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OPTICAL STUDIES OF ALKALI BOROSILICATE GLASS IRRADIATED WITH HIGH-ENERGY ELECTRONS

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The effects of the irradiation by electrons with the energy 5-10 MeV on the optical absorption and photoluminescence spectra of alkali borosilicate glass are reported. The dependences of the irradiation-induced absorption band characteristics on the electron fluence, energy, irradiation temperature and annealing are studied, the transformations of the radiation defects in glass, responsible for the changes in the optical spectra, being discussed.

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Keywords: Electron irradiation, Borosilicate glass, Absorption, Radiation defects, Annealing, Photoluminescence

1. Introduction

Among a wide variety of silicate-based glasses a special role is played by alkali borosilicate glasses due to their wide applications in optical engineering as well as possibilities for using them as matrices for embedding semiconductor microcrystals [1]. Such composites are promising for construction of optical devices (colour filters, fast optical switches etc.) and interesting due to size-quantum effects resulting from spatial confinement of charge-carriers in microcrystals [2]. The glass matrix essentially affects the optical properties of the microcrystals [3, 4]. In glasses, exposed to ionizing radiation, radiation defects (colour centres) are known to be formed, increasing the glass matrix volume [5]. In order to minimize the radiation effects on the parameters of alkali borosilicate glass, it is intentionally doped with cerium dioxide [6]. However, studies of radiation effects on the unmodified borosilicate glass parameters are of particular interest since it is this sort of glass that is most often used for embedding semiconductor microcrystals. Note that while studying the effect of radiation upon optical characteristics of commercially available borosilicate glass samples and their radiation-proof analogues mostly high-energy X-ray and gamma-radiation is applied [6-8].

The present paper is aimed at detailed studies of high-energy (5, 8, 10 MeV) electron irradiation on absorption and photoluminescence (PL) of commercially available K-8 alkali borosilicate glass at various fluence and energy of electrons, irradiation temperature as well as at subsequent annealing in order to elucidate the nature of the radiation defects being formed.

2. Experimental

K-8 alkali borosilicate glass samples were irradiated on a M-30 electron accelerator at the Institute of Electron Physics, Ukr. Nat. Acad. Sci. (Uzhhorod, Ukraine) with the electron flux 6.3×10^8–7.2×10^9 $cm^{-2} \cdot s^{-1}$ in the range of temperatures 223–293 K. The irradiating electrons were monoenergetic within 0.5 MeV. To avoid the samples heating at the irradiation they were cooled by liquid nitrogen vapour. Note that a specially constructed chamber enabled the low-temperature irradiation and sample transportation from the irradiation area to the measuring setup equipped with

UTREX cryostat without temperature increase. The optical absorption spectra were measured using standard technique at LOMO MDR-23 monochromator within 300–800 nm, PL spectra – at LOMO DFS-24 spectrometer with a photon counting system, Ar+-laser (514.5 and 488 nm) being used as the excitation source.

3. Results and discussion

Fig. 1 (a) presents the increment of K-8 glass absorbance after 10-MeV electron irradiation at 293 K for various electron fluences Φ. With the increase of the irradiation dose the absorbance increment Δα increases considerably first in the range of hν > 3.5 eV, and then – in the lower-frequency range as well. Note that the irradiation-induced absorption spectrum essentially depends not only on the electron fluence, but also on their energy *E*, this being illustrated by Fig. 1 (b).

