

Small doses γ -irradiation effect on the photoluminescence properties of porous glasses

IGOR K. DOYCHO¹, SERGEY A. GEVELYUK¹, MIKOLA P. KOVALENKO¹, LUDWIG P. PROKOPOVICH¹,
EWA RYSIAKIEWICZ-PASEK²

¹Odessa National University, Dvoryanskaya 2, 65026 Odessa, Ukraine.

²Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

The γ -irradiation effect on the photoluminescence of various types of porous silica glasses and on its change during a half-year storage has been studied. It has been revealed that the photoluminescence intensity of glasses with fine matrix and almost complete absence of silica gel does not change when irradiated at applied doses, but a long-wave shift of its maximum position is observed. The increase in photoluminescence intensity appeared to be the most stable in glasses with the thick-wall matrix. The model which explains apparent changes in photo-luminescent properties and also allows us to draw conclusions about some features of various types of porous silicate glasses structure has been presented.

Keywords: γ -irradiation, photoluminescence, porous glasses.

1. Introduction

Problems of porous materials irradiative stability and also of using radioactive irradiation as a method of technological processing of material were investigated in few studies. Most commonly, the authors of these papers studied luminescent properties of porous, silicon-containing media immediately after γ -irradiation [1] and α -irradiation [2]. In both cases the photoluminescence spectra shape was dose-independent and simultaneously their intensity I_{pl} decreased monotonously. In order to explain this effect, the authors assumed that the nanoclusters of determined size are the source of luminescence and their number or the probability of the irradiance recombination in them decreases with irradiation. Such approach is applicable to porous silicon [3] or germanium [4], which contain a sufficient amount of micro-crystallites of various sizes. These formations may be created in porous silicate glasses only as a result of additional treatment [5], [6], and that is why photo-luminescent properties of these materials require special explanation. Taking into account the fact

that porous glass is characterized by considerable development of the surface, it can be expected that even small doses of γ -irradiation may result in essential changes in the condition of the pore surface. First of all, it will have an effect on the shape and intensity of the luminescence spectra. The aim of the present paper has been to present the photoluminescence of various types of porous silicate glasses and its changes after γ -irradiation and during a half-year storage. The offered model not only explains the changes in photoluminescent properties of the glasses during the storage after irradiation, but also allows us to draw conclusions about some features of their structure.

2. Experimental

Four types of porous glasses (A, B, C and D) received by chemical leaching of alkali-borate phase from alkali borosilicate glass were used in investigations. Initial glasses differed, first of all, in the temperature of phase separation; thus for glass A samples this temperature was 490 °C and for glasses C it was 650 °C. Glasses B and D were formed from A and C ones, respectively, by additional etching in KOH for the removal of residual high-dispersed secondary silica gel. Four types of thus obtained specimens differed in porosity, surface morphology and other properties.

All types of samples were irradiated with γ -radiation from Co^{60} source (radiation energy is 1.18 MeV [7]) at doses 10^4 , 10^5 and 10^6 rad. Apart from this, initial samples of all types were maintained for comparison.

Before the irradiation the photoluminescence spectra were recorded by excitation with the ultraviolet nitrogen (wavelength 337 nm, pulse length 10 ns, repetition frequency 50 Hz) using the set-up consisting of a quartz monochromator SF-4, photomultiplier FEU-79, lock-in amplifier U2-8 and two-coordinate recorder H-307 for all specimens. All photoluminescence spectra were normalized to a luminophor-etalon spectrum having been recorded before each measurement. Next, after irradiation of specimens, the photoluminescence spectra were recorded periodically for half a year using the same set-up.

