

Role of point defects in the photosensitivity of hydrogen-loaded phosphosilicate glass

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Abstract. It is shown that point defect modifications in hydrogen-loaded phosphosilicate glass (PSG) do not play a central role in determining its photosensitivity. Photochemical reactions that involve a two-step point defect modification and pre-exposure effect are incapable of accounting for photoinduced refractive index changes. It seems likely that a key role in UV-induced refractive index modifications is played by structural changes in the PSG network. Experimental data are presented that demonstrate intricate network rearrangement dynamics during UV exposure of PSG.

Keywords: photosensitivity, phosphosilicate glass, defects in glass, photoinduced refractive index changes, two-step photochemical reaction.

1. Introduction

Phosphosilicate glass (PSG) fibres, in which the Stokes shift far exceeds that in fibres from germanosilicate glass (GSG) and other silicate glasses, are of special interest for the fabrication of Raman fibre lasers and amplifiers [1].

At the same time, the photosensitivity of PSG, needed to change its refractive index when writing Bragg gratings (BGs), is markedly lower than that of other quartz glasses [2]. For this reason, to inscribe BGs into PSG fibre, the glass is first loaded with hydrogen and the fibre is then exposed to radiation with a wavelength λ no longer than 193 nm. This procedure influences other properties of the glass; in particular, it increases the optical loss, thereby reducing the efficiency of the fibre laser or amplifier. Hydrogen loading of PSG markedly complicates the mechanism of photoinduced index changes, and the process takes the form of a two-step photochemical reaction involving three types of point defects. The process also shows up as the pre-exposure effect. A model for PSG photosensitivity should be constructed so as to account for all the effects observed so far to accompany photoinduced index changes.

There are two approaches to the interpretation of photoinduced index changes in silicate glasses [3]. One of them builds on photoinduced point defect (colour centre) modifications in the glass. The associated changes in point defect polarisability lead to index changes. This mechanism is thought to be responsible for most of the photoinduced index change (PIC)

in GSG and some other glasses. Efforts to detect such defects in PSG were however unsuccessful for a long time. Only recently have Rybaltovsky et al. [4] identified a phosphorus-related oxygen-deficient centre (PODC) having a VUV absorption band. The photosensitivity of PSG can be accounted for by changes in the state of this defect. In the other approach, PICs are interpreted in terms of glass network rearrangement. This process may be evidenced by photoinduced changes in the coordination number of the phosphorus atoms (the phosphorus atoms can be coordinated to four or five oxygens), leading to changes in the ring structures of the network. Dianov et al. [5] presented experimental evidence that 244-nm exposure changed the average coordination number of the phosphorus atoms in PSG, but no network rearrangement or PICs were detected. Hosono et al [6] assumed that the formation of phosphorus-related defects in hydrogen-loaded PSG might influence the average coordination number of the network atoms, but no evidence of PSG network rearrangement was reported. Indirect evidence of structural changes in the network of hydrogen-loaded PSG was presented in several reports. In particular, the coefficient in the Sellmeier dispersion formula, $n(\lambda)$, that depends mainly on network modifications varies in the same fluence range as the refractive index, whereas the coefficient dependent on point defect modifications remains essentially unchanged [7]. The tensile stress produced in the fibre core by BG inscription [8] also attests to PSG network rearrangement.

The objective of this work was to perform additional studies and analyse earlier data with the aim of constructing a consistent model for PSG photosensitivity.

2. Criticism of the model based on point defect modifications

2.1. Pre-exposure effect

Among the silicate glasses studied, PSG exhibits the strongest pre-exposure effect [9]. It can be accounted for by the presence of three types of point defects in PSG and a two-step photochemical reaction. It is assumed that, during UV exposure, the first photochemical reaction, involving atomic hydrogen, converts precursor defects to an intermediate form. The second photochemical reaction, without hydrogen, converts the intermediate defects to a final form, responsible for the PIC. During exposure, the concentration of precursor defects decreases, that of intermediate defects first increases and then drops, and that of final defects increases with a delay in the initial stage, which accounts for the fact that the PIC vs. fluence curve of PSG is typically S-shaped [10]. Thus, the presence of a UV-degradable precursor to the PODC identified by Rybaltovsky

