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Influence of γ-irradiation on the photoluminescent properties of porous glasses

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Influence of small doses of γ-irradiation on the features of the photoluminescence spectra of porous silica glass during long-time (several months) storage after the irradiation is investigated. The non-monotonic dependence of photoluminescence change on the dose of the glasses with a different composition and different additional pre-treatment is observed. The analysis of intensity changes and shifts of the maxima of photoluminescence spectra shows long-time oscillations. This indicates that composite catalytic processes take place on the surface of pores. Perhaps the small γ-radiation doses initiate the cyclic process of the surface state transformation on the inner side of pores.

1. Introduction

New porous glass applications appeared in the recent time, in particular different types of novel sensors. Stability of porous glass parameters to various external influences is of interest because of these new applications. In particular, studies of their radiation stability are necessary. Taking into account the fact that significant development of a surface is characteristic of porous glasses, one can expect that even small doses of γ-irradiation bring about an essential change in surface states. The present work is devoted to the study of the influence of small γ-irradiation doses on the photoluminsecnce spectra of porous glasses. In our previous paper [1], the presence of long-term changes in porous silicon layers after such an action was shown. However, in contrast to the results reported in paper [2], where degradation of the photoluminescence intensity of porous silicon after γ-irradiation was observed, we have found out its non-monotonic increase in the course of storage in air for several dozen days after exposition to irradiation. In the previous papers [3]–[5] it was shown that the properties of porous glasses in some aspects are very similar to the properties of porous silicon (partly oxidized). This allows us to expect similarity in the behaviour of these substances after small doses of γ-irradiation.

2. Experimental

Samples of porous glasses produced with the use of four various techniques were investigated. The samples of type A and B were made by etching a sodium-borosilicate glass, after thermal annealing at 490 °C, with the latter ones being additionally etched in the KOH solution for removal of a gel of secondary silica formed during the etching. Samples of type C and D were made of glass, annealed at 650 °C, and samples D were also additionally etched in KOH. Obtained in this manner the four types of specimens differ in porosity, surface morphology, *etc*, which can be seen the photographs taken with electronic microscope (Fig. 1). The porosity of particular specimens was as follows: specimen A about 38%, specimen B – about 52%, specimen C – about 41%, and specimen D – about 48%.

The samples of each type were grouped for simultaneous γ-irradiation by a ^{60}Co source with doses of 5×10^3, 1×10^4, 5×10^4, 1×10^5, 5×10^5, 1×10^6 rad (the samples are numbered respectively from 1 to 6). The non-irradiated samples of all types were also tested for reference (they were indexed with 0). The photoluminescence spectra were recorded for all specimens before irradiation together with a luminophor-etalon

