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EFFECT OF HIGH-ENERGY ELECTRON IRRADIATION ON OPTICAL SPECTRA OF LEAD SILICATE GLASS

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Optical absorption and photoluminescence spectra of lead silicate glass irradiated by 5- to 10-MeV electrons are studied. High-energy electron irradiation is shown to result in the formation of colour centres generally similar to those being formed by X-ray and γ-radiation. The most probable factors responsible for the non-sensitivity of the photoluminescence of the investigated lead silicate glass to the electron irradiation are discussed.

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1. Introduction

Radiation is known to result in essential changes of optical characteristics of glasses which are related to the formation of electron and hole colour centres induced by radiation, arising due to the generation of free charge-carriers (electrons and holes) in the glass matrix, their diffusion and capture by traps [1,2]. Broad applications of devices with optical glasses under exposure to radiation draw particular attention to their radiation strength, this being the reason for the necessity of the studies of radiation effects on the optical parameters of glasses, especially of the absorption coefficient. Such studies are well known for amorphous SiO_2, alkali silicate and borosilicate systems and their radiation-proof analogues.

Previous studies of lead-containing glasses, which are characterized by higher refractive indices, deal in most cases with the effects of X-ray and γ-radiation [3,4], but not of high-energy electron beams. The present paper is aimed at the studies of effects of 5- to 10-MeV electron irradiation on lead silicate glass and comparison of the obtained results with the available experimental data.

2. *Experimental*

We report on effects of high-energy electrons (5, 8, and 10 MeV) on optical absorption and photoluminescence (PL) spectra of F-1 lead silicate glass (74.1 mol.%. SiO_2, 19.2 mol.% PbO, 6.4 mol.% K_2O, 0.3 mol.% As_2O_3). The irradiation was carried out in the M-30 microtron of the Institute of Electron Physics, Ukrainian National Academy of Science (Uzhhorod, Ukraine) by an electron beam with the fluence density $6.3 \times 10^8 - 7.2 \times 10^9$ cm^{-2}s^{-1} at temperatures between 223 and 293 K. In order to avoid overheating the samples in the course of irradiation, they were cooled by evaporating liquid nitrogen, the temperature being controlled by a copper-constantane thermocouple. A specially constructed chamber permitted the low-temperature irradiation and sample transportation without a temperature increase during the transport from the irradiation area to the measuring setup equipped with a UTREX cryostat.

The optical absorption spectra were measured in the range 300 – 800 nm with a LOMO MDR-23 monochromator, applying a standard technique, and PL spectra with a LOMO DFS-24 spectrometer with a photon counting system, Ar^+-laser ($\lambda = 488$ nm) being used as the excitation source.

3. *Results and discussion*

Optical absorption spectrum of non-irradiated lead silicate glass is shown in Fig. 1a. The optical absorption edge of glass is described by a modified "glassy" Urbach rule [5]:

$$\alpha = \alpha_0 \exp\left\{ \frac{\gamma[h\nu - E_g(0) + \beta T]}{kT} \right\} , \tag{1}$$

where α is the absorption coefficient, which depends on temperature T and the light energy $h\nu$; α_0 and γ are constants, $E_g(0)$ is the energy gap value at 0 K and β is the energy-gap temperature coefficient, which is determined from equation $E_g(T) = E_g(0) - \beta T$.

A detailed analysis of the absorption edge in the glasses of the PbO-SiO_2 system for a broad range of composition is presented in Ref. [6] where a number of the edge parameters are given. Our measurements have shown that the energy position of the absorption edge in the lead silicate glass under investigation agrees with the results of Ref. [6], while our value of the energy width of the Urbach absorption edge $w = 0.08$ eV obtained from the measured spectra is somewhat lower than the value $w = 0.12$ eV quoted in Ref. [6] for the $0.8\,SiO_2 \times 0.2$PbO glass, whose composition is close to the composition of our glass. This parameter quantitatively characterizes predominant statical disorder in the investigated glass and is responsible for the density-of-states tails extending into the gap. The disagreement of our results and those of Ref. [6] is partly explained by the presence of a noticeable quantity of modifiers - potassium and arsenic oxides in our sample.

