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COMPOSITIONAL TRENDS IN RADIATION-OPTICAL PROPERTIES OF CHALCOGENIDE GLASSES

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The influence of chemical composition on the peculiarities of radiation-induced effects in chalcogenide glasses is analysed. It is shown that the character of the compositional dependencies for the controlled parameters depends strongly on structural dimensionality of glass network. The methodological features of radiation treatment for chalcogenide glasses are described. The review of radiation-induced phenomena investigations since early 1960-s is presented.

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1. Instead of Introduction: brief historical overview of the problem

One of the most attractive features of chalcogenide vitreous semiconductors (ChVSs) is their sensitivity to the external influences. This unique ability has no exhaustive explanations up to now. But, probably, it is associated with a high steric flexibility proper to a glassy-like network with low average coordination, relatively large internal free volume and specific lp-character of electronic states localized at a valence-band top [1]. As one of the typical examples, the well-known photoinduced effects, being the ground for ChVSs-based optical memory systems, should be mentioned here [1-3].

At the same time, the radiation-induced effects (RIEs) or, in other words, the changes of ChVSs' physical properties stimulated by high-energetic (E > 1 MeV) ionizing influences such as γ-quanta of ^{60}Co radioisotope, accelerated electrons, reactor neutrons, protons, etc., were not analyzed for a long time. Indeed, the ChVSs, since the discovery of their semiconductor properties by N.A. Goryunova and B.T. Kolomiets near half a century ago [4], were expected to be usefully distinguished from their crystalline counterparts by high radiation stability. It was supposed that these glassy materials, owing to positional (topological) and compositional (chemical) disorders frozen near a glass transition temperature T_g during melt-quenching, would not create any additional structural defects at the irradiation treatment, changing sufficiently their physical properties. Furthermore, the covalent-like built-in mechanism of ChVS structural network, keeping a full atomic saturation defined by (8-N) rule [5], speaks in favor of the above conclusion. Hence, the high radiation stability, as well as the non-doping ability were expected to be the most essential features of ChVSs.

This is why the first report on radiation tests in ChVS-based ovonic threshold switches by S. R. Ovshinsky et al. [6] at the end of the 60-s, which declared their remarkable radiation hardness, was accepted as a quite generalized one, concerning a whole variety of ChVSs, in spite of some specific experimental limitations and disadvantages including:

- the compositional restriction of the investigated samples by exceptional selection of Te-containing ChVSs with a high saturation of covalent-like chemical bonding and, consequently, a small defect formation ability;

- the technological restriction of the investigated samples by cathode-sputtered films with a too small thickness of about 10^{-6} m (only the bulk ChVS samples can accumulate a large overall RIE due to deep penetration ability of ionizing radiation);
- the limitation factors of radiation treatment (in spite of huge energies E>>1 MeV of neutron flux, X-rays or γ-quanta, accompanied sometimes by a non-controlled radiation heating, the doses Φ were chosen without consideration of to the minimum level of ChVSs' radiation sensitivity).

It should be noted that the above article [6] followed another one by J.T. Edmond et al. (1968) [7]. The latter concerned the influence of reactor irradiation, created by γ-ray flux of 5×10^{13} MeV$\cdot$cm$^{-2}\cdot$s^{-1}, as well as fast and thermal neutron fluxes of 3×10^{13} cm$^{-2}\cdot$s^{-1}, on electrical properties of liquid semiconductors in the mixed As-S-Se-Te-Ge system. No changes were detected even at the fast neutrons doses up to 1.8×10^{20} cm^{-2}. But it remained unclear whether this irradiation did not produce significant damage, or that high-temperature thermal heating (at more than 470 K) was sufficient to anneal any damage.

All these circumstances strongly restricted the observation possibilities for RIEs in ChVSs. Nevertheless, the general conclusion on their unique radiation stability was repeated often and often with enviable constancy up to that moment when the above problem on the experimental RIEs study was considered at the begining of the 1980-s by some scientific-research centers in the former Soviet Union.