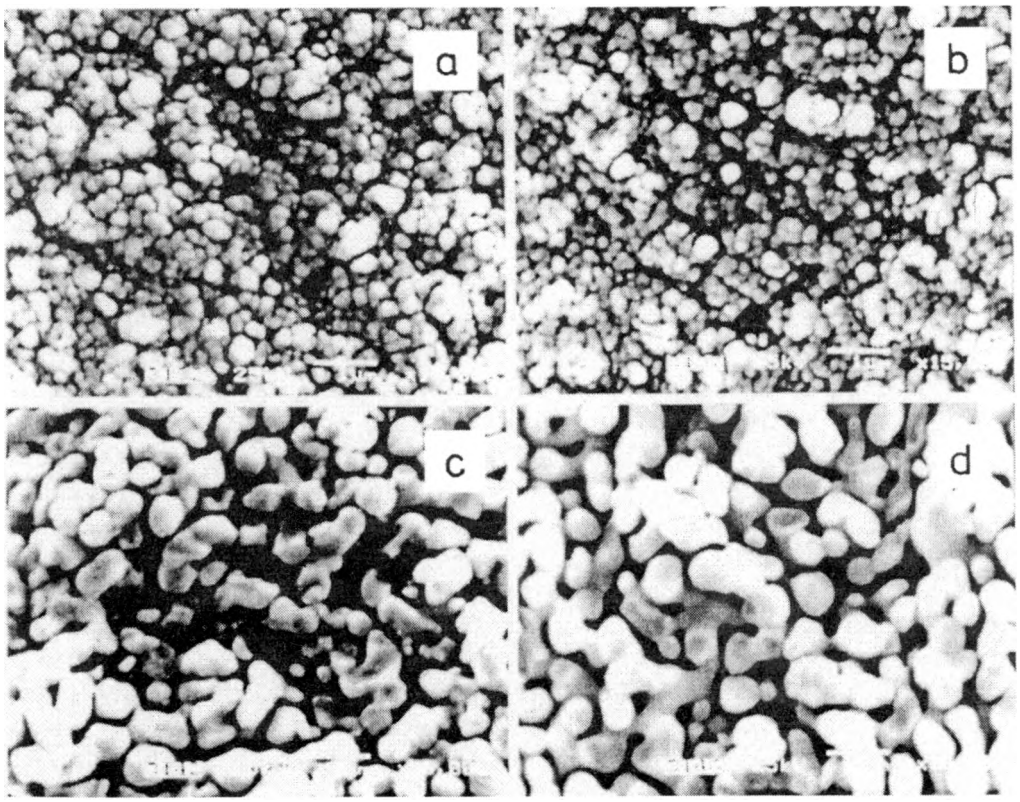

Fig. 1. Electron microscope images of the surface of porous glasses of four types: **a** – specimen A (porosity 38%), **b** – specimen B (porosity 52%), **c** – specimen C (porosity 41%), **d** – specimen D (porosity 48%).

spectrum upon excitation by the UV nitrogen laser at a wavelength of 337 nm, pulse duration 10 ns and repetition rate 50 Hz. The set-up consisting of the quartz monochromator SF-4, photomultiplier FEU-79, narrow-band amplifier U2-8 and two-coordinate recorder H-307 was utilized for taking the photoluminesene spectra. After irradiation, the photoluminesecnce spectra of all specimens were recorded periodically and the measurement time was 8 hours.

3. Results and discussion

In the absence of literature data, we were compelled to rely on our own experience from research on a similar material, namely porous silicon. The ranges of irradiation from 10^3 up to 10^6 rad made it possible to find a maximum in the dependence of photoluminescence intensity on the γ-irradiation dose for this substance [1]. One should note that the coordination in change of photoluminescent properties with time observed for irradiated samples of porous glasses was smaller than for porous silicon, which can be explained by better reproducibility of the latter due to the debugged silicon technologies.

There are peaks in the time dependences of the luminescence after irradiation. The peculiarities are observed for the luminescent efficiency I_{pl} as a function of the storage time after irradiation and in the evolution of the photoluminescence peak λ_{max} for all doses and all types of specimens. The position of this peak is supposedly connected with the evolution of Si–O, SiO_2, Si–H and Si–OH surface states on the inner surface of pores.

Although the sample behaviour seems to be chaotic, one should point to some regularity. So, the time dependences have a typical extremum in the range of 60 – 70 days of storage for all kinds of specimens. We cannot consider this result to be causal, since apart from the changes in luminescent efficiency, there are also changes in the position of its maximum, and this testifies to an evolution of the surface states.

Various irradiation doses result in identical changes of intensity for the type A specimens. Nevertheless, the rate of these changes is not the same. The evolution of λ_{max} is also different. The photoluminescence intensity generally smoothly decreases versus the storage time almost for all doses. Exception is the sample with maximum irradiation dose. The efficiency I_{pl} in this continues to rise (Fig. 2 **a**, **b**), that requires an extension of the dose ranges for this type of specimens.