3. Results

Figure 1 shows changes in the photoluminescence intensity at storage of all four types of irradiated glasses within half a year. Results are given as histograms, where each histogram bar corresponds to the photoluminescence intensity maximum over the specified storage time. Histogram bars are grouped in fours, corresponding to types of glass. Figure 1a corresponds to the γ -irradiation dose of 10^4 rad, Fig. 1b – to the dose of 10^5 rad, and Fig. 1c – to the dose of 10^6 rad. As can be seen in the figures, there is an essential increase in the photoluminescence intensity for glasses A, B and C after irradiation in comparison with the initial ones. The increase in photoluminescence intensity during storage was observed at the irradiation doses of 10^4 rad and 10^5 rad for glasses A and at the dose of 10^6 rad for glasses B, and also at all the considered

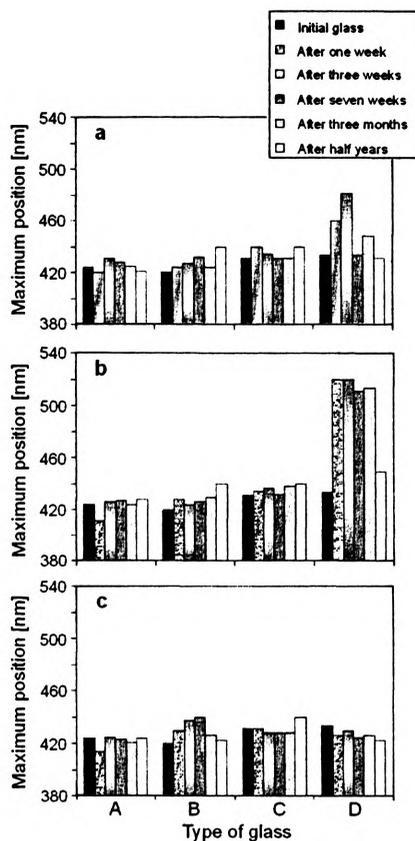
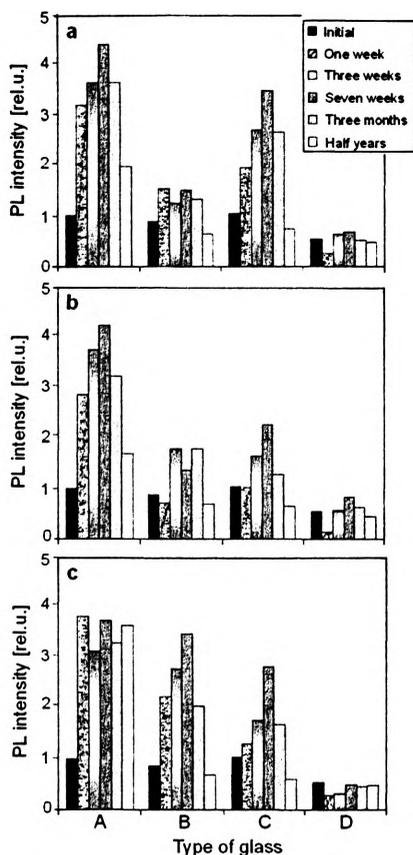


Fig. 1. Changes in the photoluminescence intensity of porous glasses on storage after γ -irradiation: a – irradiation dose of 10^4 rad; b – irradiation dose of 10^5 rad; c – irradiation dose of 10^6 rad. The intensity is normalized to the intensity of photoluminescence of the initial porous glass A (prior to irradiation).

Fig. 2. Changes in the photoluminescence maximum position intensity of porous glasses on storage after γ -irradiation: a – irradiation dose of 10^4 rad; b – irradiation dose of 10^5 rad; c – irradiation dose of 10^6 rad.

doses for glasses C. This increase was observed until the 7th week of storage, and then intensity began to decrease, as it usually happens on aging of specimens [8], [9]. On storage, the photoluminescence intensity is maintained at a high level for a long time with high irradiation doses for glasses A and at small doses for glasses B, and the changes seem random during storage. The photoluminescence intensity of glasses D almost does not show any γ -irradiation sensitivity in the studied dose range.

The histograms in Fig. 2 correspond to the changes in the photoluminescence maximum position for all four types of irradiated glasses during a half-year storage. It can be seen that the luminescence before the irradiation is localized in the blue part of spectrum (about 420–440 nm) for all types of glasses. After irradiation at all the investigated doses the photoluminescence maximum position remains in the specified limits for glasses A, B and C, while glasses D reveal the shift to the red direction of

spectrum. This shift is especially evident at the irradiation dose of 10^5 rad (up to 520 nm) and it cannot be observed practically at 10^6 rad.