It must be mentioned that the first announcements of I. A. Domoryad [8] (Institute of Nuclear Physics, Tashkent, Uzbekistan) on the changes of ChVSs' mechanical properties, caused by ^{60}Co γ-irradiation with average energy of 1.25 MeV, appeared in the early 60-s. Contrary to the above discussed radiation tests of S.R. Ovshinsky under ChVS-based Ovonic devices [6], the bulk samples of vitreous v-Se, v-As_2S_3, v-As_2Se_3 and some of their simplest quasi-binary compositions were chosen as investigated objects. As a result, it was established that the experimentally detectable RIEs in these glasses were observed at the absorbed doses of 10^5-10^6 Gy. These changes were stable at room temperature over a long period after irradiation (4-7 months), but they fully or partly restored at the annealing to respectively low temperatures near 20-30 K below glass transition point T_g. These RIEs were reversible in multiple cycles of γ-irradiation and thermal annealing with slight damping component. Then (in the 70-s), the similar radiation-induced changes were observed in photoluminescence [9], photoconduction [10] and dissolution [11] of the above ChVSs. However, any exact experimental results on microstructural origin of these phenomena were not obtained. So these investigations were rather of a semi-empirical character.

The greatest success in this field was achieved by the group of Sh. Sh. Sarsembinov (Kazakh State University, Alma-Ata, Kazakhstan) implied in the study of the influence of accelerated electrons on optical and electrical properties of As- and Ge-based ChVSs. It was shown, particularly, that electron irradiation of these samples with 2 MeV energy, 10^{17}-10^{18} cm^{-2} fluences and 10^{13} cm$^{-1}\cdot$s^{-1} flux power led to reduction of their optical transmission coefficient in the whole spectral region and long-wave shift of fundamental optical absorption edge, accompanied by characteristic slope decrease [12-13]. These changes were reversible in multiple cycles of irradiation and annealing. The other ChVS's properties such as microhardness, glass transition temperature T_g, dissolution rate, photoluminescence and photoconductivity were also sensitive to electron irradiation. Changes in electrophysical properties were attributed to electron-induced diffusion of metals, deposited at the surface of irradiated samples for electrical contacts. It must be emphasized that this group was the first to put forward one of the most practically important ideas on the electron-induced modification of ChVSs [14] and to study the physical nature of the observed RIEs, using methods as IR spectroscopy, positron annihilation technique or ESR [15]. But surface damages created with high-energetic accelerated electrons did not allow to investigate the microstructural origin of these effects directly at short- and medium-range ordering levels.

Some attempts to study RIEs at the extra-high doses of γ- and reactor neutron irradiation were made by L. F. Konorova et al. from A. F. Ioffe Physical-Technical Institute (St.-Petersburg, formerly - Leningrad, Russia) [16,17]. However, despite of a great number of experimental measurements, their scientific significance remained relatively poor and speculative because of some essential complications in radiation treatment conditions, such as uncontrolled thermal misbalance during irradiation resulting in specific structural transformations (crystallization, segregation and phase separation). Apart from the investigated samples (v-As_2S_3, v-AsSe and ternary v-AsGeSe or v-AsGe$_{0.2}$Se, additionally doped with Cu and Pb) were chosen too arbitraryly without tight connection to their structural-chemical pre-history and technological quality. Sometimes, one could doubt the accuracy of the presented results, as optical transmission spectra of non-irradiated samples in the vicinity of the fundamental absorption edge contained the specific stretched bands, proper usually to light-scattering processes caused by technological macro-inhomogeneities, voids, cracks and impurities [16]. The only experimentally proved conclusion of this group was the confirmation of chemical interaction between intrinsic structural fragments of ChVSs and absorbed impurities, stimulated by prolonged irradiation.

The similar conclusion on radiation-induced impurity processes has been put forward recently by scientists from National Centre for Radiation Research and Technology (Cairo, Egypt). It was shown, in part, that additional weak absorption bands associated with oxygen-based impurity complexes appeared in the powder of v-Ge$_{20}$As$_{30}$Se$_{50-x}$Te$_x$ (x = 0-40), irradiated by ^{60}Co γ-quanta with Φ = 0.25 MGy dose [18]. In contrast to the previous research, the small γ-irradiation dose (no more than 0.34 MGy) did not allow to observe the stronger changes. However, a number of results concerning temperature dependence of steady-state conductivity in v-As$_4$Se$_2$Te$_4$ γ-irradiated near T_g or γ-induced thermoluminescence in v-Si$_x$Te$_{60-x}$As$_{30}$Ge$_{10}$ [19] seem to be quite interesting. The authors of these publications maintain that microstructural origin of the observed RIEs is connected with specific defect centers (broken or dangling bonds, vacancies, non-bridging atoms, chain ends, etc.), created owing to atomic displacements at a high temperature by secondary electrons caused by γ-quanta [19,20].