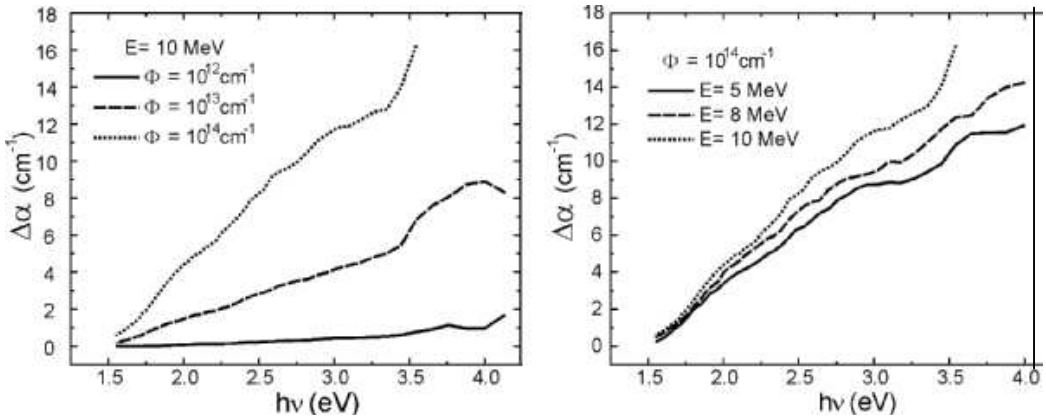

Fig. 1. Spectral dependences of irradiation-induced absorption increment of K-8 alkali borosilicate glass: (a) for different values of electron fluence Φ at irradiation temperature 293 K and electron energy E = 10 MeV; (b) at electron fluence $\Phi = 10^{14}$ cm^{-2} and irradiation temperature 293 K for different electron energy values.

The absorbance increment spectrum has a complex shape, evidently resulting from the presence of several absorption bands in the spectral range under investigation. While the spectrum being approximated by elementary gaussian contours the best fit was obtained for three absorption bands centered at 2.03, 2.73 and 4.0 eV with halfwidths 0.46, 0.83 and 1.20 eV, respectively, as shown in Fig. 2.

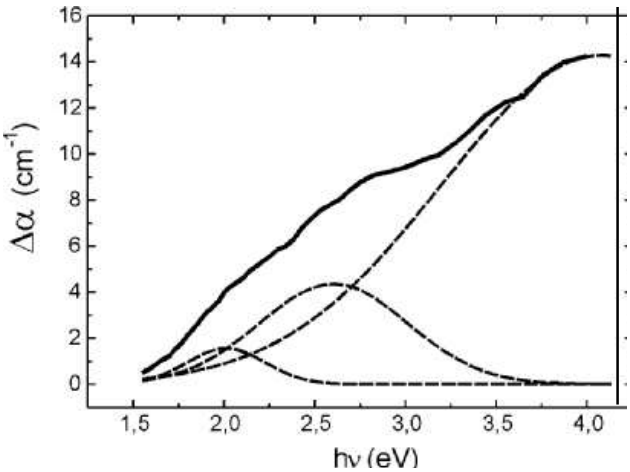

Fig. 2. Irradiation-induced absorption increment spectrum of K-8 alkali borosilicate glass irradiated at 293 K with the fluence $\Phi = 10^{14}$ cm^{-2} of 10 MeV electrons and its simulation by elementary gaussian curves.

Note that $\Delta\alpha(h\nu)$ spectra of γ-irradiated K-8 glass have a similar outlook [7], the energy positions of the additional absorption bands being in good agreement with our results. Similar bands are observed in alkali borosilicate glass spectra after UV-irradiation [8, 9]. In this case not only the energy positions, but also the halfwidths of the corresponding absorption bands are close to those obtained here (Table 1). This enables us to conclude the spectrum of additional absorption induced by high-energy electron irradiation, like in the case of heavy γ- or UV-irradiation, to be determined by superimposing of the known intrinsic hole radiation colour centres H_3^+, H_2^+, H_4^+.

Table 1. Characteristics of colour centres.

Colour centre	Peak energy position, eV			Halfwidth, eV	
	Our results	[7]	[8]	Our results	[8]
H_3^+	2.03	2.0	1.96	0.46	0.50
H_2^+	2.73	2.8	2.72	0.83	0.95
H_4^+	4.0	4.1	4.0 [10]	1.20	…

One of the methods of uncovering the structure of the absorption increment spectra lies in studying their variation at thermal decolouring. For this purpose we performed isochronal (20 min) annealing studies of the samples within 300–800 K temperature range with a step of 25 K. The corresponding $\Delta\alpha(h\nu)$ spectra, measured at room temperature, are shown in Fig. 3. The annealing is seen to result in the decrease of the radiation-induced absorbance in the whole temperature range, the spectrum transformation being non-uniform in the course of annealing.