4. Discussion

The γ -radiation energy from Co^{60} source is not sufficient for the formation of electron–positron pairs, but the energy of the fast electrons created by photo-effect and Compton effect is adequate enough for the occurrence of short-range disorder similar to Frenkel defects in crystals [10]. During storage migration of these disorders towards the surfaces or their stabilization due to relaxation or distortion of the nearest surrounding of the defect are possible. Stabilization is improbable in the fine-dispersed secondary silica gel and it is quite possible in a matrix of the glass.

The more fine-dispersed alkali-borate phase in the initial glass gives rise to lower sensitivity to γ -irradiation in the obtained porous glass, as there are multiple short range order disorders observed initially in its matrix. The changes due to irradiation are visible in comparison to these disorders. The irradiation causes only ionization of some elements of the matrix, and the resultant broken bonds may lead to the formation of silicon clusters, which contribute to the red shift of the luminescence peak without any essential changes in its intensity.

Glasses C and D were obtained from glasses treated with high temperature. Their structure is characterized by considerable fragments of the skeleton with simultaneous formation of fine matrix parts which are interconnected. The figures show that no essential photoluminescence intensity changes were observed at the investigated irradiation doses for samples D in which the secondary silica gel was removed, but at small irradiation doses the photoluminescence peak was shifted to the red direction of spectrum almost at 80 nm.

Glasses C, in contrast to the D ones, initially contain large amounts of the secondary silica gel, and they are characterized by the “bell-shaped” histogram of the photoluminescence intensity change during prolonged storage in the investigated dose range. At the same time the luminescence peak position does not change, what indicates small reconstruction of the silica matrix in comparison with changes in the silica gel. In fact, the changes in the luminescence spectra of the samples C during the storage after γ -irradiation are associated with the changes in the secondary silica gel. It can be seen that the irradiations are followed immediately by a sharp increase in the photoluminescence intensity associated with the defects formation inside the gel. During storage, the luminescence intensity continued to increase for 7 weeks, what apparently corresponded to the defects migration onto the surface of the gel particles. This time-length is apparently associated with the sizes of the gel particles which are determined by the etching technology. After reaching, the surface the defect disappears and a slow decrease in the luminescent intensity, characteristic of the aging process of the glass, begins.

Glasses A and B are obtained at the low phase separation temperature and their structure is characterized by fine, but densely packed fragments of the matrix skeleton.

The stabilization of the defects, being the competitive mechanism to their migration, is rather probable for such a matrix. That is why the histogram of the photoluminescence intensity change during the prolonged storage may not have the particular shape in some cases. It is seen especially well on histograms for glasses B, which contain small amounts of the secondary silica gel. These glasses are not characterized by any regular pattern of the photoluminescence intensity change during prolonged storage at small irradiation doses. The increase of intensity is only seen in comparison with the initial sample. The histogram for glasses B becomes "bell-shaped" at the γ -irradiation dose of 10^6 rad. Apparently, the migration processes taking place in the remainder secondary silica gel (which usually has not been etched completely [11]) begin to prevail over the defects stabilization processes in the matrix at this irradiation dose. Glasses A initially contain high amount of secondary silica gel (more, than glasses C [12]) and they behave in a similar way to samples C at small irradiation doses. At the γ -irradiation dose of 10^6 rad there occur many stabilized defects in the matrix of glass A with simultaneous intensive migration of the defects in silica. The increase in the photoluminescence intensity is maintained much longer in this case.

It should be noted that the silicon clusters are not formed at γ -irradiation for glasses A, B and C, what is confirmed by the absence of the photoluminescence peak shift to the red direction of spectrum.

5. Conclusions

The γ -irradiation affects the silica matrix of porous glass and the silica gel present inside the pores in different ways. Inside the silica gel particles there are formed disorders similar to Frenkel defects in crystals. During storage these disorders migrate to the surface. The relaxation or distortion of the nearest surrounding around the defects inside the silica matrix lead to their stabilization. The seven-week period of the photoluminescence intensity increase in glasses with sufficient content of the silica gel corresponds to the defects migration to the surface of the gel particles. The fine-structured matrix is less sensitive to γ -irradiation. Thus, glasses D, which are characterized by the fine matrix and almost complete absence of the silica gel, are insensitive to irradiation and the increase in the photoluminescence intensity is the most stable for the thick-wall glasses A at the irradiation dose of 10^6 rad.

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