Other important research as in this field includes effect of γ-induced electrical conductivity in v-As-S(Se)-Te studied by T. Minami et al. (1972) [21], X-ray diffraction study of γ-induced structural transformations in v-As$_2$S$_3$ and v-As$_2$Se$_3$ by Yu.G. Poltavtsev et al. (1973) [22], first observation of electron-induced long-wave shift of fundamental optical absorption edge in v-As$_2$S$_3$ and v-As$_2$Se$_3$ by A. V. Moskalionov (1976) [23], effect of thermally-stimulated conductivity in γ-irradiated v-AsS$_{3.5}$Te$_{2.0}$ investigated by T. Minami et al. (1977) [24], neutron-induced effects in v-GeS$_x$ and v-As$_2$S$_3$ observed by P. Macko et al. (1977) [25,26]; ESR study of paramagnetic counterparts of radiation-induced defects in ChVS by P.C. Taylor et al. (1978) [27], N. Kumagai et al. (1984) [28], I.V. Chepeleva (1987) [29] and E.A. Zhilinskaya et al. (1990) [30], γ-induced structural relaxation in v-Se studied by R. Calemczuk et al. (1981) [31], radiation-induced effects in ChVS-based optical fibers observed by A.M. Andriesh et al. (1984) [32] and A. Ya. Vinokurov at al. (1988) [33], electron-induced crystallization in the ternary Ge-Sb-Se glasses investigated by S. I. Kalinich et al. (1986) [34].

In early 80-s, the complex and comprehensive experimental investigations of RIEs in As$_2$S$_3$-based ChVSs, caused by ^{60}Co γ-irradiation, has been started in the Institute of Materials of Scientific-Research Company “Carat” (Lviv, Ukraine). Apart from a great number of experimental measurements of RIEs (their compositional, dose, temperature and spectral dependences) [35-42], the physical nature of the observed radiation-structural transformations was treated using IR Fourier spectroscopy [43-45] and EPR [46] data at the example of v-As$_2$S$_3$ - the typical glass-forming model compound with high radiation sensitivity and well-studied structural parameters. The observed RIEs were explained by two interconnected processes. The first one was the process of coordination topological defects (CTDs) formation associated with covalent chemical bonds switching [47,48], and the other one, the process of radiation-induced chemical interaction between intrinsic ChVS structural fragments and absorbed impurities [49]. Having developed the model of radiation-induced CTDs [47,48], the theoretical principles of topological-mathematical simulation for destruction-polymerization transformations in the complex ChVS-based systems were introduced for the first time [50]. As some of the main important practical results of these investigations, the previously stated idea on radiation modification took on a new sense [33,50], as well as the possibilities for ChVSs using in industrial dosimetry were given in scientific ground [51]. In late 90-s, this group was close to the resolution the actual problem on compositional description of RIEs in physically different multicomponent ChVS systems [40-42,52].

The most illustrative and usable from the point of practical application are radiation-induced optical effects (RIOEs). Let’s consider the compositional trends of RIOEs in ChVSs at the example of one of the typical topologically disordered model objects such as v-As_2S_3 and As_2S_3-based ChVSs.

2. Methodological features for RIOEs observation

We usually used ChVS samples of various chemical compositions prepared from high-purity elemental constituents by direct synthesis in evacuated quartz ampoules. The standard rocking furnace technique followed by air quenching was applied [5]. After synthesis all ingots were air-annealed at a temperature of 420 to 430 K during 3 to 5 h and cut into plates about 1 to 2 mm in thickness. The sample surfaces were polished with 1 μm alumina. Samples for acoustooptical measurements were cut into rectangular 10 × 10 × 15 mm^3 parallelepipeds. X-ray diffraction measurements confirmed that phase separation and crystallization did not occur in each sample.

The optical absorption spectra were obtained with “Specord M-40” spectrophotometer in the wavelength region from 200 to 900 nm. The IR absorption measurements were carried out using “Specord 75 IR” spectrophotometer (2.5 to 25 μm wavelengths).

The radiation-structural transformations were studied using “differential” Fourier-spectroscopy technique in a long-wave IR region (400-100 cm^{-1}). The observed radiation-structural transformations were associated with reflectivity changes ΔR in the main vibrational bands of the investigated ChVS samples. The positive values of $\Delta R>0$ correspond to complexes appearing under irradiation, and negative ones of $\Delta R<0$, on the contrary, correspond to complexes disappearing under irradiation. The advantage of this experimental technique consists in the fact that only a small part of the vibrational spectrum induced by γ-irradiation is investigated, but not the whole spectrum. Multiple accumulation of this additional reflectivity signal, when fast Fourier transformation is used, allows us to achieve the sensitivity at the breaking bonds level of ~1 %.