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et al. [4] is a necessary condition for this centre to contribute to PICs. It is reasonable to assume that the precursor defect is oxygen-deficient, like the PODC. The known oxygen-deficient centres in silicate glass include ODC1 and ODC2 [11]. The 5.05-eV absorption band of ODC2 is however missing in the spectrum of hydrogen-free PSG [4], and the absorption band of ODC1 (7.6 eV) remains unchanged during UV exposure of hydrogen-loaded PSG [12], meaning that these defects are not involved in the photochemical reaction in question. Therefore, PODC formation can only be accounted for by PSG network degradation. This requires three photochemical reactions near a phosphorus atom: removal of the oxygen from the Si–O–P bridges in two steps and breaking of one bond of the phosphorus atom. Such a multistep reaction in one cluster appears unlikely.

That the PODC is involved in a two-step photochemical reaction might be evidenced by the photoinduced loss vs. fluence curve (whose shape is determined by the PODC concentration) being S-shaped, in common with the PIC vs. fluence curve of PSG. Figure 1 compares such curves taken from Rybaltovsky [12] (for convenience of comparison, the curves are scaled to roughly the same level, and the loss and PIC are given in arbitrary units). The fluence dependence of the PIC [curve (2)] is seen to be S-shaped, in contrast to that of the photoinduced loss [curve (1)], which is determined by the PODC concentration. Therefore, the PODC does not result from any two-step photochemical reaction and, hence, is not directly related to PICs (it may result from other reactions).

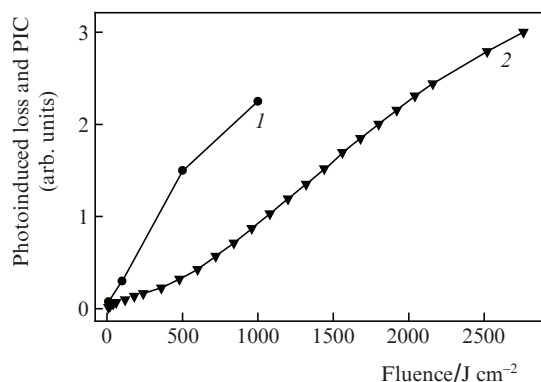


Figure 1. (1) Photoinduced loss and (2) PIC as functions of fluence [12].

2.2. Discrepancy between calculated and measured PIC values in PSG

The photoinduced loss values reported by Rybaltovsky [12] for the band at ~ 180 nm can be used to assess the influence of the defects in question on the PIC in bulk PSG. After exposure to a fluence of 1 kJ cm^{-2} , the photoinduced loss in this band was $\sim 800 \text{ cm}^{-1}$, exceeding that in the other absorption bands by two orders of magnitude. Using the simple and sufficiently accurate relation for PICs derived by Sokolov and Sulimov [13] from the Kramers–Kronig relationship, $\delta n = (\lambda/2\pi^2)(\Delta/\omega)\delta\alpha_{\text{max}}$ (where $\delta\alpha_{\text{max}}$ is the maximum photoinduced absorption at frequency ω ; Δ is the effective absorption band width; and $\lambda = 2\pi c/\omega$), we can estimate the PIC near $1.5 \text{ }\mu\text{m}$: $\delta n \sim 1 \times 10^{-4}$ [at $\hbar\Delta \sim 1 \text{ eV}$, $\delta\alpha_{\text{max}} = 800 \text{ cm}^{-1}$ [12] and $\hbar\omega = 6.9 \text{ eV}$ ($\lambda = 180 \text{ nm}$)]. The same value was obtained using the Kramers–Kronig relationship [12]. It is an order of

magnitude lower than the measured value (1×10^{-3}) for a fibre sample exposed to the same fluence [12]. The discrepancy between the measured and calculated PIC values is attributed by Rybaltovsky [12] to the potentially higher refractive-index modification efficiency in fibres compared to bulk material because the fibres experience tensile stresses. According to the model used by Rybaltovsky [12] to interpret the PIC in PSG, this means that mechanical stress should raise the PODC concentration in the fibre. Since GSG fibres and bulk samples do not differ in point defect concentration after UV exposure [14], additional experimental evidence is needed to confirm that the defect concentration in PSG fibres exceeds that in bulk PSG.

