

# Defects of a phosphosilicate glass exposed to the 193-nm radiation

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

**Abstract.** Induced absorption is measured in a hydrogen-unloaded phosphosilicate glass (PSG) in spectral ranges from 140 to 850 nm and from 1000 to 1700 nm before and after its exposure to the 193-nm radiation. It is shown that the induced-absorption bands in the range between 140 and 300 nm do not coincide with the bands observed earlier after exposing a PSG to X-rays. It is assumed that the photorefractive effect in the PSG is related to variations induced in the glass network rather than to defects responsible for the induced-absorption bands.

**Keywords:** photosensitivity, phosphosilicate glass, glass defects, induced refractive index, excimer laser.

## 1. Introduction

Phosphosilicate fibres are promising for applications in Raman converters and optical amplifiers [1]. Unfortunately, a comparatively low photosensitivity of phosphosilicate glasses (PSGs) hampers their use in fibreoptic communication lines because the fabrication of refractive-index gratings in them is complicated for this reason. Therefore, the study of the mechanism of photosensitivity of PSGs with the aim to increase it is of current interest.

The photoinduced effect (the UV light-induced change in the refractive index) was first discovered in a germanosilicate glass. Later, this effect was found in other silicate glasses, in particular, in a PSG. However, this effect in PSGs was observed only in hydrogen-loaded samples and only upon irradiation at 193 nm by excimer lasers [2]. And only after 10 years it was found [3] that the photoinduced effect can be also observed in hydrogen-unloaded PSGs irradiated by 6–8-ns laser pulses providing a high energy density ( $\sim 300 \text{ mJ cm}^{-2}$ ). In this case, the effect is induced probably due to two-photon absorption. The maximum value of the induced refractive index achieved in [3] was  $5 \times 10^{-4}$  for the exposure dose  $\sim 5 \text{ kJ cm}^{-2}$ .

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It is assumed that the photoinduced effect appears in doped silica glasses due to the presence of defects in them. The existence of energy levels within the forbidden band related to defects provides the absorption of light in the one-photon process. In addition, the intrinsic defects of a glass cause the appearance of new or modified defects and the rearrangement of the glass structure, thereby changing its refractive index.

The nature of induced point defects in PSGs (hydrogen-unloaded) was established in the early 1990s by exposing glasses to X-rays [4]. Four types of phosphorous defects were found in the energy range between 0.5 and 6.2 eV. These types of defects are mentioned and discussed virtually in all papers devoted to the study of defects in PSGs exposed to UV radiation as well. However, the question about the identity of defects produced in PSGs exposed to X-rays or UV radiation and their relation to the photorefractive effect still remains open.

The role of phosphorous defects in the refractive-index induction was analysed in paper [5] where hydrogen-loaded and pure glasses exposed to the 193-nm radiation were studied. The existence of two of the four phosphorous defects found in [4] in hydrogen-unloaded PSGs was confirmed. In addition, the models of defects produced in the PSG upon its loading with hydrogen, which are responsible, in the opinion of the authors of [5], for the photorefractive effect, were proposed in [5].

Variations in the structure of hydrogen-unloaded PSGs induced by the 248-nm UV radiation were studied in papers [6, 7]. However, these variations were not accompanied by the refractive-index induction. The observation of the photorefractive effect in hydrogen-unloaded PSGs rekindles interest in the initial and modified defects of these glasses and the mechanism of their involvement in the refractive-index induction.

The aim of our paper was to study the formation of defects in a PSG exposed to the 193-nm UV radiation. Measurements were performed in the same spectral ranges as in [4] and in the VUV region. In [4], the VUV region was not studied due to strong scattering of light by glasses after their exposure to X-rays.

## 2. Experimental

We studied bulk phosphosilicate glasses and phosphosilicate fibres with low losses fabricated by the MCVD method [8]. Bulk samples were 0.2–1-mm-thick glass plates cut out of the fibre preforms perpendicular to their axis. The molar content of phosphorous oxide in the core of all samples

under study was  $\sim 12\%$ . The core diameter in bulk samples was 0.4–1 mm. Optical fibres were drawn from preforms that were similar to those for fabricating bulk samples. The difference between the refractive indices of the fibre core and cladding was  $\Delta N = 0.01$ , and the cut off wavelength was  $\lambda_c = 1.1 \mu\text{m}$ .

