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RAMAN SCATTERING AND OPTICAL ABSORPTION STUDY OF RADIATION EFFECTS IN ALKALI ZINC BOROSILICATE GLASS

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Abstract

Raman scattering and optical absorption studies of alkali zinc borosilicate glass irradiated with X-rays (up to 1100 Gy) or 7-MeV electrons $(\text{up to } 10^{15}\text{cm}^{-2})$ are reported. We did not observe any Raman evidence for the radiation-induced changes in the glass structure, which could be related to the increasing number of three-member silicate rings and decreasing the average Si–O–Si bond angle. Optical absorption spectra show the formation of three types of colour centres $(H_3^+, H_2^+, \text{ and } H_4^+)$ in alkali zinc borosilicate glass similar to other amorphous materials. The observed radiation colour centres partly anneal at post-irradiation storage at room temperature and completely disappear at annealing to 550K.

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1. Introduction

Radiation-induced changes in the optical spectra of glasses are usually related to the formation and transformation of electron and hole colour centres, which emerge in the glass exposed to high-energy irradiation [1-3]. Broad applications of devices with optical glasses under the action of high-energy radiation set extra requirements to their radiation strength. This determines the practical importance of studies devoted to the influence of irradiation on the optical parameters of glasses, first of all on their absorption coefficient, and elucidation of the structure and mechanism of formation of radiation colour centres.

Radiation-induced centres in glass are usually related to non-bridging oxygen atoms [4-7]. For the most extensively studied amorphous SiO_2 various centres of this type have been identified and studied – a single non-bridging oxygen atom (hole centre) [8], E' centre (an oxygen vacancy, i.e., a silicon atom bound to just three oxygen atoms in the glass network) [4, 9, 10], a peroxy radical O_2^- bound to a Si atom in the glass network [11]. In glasses with more complicated chemical structure, various radiation-induced centres are known [2, 12-15], revealed as additional bands in the optical absorption spectra of the irradiated glass samples. In particular, the effect of high-energy irradiation was studied rather extensively for alkali silicate and alkali borosilicate glasses [6, 12-17]. However, zinc-containing borosilicate glasses have been much less studied so far. In particular, to our knowledge, no targeted studies of irradiation effect on the optical spectra of zinc-containing borosilicate glasses have been reported though glasses of this sort are extensively used as optical and engineering materials, display glasses, neutron absorbers [18] as well as host matrices for embedding II–VI semiconductor nanocrystals [19, 20].

The present paper reports on the study of the effect of high-energy electron and X-ray irradiation as well as post-irradiation annealing on the optical absorption spectra of zinc alkali borosilicate glass.

2. Experimental

The samples of $Na_2O–K_2O–ZnO–B_2O_3–SiO_2$ glass were prepared by co-melting of the initial mixture in an oven at 1500K and subsequent rapid quenching. An X-ray irradiation was carried out by using an X-ray tube with a Mo anticathode (40kV, 20mA). 7-MeV electron irradiation was performed by using an M-30 electron accelerator at the Institute of Electron Physics (Uzhhorod, Ukraine). The electron fluence Φ varied from 10^{11} to $10^{15}cm^{-2}$. In order to avoid the sample overheating above the room temperature, the irradiated samples were cooled by evaporating liquid nitrogen, their temperature being controlled by a copper-constantane thermocouple. Optical absorption spectra were recorded at room temperature within 2h after the irradiation using a LOMO MDR-23 monochromator with a FEU-100 phototube. Raman scattering spectra were measured by using a LOMO DFS-24 double monochromator and a FEU-79 phototube. The excitation was provided by a 514.5nm line of an Ar^+ion laser.

3. Results and Discussion

Figure 1 illustrates a Raman spectrum of the alkali zinc borosilicate glass under investigation with broad bands typical for disordered systems, in particular, glasses and a rather intense scattering in the low-frequency range determined by the presence of the glass boson peak. A rather broad continuum observed in the range of 300-700cm^{-1} with several maxima (the most pronounced ones at 477 and 544cm^{-1}) and shoulders, is in agreement with the data reported by other authors for silica glass [21, 22], silicate [23], and borosilicate [18, 24] glasses. Raman scattering in this spectral range is related to delocalized vibrations of Si–O–Si bridges between tetrahedral $Q^n = [Si(O_{1/2})_n O_{4-n}]^{-(4-z)}$ structural groups, where $O_{1/2}$ denotes a bridging oxygen atom between two silicon atom while O stands for a non-bridging oxygen atom [23]. Note that the observed complicated scattering continuum in the range up to 500cm^{-1} can also contain contribution from the vibrations of Zn–O and B–O bonds, though the nature of the corresponding band observed in the Raman spectra of vitreous B_2O_3 near 500cm^{-1} [25] remains unclear. A shoulder near 625cm^{-1} can be due to the contribution of vibrations of borosilicate rings with B–O and Si–O bonds [24, 26].

