

Rearrangement of a phosphosilicate glass network induced by the 193-nm radiation

Yu.V. Larionov, V.O. Sokolov, V.G. Plotnichenko

Abstract. The IR absorption and Raman spectra of phosphosilicate glass (PSG) are measured during its exposure to radiation at a wavelength of 193 nm. The obtained data demonstrate the complicated rearrangement dynamics of the glass network around phosphor atoms and of the glass network as a whole. The experimental dependences are explained by the model of the PSG network based on the concepts of the theory of rigidity percolation.

Keywords: photosensitivity, phosphosilicate glass, glass network, induced refractive index, rigidity percolation.

1. Introduction

Although the photoinduced change in the refractive index of a germanosilicate glass caused by UV radiation was discovered more than 25 years ago [1] and has been extensively studied since then, the mechanism of this phenomenon still remains unclear in many aspects. The mechanism of this effect is even more unclear for silicate glasses of other compositions. However, it is established reliably that point defects appearing upon doping play a key role in this mechanism in most photosensitive silicate glasses.

At present it is established that this effect can be explained only by the simultaneous action of several factors. The determining factor is a change in the polarisation of defects and their number (according to the Clausius–Mosotti equation), i.e. of elements of the glass network that are most easily changed by the action of UV radiation [2]. In addition, it was found that the structure of the doped glass network could change during exposing to radiation, by making a contribution to the induced refractive index. Thus, it was shown in [3] that the network of a number of silicate glasses, in particular, a phosphosilicate glass (PSG) was tightened after exposing to light, the degree of densification increasing with increasing doping level.

There exist two mechanisms proposed for explaining the

rearrangement of the glass network induced by UV radiation. According to the first mechanism, the rearrangement involves point defects of the glass and, therefore, is initially local. It is assumed that the local densification can be caused, in particular, by germanium oxygen-deficient centres capable of reconstructing the SiO_4 tetrahedra in the nearest coordination sphere to denser structures – the SiO_6 octahedra (structural members of stishovite) [4]. The crystalline stishovite structure was observed in PSG experimentally during devitrification of this glass at the normal pressure [5]. The mechanism of this effect remains unknown in details. One can assume that this phase will be also formed upon irradiation by UV light, which reduces the rigidity of the PSG network. It is assumed that the region of rearrangement of the network structure around a local densification can encompass a few tens of SiO_4 tetrahedra. In [6], this process was explained by the delocalisation of one of the valence electrons during the decomposition of oxygen-deficient centres. The rearrangement of the glass network of this size can be also caused by photoexcitation and relaxation of the stretched Si–O–Si linkages at cluster boundaries, which can result in the formation of the glass structure similar to that of crystalline quartz [4].

There also exists, however, another explanation of the glass network rearrangement induced by UV radiation based on the study of the nature of photosensitivity of quartz glasses. This approach does not relate the photosensitivity of glasses directly to defects in them and to the formation of local densifications in the glass network [7]. The densification is explained in this model by the ordering of the glass network, approaching the network of crystalline quartz. It is assumed that the network rearrangement is caused by the excess energy stored in linkage (Si–O–Si) bonds of the network during glass cooling. This energy determines the number of groups of rings into which SiO_4 tetrahedra are combined [7]. It is assumed that the glass densification occurs due to a decrease in the size of interstices in the middle of the rings due to a decrease in the number of their groups. The network rearrangement occurs due to the relaxation of internal stresses in quartz glass when interatomic covalent bonds are weakened during exposing to UV light [8]. It seems that point defects contained in the network can change the rearrangement rate and even its type. Thus, a decrease in the density of hydrogen-impregnated quartz glasses observed at some exposure stages was explained by the presence of point defects in them [8].

A disadvantage of the first approach is the neglect of variations in the network taking place in the regions

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between local densifications, which together with local densifications change the glass density. A disadvantage of the second approach is the absence of the detailed picture of the network rearrangement at the microscopic level, including the influence of defects on this rearrangement.