3. Experimental

The low-loss PSG fibres and bulk samples studied were similar to those described elsewhere [10]. UV irradiation of the samples was performed using a CL5000 excimer laser (wavelength, 193 nm; pulse duration, 6–7 ns; pulse energy density, 25–150 mJ cm^{-2} ; pulse repetition rate, 10 Hz or varied from 5 to 50 Hz). Absorption spectra were measured on a Bruker IFS-113V Fourier transform IR spectrometer equipped with an IR microscope, which enabled the beam to be focused to a spot diameter of 0.4 mm. In Raman measurements, excitation was provided by the 514.5-nm argon laser line (Spectra-Physics Stabilite 2017). Raman spectra were taken on a Jobin-Yvon T64000 triple spectrograph. The transmission and Raman spectra were measured before UV exposure and after each UV exposure. The fibres were loaded with molecular hydrogen in a chamber at 100 atm. To accelerate hydrogen diffusion, the samples were maintained at $100 \text{ }^\circ\text{C}$ for 12 h. To eliminate the PIC, pieces of the fibres with inscribed BGs were thermally annealed at $500\text{--}600 \text{ }^\circ\text{C}$. The automatic apparatus and procedure used to anneal the fibres were similar to those described by Bozhkov et al. [15].

4. Results and discussion

4.1. Thermal decay of PICs

The annealing behaviour of PICs may provide insight into the mechanism of PSG photosensitivity. The annealing-induced PIC decay was quantified using two parameters (like in Bozhkov et al. [15]): Δn_{mod} (peak-to-valley index modulation, evaluated as the index difference between the UV-exposed and unexposed parts of the BG fringes) and Δn_{av} (PIC averaged over the grating length, evaluated from the spectral position of the Bragg peak). The $\Delta n_{\text{mod}}(T)$ data were obtained from the difference between the Bragg peak heights at the annealing and initial temperatures. To determine $\Delta n_{\text{av}}(T)$, the BGs were annealed twice. The first anneal led to an incomplete grating decay, which allowed us to anneal the grating a second time. Since the second anneal had no effect on the PIC (the Bragg peak height was temperature-independent), the Bragg peak position was determined by the temperature variation of the initial refractive index, $n_0(T)$. The change in the Bragg wavelength in the second anneal relative to that in the first anneal ($\Delta\lambda/\lambda$) can be used to determine the average PIC: $\Delta n_{\text{av}}(T) = n_0(T)\Delta\lambda/(\lambda\eta)$, where η is the fraction of light that propagates within the fibre core.

Figure 2 illustrates the annealing-induced decay of Δn_{av} and Δn_{mod} in hydrogen-loaded PSG and GSG fibres. When photosensitivity is due to point defects, annealing reduces the

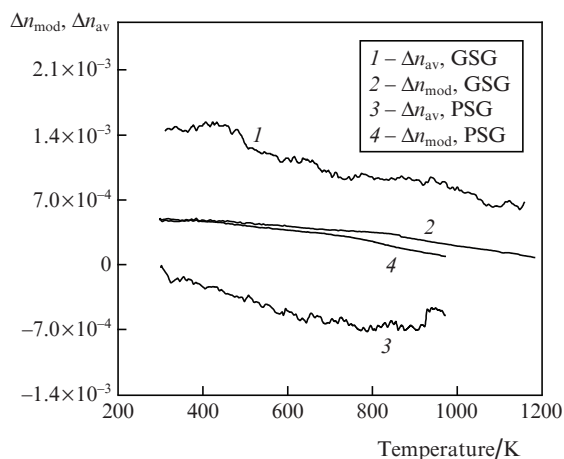


Figure 2. Annealing-induced decay of Δn_{av} and Δn_{mod} in hydrogen-loaded (1, 2) GSG and (3, 4) PSG fibres.