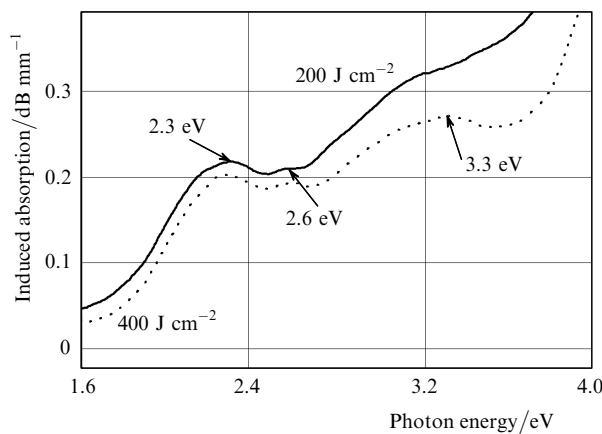
Samples were irradiated by 193-nm, 6–7-ns pulses from a CL5000 excimer laser [9]. The pulse energy density was 25–150  $\text{mJ cm}^{-2}$ . The pulse repetition rate was, as a rule, 10 Hz and was changed in some cases from 5 to 50 Hz. Induced absorption was measured by using an AQ6317 spectrum analyser (ANDO).

The UV transmission spectra of bulk samples were measured before and after their irradiation by using a LAMBDA 900 spectrophotometer (Perkin-Elmer) (beginning from 190 nm) and a VUVaS 1000 vacuum spectrophotometer (McPherson) (beginning from 116 nm). The transmission spectra recorded with these spectrophotometers could be compared in the wavelength region above 200 nm. The time intervals between the exposure of a sample and measurement of its spectra were from a few hours up to a few days, and between the successive exposures – from a few days up to a week. The EPR spectra of some bulk samples were also recorded before and after their irradiation.

### 3. Experimental results

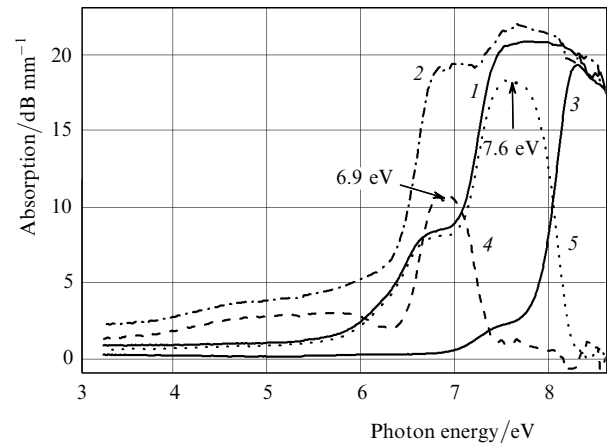
Figure 1 shows the induced-absorption spectra of a bulk PSG sample exposed to 200- and 400- $\text{J cm}^{-2}$  radiation doses, recorded with a LAMBDA 900 spectrophotometer. One can see that exposure gives rise to absorption bands at 2.3, 2.6, and 3.3 eV. These values correspond approximately to those reported in [4]. A similar absorption spectrum was obtained in [5] for a pure PSG sample containing 1.7% of phosphorous oxide irradiated by an excimer laser at 193 nm. However, the 2.6-eV band in the absorption spectrum in [5] was absent.

The absorption spectra of the same sample recorded with a vacuum spectrophotometer are presented in Fig. 2. One can see that absorption in the PSG (core) drastically increases in the energy range between 6.3 and 7.3 eV compared to that in the silica cladding [curves (1) and



**Figure 1.** Induced-absorption spectra of the PSG for exposure doses of 200 and 400  $\text{J cm}^{-2}$  (the arrows show the positions of induced-absorption bands).

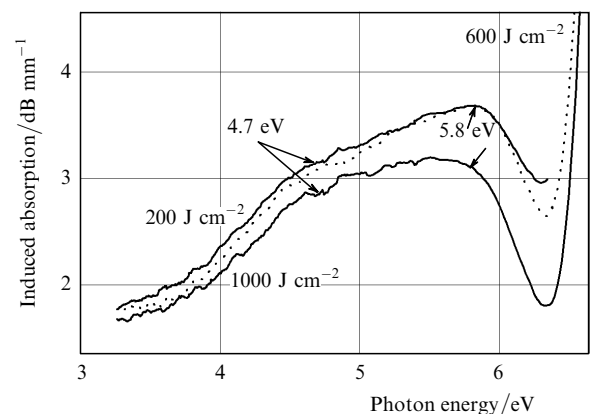
(3), respectively; curve (5) is the difference of curves (3) and (1)]. The appearance of the absorption band at 6.9 eV and a noticeable increase in the intensity of the 7.6-eV band lead to the red shift of the fundamental absorption band of the PSG. The absorption spectrum observed after exposing the sample to the 400- $\text{J cm}^{-2}$  dose is shown by curve (2). The corresponding induced absorption is shown by curve (4). One can see that the induced-absorption spectrum of the PSG consists of a broad band located in the range from 4 to 6 eV and a narrower band at 6.9 eV.