The phosphosilicate glass occupies a special place among silicate glasses because its photosensitivity is assumed low, as that of quartz glass ($\Delta n \sim 5 \times 10^{-5}$) [9] (however, it noticeably increases, achieving $\Delta n \sim 5 \times 10^{-4}$ with decreasing a laser pulse duration [10]). The dependence of the induced refractive index of PSG on the exposure dose looks strange and does not correlate with the dose dependence of the concentration of main point defects [11]. Note that the increase in the PSG density during irradiation is described by the unusual quasi-step law (see Fig. 2 in [12]). It was assumed in [11] that this is explained by the fact that, unlike germanosilicate glass, the induced refractive index in PSG is mainly determined by photoinduced changes in the PSG network, as in quartz glass.

The aim of our paper is to study photoinduced variations in the PSG network by the methods of IR and Raman spectroscopy to confirm this assumption.

2. Experimental

We investigated bulk and fibre PSG samples with low losses, as in paper [10]. As in [10], samples were irradiated by 6–7-ns, 25–150-mJ cm⁻² pulses from a CL5000 excimer laser at 193 nm with a pulse repetition rate of 10 Hz (sometimes from 5 to 50 Hz). In addition, irradiation was performed by 20-ns, 300-mJ cm⁻² pulses from a CL7000 laser at 193 nm. Absorption spectra were recorded with a Bruker IFS-113V IR Fourier spectrometer with a microscopic attachment (the light beam diameter was 0.4 mm). Raman spectra of the PSB excited by a Spectra-Physics Stabilite 2017 argon laser at 514.5 nm were recorded with a Jobin-Yvon T64000 triple spectrograph. Transmission and scattering spectra were recorded before and after each exposure of samples. Time intervals between the exposure of a sample and recording its spectra were from several hours up to several days, and between the successive exposures – from a few days up to a week.

3. Results of the study

3.1 Induced IR absorption

The absorption spectra of a bulk PSG sample are presented in Fig. 1. Curves (1) and (2) show the spectra of the sample before irradiation and after irradiation by the dose 180 J cm⁻², respectively. The inset presents these spectra in the frequency range from 3000 to 4500 cm⁻¹. Both curves exhibit absorption bands at frequencies ~ 3670 , 2646, 2467, and 2270 cm⁻¹, respectively. Curve (2) also has a relatively weak but broad absorption band at 3280 cm⁻¹. All these bands are well known and almost all of them are identified [13–15]. The bands at 3670 and 3280 cm⁻¹ are caused by vibrations of hydroxyl OH groups in the glass. The first band is related to their vibrations in silanol (Si–O)₃ ≡ Si–OH centres and the second band – to their vibrations in silanol centres coupled by the hydrogen bond with non-bridge oxygen atoms in phosphorus (Si–O)₃ ≡ P=O centres [13]. The bands at 2646 and 2467 cm⁻¹ correspond to phosphorus centres. The first

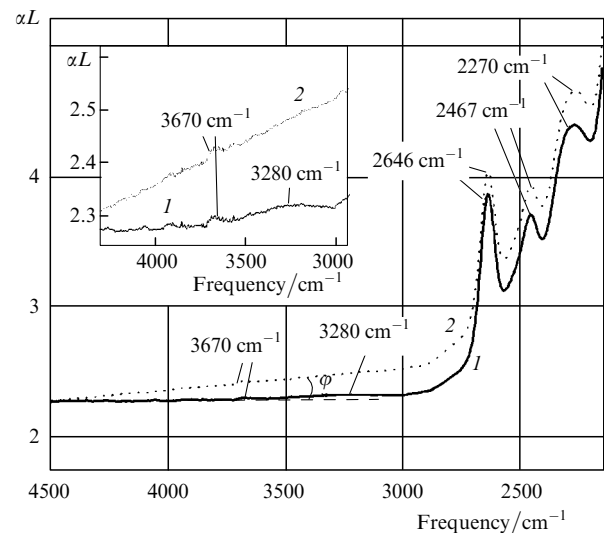


Figure 1. Infrared absorption spectra of the initial PSG sample (1) and the PSG sample exposed to the 0.18-kJ cm⁻² radiation dose (2). The sample length is L , α is the absorption coefficient. The inset shows the part of the IR spectrum in the frequency range from 3000 to 4500 cm⁻¹.