There are some interesting features in the samples B behaviour. As it follows from Fig. 3 **a**, **b**, the I_{pl} time dependences for each radiation dose have at least three peaks. The largest effect is from minimum and maximum irradiation doses. In both cases the shape of I_{pl} curves is similar. The curves have similar peaks within the same time frames. Two maxima are visible, but for a minimal dose the greatest effect corresponds to the first maximum (shorter storage time), and for a maximal dose to the second one (to 60 – 70 days of storage). Apparently, this can be explained as being due to the action of the same mechanisms during irradiation having various efficiencies.

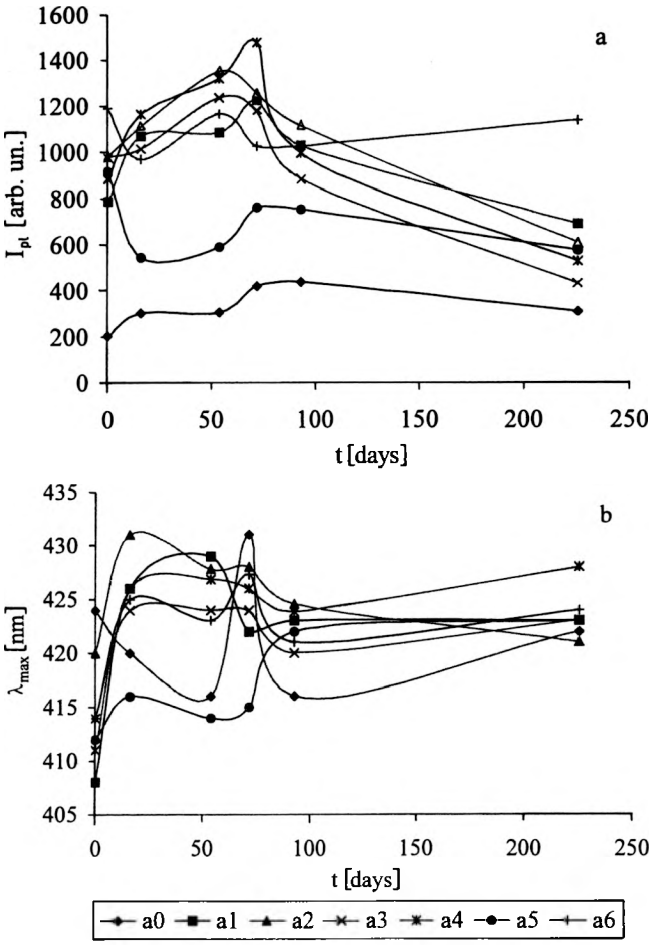

Fig. 2. Storage time dependences of the photoluminescence intensity I_{pl} (**a**) and of the spectral peak position shift λ_{max} (**b**) for A-type specimens.

The final decay of I_{pl} for samples A and B occurs rather synchronously, although the comparison of the relevant evolution curves λ_{max} shows that the sizes of luminescent centres change in an antiphase. This testifies to a variety of competing processes on the inner surface of pores in samples C and D.

After irradiation the behaviour of specimens C and D becomes more similar. Thus, the influence of pre-treatment of glass at the stage of phase separation on the properties of porous glasses is obvious.

In case of type C specimens, the non-monotonic (with several peaks) dependence of I_{pl} is registered both as a function of the irradiation dose and of the storage time. In the latter case, the intensity decreases with time. Corresponding samples can be divided into two subgroups: the evolution of λ_{max} in the first subgroup is towards the short-waves, while in the second one λ_{max} shifts to the long-waves (Fig. 4**a**, **b**).

