On the structural-optical correlations in radiation-modified chalcogenide glasses

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Abstract. In this work, we report our recent results on the $\gamma$-irradiation-induced structural transformations in the Ge-Sb-S glasses as observed from the structural studies using high-energy synchrotron x-ray diffraction and extended x-ray absorption fine structure spectroscopy in comparison with the optical measurements using VIS/IR spectroscopy techniques. The structural-optical correlations in the radiation-induced effects are established. The structural changes upon irradiation are explained in the frames of the concept of coordination topological defects formation.

1. Introduction
Chalcogenide glasses are known as perspective optoelectronic materials with unique physical and chemical properties, induced phenomena, etc. [1]. Their attractive application in optoelectronics is tightly related to the externally induced structural defects.

The concept of coordination topological defects (CTDs) was applied to interpret both photo- and radiation-induced phenomena in amorphous chalcogenides [2]. Infrared (IR) Fast Fourier Transform spectroscopy [3] is a sensitive method for CTDs’ detection due to direct relation between intensity of vibrational mode and concentration of oscillating centres/chemical bonds. Recently, it has been shown [4] that Raman scattering in depolarized configuration is also an informative tool for CTD identification. However, application of vibrational methods is limited because they provide information on the statistics of chemical bonds only and help to construct possible topological CTD-related schemes, but no information on the local atomic structure in the vicinity of CTD can be obtained. Besides, the sensitivity of IR and Raman spectroscopy is rather low if oscillating complexes are present in the glass matrix in a small amount, while the role of these complexes in the externally induced defect formation processes could be significant.

The goal of the present work is to apply direct structural techniques such as high-energy synchrotron x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS) spectroscopy in combination...
with optical VIS/IR measurements in the visible (VIS) and infrared (IR) spectral ranges for the study of radiation-modified chalcogenide glasses on the example of Ge-Sb-S ternary system.

2. Experimental
The bulk Ge$_x$Sb$_{40-x}$S$_{60}$ samples of chalcogenide glasses with $x = 5, 25, 27$ and $35$ were prepared by a standard melt-quenching method. Radiation treatment of the samples with accumulated dose of $2.41$ and $7.72$ MGy was performed at the normal conditions of stationary radiation field, created in a closed cylindrical cavity by a number of concentrically established $^{60}$Co radioisotope capsules as shown schematically in Fig. 1. No special measures were taken to prevent uncontrolled thermal annealing of the samples, but maximum temperature in the irradiating camera did not exceed $320-330$ K during prolonged $\gamma$-irradiation (more than 30 days), providing absorbed dose power $P < 5$ Gy/s. Principal advantages of $\gamma$-irradiation as a structure modification factor for amorphous chalcogenides among other types of ionizing irradiation are discussed elsewhere [5].

![Figure 1](image)

**Figure 1.** Setup for radiation treatment of the chalcogenide glasses.

High-energy XRD experiments were performed at the synchrotron experimental station BW5 at HASYLAB, DESY in Hamburg (Germany). EXAFS measurements at Ge K-edge were carried out at the synchrotron beam line X1 (HASYLAB) in transmission mode using Si (111) double-crystal monochromator. The measuring time was $k$-weighted during collection of the signal. The experimental data were treated using VIPER program [6] and FEFF8.4 code [7]. VIS optical transmission measurements were performed with “Specord M40” spectrophotometer. Far IR optical reflectance measurements were conducted with IR spectrometer “KSDI-82”.

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3. Results and discussion

Fig. 2 shows parts of the pair distribution functions $g(r)$ in the range of 2.0-3.0 Å for Ge$_{25}$Sb$_{15}$S$_{60}$ and Ge$_{35}$Sb$_{5}$S$_{60}$ glasses in the unmodified and $\gamma$-irradiation-modified states [8]. The main peak at 2.26 Å corresponds to the Ge–S first neighbor correlations; the shoulder for Ge$_{25}$Sb$_{15}$S$_{60}$ and peak for Ge$_{35}$Sb$_{5}$S$_{60}$ at 2.65 Å corresponds to the Ge–Sb first neighbor correlations. The radiation-induced structural changes in the Ge–S correlations are more pronounced for composition with 25 at.% of Ge, while the changes in Ge–Sb correlations are better detectable for the alloy with 35 at.% of Ge.