PIC to nearly zero [Fig. 2, curves (1, 2)]. At the same time, the $\Delta n_{av}(T)$ of the PSG fibres is negative ($\Delta n_{av} \approx 0$ only at the initial temperature $T \approx 293$ K), indicating an increase in PIC. The increase in the magnitude of Δn_{av} is accompanied by a reduction in Δn_{mod} [curve (4)]. Therefore, the mechanism of PIC decay in hydrogen-loaded PSG differs from that in GSG. One possible reason for this is that the annealing-induced stress in PSG leads to plastic deformation of the UV-exposed region of the grating, thereby increasing n_0 and/or the BG period. As a result, the Bragg wavelength increases to above its initial level at all temperatures, leading to negative Δn_{av} values. At the initial annealing temperature (293 K), this increase only compensates for the decrease in Bragg wavelength due to the PIC decay. Plastic deformation of PSG may be due to the photoinduced disruption of network connectivity, which persists until annealing [16].

4.2. Quasi-periodic fluence dependence of bond densities

Photoinduced glass network rearrangement in hydrogen-free PSG may be evidenced by quasi-periodic fluence dependences of point defect and bond densities [16]. Figure 3 shows the fluence dependences of the UV-induced absorption (for a bulk sample) and UV-induced Raman scattering (for a fibre sample) due to changes in the P=O bond density in hydrogen-loaded PSG. As seen in Fig. 3a, the UV-induced absorption in hydrogen-loaded PSG varies quasi-periodically. Such behaviour was observed under various exposure conditions and is, therefore, reproducible. The Raman scattering intensity for the fibre sample also varies quasi-periodically (Fig. 3b). The fact that the maxima and minima in Figs 3a and 3b occur at different fluences is attributable to the distinctions between the samples used.

A quasi-periodic variation of UV-induced absorption was also observed for other bands in the spectrum of PSG (Fig. 4). The broad band near 2300 cm^{-1} is presumably composed of two components, centred at 2260 and 2320 cm^{-1} , which arise from Si-H and P-H bond vibrations. Decomposing this band into two Gaussians centred at these frequencies and determining their heights as functions of laser fluence, we assessed the variation of the absorption in the two components, which are directly related to the variations in the density of the bonds in question. The P-H and Si-H bond densities have a maximum at a fluence of $\sim 2\text{ kJ cm}^{-2}$. The phosphorus

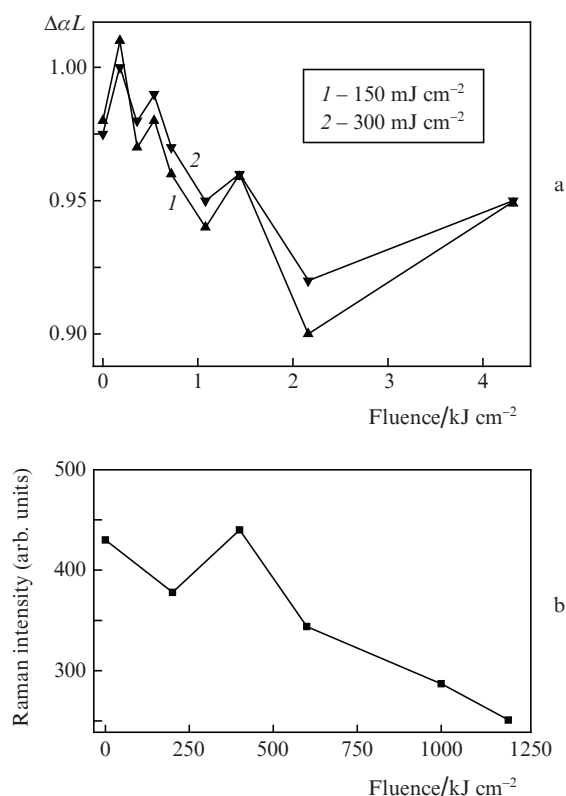


Figure 3. Fluence dependences of the UV-induced absorption in the 2646-cm^{-1} band (second harmonic of P=O bond vibrations) for a bulk sample ($\Delta\alpha$ is the induced absorption coefficient and L is the sample length); (b) fluence dependence of the Raman intensity in the 1325-cm^{-1} band for a fibre sample.

atoms more actively react with hydrogen: with increasing fluence, the density of P-H bonds rises more rapidly than that of Si-H bonds. Also shown in Fig. 4 is the fluence dependence of the UV-induced absorption in the Si-OH band. The three curves have a minimum at a fluence of $1.2\text{--}1.4\text{ kJ cm}^{-2}$.