band is related to the second vibrational harmonic of the P = O bond, while the second band is not identified in the literature. It is assumed that the absorption band at ~ 2270 cm⁻¹ is related to the second harmonics of a group of oxygen vibrations in Si–O–Si, Si–O–P, and P–O–P linkages (hereafter, linkage vibrations) [13].

The slope of curve (2) in the frequency range from 4500 to 3000 cm⁻¹ exceeds that of curve (1) and curve (2) has no absorption band at 3280 cm⁻¹. The increase in the curve slope can be explained, in our opinion, by the increase in the intensity of a broad and intense absorption band in the range from 1020 to 1150 cm⁻¹ related to the fundamental vibrations of the Si–O–Si, Si–O–P, and P–O–P, linkages, on which tail the absorption bands presented in Fig. 1 are located. This assumption is confirmed by a strong dependence of this slope on the UV radiation power density, i.e. on the contribution of two-photon absorption, which can break and reconstruct the linkages.

Figure 2a shows the dependences of induced absorption in the 2646-cm⁻¹ band and of the slope φ of curve (2) in Fig. 1 in the frequency range 4500–3000 cm⁻¹ on the exposure dose. Absorption in the bands was calculated as the difference of absorptions at the band maximum and its base. The absorption at the band base was determined by the ordinate of a point with abscissa coinciding with the frequency of the band maximum. Figure 2b shows the dependences of the shift of absorption bands at 2467 and 2270 cm⁻¹ on the exposure dose.

One can see from Fig. 2a that the values of $\tan \varphi$ and $\Delta \alpha L$ change quasi-periodically with increasing the exposure dose. Note that curves (1) and (2) change most noticeably after the first exposure. Another important feature of the behaviour of these curves is their anticorrelation in the energy density range up to 2.5 kJ cm⁻². Figure 2b demonstrates the correlation of the shifts of the 2467-cm⁻¹ and 2270-cm⁻¹ absorption bands.

The curves presented in Fig. 2 were obtained by exposing the bulk PSG sample to radiation with the energy density of 300 mJ cm⁻². When such samples were exposed to radiation with the energy density lower than

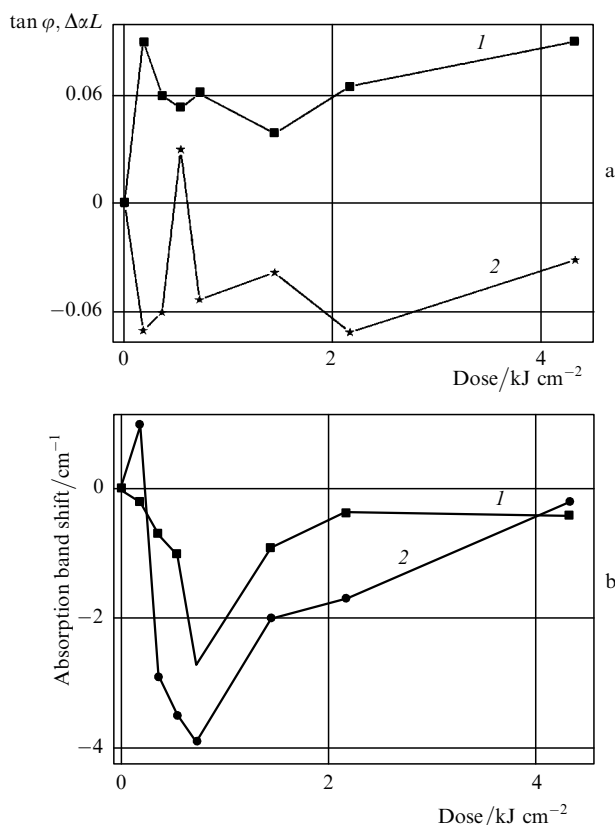


Figure 2. Dose dependences of the slope ϕ of curve (2) in Fig. 1 in the frequency range from 4500 to 3000 cm^{-1} (1) and the induced absorption ΔzL in the 2646- cm^{-1} band (2) (a), and shifts of the 2467- cm^{-1} (1) and 2270- cm^{-1} bands (2) (b).