A maximum in the Raman spectrum at 781cm^{-1} (see Figure 1) is most likely related to the vibrations of boron and oxygen atoms in the glass. Bands at similar frequencies are observed in the spectra of borosilicate glasses and attributed to the vibrations of borate rings with $[BO_{4/2}]^-$ tetrahedrons [18, 24, 26, 27] and their intensity is known to increase with boron content in the glass [27]. Higher-frequency Raman bands in the range $900\text{-}1200 \text{cm}^{-1}$ are related to symmetrical stretching vibrations of Q^n silicate tetrahedra [23, 24, 26]. As follows from the comparison with the data of other authors for borosilicate glasses, the band at 945cm^{-1} corresponds to the vibrations of Q^2 tetrahedra, while the one at 1096cm^{-1} is related to the Q^3 tetrahedra [24, 26]. Note that for electron-irradiated silica [22] and borosilicate [28] glasses, the authors observed transformation of some Raman bands in this spectral range under irradiation, which is related to the increasing number of three-member silicate rings and decreasing the average Si–O–Si bond angle.

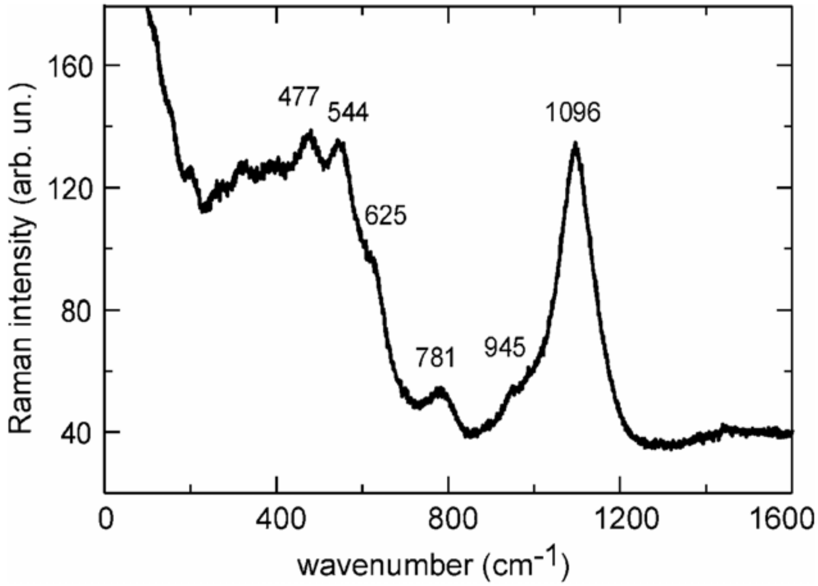

Figure 1. Raman spectrum of the alkali zinc borosilicate glass at room temperature.

However, our measurements of the Raman spectra of alkali zinc borosilicate glass irradiated by the fluence of $10^{14}\,cm^{-2}\,7$ - MeV electrons did not reveal any noticeable changes in the spectral positions and intensities of the observed maxima. Slight deviations in the intensity ratios for some maxima are, in our opinion, related rather to laser power fluctuations in the course of measurement and in our case cannot testify for any radiation-induced changes in the Raman spectra. Evidently, Raman measurements using spectrometers with CCD cameras providing multichannel signal registration are required to avoid the effect of laser power instability.

Much more noticeable changes under irradiation with high-energy electrons were expected in the optical absorption spectra of alkali zinc borosilicate glass. As can be seen from Figure 2, in the spectrum of the non-irradiated sample, the optical absorption edge of the glass is described by the modified so-called "glass-like" Urbach rule [29]. After irradiation by 7-MeV electrons $(\Phi = 10^{15}\,cm^{-2})$, the absorption coefficient increases in the whole visible spectral range. As shown in the insert, the spectral dependence of the irradiation-induced absorption increment is observed to be well simulated by a superposition of three Lorentzian peaks centred at 1.9, 3.1, and 4.6eV with halfwidths 0.4, 1.1, and 1.2eV, respectively.

