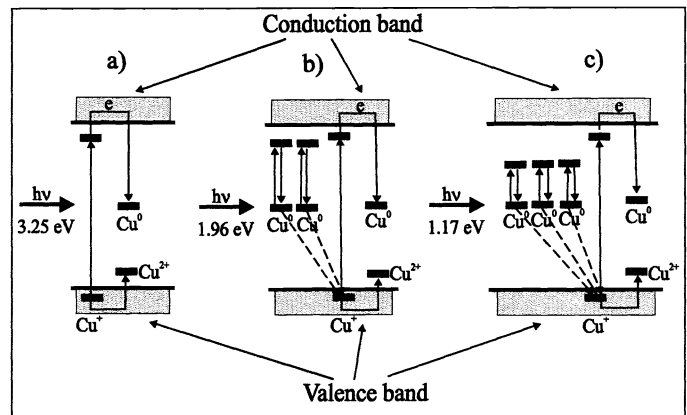

Fig. 14. Energy diagram for color center generation in CuCl-doped glass. a) – single-photon ionization of exciton. b) and c) two- and three-photon cooperative self-multiplication of color centers

Explanation of these phenomena is shown in Fig. 14. Two color centers created by previous UV exposure absorb two visible photons and transgress to the excited states. Then they contemporary relax to the ground state and transfer summarized energy to Cu^+ center in a nonradiative process. Exciton resulted from this action releases electron which creates a new color center. Concentration of color center increases, visible radiation is absorbed more efficiently, and coloration rate increases. We called the process "cooperative self-multiplication of color centers." Thus, this is two-photon nonlinear process but no transitions through virtual levels occur in this case. This is why this process is very efficient at very low irradiance in the range of 1 W/cm^2 (watt, not kilowatt). Moreover, three-photon self-multiplication of color centers was detected under excitation by Nd-laser at 1064 nm (Fig. 14). However, in the last case irradiance above 10^6 W/cm^2 is necessary. Thus, this example shows that color centers generated in material can participate in the further process not only because of linear bleaching by laser radiation but can contribute to very unusual mechanisms of additional photosensitivity. It is important that cooperative processes are very efficient at significantly lower irradiance compare to multiphoton processes.

4.4. Ionization by spectral broadening (ISB) of femtosecond laser pulses

Let us consider an opposite case of silicate and borosilicate glasses coloration by high-power femtosecond laser pulses [36, 37] with λ=850 nm (1.5 eV) and very high irradiance above 10^{12} W/cm^2. It was found in sodium-silicate glasses that exposure below laser damage threshold and below selffocusing threshold 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. Unusual feature of this phenomenon depicted in Fig. 15 does not allow ascribing the process to any type of multiphoton absorption. It was shown in Section 4.1 that coloration under two-photon excitation generates in the vicinity of focal plane with maximal concentration of laser radiation (maximal irradiance). However, in the case of femtosecond irradiation, no induced absorption was detected near the focal plane of laser beam placed before the entrance
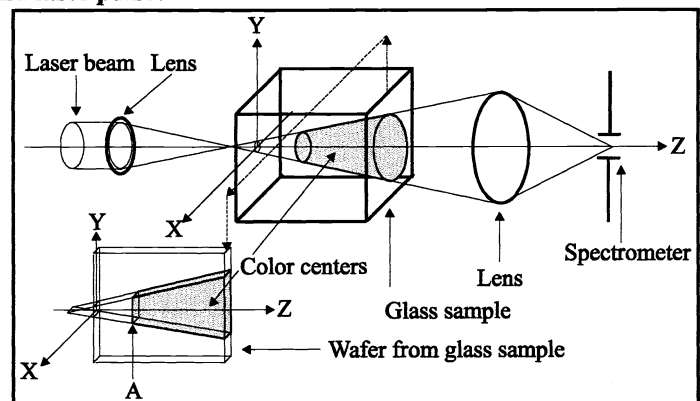

Fig. 15. Geometry of color center generation in glass under exposure to the femtosecond IR laser pulses. Lens and spectrometer are for the transmitting and emitting radiation detection

surface of the specimen, but colored area spread out starting from some distance under the surface. One can expect that some properties of the laser beam should be changed before glass ionization occurs. Measurement of spectrum of transmitted beam has shown that not only well-known white light generation results from femtosecond beam propagation in the glass sample but UV radiation up to 220 nm (5.6 eV) was detected. It is remarkable that even for commercial glass with extrinsic absorption edge at 330 nm this far UV radiation was detected. This means 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. No multiphoton ionization of silicate glasses was detected under exposure to femtosecond laser pulses.