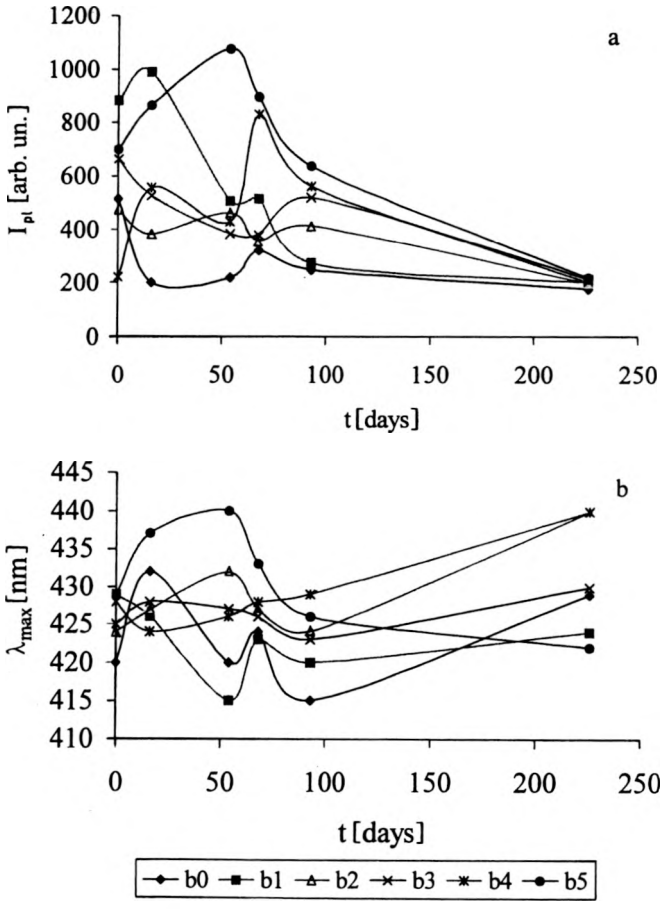

Fig. 3. Storage time dependences of the photoluminescence intensity I_{pl} (a) and of the spectral peak position shift λ_{max} (b) for B-type of specimens.

The I_{pl} dependence on irradiation dose is best ordered for samples D (Fig. 5 **a**, and **b**). It has one maximum at 10^5 rad, therefore it is possible to speak about an optimality of the chosen γ-irradiation doses for this kind of porous glasses. In this group of specimens, the position of maximum also monotonously shifts towards the short-waves with decreasing I_{pl} dependence on storage time, which may be explained by the evolution of surface states inside the pores due to surface oxidation. For other kinds of samples the dependences discussed are more complicated, which may be explained by precipitation of a high-dispersed secondary silica gel within pores.

In papers [2] and [6], which deal with γ- and α-irradiation of structures containing porous silicon, stabilisation of the photoluminescence spectra shape is shown for the various doses characterized by a monotonic decrease intensity. It has been concluded on such basis that light is radiated by nanostructure of the particular sizes and that either their quantity or probability of an emissive