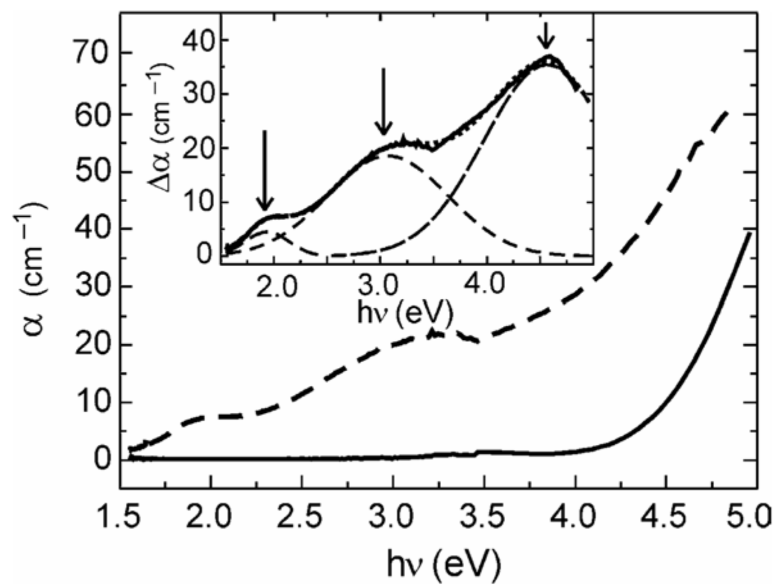

Figure 2. Optical absorption spectra of non-irradiated (solid curve) and irradiated with 10^{15}cm^{-2} of 7-MeV electrons (dashed curve) alkali zinc borosilicate glass. The insert shows the spectral dependence of the irradiation-induced absorption increment $\Delta\alpha$ (solid curve) along with its approximation by three Lorentzian peaks (dashed curves), their maximum positions being shown by arrows.

From the observed spectra, one can suppose irradiation-induced formation of three types of radiation colour centres in alkali zinc borosilicate glass. Such conclusion is supported by the comparison with our earlier studies of 10-MeV electron-irradiated alkali borosilicate glass [16], where three irradiation-induced absorption maxima at 2.0, 2.7, and 4.0eV were observed, attributed to H_3^+, H_2^+, and H_4^+ colour centres. In our case, due to the presence of a noticeable (13%) amount of zinc in the glass, the spectral positions of the absorption bands somewhat differ from the case of [16]; however, the band halfwidths and intensity ratios agree fairly well with the case of alkali borosilicate glass. Therefore, formation of radiation colour centres of the same types in the zinc-containing glass can be assumed.

As seen from Figure 3, irradiation of alkali zinc borosilicate glass by X-rays results in similar changes in the absorption spectrum. The positions (1.9, 3.0, and 4.3eV), bandwidths, and ratio of intensities of the X-ray-induced absorption maxima almost coincide with those observed under high-energy electron irradiation. Such mechanism of radiation defect formation is generally typical for glasses. For example, a similar situation was observed earlier for zinc-free borosilicate glass, where ultraviolet [30], gamma-ray [2], and 10-MeV electron [16] irradiation produces the same colour centres.