4.5. Thermal ionization by laser radiation

We have considered a number of different mechanisms of photoionization of wide bandgap dielectric glasses by photo-excitation of electrons to the levels placed above the electron mobility threshold. However, this is not a single way to produce movable carriers. An example of alternative mechanism was demonstrated in Ref. [38]. The glass plate was exposed to radiation of CW CO_2 laser at 10.6 μm heating the sample up to high temperatures above melting point. Before the melted sample trickled down, pulse of Nd-laser was used for the measurements of transmission and laser induced breakdown at 1.06 μm. It was found that opaqueness temperature for borosilicate glass is in the range of 1700 K and 2800 K for fused silica. One can propose the mechanism of total opaqueness depicted in Fig. 16. Heating of wide bandgap dielectric initially (up to 1300 K) does not cause visible emission and coloration. However, a gradual overlay of bandgap at increasing temperature by electronic and vibrational states results in increasing of absorption and, consequently, emission. Finally, overlapping of occupied and empty levels creates metal-like structure with mobile carriers.
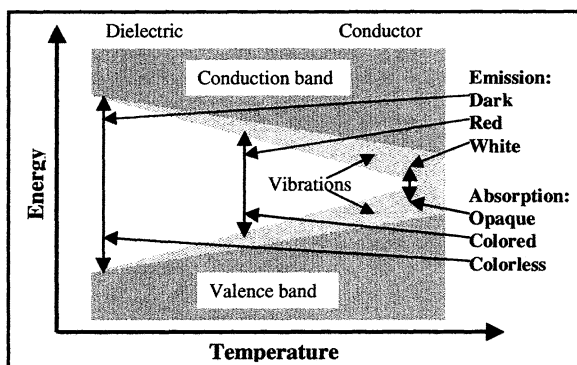

Fig. 16. Thermal transformation of electronic level structure in wide-bandgap dielectric

This mechanism of thermal ionization results in plasma "bullet" generation in glasses under 1.06 μm laser pulses of several milliseconds width [39]. This opaque plasma cone arose in the focal plane and propagated in glass volume toward the laser beam with speed about 100 m/s. Estimated temperature of the plasma cone was approximately 2700 K. Obviously, this ionization is primed by linear absorption of laser radiation by glass (in this case it is absorption of Fe^{2+} shown in Fig. 5). However, strong heating causes nonlinear increasing of absorption coefficient and temperature and finally produces extremely nonlinear plasma generation.

Thermal ionization plays main role in nonlinear behavior of glasses with absorbing inclusions exposed to pulsed laser radiation[40]. Inclusion heated by linear absorption of laser radiation up to temperature of opaqueness heats the adjacent to inclusion layer of glass by thermal conductivity and converts it to the opaque state (Fig. 16). Actually this means increasing of the inclusion size and triggering of nonlinear process of heating and consequent breakdown. This type of ionization can be responsible for many phenomena cumulated in glass under multiple laser irradiation. The process shows exponential dependence on irradiance and can be confused with different types of power functions symbolizing different multiphoton processes.

4.6. Laser ionization of the glass surface

The most insidious mechanism which can cause phenomena looking like different types of photoionization of glass itself, is surface plasma generation under laser irradiation. Charged particles emission from surface [41] and luminosity of surface [42] under exposure to pulsed laser radiation significantly below the threshold of laser-induced breakdown was revealed in the beginning of laser era and are under investigation until now. The main role in the process of surface ionization plays the surface layer deposited on the glass surface. Its contribution to absorption and linear photoionization was discussed in Sections 2 and 3. Initial stage of this process is burning of this surface layer exposed to laser radiation. Complexity of the process is determined by both unknown composition of the layer and uncertain geometry of irradiation (irradiance distribution, surface cracks, etc.). Finally the nidus of plasma generation moves from the deposited extrinsic surface layer to

the adjacent layer of glass itself. Everybody can observe this process visually by looking in darkness to the surface exposed to laser radiation with intensity several times below the surface damage threshold. A blue cloud flies off the glass surface while no residual damage can be detected. Luminosity of the cloud decreases from pulse to pulse. However it is restored after exposure to atmosphere for several minutes. Actually, this cloud represents a shock wave propagating in the air with supersonic speed up to 1 km/s (Fig. 17). Combination of optical emission and charged particles from spreading plasma can cause a chain of phenomena starting from defect generation (including all types of intrinsic centers) and finalizing with Coulomb explosion. We will not discuss in details interaction of laser radiation with surface because this is a completely separated vast topic. It is important from the point of view of laser-induced intrinsic processes in glass volume, that intensity of surface emission nonlinearly depends on irradiance and can be easily confused with different power functions distinctive for multiphoton processes.
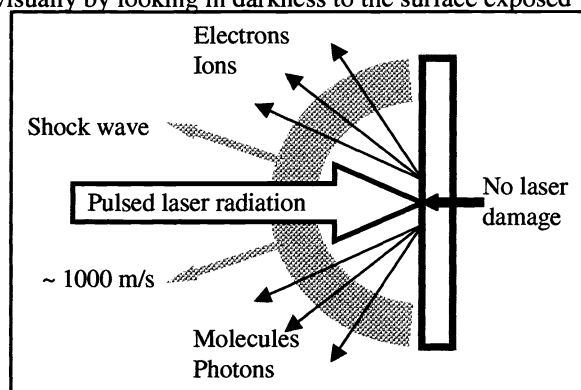