150 mJ cm^{-2} , the correlation between the corresponding dose dependences disappeared.

3.2 Raman spectra

Figure 3 presents the typical dose dependences for Raman bands at 1325, 1060, 1020, and 606 cm^{-1} in a PSG fibre.

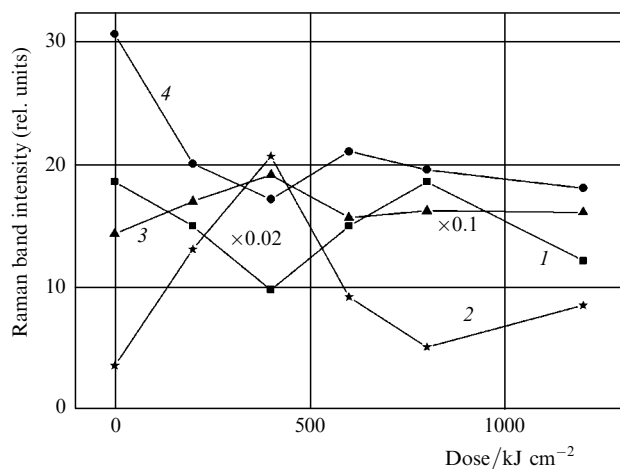


Figure 3. Dose dependences of the Raman bands related to the $\text{P}=\text{O}$ vibrations (1, 1325 cm^{-1}), vibrations of the $\text{Si}-\text{O}-\text{P}$ linkage including pentacoordinated phosphorus atoms (2, 1060 cm^{-1}), breathing vibrations of three-membered rings (3, 606 cm^{-1}), and vibrations of the $\text{P}-\text{O}-\text{P}$ linkage (4, 1020 cm^{-1}).

These bands were assigned [13] to the vibrations of the non-bridge oxygen bonded to phosphorus atoms ($\text{P}=\text{O}$); the $\text{Si}-\text{O}-\text{P}$ linkages including pentacoordinated phosphorus atoms; totally symmetric (breathing) vibrations of structures in the form of three-membered rings combining SiO_4 tetrahedra; and the $\text{P}-\text{O}-\text{P}$ linkages, respectively. The intensity of Raman bands was calculated as the intensity of IR absorption bands.

One can see the band intensities in Fig. 3 change quasi-periodically, as in Fig. 2. Other important features of curves in Fig. 3 are correlation in pairs of curves (1), (4) and (2), (3) and anticorrelation between these pairs.

4. Discussion of the results

The most important feature of the curves in Figs 2 and 3 is their quasi-periodic change with increasing exposure dose. We observed the similar dynamics of the dose dependences for three UV absorption bands in PSG samples [10]. As in the case of IR absorption spectra, the strongest changes in the spectra were induced during the first exposure. Note that, as far as we know, such dependences of the concentration of point defects and the concentration of interatomic bonds in quartz glasses on the exposure dose were not observed earlier and were not assumed in theoretical models.