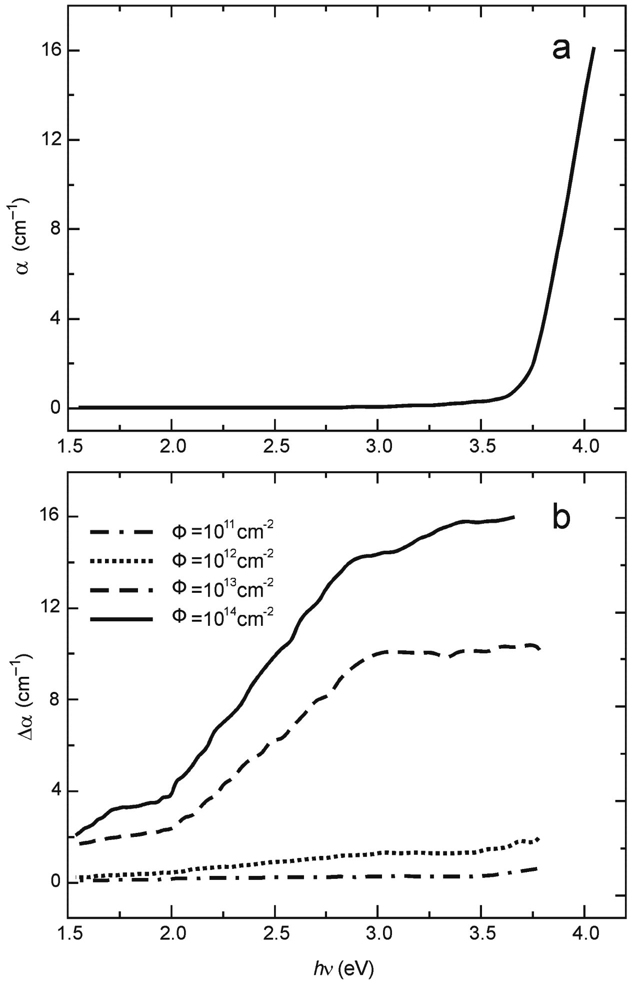

Fig. 1. (a) Optical absorption spectrum of F-1 lead silicate glass and (b) spectral plots of radiation-induced absorption increment for F-1 glass, irradiated at 293 K *by different fluences of* 10-MeV *electrons.*

The performed measurements have shown that the irradiation of lead silicate glass by electrons of different energies results in qualitatively the same changes – additional absorption near the edge and in the transparency range. That is generally in a qualitative agreement with the results for X-ray- and γ-irradiated lead silicate glasses [4,7]. Figure 1b illustrates the increment of absorption $\Delta\alpha(h\nu)$ induced by radiation of the F-1 glass at room temperature by 10-MeV electrons for different values of the electron fluence, Φ. As seen in the figure, with the increase of Φ, some selective absorption features appear against the background of a continuous absorption increment. The lowest-energy band is observed at 1.7 eV. It should be noted that a correct identification of the higher-energy bands and determination of their parameters is encumbered by the presence of radiation-induced tails of the density of electron states, whose contribution to the $\Delta\alpha(h\nu)$ spectrum also increases with Φ.

In the absorption spectra of X-ray- and γ-irradiated lead silicate glasses, three bands have been reported, centered at 1.7, 2.3 and 3.3 eV, corresponding to the radiation colour centres [4, 7]. The increase of their intensity with greater percentage of lead oxide in the glass is related to the spectrum of 6s Pb molecular orbital in the energy gap of $[Si_4O_4PbO_2Si_2]^{+14}$-fragment with the increase of the number of non-bridging oxygen atoms in the vicinity of Pb_2^+ ions and possible localization of electrons at these molecular orbitals [4].