The release of bound hydrogen from the glass network during UV exposure appears unusual, but it is confirmed by the increase in the concentration of Si-OH silanol groups

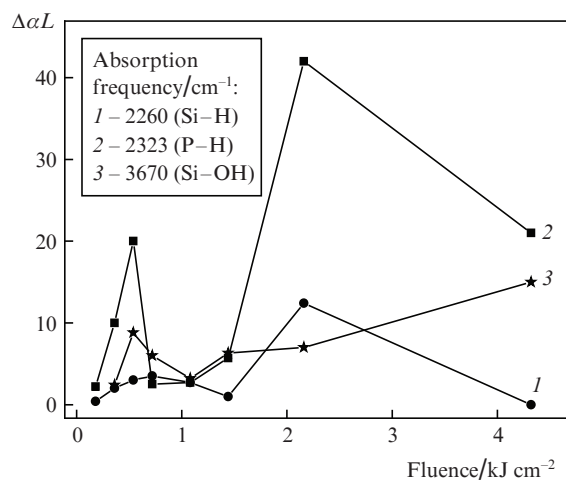


Figure 4. Fluence dependences of the UV-induced absorption in the bands at (1) 2260 (Si-H), (2) 2323 (P-H) and (3) 3670 cm^{-1} (Si-OH).

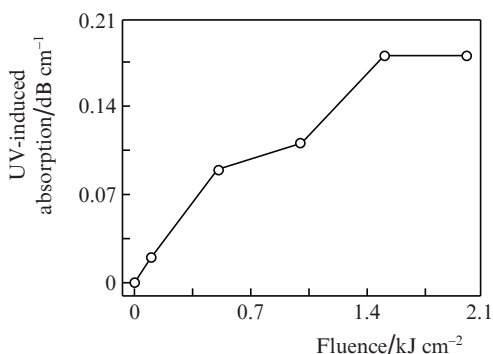


Figure 5. Fluence dependence of the UV-induced absorption in the 1.39- μm band (second harmonic of Si–OH vibrations) for a pre-exposed fibre sample free of molecular hydrogen.

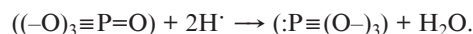
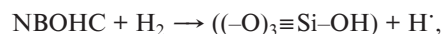
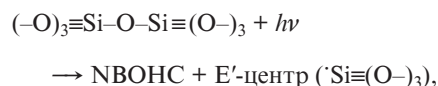
during re-exposure of samples known to contain no molecular hydrogen. Figure 5 illustrates the increase in UV-induced 1.39- μm absorption, which can be accounted for by the release of atomic hydrogen from the glass network and reaction of the hydrogen with UV-induced nonbridging oxygen hole centres (NBOHCs, $(\text{O})_3\equiv\text{Si}-\text{O}$): $\text{NBOHC} + \text{H}^\cdot \rightarrow (\text{O})_3\equiv\text{Si}-\text{OH}$. It seems likely that UV exposure predominantly breaks Si–H bonds (relative to the P–H bonds) and drives the resulting atomic hydrogen from the glass network to interstitial positions, causing it to participate in the above photochemical reaction. Hydrogen incorporation into and release from the network should change the network rigidity, which might influence the photochemical reaction and refractive index modification [16].

5. Model of a two-step point defect reaction in hydrogen-loaded PSG

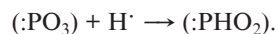
The above evidence that the glass network actively participates in the photochemical reaction initiated by UV exposure leads us to re-examine the role of phosphorus-related point defects as the only sources of PICs. At the same time, point defects (and possibly network modifications) may be involved in a two-step reaction that would account for the pre-exposure effect.