**Figure 2.** Absorption spectra of the PSG (core) and cladding (silica glass) recorded with a vacuum spectrophotometer (the arrows show the positions of induced-absorption bands): (1) initial absorption in the core; (2) absorption in the core after irradiation by the 400- $\text{J cm}^{-2}$  dose; (3) initial absorption in the cladding; (4) induced absorption; (5) difference of absorptions in the cladding and core.

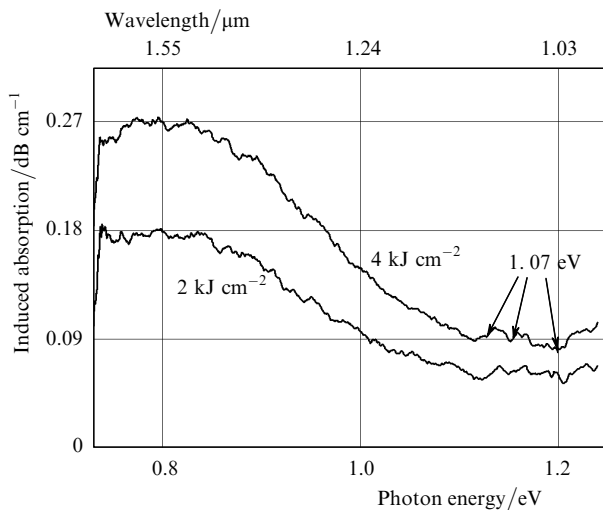
The induced-absorption band in the range between 4 and 6 eV is shown in more detail in Fig. 3. It seems that this band consists at least of two bands with maxima at 4.7 and 5.5 eV and width  $\sim 1.1$  eV.

Figure 4 presents the IR absorption spectra of a phosphosilicate fibre recorded after exposing the fibre to two irradiation doses. One can see that the induced-absorption band at  $\sim 0.8$  eV ( $\lambda = 1.57 \mu\text{m}$ ) (corresponding approximately to the 0.79-eV induced-absorption band in [4]) increases with increasing dose. The width of this band,



**Figure 3.** Induced-absorption spectra of the PSG in the energy range from 4 to 6 eV after exposure doses 200, 600, and 1000  $\text{J cm}^{-2}$ .

according to our data, is  $\sim 0.6$  eV. The 1.07-eV induced-absorption band ( $\lambda = 1.16 \mu\text{m}$ ) observed in [4] is present in Fig. 4 in the distorted form (without the distinct maximum at  $1.07 \mu\text{m}$ ). The width of this band is smaller than the value 0.32 eV presented in [4] and its shape does not change with increasing dose.



**Figure 4.** IR induced-absorption spectra of the PSG fibre (the arrows indicate the position of the band of the distorted shape) for radiation doses 2 and  $4 \text{ kJ cm}^{-2}$ .

#### 4. Discussion

Let us compare our results with those obtained in [4]. The differences between them are caused by different radiation wavelengths used for exposing samples, different methods of fabrication of bulk samples, and different conditions of measuring spectra after exposing. Bulk PSG samples were prepared in [4] by the plasma-chemical method (sputtering and deposition of particles of the proper chemical composition in an oxygen plasma). In our paper, samples were prepared by the MCVD method (the molar content of phosphorous oxide in our samples (12%) and in [4] (10%) was approximately the same). The induced-absorption bands were determined in [4] from the difference of spectra obtained directly after exposure and after annealing of samples at the temperature 823 K. Samples were exposed to light and their spectra were measured in [4] at the temperature 80 K. We irradiated samples and measured their spectra under normal conditions (i.e. conditions for FBG writing in fibres), and determined induced absorption from the difference between the absorption spectra of sample after and before irradiation.