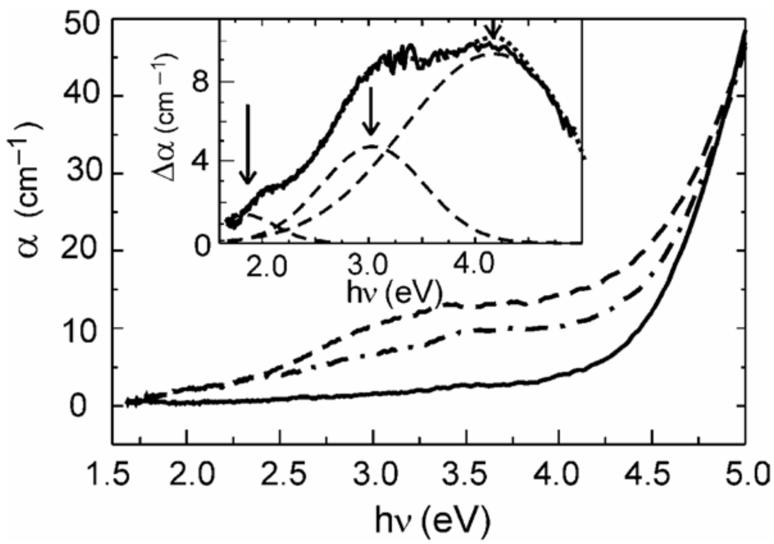

Figure 3. Optical absorption spectra of non-irradiated (solid curve) as well as X-ray irradiated with the dose D = 550 Gy (dash-and-dotted curve) and 1100 Gy (dashed curve). The insert shows the spectral dependence of the 1100 Gy irradiation-induced absorption increment $\Delta\alpha$ (solid curve) along with its approximation by three Lorentzian peaks (dashed curves), their maximum positions being shown by arrows.

The radiation-induced additional absorption features attributed to radiation colour centres in glasses usually undergo thermal decolouring. Note that in our case, variation of the optical absorption spectra of the electron-and X-ray irradiated glass samples is observed even after their storage at room temperature for a period of 20 days. As can be seen from Figure 4, the absorption coefficient value α_t measured in a broad spectral range 20 days after the irradiation, is noticeably below the value measured immediately (within 2h) after the irradiation. The spectral dependence of the absorption decrement $\alpha_t - \alpha_0$ due to the radiation-induced colour centres annealed during the 20-days room-temperature storage is shown in the insert. It clearly reveals the presence of the three maxima, corresponding to the H_3^+, H_2^+, and H_4^+ colour centres what is the evidence for the processes of post-irradiation relaxation in the glass resulting in the decay and/or transformation of the radiation-induced colour centres. The comparison of the ratio of intensities of the maxima, related to the three types of centres shown in the inserts of Figure 2 and Figure 3 shows that H_4^+ colour centres are more stable than H_3^+ and H_2^+. However, the absorption spectrum of the irradiated sample after 20 days of storage still preserves the features related to the radiation colour centres.

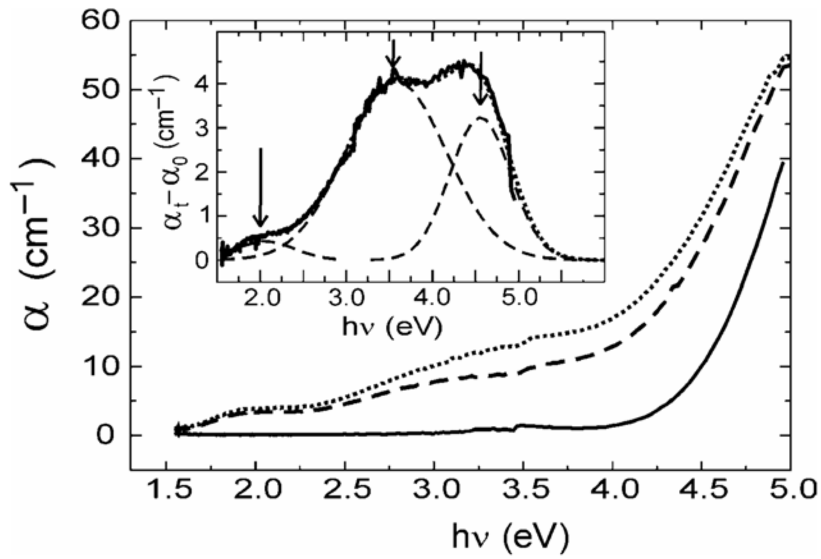

Figure 4. Optical absorption spectra of non-irradiated (solid curve) as well as irradiated with $10^{14}\,cm^{-2}$ of 7-MeV electrons alkali zinc borosilicate glass, measured 2h (dotted line) and 20 days (dashed line) after the irradiation. The insert shows the spectral dependence of the absorption decrement due to the 20-days storage (solid curve) along with its approximation by three Lorentzian peaks (dashed curves), their maximum positions being shown by arrows.

The studies of isochronal (20 min) annealing of the irradiated alkali zinc borosilicate glass in the 300-700K temperature range (Figure 5a) show that the irradiation-induced absorption increment $\Delta\alpha$ decreases with annealing temperature T_a in the whole spectral range under investigation, though the behaviour of $\Delta\alpha(T_a)$ differs for different spectral intervals.