4.1 Dynamics of the concentration of phosphorus atom bonds

It is known [13] that a considerable part of phosphorus atoms in the PSG are in the tetracoordinated state with the $\text{P}=\text{O}$ bond and a relatively small part of these atoms is in the pentacoordinated state. The UV irradiation of PSG leads to the dissociation of the $\text{P}=\text{O}$ bonds followed by the formation of pentacoordinated phosphorus atoms [13]. In principle, the reverse reaction is also possible, which leads to the formation of the $\text{P}=\text{O}$ bond after the decomposition of pentacoordinated phosphorus atoms. We have managed to observe experimentally multiple changing of one reaction by another during irradiation of PSG. The nonmonotonic dynamics of the dose dependence of the concentration of atoms coupled by the $\text{P}=\text{O}$ bond (hereafter, the $\text{P}=\text{O}$ bond concentration) was observed by the methods of IR absorption spectroscopy [curve (2) in Fig. 2a] and Raman spectroscopy [curve (1) in Fig. 3]. The extrema of these dependences were achieved at different doses, which is explained, in our opinion, by the fact that in the first case, we studied a bulky sample, while in the second case, we studied a fibre sample. In addition, the exposure doses were different (300 mJ cm^{-2} in the first case and 50 mJ cm^{-2} in the second case). Similar dose dependences of the $\text{P}=\text{O}$ bond concentration obtained by two different methods demonstrate the reliability of these results. The dissociation of $\text{P}=\text{O}$ bonds should reduce the intensities of bands caused by vibrations of the part of this group of atoms coupled by the hydrogen bond with oxygen atom of hydroxyl groups in silanol centres. This is manifested in the disappearance of the 3280- cm^{-1} absorption band in the inset in Fig. 1.

The transition of a phosphorus atom from the tetracoordinated to pentacoordinated state should lead to the appearance of additional rings bonding the given atom with other atoms in the network and also possibly to a change in the number of ring members into which this atom was

already included, if these rings were 'stressed'. If the concentration of phosphorus atoms in the glass is high enough, these changes will cause the rearrangement of the entire PSG network. The experimental data presented below demonstrate such a rearrangement.

It was shown in paper [13] that a considerable part of tetracoordinated phosphorus atoms in PSG are bonded in pairs by P – O – P oxygen linkages. Curve 4 in Fig. 3 shows that the concentration of P – O – P linkages during irradiation correlates with the P=O bond concentration [curve (1)]. It may seem that this result contradicts the course of the photochemical reaction because the dissociation of P = O bonds should lead to the increase in the number of P – O – P linkages. This contradiction can be explained by the fact that, according to [13], the Raman scattering intensity determined by P – O – P linkages between tetra-coordinated phosphorus atoms exceeds the Raman scattering intensity determined by linkages between penta-coordinated atoms, and the contribution to the total scattering intensity at a frequency of 1020 cm⁻¹ from newly formed P – O – P linkages coupling new or previously existed pentacoordinated phosphorus atoms is relatively small.

4.2 Dynamics of variations of the structural elements of the PSG network near phosphorus atoms

The absorption spectra of PSGs with different concentrations of phosphorus oxide recorded in the region from 2.5 to 5 μm are presented in [16]. The spectra show that the 2260-cm⁻¹ absorption band (λ ~ 4.42 μm) shifts to ~ 2336 cm⁻¹ when the molar concentration of P₂O₅ is increased from 0 to 16.5%. On the other hand, the position of the 2467-cm⁻¹ absorption band (λ ~ 4.05 μm) changed weakly, while its intensity increased monotonically. As mentioned above, the first of these bands is related to vibrations of the Si – O – Si, Si – O – P, and P – O – P linkages, while the nature of the second band was not explained in the literature [13].

We assume that the second band is determined by vibrations of the same linkages, but in the presence of phosphorus atoms in the nearest coordination sphere. This assumption was verified with the help of quantum-chemical calculations of vibrations of the Si – O – Si, Si – O – P, and P – O – P linkages performed by using the GAMESS program (US) [17] within the framework of the cluster model of the glass network. The structure of cluster used in calculations is shown in Fig. 4. The broken bonds of the external Si and P atoms were saturated with hydrogen atoms. The calculations showed that in the case of asymmetric extension of the Si – O and (or) P – O bonds in the Si – O – P and P – O – P linkages, the vibrational overtone frequency was greater than the doubled frequency of the fundamental vibration and was ~ 2500 cm⁻¹, i.e. close to the experimental value 2467 cm⁻¹. As the concentration of phosphorus atoms was increased, the number of asymmetrically extended bonds increased and, therefore, the intensity of the 2467-cm⁻¹ absorption band also increased, whereas the intensity of the 2270-cm⁻¹ band did not change because the total number of the Si – O – Si, Si – O – P, and P – O – P linkages remained almost invariable after doping the glass with phosphorus atoms. The correlation of the curves in Fig. 2b additionally confirms the assumption about the same nature of the absorption bands at 2467 and 2270 cm⁻¹.