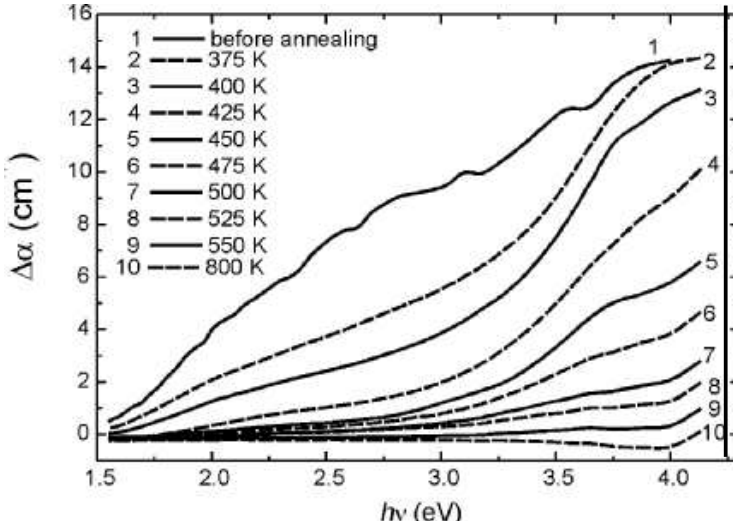

Fig. 3. Effect of annealing on the spectral dependences of irradiation-induced absorption increment of K-8 alkali borosilicate glass irradiated at 293 K with the fluence $\Phi = 10^{14}$ cm^{-2} of 8 MeV electrons.

The analysis of the absorption increment spectrum behaviour under annealing, carried out by simulation of the measured spectra by multiple gaussian contours, enabled us to plot the energy positions, halfwidths and integrated intensities of the additional absorption bands against the annealing temperature, what is illustrated by Fig. 4. Annealing at 350-400 K practically does not affect the spectral position of the bands at 2.0, 2.7 and 4.0 eV and their halfwidths as well as the intensity of the band at 4.0 eV, while the intensity of the lower-energy bands noticeably decreases. At T_a = 425 K in the absorption increment spectrum the bands at 2.1 and 2.8 eV are replaced by a band centered at 2.47 eV with the halfwidth of 0.6 eV. At further annealing in the range 450–475 K its peak position and halfwidth decrease to 2.42 and 0.5 eV, respectively, accompanied by the decrease of intensity. At T_a >

475 K this additional absorption band disappears. Quite similar behaviour is observed at the annealing of the 5 MeV electron-irradiated sample.