From the available data [4,7], it is not clear how the contribution of the density-of-states tails was taken into account. The $\Delta\alpha(h\nu)$ experimental spectra were approximated by a set of elementary contours. However, if high-energy electron irradiation of lead silicate glass is assumed to result in the same types of radiation-induced colour centres as those induced by γ-, X-ray- and UV-radiation [3,4,7] (as is known for the alkali silicate glasses [8]), it seems reasonable to simulate the experimental $\Delta\alpha(h\nu)$ spectra of the electron-irradiated lead silicate glass taking into account the values of the band parameters of radiation-induced colour-centre absorption presented in Refs. [3,4,7]. Hence, for the samples irradiated with the fluences $\Phi \geq 10^{13}$ cm^{-2} of 5-MeV, 8-MeV and 10-MeV electrons, the experimental $\Delta\alpha(h\nu)$ spectra were approximated by a superposition of an exponential curve (the density-of-states tails) and Gaussian contours (the known bands, related to the radiation-induced centres). The calculations have shown that all experimental spectra are well described by that approximation (e.g., Fig. 2). In all cases, the energy positions of the radiation-induced higher-energy absorption bands were (2.5 ± 0.1) and (2.9 ± 0.1) eV, what differs from the data in Refs. [4,7] by +0.2 and -0.4 eV, respectively. That disagreement can be explained either by the different approximation procedure used in the analysis of the experimental spectra, or by the fact that the types of colour centres formed in the lead silicate glass under high-energy electron bombardment differ from those induced by less energetic UV and γ-radiation. However, the basic net-former in the investigated lead-silicate glass is silicon dioxide, and the experimental studies of electron-irradiaied glassy SiO_2 [2,7] and alkali silicate glasses on its base [8] have shown that in these materials different type of radiation results in formation of the centres of the same type. Besides, the energy position of the absorption band centered at 1.7 eV, observed in electron-irradiated lead silicate glass at $\Phi = 10^{14}$ cm^{-2}, coincides with the data of Refs. [4,7]. Note that while studying transient absorption of the lead silicate glass of a similar composition under UV pulsed irrradiation [3], the absorption bands centred at 2.7 and 2.9 eV were revealed. Hence, we relate the observed features induced by high-energy electron irradiation to the same colour centres as those caused by less energetic radiation.

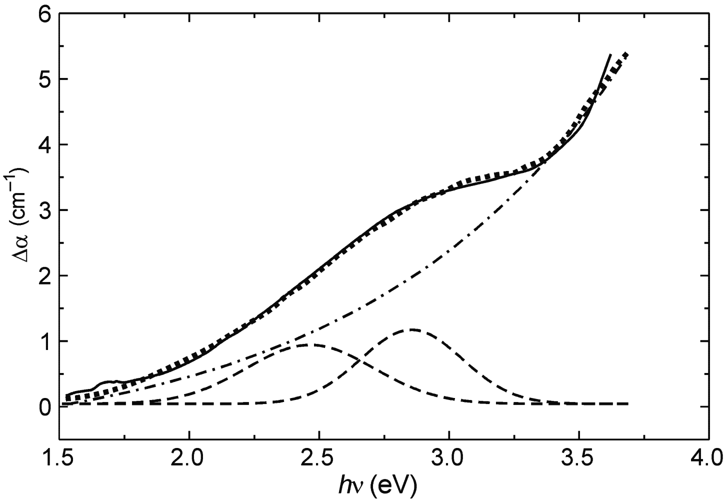

Fig. 2. Experimental spectrum of absorption increment in F-1 lead silicate glass, irradiated at 293 K by $\Phi = 10^{14}$ cm^{-2} of 5-MeV electrons (solid curve), and its approximation by the superposition of two Gaussian contours (dashed curves) and an exponential density-of-states tail (chain curve). The result of the approximation is shown by the dotted curve.

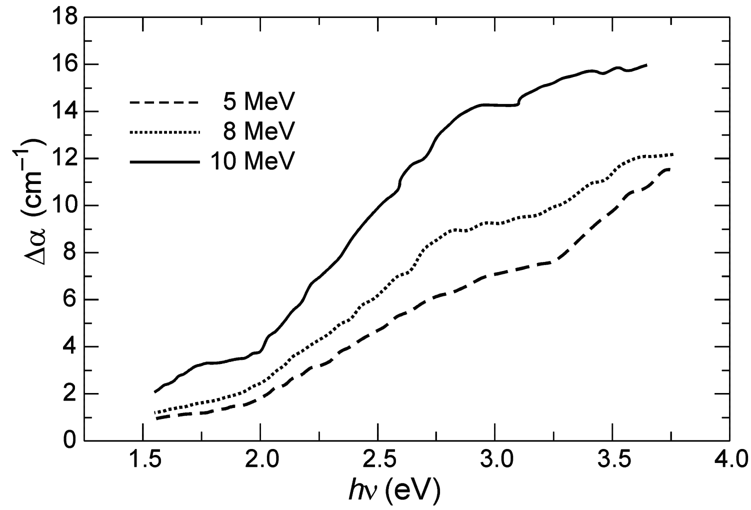

Fig. 3. Spectral plots of radiation-induced absorption increment for F-1 lead silicate glass, irradiated at 293 K by the fluence $\Phi = 10^{14}$ cm^{-2} electrons at different electron energies.

As seen in Fig. 3, the increase of the incident electron energy E from 5 to 10 MeV, while retaining the same electron fluence Φ, resulted in an increase of the absorption increment by a factor of two in the whole spectral range under investigation.