Fig. 17. Surface ionization by pulsed IT radiation

5. 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 completely overlapped spectra of ferric (Fe^{3+}), ferrous (Fe^{2+}), and hydroxyl (OH^-) ions. Specific absorption spectra of all components are determined, algorithm for total absorption spectra is developed. Intrinsic absorption edge for lead silicate glasses is placed at ~300 nm.

- Photoionization of glass matrix occurs under excitation by photons with hv>5.2 eV (λ<235 nm). Irradiation with hv>5.9 eV (λ<210 nm) results in electron excitation to delocalized states. Consequent electron and hole trapping by glass matrix defects results in intrinsic color center generation. Presence of intrinsic hole centers is an evidence of glass matrix ionization. Ionization of lead-silicate glasses occurs at hv>6.2 eV (λ<200 nm)

- Decreasing of photoionization threshold down to 3.1 eV (400 nm) is possible by introducing some donor ions in glass composition. No intrinsic hole centers can be generated in this case.

- Two-photon ionization of glass matrix occurs at irradiance above 10^6 W/cm^2 and photon energy above 3 eV (½ of bandgap for silicate and borosilicate glasses). No multiphoton ionization with photon number above 2 observed in those glasses. Three-photon ionization was observed at photon energy above 1/3 of bandgap for lead-silicate glass only.

- Two- and three-photon 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/cm^2 resulted from glass ionization by spectral broadening (ISB).

- Thermal ionization of glass matrix results from linear absorption of laser radiation by impurities or inclusions and heating above 1700 K.

- Surface plasma generation by burning of impurities layer deposited on glass surface results in shock wave, emission of charged particles and short wavelength radiation which cause glass ionization.

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Optical absorption and ionization of silicate glasses (4347-5)

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Q. You showed a picture of polarization versus temperature for different incident wavelengths of light. Can you say a little bit more about the geometry of the set up and the mechanisms involved? That was very interesting.

A. This is a combination of circumstances. At the first action of light you produce excitation of an electron to the upper state and then migration of the electron to the defect level. After some time this electron comes back and recombines with the hole. If the hole is at the same place and with the same orientation, you will see polarized luminescence. If during this time your hole jumped to the other position, or rotated its orientation in the same position, you will lose polarization luminescence. Therefore, this gives evidence of stable or mobile hole centers in this glass. And you can see that if the temperature is more than a critical value, the holes become mobile.

Q. You showed an example of a femtosecond pulse going through glass and being broadened by self phase modulation and producing enough spectral width then that 2 and 3 photon transitions took place. My question is how thick was the glass and can you do this at an intensity low enough that you don't damage the glass?

A. You can produce enough photon energy even for single photon ionization because if you have a piece of glass, and normal commercial glass is not transparent in ultraviolet, and you illuminate it by an ultraviolet laser you have nothing here. If you illuminate it by an infrared laser you have ultra violet here, after almost 200 nanometers.

Q. I just want to repeat the question in my Russian - English. In your experiment that you did, how thick was the glass and did you do any damage when you saw this coloration?

A. No, we did damage but this is separate. This is significantly below the damage threshold. No damage was seen after multiple exposure at this power density.

Q. And the thickness of the glass?

A. From one to ten millimeters.

Q. Thank you for an interesting presentation. I have just a conceptual question. Before ionization, when you excite within the H band, you do have shifted luminescence? Could we use the concept of a self-trapped exciton in this case because it looks like it's trapped from the bulk exciton which stops the luminescence shift of the bulk because the electron and hole are not far away.

A. From my point of view this is not a physical question, this is linguistic. Because in one language it is a self-trapped electron, in the other language it is excitation in the localized states. Actually it is the same as a self-trapped exciton. And we have very strong atomic relaxation for the excited electron in the upper state.

Q. You showed a graph, I think it was contributed by one of your colleagues. It showed 3-photon excitation for the time duration that you showed for the pulse width. It appeared to me that the time duration of the three-photon excitation was about the same as that of the pulse duration.

A. Yes, it follows the intensity distribution of the pulse.

Q. Would you expect a shorter pulse rate?

A. No, I don't believe so.

Q. But I think the pulse could be shortened a lot.

A. There is no other shortening of the pulse.