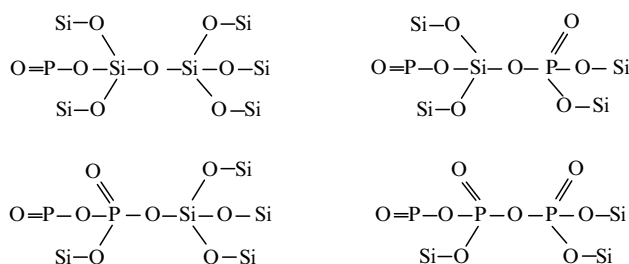


Figure 4. Structure of clusters of the PSG network used in quantum-chemical calculations for assigning the 2467-cm⁻¹ absorption band (λ ~ 4.05 μm).

The shift of the 2260-cm⁻¹ band is explained in [13] by a change in the valence angle at the oxygen atom in the Si – O – Si linkage. The presence of the minimum in both curves in Fig. 2b at a dose of ~ 500 J cm⁻² suggests that the average value of this angle in the Si – O – Si, Si – O – P, and P – O – P linkages first decreases and then increases during irradiation, which indirectly points to a change in the number of members in the ring system and, therefore, to the rearrangement of the glass network.

4.3 Dynamics of variations of the structural elements of the PSG network not bonded with phosphorus atoms

Changes occurring in the PSG network exposed to radiation involve not only the bonds of phosphorus atoms with neighbouring atoms. Curve (3) in Fig. 3 reflects the change in the concentration of SiO₄ tetrahedra combined in three-membered rings. One can see that this curves correlates with the change in the concentration of pentacoordinated phosphorus atoms in PSG. Note that three-membered rings of SiO₄ tetrahedra and pentacoordinated phosphorus atoms are locally stressed structures. The correlation of the dose dependences of the concentration of stressed structural elements of the PSG network suggests that the repeated ranges of increasing stresses followed by relaxation appear over the entire network during irradiation.

The change in the entire glass network during irradiation is also confirmed by the similarity of the obtained quasi-periodic dependences with the dose dependences of the concentration of point defects in PSG not related to phosphorus atoms, i.e. of non-bridge oxygen-hole centres (NOHCs) and E' centres [10]. Variations in the concentration of these point defects are probably caused by the network rearrangement. This is also confirmed by the dependence of the correlation of changes in different parts of the network on the radiation energy density (i.e. on the increase in the number of breaks in Si – O – Si, Si – O – P, P – O – P linkages caused by two-photon absorption).

Thus, the data obtained in our study give the self-consistent picture of changes in the bonds of phosphorus atoms, structural elements of the PSG network near phosphorus atoms and network elements not related to phosphorus atoms (including point defects of the quartz sublattice).

5. Model of the photoinduced change of the PSG network

We interpreted our experimental data by using the concepts of mobility (rigidity) of the bonds between objects in

disordered media, which were developed in the theory of rigidity percolation described, for example, in [18]. These concepts have been already used to explain and predict the properties of glasses [19] by describing changes in the state of their network. The mobility of the glass network (the ability of interatomic bonds to switch from one pair of atoms to another) is determined in the percolation theory by the average coordination number n_c for all atoms of the network. If n_c is small, the glass network is relatively 'soft', which facilitates the bond switching and relaxation of stressed bonds. As n_c is increased, the network undergoes a comparatively abrupt transition to the 'rigid' state in which bond switching between atoms and relaxation processes cease. This transition is similar to the phase transition of the second kind [18]. The value of n_c at which the network undergoes an abrupt transition to the rigid state (hereafter, threshold) can be calculated comparatively simply for pure quartz glass or P_2O_5 glass. However, the calculation of the threshold for multicomponent glasses and in the presence of defects becomes complicated, and it was not performed for PSG.