The RIOEs can be produced in the bulk ChVS samples by high-energetic (E>1 MeV) ionizing irradiation of different kinds, but γ-quanta irradiation of ^{60}Co radioisotope, the typical example of high-energetic photon flux treatment, has a number of significant advantages over others. These advantages are as follows [53]:

- the average energy of ^{60}Co γ-quanta (1.25 MeV) is greater than the dual rest energies of electrons (1.02 MeV), which determines the high-energetic character of the observed RIEs;
- the γ-irradiation is characterized by a high penetration ability and, consequently, a high uniformity of the produced structural changes throughout the sample thickness;
- the γ-irradiation does not cause the direct atomic displacements resulting in surface macro-damages, craters or cracks, proper to high-energetic corpuscular radiation (accelerated electrons, protons, neutrons, etc.);
- the nuclear transmutations, induced by reactor neutrons and essentially limiting the experimental possibilities for RIEs observation, do not take place during γ-irradiation.

So, we shall pay attention in the below consideration only to the RIEs stimulated by ^{60}Co γ-irradiation. This radiation treatment is performed in the normal conditions of stationary radiation field, created in a closed cylindrical cavity by concentrically established ^{60}Co (E = 1.25 MeV) radioisotope capsules. The accumulated doses of $\Phi = 0.1\text{-}10.0$ MGy were chosen with due account of the previous results of I.A. Domoryad’s investigations [8-11]. The absorbed dose power P was chosen from a few up to 25 Gy/s. This *P* value determined the maximum temperature of accompanying thermal heating in irradiating chamber. This temperature did not exceed 310-320 K during prolonged γ-irradiation (more than 10 days), provided the dose power P<5-10 Gy/s. However, it reached approximately even 380-390 K at the dose power of ~25 Gy/s. The process of γ-irradiation is illustrated in Fig. 1.

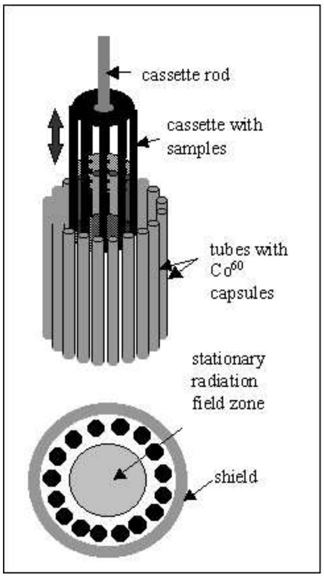

Fig. 1. The γ-irradiation chamber.

3. Results and discussion

As it was shown repeatedly the considerable changes in optical properties of v-As_2S_3 appear after γ-irradiation at the absorbed doses of Φ>0.5 MGy [12,13,35-39].

The γ-induced long-wave shift of the optical transmission coefficient curve $\tau(h\nu)$, or the so-called radiation-induced darkening effect, was observed in the fundamental optical absorption edge region of As_2S_3-based ChVSs (Fig. 2). This shift, as a rule, was close to parallel one for the most ChVS compositions. However, in the case of some glasses with increased spatial dimensionality, characterized by a high average coordination number Z>2.7 (the number of covalent chemical bonds per one atom of glass formula unit), the slope of the $\tau(h\nu)$ curves additionally decreased after radiation treatment [40-42]. Apart from this shift, some changes in the optical transmittance (in the long-wave spectral range just behind optical absorption edge) are often observed in γ-irradiated ChVS samples [12,13,16,17,40-42]. The latter effect can be positive (transmittance increase) or negative (transmittance decrease) depending on glass composition and its thermal pre-history. The spectral dependences of optical transmission differences $\Delta\tau$ in the γ-irradiated v-As_2S_3 samples are presented in Fig. 3.