![Diagram](image)

**Figure 2.** Parts of the pair distribution functions $g(r)$ in the range of 2.0-3.0 Å for Ge$_{25}$Sb$_{15}$S$_{60}$ (top) and Ge$_{35}$Sb$_{5}$S$_{60}$ (bottom) glasses in unmodified and $\gamma$-irradiation-modified states.

IR optical reflectance measurements [9] support the changes observed on $g(r)$’s, but only for the Ge–S correlations (Fig. 3). Indeed, only the strong peak at 370 cm$^{-1}$ corresponding to the bond stretching modes in GeS$_4$ tetrahedra (vibrations of Ge–S bonds) [10] is modified upon irradiation. The peak at 290 cm$^{-1}$ (well resolved for the glass with 25 at. % Ge) corresponds to the bond stretching modes in SbS$_3$ pyramids (vibrations of Sb–S bonds) [11]. A shoulder at 330 cm$^{-1}$ (better seen at higher Ge content) is assigned to the bond stretching modes in SbS$_3$ pyramids [12]. The Sb–S correlations are found to be stable to radiation impact. The Ge–Sb vibrations are not resolved in the IR spectral region studied probably due to a small amount of these groups in the glass matrix of Ge–Sb–S ternaries as it was predicted earlier by Feltz [13] and observed experimentally in the XRD [8] and EXAFS [14] studies.
In the frames of the concept of coordination topological defects [2], the radiation-induced defective structural transformations detected in the XRD and IR studies of the Ge$_{25}$Sb$_{15}$S$_{60}$ and Ge$_{35}$Sb$_{5}$S$_{60}$ glasses can be explained by the formation of CTDs as a result of chemical bond distortion and switching upon irradiation. The changes in Ge–S correlations can be an indicative of the distortion of Ge–S bonds with switching and creation of negatively charged under-coordinated Ge$_3^-$ and positively charged over-coordinated S$_3^+$ defects. Schematically this mechanism is illustrated in Fig. 4 (left) [8]. The radiation-induced non-defective structural transformations detected only from XRD study are connected with formation of Ge–Sb bonds with normal atomic coordination (Ge$_4^0$, Sb$_3^0$, S$_2^0$) in their vicinity with intermediate configuration accompanied by appearance of unstable Ge$_3^-$ and S$_3^+$ CTDs as shown in Fig. 4 (right) [8]. The nature of Sb atoms (property of Sb to annihilate a wrong coordination defect in its vicinity) plays a key role for occurrence of the non-defective mechanism.

**Figure 4.** Radiation-induced defective (left; formation of Ge$_3^-$ and S$_3^+$ CTDs) and non-defective (right; formation of Ge–Sb bonds with normal atomic coordination (Ge$_4^0$, Sb$_3^0$, S$_2^0$) in their vicinity with intermediate configuration accompanied by appearance of unstable Ge$_3^-$ and S$_3^+$ CTDs) structural transformations in Ge–S sub-system of Ge–Sb–S glasses.
It is understandable that the main radiation-induced structural transformations (defective and non-defective) take place in Ge–S sub-system, whereas no changes in Sb–S correlations demonstrate radiation stability of Sb–S sub-system.

The EXAFS $\chi(k)k^3$ Ge K-edge spectra and their Fourier transforms for Ge$_{27}$Sb$_{13}$S$_{60}$ glass in the unmodified and $\gamma$-radiation modified states (Fig. 5) give an evidence for the conclusion on the changes in the Ge–S sub-system. Indeed, the first nearest neighbor distance $r = 2.24$ Å detected in the first coordination shell is attributed to the Ge–S bonding [15]. Upon irradiation, the coordination number of Ge atoms $N_{\text{GeS}}$ decreases by 1.3 % and Debye-Waller factor $\sigma_{\text{GeS}}^2$ or MSRD increases by 4.4 % that support the appearance of CTDs or atomic pairs with wrong coordination and static disorder.

The radiation stability or non-sensitivity of Sb–S sub-system is evidenced also from optical transmission measurements as illustrated in Fig. 6. It is clearly seen that the red shift of optical transmittance (or radiation-induced darkening effect) is detected for the Ge-rich composition with 27 at.% Ge and no effect is observed for the Sb-rich alloy with 35 at.% Sb.

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**Figure 5.** EXAFS $\chi(k)k^3$ Ge K-edge spectra and their Fourier transforms (without phase shift correction) for Ge$_{27}$Sb$_{13}$S$_{60}$ glass in unmodified and $\gamma$-irradiation-modified states.