According to a previous model [10], the index modification conditions in the second step of the reaction result from the dissociation of an assumed intermediate defect, produced in the first step in the presence of hydrogen. In an earlier study [10], UV exposure first increased the concentration of this defect in PSG and then reduced it (with a maximum near 2 kJ cm^{-2}), but its structure was not identified [10]. In a more recent study [12], the fluence dependence of the UV-induced absorption for hydrogen-loaded PSG was shown to be monotonic for all the observed absorption bands in the spectral range 0.18–3 μm . At the same time, the dependence for the absorption band at 2646 cm^{-1} , which is due to P=O bond vibrations and was not examined by Rybaltovsky [12], is non-monotonic (Fig. 3a). It may be that it is this centre which participates in the two-step reaction in PSG. Consider a hypothetical photochemical reaction involving it. Its first step yields atomic hydrogen. It may originate from NBOHCs, which cause molecular hydrogen to dissociate [11]. NBOHCs result from Si–O–Si bridge breaking via photon absorption ($h\nu$). The next step is P=O bond breaking and the formation

of three-coordinate phosphorus atoms, each having a lone electron pair ($:\text{P}\equiv(\text{O}-)_3$):



These reactions yield E'-centres, $\equiv\text{Si}-\text{OH}$ silanol groups and water molecules. The growth of the E'-centre concentration was documented by Rybaltovsky [12]. The increase in silanol group concentration, which can be assessed from the variation in the UV-induced absorption at 3670 cm^{-1} , is illustrated in Fig. 5. Since the P=O bond density has a minimum at a fluence of $\sim 2 \text{ kJ cm}^{-2}$ (Fig. 3a), the $(:\text{P}\equiv(\text{O}-)_3)$ concentration must have a maximum at the same fluence. Therefore, the fluence dependence of the concentration of these phosphorus centres must be similar in shape to that of the concentration of assumed intermediate defects [10]. The next reaction is presumably



According to quantum-chemical modelling results, the $(:\text{PHO}_2)$ centre has an absorption band near 176 nm, in excellent agreement with the $\sim 180 \text{ nm}$ found in experiments [12]. Excited-state energies were calculated using the GAMESS program [17], like in Rybaltovsky et al. [4]. The dangling bonds on the cluster surface were saturated with hydrogen. The cluster geometry was optimised by the Hartree–Fock method. The uncertainty in the excited-state energies obtained was 15%–20%. The structure of the cluster is shown in Fig. 6.

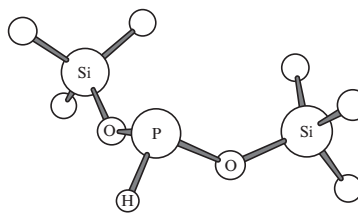


Figure 6. Simulated configuration of the $(:\text{PHO}_2)$ centre.

The $(:\text{PHO}_2)$ centre possesses all features of a defect capable of accounting for the PIC in the point defect modification model: it forms from an intermediate centre, with a characteristic nonmonotonic fluence dependence of its concentration; it results from interaction with hydrogen in the second step of the reaction; and it has an absorption band near 180 nm (i.e., near the only induced absorption band that can account for PICs). Moreover, this centre emerges together with other defects, as identified in UV-exposed samples: E'-centres and $\equiv\text{Si}-\text{OH}$ groups. Since the reaction involving the $(:\text{PHO}_2)$ centre is two-step, the associated absorption band should have an S-shaped fluence dependence. This is however not so (Fig. 1). Therefore, the centre under consideration is incapable of markedly changing the refractive index. It seems likely that the two-step reaction in PSG involves not several types of

point defects but sequentially varying network structures, transitions between which result in refractive index modifications. The data presented in Fig. 4 attest to the possibility of dynamic changes in network structure during hydrogen incorporation into and release from the network.

6. Conclusions

No evidence has been found that any point defects are responsible for UV-induced refractive index modifications in hydrogen-loaded PSG, in contrast to the model presented in Larionov et al. [10].

The phosphorus-related point defect proposed here can be responsible for a two-step photochemical reaction. Unfortunately, the UV-induced modification of this defect, traced in this study, cannot account for UV-induced refractive index modifications within a point defect mechanism. It seems, therefore, likely that the PIC and two-step reaction in PSG are associated with glass network modifications.

Some of the present experimental results (the observed distinction between the photoinduced index contrast and average PIC upon Bragg grating annealing and the quasi-periodic fluence dependence of the concentration of phosphorus bonds to other atoms) provide indirect evidence of PSG network modifications. UV exposure may cause both the incorporation of atomic hydrogen into the glass network and hydrogen release. This may lead to a dynamic network rearrangement and seems to account for the characteristic S-shaped fluence dependence of the PIC in PSG. The present results offer further insight into photoinduced PSG network modifications [6] via a two-step photochemical reaction.

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