Nevertheless, despite these differences in the preparation of samples and experimental conditions, our results are in good agreement with the data presented in [4]. Thus, the induced-absorption bands observed at 2.3, 2.6, and 3.3 eV in our experiments are close to the absorption bands at 2.2, 2.5, and 3.1 eV obtained in [4]. The widths of the compared bands at 2.3 and 3.3 eV are also close. The energies and widths of the bands and the types of defects are presented in Table 1. The induced-absorption bands are explained in [4] by the formation of a phosphorous oxygen–hole centre (POHC). The appearance of induced POHCs after irradiation is confirmed by our EPR data. The absorption band at

**Table 1.**

$E/\text{eV}$ [4] ( $E/\text{eV}$ , this paper)	Band width/eV [4] (defect type [4])	Band width/eV (this paper)	Band width/eV (defect type) [10]
0.45	0.8 (–)	–	–
0.79	0.29 (P1)	$\sim 0.6$	–
1.07	0.32 (–)	0.01 – 0.04	–
2.2 (2.3)	0.35 (POHC)	$\sim 0.4$	–
2.5 (2.6)	0.63 (POHC)	$\sim 1.3$	–
3.1 (3.3)	0.73 (POHC)	$\sim 0.7$	–
4.5 (–)	1.27 (P2)	–	–
4.8 (4.7)	0.41 (P4)	$\sim 1.1$	1.05 (NBOHC)
5.05 (5.1)	0.88 ( $E'(P)$ )	$\sim 0.4?$	0.3 (ODC 2: $S_1 - S_0$ )
5.3 (5.0–5.3)	0.74 (POHC)	?	–
– (5.8)	– (–)	$\sim 1.1$	0.8( $E'$ )
7.0 (6.9)	2.76 (–)	$\sim 0.7$	0.4 (ODC 2: $S_1 - S_0$ )

Note: blank corresponding to the defect type means that the defect is absent or has not been identified; POHC is a phosphorous oxygen–hole centre; P1, P2, and P4 are phosphorous defects [4]; NBOHC is a non-bridge oxygen–hole centre;  $E'(P)$  is a  $E'$  centre in the PSG near the centre of the phosphorous atom; the band full width at half-maximum;  $S_{0,1,2}$  are singlet levels of a defect; the question sign means the unreliable result of decomposition of the band into Gaussian components;  $E$  is the band energy.

5.3 eV observed in [4] is also assigned to this defect. Unfortunately, due to the ambiguity of decomposition of the induced-absorption band into four Gaussian components, we have failed to confirm reliably the presence of this band in our spectra (see Fig. 3).

As mentioned above, our spectra exhibit at least two bands in the range between 4 and 6 eV, one of which (at 5.8 eV) was not observed in [4], while the other (at 4.7 eV) is close to the 4.8-eV band observed in [4]. The latter band, however, should be absent in our spectra because, according to EPR spectroscopy, the P4 defects [4] responsible for this absorption band [5] are absent in hydrogen-unloaded PSGs. The 4.5-eV band is located relatively close to the 4.8-eV band in [4] (see Table 1). The P2 defect responsible for the 4.5-eV band should also be absent in our hydrogen-unloaded samples [5]. The decomposition of the broad induced-absorption band in the range from 4 to 6 eV into three Gaussian components gives, along with the absorption bands at 4.7 and 5.8 eV, a relatively weak and narrow band of width 0.4 eV located at 5.1 eV. However, we have failed to determine reliably the parameters of all the bands by decomposing the broad band into four Gaussian components (taking into account the assumed band at 5.3 eV).

In the energy region above 6 eV, we observed the induced-absorption band of width  $\sim 0.7$  eV at 6.9 eV (Fig. 2 and Table 1); in [4], the induced-absorption band of width 2.76 eV was observed at 7 eV in this region. A great difference between the widths of these bands probably indicates that they are related to different defects.

One can see from Fig. 4 that the width of the 0.8-eV band ( $\lambda = 1.57 \mu\text{m}$ ) is approximately 0.6 eV, unlike 0.28 eV for the band in [4]. According to the EPR data [5], the P1 defects responsible for this band should be also present in our hydrogen-unloaded PSG. To explain the difference between the widths of these absorption bands, additional studies are required.