**Figure 6.** Optical transmission spectra for Ge$_{27}$Sb$_{13}$S$_{60}$ and Ge$_{5}$Sb$_{35}$S$_{60}$ glasses in unmodified and $\gamma$-irradiation modified states.
4. Conclusion

We report our recent results on the $\gamma$-irradiation-induced structural transformations in Ge-Sb-S glasses as observed from the structural studies using high-energy synchrotron XRD and EXAFS in comparison with the optical investigations using VIS/IR spectroscopy techniques. The structural-optical correlations in the radiation-induced effects are established. In contrast to the IR optical measurements, XRD study reveals the role of heteronuclear metal-metal chemical bonding (Ge-Sb), which cannot be negligible in the radiation-induced structural transformations in the glass system investigated. It is concluded that both defective and non-defective mechanisms of the radiation-induced structural changes might be responsible for the effects observed in the XRD and IR experiments. The radiation-induced structural changes can be plausibly explained with the coordination topological defects formation concept.

Acknowledgments

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References

[1] Shimakawa K, Kolobov A and Elliott S R 1995 Photoinduced effects and metastability in amorphous semiconductors and insulators Adv. Phys. 44 475-588
[2] Shpotyuk O I 1996 Photo- and radiation-induced coordination defects in amorphous chalcogenides Proc. SPIE 2968 246-255
[3] Golovchak R Ya and Shpotyuk O I 2005 Radiation-induced bond switching in mixed Ge-As sulphide glasses Philos. Mag. 85 2847-2860
[4] Kavetskyy T, Vakiv M and Shpotyuk O 2007 Charged defects in chalcogenide vitreous semiconductors studied with combined Raman scattering and PALS methods Radiation Measurements 42 712-714
[5] Kavetskyy T, Shpotyuk O, Kaban I and Hoyer W 2007 Atomic- and void-species nanostructures in chalcogenide glasses modified by high energy gamma-irradiation J. Optoelectron. Adv. Mater. 9 3247-3252
[6] Klementev K V 2001 Extraction of the fine structure from x-ray absorption spectra J. Phys. D: Appl. Phys. 34 209-217
[7] Ankudinov A L, Ravel B, Rehr J J and Conradson S D 1998 Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure Phys. Rev. B 58 7565-7576
[8] Kavetskyy T, Shpotyuk O, Kaban I and Hoyer W 2008 Radiation-modified structure of Ge$_{25}$Sb$_{15}$S$_{60}$ and Ge$_{35}$Sb$_{5}$S$_{60}$ glasses J. Chem. Phys. 128 244514-1-244514-8
[9] Kavetskyy T, Shpotyuk O, Balitska V, Dovbeshko G, Blonskyy I, Kaban I, Hoyer W, Ivov M and Andriesh A 2008 Vibrational and structural properties of unmodified and radiation-modified chalcogenide glasses for advanced optical applications Proc. SPIE 7142 71420B-1-71420B-8
[10] Vahalova R, Tichy L, Vlcek M and Ticha H 2000 Far infrared spectra and bonding arrangement in some Ge-Sb-S glasses Phys. Stat. Solidi A 199 199-209
[11] Ticha H, Tichy L, Rysava N and Triska A 1985 Some physical properties of the glassy (GeS$_2$)$_x$(Sb$_2$S$_3$)$_{1-x}$ system J. Non-Cryst. Solids 74 37-46
[12] El Idrissi Raghni M A, Lippens P E, Olivier-Fourcade J and Jumas J C 1995 Local structure of glasses in the As$_2$S$_3$-Sb$_2$S$_3$ system J. Non-Cryst. Solids 192-193 191-194
[13] Feltz A 1986 Amorphous and Vitreous Inorganic Solids (Moscow: Mir)
[14] Cervinka L, Smotlacha O, Bergerova J and Tichy L 1991 The structure of the glassy Ge-Sb-S system and its connection with the MRO structures of GeS$_2$ and Sb$_2$S$_3$ J. Non-Cryst. Solids 137-138 123-126
[15] Sen S, Ponader C W and Aitken B G 2001 Atomic structure and chemical order in Ge-As sulphide glasses: a combined Ge and As K-edge EXAFS study J. Non-Cryst. Solids 293-295 204-210