The increase of the additional absorption is also observed when the irradiation temperature was reduced to 223 K. The absorption spectrum is of the same form as of the room-temperature irradiated sample, but the absolute value of the radiation-induced absorption increment is considerably higher in the whole investigated spectral range (see Fig. 4). Thus, one may conclude that the irradiation at 223 K results in the formation of the same colour centres as those formed by irradiation at room-temperature. However, at 293 K, the radiation-induced centres are partly annealed already during the irradiation.

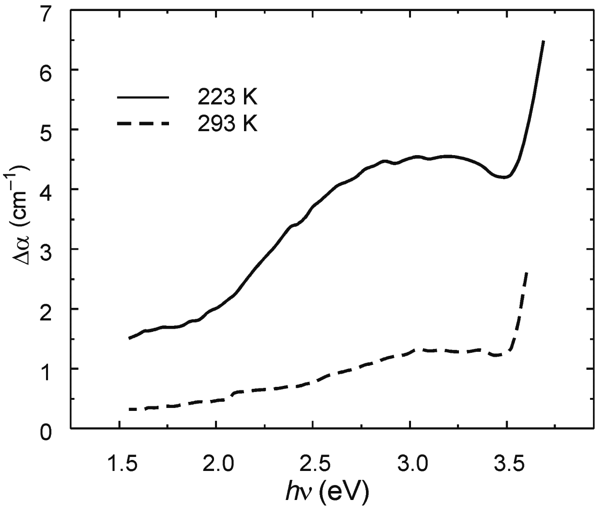

Fig. 4. Spectral plots of radiation-induced absorption increment for F-1 lead silicate glass, irradiated at 223 *and* 293 K *by the fluence* $\Phi = 10^{12}$ cm^{-2} *of* 10-MeV *electrons.*

The isochronal annealing studies of the absorption coefficient after the low-temperature irradiation have shown that the absorbance recovers gradually in the whole temperature range 223 – 293 K. We have also performed the measurements of isochronal annealing of the samples, irradiated at room temperature by the fluence $\Phi = 10^{14}$ cm^{-2} of 5-, 8- and 10-MeV electrons, in the temperature range 350 – 800 K. As seen in Fig. 5, annealing results in a decrease of the radiation-induced absorption increment. The main part of the absorption increment is annealed below 425 K. Contrary to the alkali silicate glasses, where annealing reveals an additional band in the radiation-induced absorption spectrum [8,9], in the lead silicate glass no new features in the additional absorption spectrum were observed under annealing. One can conclude that there is a durable annealing stage 275 – 425 K for both radiation-induced absorption bands (at 2.5 and 2.9 eV) and the density-of-states tails.

Photoluminescence (PL) measurements of non-irradiated lead silicate glass (solid curve in Fig. 6) have revealed the presence of two bands centered at 1.75 eV (710 nm) and 2.10 eV (590 nm). Note that under irradiation with the fluences

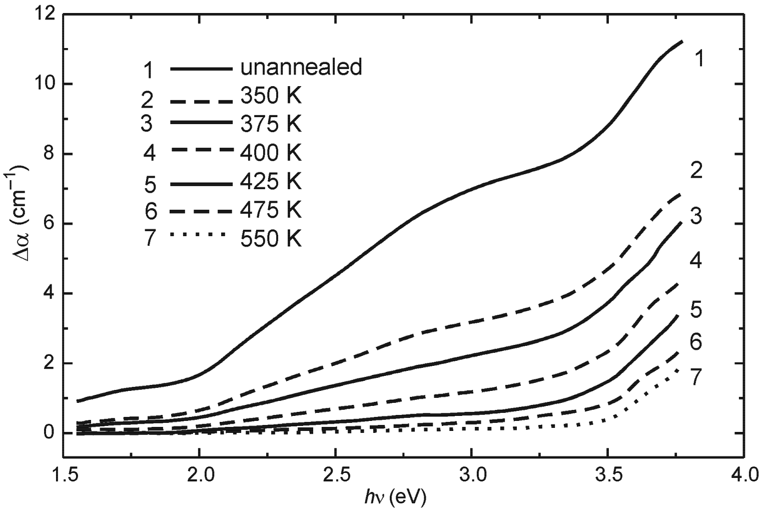

Fig. 5. Effect of isochronal annealing on the spectral plots of radiation-induced absorption increment for F-1 lead silicate glass, irradiated at 293 K *by the fluence* $\Phi = 10^{14}$ cm^{-2} *of* 5-MeV *electrons.*