Figure 2 shows that the absorption spectrum of a silica glass doped with phosphorous exhibits two bands at 7.6 and 6.9 eV of widths  $\sim 0.9$  and 0.7 eV, respectively. The

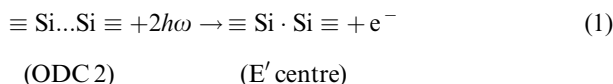
positions and widths of these bands are close to those of the absorption bands of silicon oxygen-deficient centres ODC1 and ODC2 in silica glasses at 7.6 and 6.9 eV of widths 0.62 and 0.4 eV [10]. The 6.9-eV absorption band of the ODC2 corresponds to the  $S_0 - S_2$  singlet transition. However, the absorption band at 5.05 eV corresponding to the  $S_0 - S_1$  singlet transition should be also observed, but this band is absent in the absorption spectra recorded before irradiation of samples (see Fig. 2). This can be explained by assuming that a greater part of silicon ODC2s in PSG preforms are initially bound to phosphorous atoms, resulting in the formation of POHCs described in [11]. It was shown in [11] that the POHC band at 6.9 eV in the absorption spectrum of PSGs is not accompanied by the 5.05-eV band.

How are ODCs involved in the formation of POHCs produced in PSGs? It is known that ODC2s are formed in the core of a germanosilicate preform [12]. This occurs due to the removal of a part of oxygen atoms from the surface layer of a preform during its collapse. It is possible that a similar (but more complicated) process also occurs in phosphosilicate preforms during their collapse.

We can assume that ODC2s that were absent initially are formed after exposing PSGs to light. As mentioned above, the decomposition of the induced-absorption band in the range from 4 to 6 eV (Fig. 3) into three Gaussian components reveals a relatively weak absorption band at 5.1 eV, which can indirectly confirm the appearance of these defects in irradiated samples. However, according to [10], the oscillator strength for the 6.9-eV band related to the second singlet transition is only approximately twice as large as that for the 5.05-eV band related to the first singlet transition. However, the intensity ratio for these induced-absorption bands in our experiments exceeds 10. This discrepancy can be explained by assuming that POHCs are produced together with ODC2s during irradiation of samples.

The 4.7-eV and 5.8-eV induced-absorption peaks observed in our experiments can be related, according to [10], to defects in silica glasses such as non-bridge oxygen-hole centres (NBOHCs) and  $E'$  centres with bands of widths 1.05 and 0.8 eV, respectively, which are close to the widths observed in our experiments (Fig. 3).

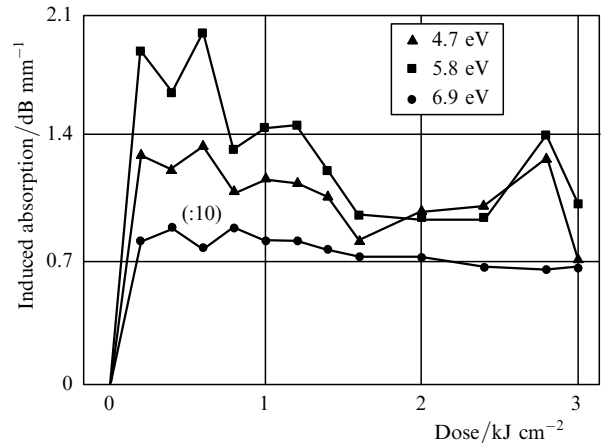
The generation of  $E'$  centres in our samples confirms the appearance of ODC2s in PSGs, because, according to [10], the reaction



takes place.

It seems that a part of  $E'$  centres are formed due to the destruction of ODC2s during irradiation. However, we can assume that the 5.8-eV band can also appear due to the decomposition of POHCs caused by the dissociation of a relatively weak bond between phosphorous atoms and ODC2s, which is formed during the formation of POHCs.

The involvement of defects responsible for induced-absorption bands at 4.7, 5.8, and 6.9 eV in the general photochemical reactions in the silica glass network is confirmed by the dose dependences of the intensity of these bands shown in Fig. 5. One can see that variations in the intensity of the 4.7-eV and 5.8-eV bands are correlated, while variation in the intensity of the 6.9-eV band is anti-correlated with respect to the first two bands. The correlation between the first bands can be explained by the



**Figure 5.** Dose dependences of induced absorption for the 4.7-, 5.8-, and 6.9-eV bands (270, 214, and 180 nm, respectively). The ordinate for the lower curve is divided by 10.

simultaneous production of the NBOHCs and  $E'$  centres due to dissociation of the Si-O-Si bonds caused by two-photon absorption of light, while the anti-correlation between the third and second and (indirectly) first band can be explained by the destruction of ODC2s and POHCs caused by two-photon absorption of light.