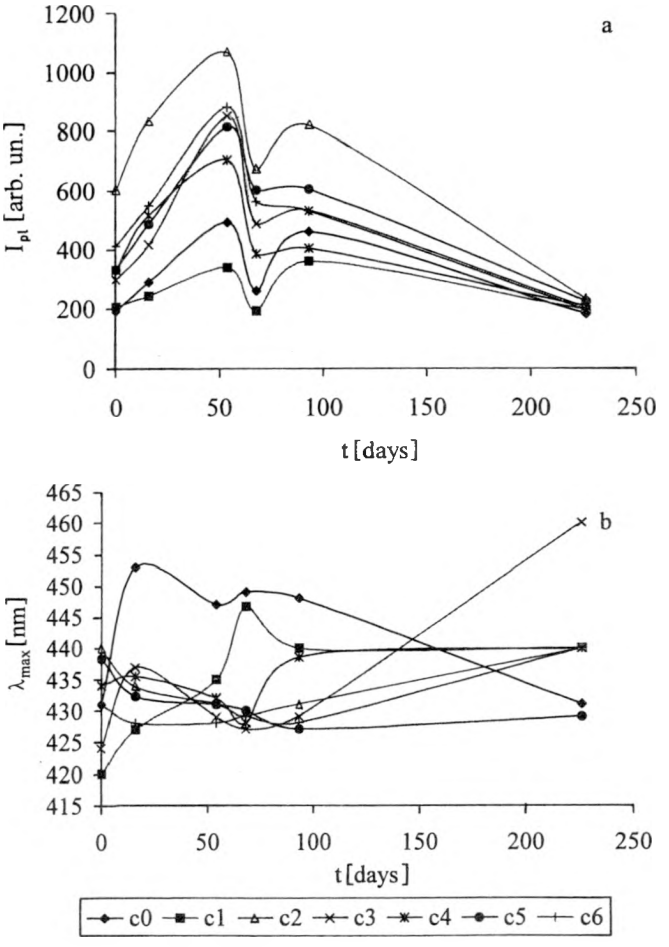

Fig. 4. Storage time dependences of the photoluminescence intensity I_{pl} (a) and of the spectral peak position shift λ_{max} (b) for C-type of specimens.

recombination due to diminution of lifetime of non-equilibrium charge carriers in these structures decrease as a result of irradiation. However, all measurements reported in both papers were done immediately after irradiation. In our work [1] it is shown that during a long-time storage of the irradiated porous silicon the time dependences I_{pl} and λ_{max} are more complicated.

A similar studies of porous glasses performed in this work revealed even more complicated dependences. The basic role in porous glass photoluminescence play the residual silica gel. A variety of light emission processes take place in porous glasses unlike the case of porous silicon where we deal only with silicon nanolcusters and their oxidized surfaces. All that was specified proves to be true by the presence of several maxima in the I_{pl} dependence on irradiation dose, and also by non-monotony of the I_{pl} time dependence during storage.

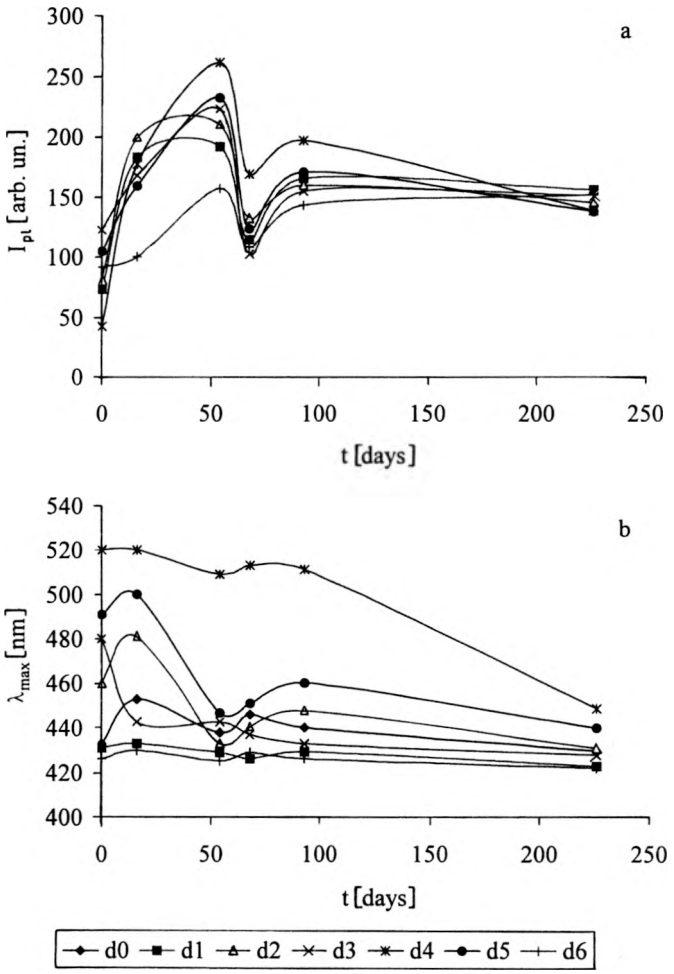

Fig. 5. Storage time dependences of the photoluminescence intensity I_{pl} (a) and of the spectral peak position λ_{max} (b) for D-type of specimens.