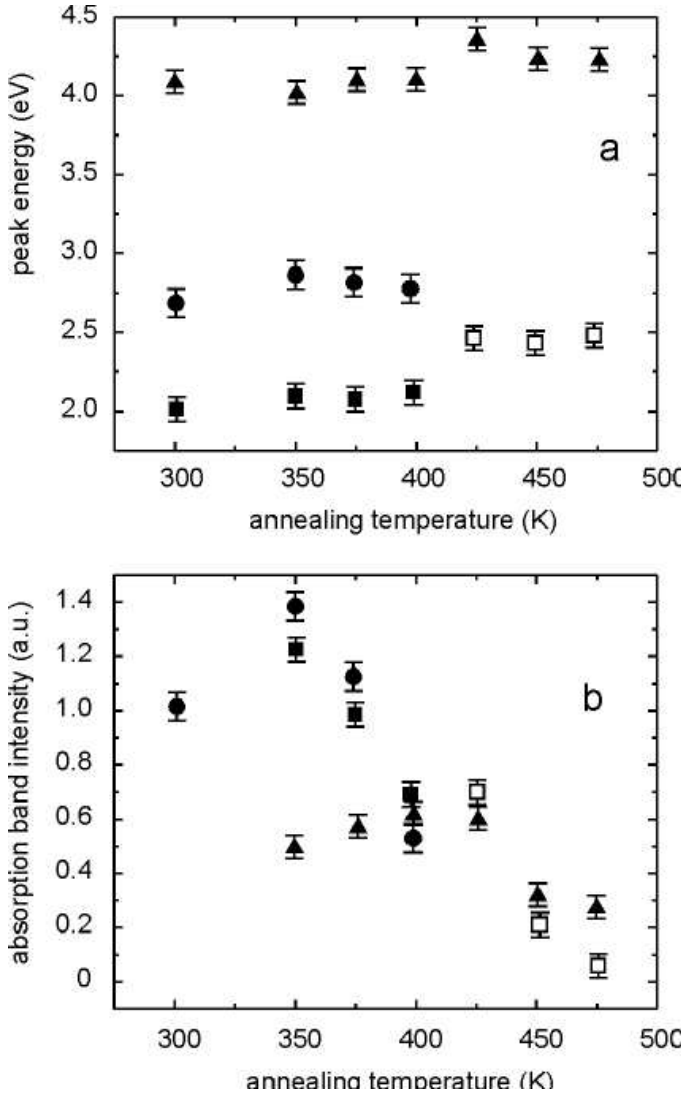

Fig. 4. Dependence of energy positions (a) and integrated intensities (b) of absorption increment bands for K-8 alkali borosilicate glass irradiated at 293 K with the fluence $\Phi = 10^{14}$ cm^{-2} of 8-MeV electrons, on the annealing temperature. Black triangles correspond to the band centered at 4.0 eV, black circles: 2.73 eV, black squares: 2.03 eV, open squares: 2.4 eV. The integrated intensities are normalized by the corresponding band intensities for the unannealed sample.

It should be noted that in [8] annealing at 475 K has also revealed a band centered at 2.4 eV with the halfwidth 0.45 eV in the additional absorption spectrum of UV-irradiated alkali borosilicate glass. The agreement of the band spectral characteristics and the annealing stage with our results is an additional evidence for UV and electron irradiation, evidently, resulting in the formation of the same absorption centres in alkali borosilicate glass, revealed in the visible spectral range.

Note that low intensity of this absorption band with respect to the known bands at 2.0 and 2.7 eV, large halfwidths and close positions of the discussed bands explain the fact that the absorption increment spectra of glass samples unannealed and annealed at T_a < 425 K, are well approximated by three absorption bands with the above characteristics. With increasing the annealing temperature to 425–475 K, the bands corresponding to H_3^+ and H_2^+ centres, vanish due to their decay, this resulting in

the visualization of the band at 2.4 eV, corresponding to the centres with higher thermal stability. As shown in [8], the band at 2.4 eV is related not to the transformation of the known radiation defects in the course of annealing, but to the formation of a new type of hole colour centres upon irradiation.

The band, corresponding to H_4^+ centres, with the maximum at 4.0 eV, is shown to decrease in intensity after annealing at T_a > 425 K. Annealing to 550 K results in complete recovery of the initial spectrum, and at higher annealing temperatures negative values of $\Delta\alpha$ are observed practically in the whole spectral range under investigation, especially near 4.0 eV. In our opinion this can be explained by the fact that at such temperature not only radiation-induced defects, but also intrinsic defects are annealed. In particular, it concerns H_4^+ centres, whose initial concentration is, probably, rather high, what is confirmed by the presence of the corresponding band in the non-irradiated sample spectrum.

We have performed spectroscopic studies of alkali borosilicate K-8 glass, irradiated with 10 MeV electrons at 223 K (see Fig. 5).

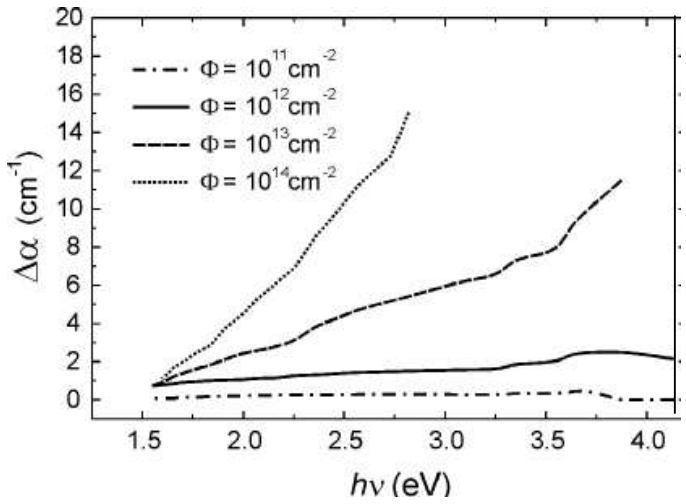

Fig. 5. Spectral dependences of irradiation-induced absorption increment of K-8 alkali borosilicate glass for different values of electron fluence Φ at irradiation temperature 223 K and energy of electrons 10 MeV.