We explain our experimental results by using the model of changing rigidity of the PSG network. The introduction of phosphorus atoms into a quartz glass, which are bonded with the glass network only by three covalent bonds [13], reduces the value of n_c . It is assumed that for the molar concentration of phosphorus $\sim 12\%$, the value of n_c becomes close to the threshold, remaining, however, somewhat higher, corresponding to the rigid state of the network. At the initial exposure stage, the rigidity threshold is achieved due to the break of Si–O–Si, Si–O–P, and P–O–P linkages and the network undergoes the transition to the soft state. The number of stressed structural elements of the network in the soft state (in particular, pentacoordinated phosphorus atoms and three-membered tetrahedron rings) decreases.

In the case of a soft network, breaks in the Si–O–Si, Si–O–P, and P–O–P linkages accumulated during irradiation until the achievement of the rigidity threshold become to restore. As a result, n_c gradually increases. The value of n_c also increases in the soft network due to the nonmonotonic decrease in the excess number of tetraordinated phosphorus atoms (compared to the number of pentacoordinated atoms existing in the initial PSG state) and due to 'healing' of initial structural imperfections of the network, resulting in the approach of its structure to crystalline. It is assumed that n_c achieves the threshold value due to these processes and the network rigidity increases. As a result, dynamic processes in the network cease and structural imperfections caused by the dissociation of bonds again begin to accumulate. Pentacoordinated phosphorus atoms and tree-unit tetrahedron rings are formed and point defects (NOHCs and E' centres) are also formed and accumulated due to the break of Si–O–Si linkages. The cycle of a change in the network rigidity repeats. However, it does not completely repeat the first cycle because the network structure after its termination becomes closer to the equilibrium state. Because of this, the subsequent cycles of the rigidity change during prolonged irradiation are less pronounced. We observed in our experiments only several first cycles.

The network rearrangement processes described above can also explain variations in the concentration of point defects observed in [10]. The NOHCs and E' centres are

formed in a rigid network, and when the network undergoes the transition to the soft state, these centres begin to relax with the formation of phosphorus oxygen-deficient centres. This could explain the anticorrelation of the dose dependences of the concentration of these defects (see Fig. 5 in [10]). The rearrangement process repeats, giving rise to several such cycles determined by the network rigidity. Periodic variations in the network rigidity can also modulate the relaxation of other defects absorbing UV radiation. If the network is rigid, the breaks in the Si–O–Si linkages are accumulated, while in the soft network the number of breaks decreases.

6. Conclusions

The network structure of PSG exposed to laser radiation at 193 nm exhibits unusual quasi-periodic variations. This effect becomes more pronounced when the radiation energy density is increased (i.e. the two-photon absorption of light increases). The network rearrangement can explain quasi-periodic variations in the concentration of point silicon defects in PSG observed earlier in [10] and also the correlation of all the observed variations and the dependence of this correlation on the radiation energy density.

The model, which we proposed to explain unusual changes in the PSG network, is based on the concept of the quasi-periodic change in the network rigidity induced by UV radiation. Initially, the network is in the rigid state, but near the rigidity threshold. During irradiation, the network undergoes the abrupt transition from the rigid to soft state due to the accumulation of breaks in the Si–O–Si, Si–O–P, and P–O–P linkages. The network structure in this state is comparatively rapidly reconstructed, which leads to a change in the type of increase in the concentration of point defects. However, the ordering of the network structure in the soft state leads to the rearrangement of the rigid state of the network during the next time interval. The cycle of variation in the PSG network rigidity during irradiation can be repeated many times.

The model that we proposed is to some extent a synthesis of models considered in Introduction. This model is devoid of the disadvantages mentioned in Introduction: the model of local densifications is supplemented by the consideration of the network changes in regions between these densifications, while the model of the network structure ordering is supplemented by the consideration of defects capable of changing the rearrangement rate.

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