Thus, some chaotic character of I_{pl} dependence on the irradiation dose for specimens A and B is due to manufacturing conditions at the stage of the phase separation and formation of residual silica gel. The similarity of the above time dependences to those obtained for specimens C and D is explained by the same processes of thermal phase separation, and the differences of specimens D may be explained by almost total absence of secondary silica gel in these samples. At the same time the synchronism of the I_{pl} decrease with time and the shift of λ_{max} towards the short-waves allows us to assume for the D-type glasses the evolution of surface states inside the pores whereas a similar effect is obtained in porous silicon by irradiation [1] or artificial aging [7], [8] due to oxidizing process in the silicon nanoclusters.

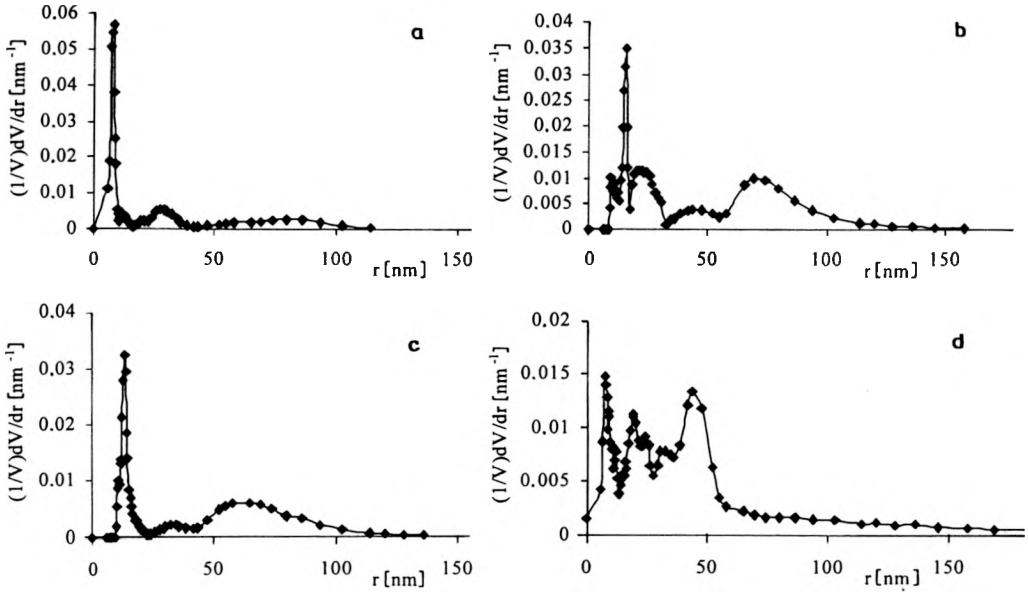

Fig. 6. Pore-size distribution for four types of porous glasses: **a** – specimen A, **b** – specimen B, **c** – specimen C, **d** – specimen D.

Morphology of the inner surface of specimen and chemical composition of residual silica gel are different, as well as surface development for different types of glasses is different, which one can see from the pores-size distribution diagrams (Fig. 6).

4. Conclusions

The observed long-term oscillations of the photoluminescence intensity as a function of the storage time after the irradiation are an indication of complicated catalytic process on the highly developed surface on the porous glass. Similar processes take place in porous silicon [9]. We argue that the revealed peculiarities are connected with the secondary silica gel at the inner surface of pores.

The luminescencet efficiency I_{pl} increases stronger after irradiation of samples A, B and C. The increase is weaker for samples B compared with specimens C (for D specimens this is by 4–6 times less). This shows that the residual silica gel in the porous glass contributes to the luminescence and is responsible for complicated radiation stimulated processes.

It is possible to optimize the γ-irradiation doses to achieve stable photoluminescence of the D type porous glasses.

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