By approximating the experimental $\Delta\alpha(h\nu)$ dependences by combinations of elementary Gaussian contours, we analyzed the behaviour of the characteristics of the radiation-induced absorption bands (energy positions, halfwidths, and intensities) with annealing. The corresponding dependences are plotted in Figure 5b. The intensities of the radiation-induced absorption bands gradually decrease with T_a in the range 350-500K. Note that the absorption maxima attributed to H_3^+ and H_2^+ colour centres completely anneal by 500K while that of H_4^+ is still observable up to 550K what is consistent with the conclusion of somewhat higher stability of the latter made from the studies of the room-temperature post-irradiation storage effect.

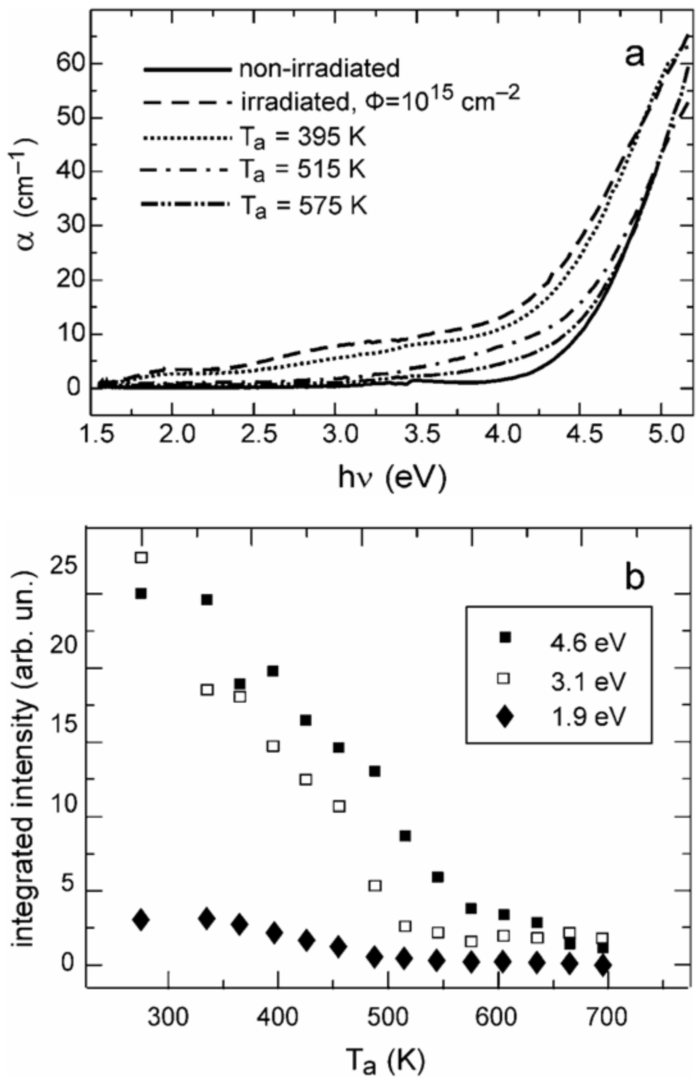

Figure 5. (a) Optical absorption spectra of non-irradiated, irradiated with $10^{15}\,cm^{-2}$ of 7-MeV electrons, and annealed at 395, 515, and 575K alkali zinc borosilicate glass; (b) dependences of the integrated intensities of the radiation-induced absorption maxima related to H_3^+(1.9 eV, ♦), H_2^+(3.1 eV, □), and H_4^+(4.6 eV, ■) on the temperature of isochronal annealing of alkali zinc borosilicate glass, irradiated with $10^{15}\,cm^{-2}$ of 7-MeV electrons.

4. Conclusion

Raman scattering and optical absorption studies of alkali zinc borosilicate glass irradiated with X-rays (up to 1100 Gy) or 7-MeV electrons (up to $10^{15} cm^{-2}$) were performed. We did not observe reliable Raman evidence for the radiation-induced changes related to the increasing number of three-member silicate rings and decreasing the average Si–O–Si bond angle reported earlier for amorphous silica [22] and other types of borosilicate glasses [28].

On the contrary, optical absorption spectra clearly show the formation of three types of colour centres (H_3^+, H_2^+, and H_4^+) in alkali zinc borosilicate glass under irradiation with X-rays or 7-MeV electrons, which is basically similar to other borosilicate glasses and typical for amorphous materials in general. The observed radiation colour centres in the alkali zinc borosilicate glass partly anneal at post-irradiation storage at room temperature and completely disappear at annealing to 550K, the H_4^+ centre being somewhat more stable.

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