It should be noted that the general outlook of the spectra and their dose behaviour are similar to those of the samples irradiated at room temperature. However, it should be noted that the comparison of the experimental spectra of the samples irradiated by the same electron fluence at 223 and 293 K (Fig. 6) has shown the effect of the low-temperature irradiation to be much more noticeable at lower Φ values. At $\Phi = 10^{12}$ cm^{-2} the absolute value of transmittance is seen to decrease (hence, the absorbance increases) much more in case of irradiation at 223 K (dotted curve 2), than at room-temperature irradiation (solid curve 2). With the increase of the electron fluence this difference decreases, and at $\Phi = 10^{14}$ cm^{-2} the spectra of the samples, irradiated at 223 and 293 K, are practically similar (dotted and solid curves 4). This fact implies that primary radiation defects, formed in alkali borosilicate glass, irradiated at 223 K, are mobile already at the irradiation temperature, their ability to form secondary, more stable radiation defects being dependent not only on temperature, but also on their concentration. Irradiation of samples with the fluence of 10^{14} electron/cm^{-2} introduces such concentration of primary radiation defects that even at low temperature they are transformed into secondary radiation defects.

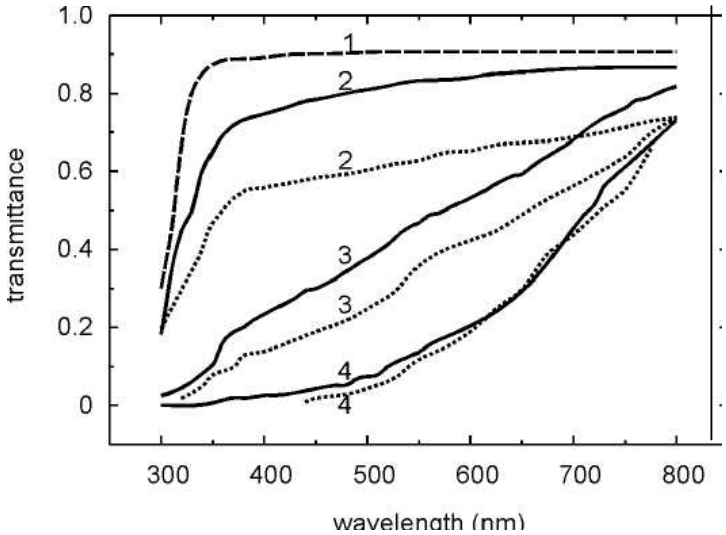

Fig. 6. Optical transmission spectra of 3-mm thick samples of K-8 alkali borosilicate glass irradiated at 223 K (dotted curves) and 293 K (solid curves) with the fluences $\Phi = 10^{12}$ cm^{-2} (2), 10^{13} cm^{-2} (3) and 10^{14} cm^{-2} (4) of 10 MeV electrons. Dashed curve 1 denotes the non-irradiated sample transmittance.