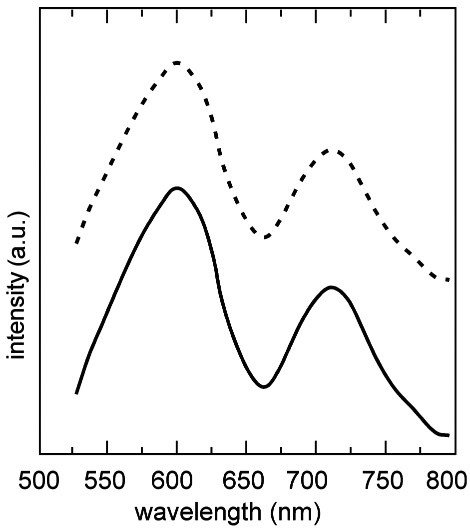

Fig. 6. Photoluminescence spectrum of F-1 lead silicate glass: non-irradiated (solid curve) and irradiated at 293 K *by the fluence* $\Phi = 10^{14}$ cm^{-2} *of* 5-MeV *electrons (dashed curve).*

up to 10^{14} cm^{-2} of 5-MeV electrons, the PL spectra remain practically the same (dashed curve in the same figure).

In silicate glass, the photoluminescence in the red spectral range is, as a rule, determined by the ions of iron which is the most important uncontrollable impurity in this material [10]. Radiation changes the valence of the iron ions present in the glass. In the non-irradiated glass, Fe^{3+} ions are considered to occupy energetically more favourable sites in tetrahedral coordination and to be responsible for the band at 1.80 eV [10]. It should be noted, however, that, evidently, radiation-induced recharging of iron impurity ions $Fe^{3+} \rightarrow (Fe^{3+})^-$ is not the only mechanism determining the behaviour of silicate-glass luminescence after high-energy electron irradiation. In this spectral range, luminescence bands related to non-bridging oxygen atoms (1.9 eV [2]) or interstitial O_2 (1.62 eV [11]) or O_3 (1.9 eV [12]) molecules have been reported. Note that the spectral position of the PL maximum is determined not only by the structure of the corresponding recombination centres, but also depends on the presence of modifiers in the glass and on the PL excitation method.

The intensity of the PL band centred at 1.75 eV, as well as that of the higher-energy one at 2.15 eV, does not vary with irradiation. Hence, one can suppose that either (i) for electron irradiation, the two competing processes compensate each other (the PL quenching due to the radiation-induced recharging of iron ions and the PL intensity increase due to the formation of non-bridging oxygen atoms and radiolytic molecule formation from the bridging oxygen atoms), or (ii) for the given fluences and energies of incident electrons, no radiation-induced charge-state transformations of the iron ions occur, while the contributions of other processes are negligible. The last assumption seems more probable since no changes in the PL band shape were observed, what could be expected in the presence of competing processes. It is known that for iron ions in silicate glass, the character of the charge-state transformations can be strongly dependent on its initial coordination (the number of oxygen atoms among the nearest neighbours), and on the presence of other variable-valence ions in the glass, what is determined by the corresponding modifiers (in this case primarily the lead oxide).

4. *Conclusions*

The experimental studies of optical absorption spectra of lead silicate glass irradiated by high-energy electrons have shown that the radiation-induced additional absorption arises due to the superposition of absorption bands, related to the known radiation-induced colour centres, and disorder-induced tails of the density of electron states. The comparison of the corresponding band parameters with the reference data, the analysis of their dose and energy behaviour as well as the recovery of the initial transmission spectra at isochronal annealing enabled us to conclude that in lead silicate glass electron irradiation produces the same colour centres as in the treatment by lower-energy radiation.

Photoluminescence studies of lead silicate glass show that the non-sensitivity of the PL spectra to the electron irradiation is most probably related to the specific features of uncontrollable iron impurity coordination in the silicate-glass structural network, modified by lead, as well as the to the presence of other variable-valence atoms.

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UČINAK OZRAČIVANJA ELEKTRONIMA VISOKE ENERGIJE NA OPTIČKA SVOJSTVA OLOVNOG STAKLA

U vidljivom smo području proučavali apsorpciju i fotoluminescentne spektre olovnog stakla ozračenog elektronima energije 5 do 10 MeV. Pokazuje se da to ozračivanje stvara centre boje vrlo slične onima koji se postižu ozračivanjem X- i γ-zračenjem. Raspravljamo o najvjerojatnijim uzrocima neosjetljivosti fotoluminescencije na ozračivanje elektronima.