The interesting features of the dose dependences of the induced absorption presented in Fig. 5 is its drastic increase for the first minimal exposure dose  $200 \text{ J cm}^{-2}$  and the quasi-periodic behaviour of the curves in the dose region up to  $1 \text{ kJ cm}^{-2}$ . We are not aware of the observation of such dose dependences of the induced-absorption bands (and the concentration of the corresponding defects) in glasses. These dependences can be explained by assuming that point defects experience the action from the glass network, which changes due to relaxation processes occurring during exposure (the glass structure changes due to drastic variations in mechanical stresses). It is possible that photochemical processes, proposed above to explain the correlation of curves in Fig. 5, are also controlled by the state of the glass network.

It is important to elucidate the relation between the induced-absorption bands observed in our experiments and the induced refractive index in PSGs. It is known [3] that the dose dependence of the induced refractive index in the hydrogen-unloaded PSG is a monotonically increasing function in the region at least up to  $5 \text{ kJ cm}^{-2}$ . Already for this reason, the induced-absorption bands in Fig. 5 (and, hence, the corresponding point defects) cannot be directly related to the refractive-index induction. At the same time, the energy of absorption bands corresponding to phosphorous defects P1, P2, P4, and POHC observed in [4] (Table 1) does not exceed 5.3 eV, i.e. these defects can be destroyed upon one-photon absorption of photons with energy 6.4 eV ( $\lambda = 193 \text{ nm}$ ). For this reason, they cannot be directly responsible for the refractive-index induction upon two-photon absorption. It seems that the glass network plays a decisive role in the refractive-index induction in hydrogen-unloaded PSGs.

## 5. Conclusions

The formation of defects in hydrogen-unloaded PSGs fabricated by the MCVD method and exposed to the

193-nm radiation noticeably differs from the production of defects in PSGs exposed to X-rays in [4]. The greatest differences have been found in the spectral energy above 4 eV (the wavelength is less than 0.3  $\mu\text{m}$ ).

A broad induced-absorption band has been observed in the region between 4 and 6 eV, as well as narrower bands at 6.9 and 7.6 eV, which appear in the PSG before exposure and are tentatively related to ODC1 and PODCs produced in the silica glass after doping with phosphorous oxide. The intensity of the 7.6-eV induced-absorption band almost does not change during exposing the PSG, whereas the intensity of the 6.9-eV absorption band drastically increases at the beginning of the exposure and then decreases. In our opinion, these variations are related to variations in the concentration of ODC2s and POHCs.

The broad induced-absorption band (4–6 eV) can be decomposed into Gaussian components located at 4.7, 5.1, and 5.8 eV, the two last components appearing only due to two-photon absorption. The intensity of the 5.1-eV band is considerably lower than that of other bands. We assume that the intensity of the 4.4-eV and 5.8-eV bands increases during two-photon absorption due to the formation of silica defects: the non-bridge oxygen–hole and  $E'$  centres, respectively. Variations in the 6.9-eV band intensity during irradiation anti-correlate with variations in the intensity of the 4.7-eV and 5.8-eV bands. This indicates that defects corresponding to these bands are involved in one or several coupled photochemical reactions proceeding in the PSG during two-photon absorption of light.

The broad induced-absorption band in the region between 4 and 6 eV differs from the band observed in [4] because the latter is related to phosphorous defects P2 and P4, which, according to EPR studies, are absent in our PSG samples. As a whole, the induced-absorption bands in the region above 4 eV observed in our paper strongly differ from the absorption bands observed in [4], and to identify reliably defects responsible for these bands, additional studies are required.

The induced-absorption bands at energies below 4 eV observed in [4] better correspond to the absorption bands observed in our paper, although their parameters somewhat differ. We assume that these bands in the absorption spectra of our samples are also related to P1 centres and POHCs.

Although the variation dynamics of point defects in the PSG with the excitation energy above 4 eV is determined by two-photon absorption (as the increase in the refractive index), the type of these variations and dose dependences of the refractive index are substantially different. Therefore, these defects cannot be a direct source of the induced refractive index. Because variations in phosphorous defects in PSGs found in [4] are not related to two-photon absorption, they also cannot be directly responsible for the refractive-index induction. It seems that the refractive index is induced in PSGs due to variations in the glass network.

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