Photoluminescence spectrum of silicate glass, in particular, K-8, is known to depend essentially not only on its composition and impurities (both intentionally and uncontrollable introduced), but also on the energy of the exciting light [9, 11–13]. Fig. 7 presents the photoluminescence spectra measured at 293 K of non-irradiated and irradiated samples of K-8 alkali borosilicate glass with the fluence of $\Phi = 10^{14}$ cm^{-2} 10 MeV electrons using Ar^+ laser (λ = 488 nm) as excitation source. The spectrum of non-irradiated K-8 glass consists of two broad bands centered at 2.1 eV (590 nm) and 1.8 eV (690 nm) with the halfwidths of 0.5 and 0.1 eV, respectively. Irradiation results in total quenching of photoluminescence band at 2.1 eV, while the intensity of the band at 1.8 eV remains practically unchanged. The luminescence band in the red spectral range of K-8 glass is considered to be related to the internal transitions at iron impurity ions, being the most significant uncontrollable impurity in silicate glasses [14]. By irradiation the valence of the iron ions in glass is changed. In the non-irradiated glass Fe^{3+} ions are considered to occupy more energetically convenient sites in tetrahedral coordination, and are responsible for the band at 1.8 eV [14]. However, it should be noted that radiation-induced recharging of iron impurity ions $Fe^{3+} \rightarrow (Fe^{3+})^-$ is not the only mechanism, responsible for the luminescence behaviour in high-energy electron-irradiated silicate glass, since we have observed the radiation quenching of the band with the maximum at 2.1 eV, while the authors of [14] report the additional luminescence band appearing in this range after γ-irradiation. Meanwhile the intensity of the band, centered at 1.8 eV, does not decrease with irradiation. This enables us to assume that the changes of iron atoms valence in glass under irradiation can essentially depend on their initial coordination (number of oxygen atoms among the nearest neighbours) and on the presence of other variable-valence ions. Besides, it is known that in glassy SiO_2 in this spectral range (1.62 eV) a luminescence band is reported, resulting from radiative transition from the second excited state of interstitial O_2 molecules to the ground state, $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$, these interstitial molecules being able to be formed radiolytically from the oxygen bridge atoms, forming SiO_2 structural network [13]. Hence, the band at 1.8 eV in K-8 glass can be a superposition of contours caused by different factors. The detailed study of the irradiation factors (type, energy, fluence of irradiating particles) and concentration of impurities (both uncontrollable and intentionally introduced) upon the borosilicate glass luminescence deserves additional investigations.

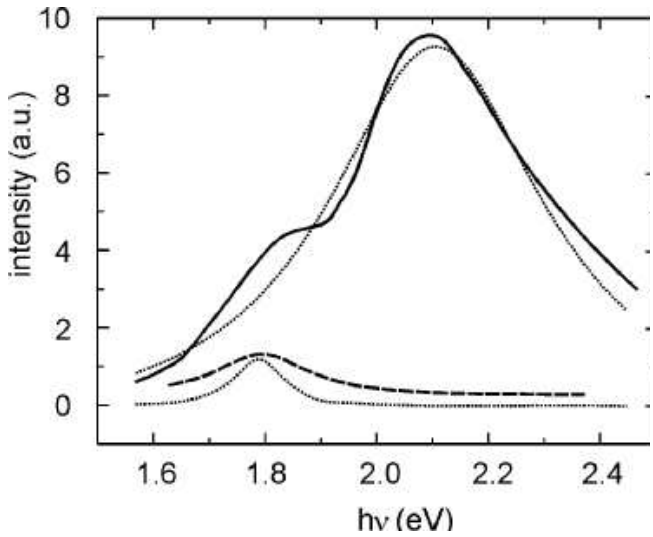

Fig. 7. Photoluminescence spectra of non-irradiated (solid curve) and irradiated at 293 K with the fluence 10^{14} cm^{-2} of 10 MeV electrons (dashed curve) K-8 alkali borosilicate glass. Dotted curves show the non-irradiated sample spectrum simulation by elementary gaussian curves.

4. Conclusions

The performed optical measurements have shown that at high-energy electron irradiation in K-8 alkali borosilicate glass the same types of defects (H_3^+, H_2^+, H_4^+), active in the absorption spectra in visible range, are formed, as under irradiation with lower-energy γ-, X- and UV-rays. The increase of dose and energy of the irradiating electrons results in the increase of the defect concentration.

In alkali borosilicate glass, irradiated at 223 K by low fluences of electrons ($\Phi \leq 10^{12}$ cm^{-2}), when the concentration of primary radiation defects is rather low, they anneal below room temperature, more thermally stable secondary defects having not yet been formed. At higher concentrations of primary radiation defects or at higher irradiation temperatures secondary radiation defects are formed, H_3^+ and H_2^+ annealing at 350–425 K, and H_4^+ – at 425–550 K. In the course of annealing in the absorption spectra a band centered at 2.4 eV, is visualized, corresponding to intrinsic hole-type radiation colour centres, annealing at 425–475 K.

High-energy electron irradiation results in the quenching of photoluminescence band centered at 2.1 eV, while the band centered at 1.8 eV, remains practically inaffected. The elucidation of the nature of the discussed bands requires further studies.

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