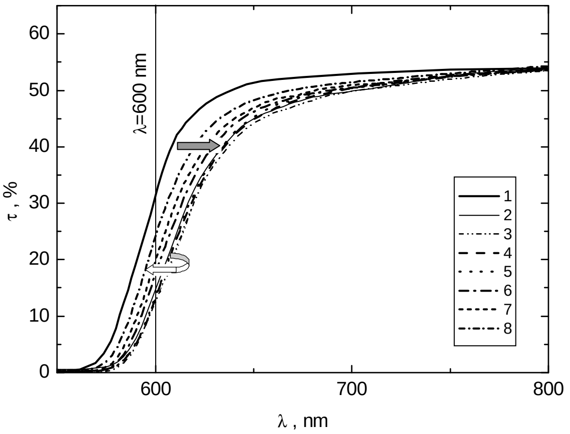

Fig. 2. Optical transmission spectra of the v-As_2S_3 (d=1 mm) before (curve 1) and after (curve 2) γ-irradiation (Φ=10.0 MGy, P=25 Gy/s), as well as with further thermal annealing at 330 (curve 3), 370 (curve 4), 380 (curve 5), 395 (curve 6), 420 (curve 7) and 440 K (curve 8).

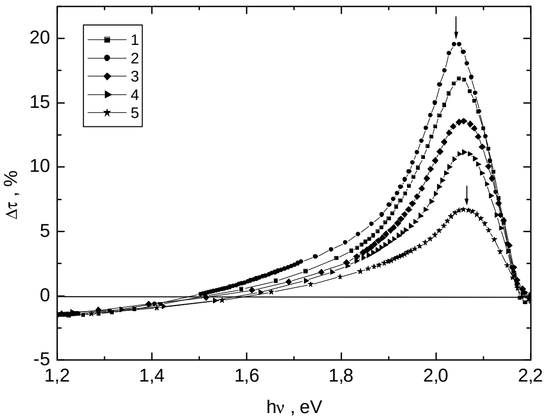

Fig. 3. Spectral dependences of optical transmission differences Δτ in the γ-irradiated (Φ=10.0 MGy, P=25 Gy/s) v-As_2S_3 samples (curve 1) and with further thermal annealing at 330 (curve 2), 370 (curve 3), 380 (curve 4), 395 (curve 5), 420 (curve 6) and 440 K (curve 7).

Despite of a great number of experimental research fulfilled, the compositional dependence of RIOEs has been remaining further as the most controversial point in this field. The matter is that these effects, being well pronounced, as a rule, in v-As_2S_3 and some other simplest As_2S_3-based ChVS compositions, are strongly determined by structural-chemical peculiarities of a glassy-like network, likely to known photoinduced optical changes in thin ChVS films [1-3]. Having determined exactly these peculiarities, the quite correct comparable analysis of RIOEs can be derived for different ChVS systems. At the same time, we have to admit that a number of faults in the selection of the investigated samples compositions were often permitted in the previous experimental research [7,16-18].

Let’s consider this problem more precisely for the following sequence of compositionally different ChVS species:

- quasibinary stoichiometric sulphide systems;
- non-stoichiometric sulphide systems with wide deviation of average coordination number Z (calculated as a number of covalent chemical bonds per one atom of glass formula unit);
- v-As_2Se_3 and quasibinary As_2Se_3-based ChVSs.

Now, the RIEs are relatively well-studied in stoichiometric ChVS systems, formed by two (or more) glass-forming units of the simplest binary sulphide-based compounds. Such systems have been studied yet since the first experiments of I.A. Domoryad et al. [54]. The main conclusion in respect to these objects is that the quantitative features of RIEs change smoothly with their chemical composition. It can be easily proved using the spectral dependences of γ-induced (Φ = 1.66 MGy, P = ~1 Gy/s) optical transmission decrease Δτ(hν) in the fundamental absorption edge region for the bulk $(As_2S_3)_x(Sb_2S_3)_{1-x}$ glasses [55] (Fig. 4). It is obvious that $\Delta\tau_{max}$ values (or, in other words, the top of bell-shaped Δτ(hν) spectral dependence) measured 1 day just after γ-irradiation decay slowly with Sb_2S_3 content from 6.8 % for v-As_2S_3 to 1.1 % for v-$(As_2S_3)_{0.7}(Sb_2S_3)_{0.3}$. The low-energetic “tail” of this curve approaches to 0 % for v-As_2S_3 and then changes its sign tending to –2 % in the glasses with maximal Sb_2S_3 concentration (x = 0.7). The latter feature has an irreversible character. It is caused by a mixed radiation-thermal influence, resulting in some atomic displacements towards more homogeneous state without crystallization (disappearing of technological imperfections frozen at melt quenching, in part).

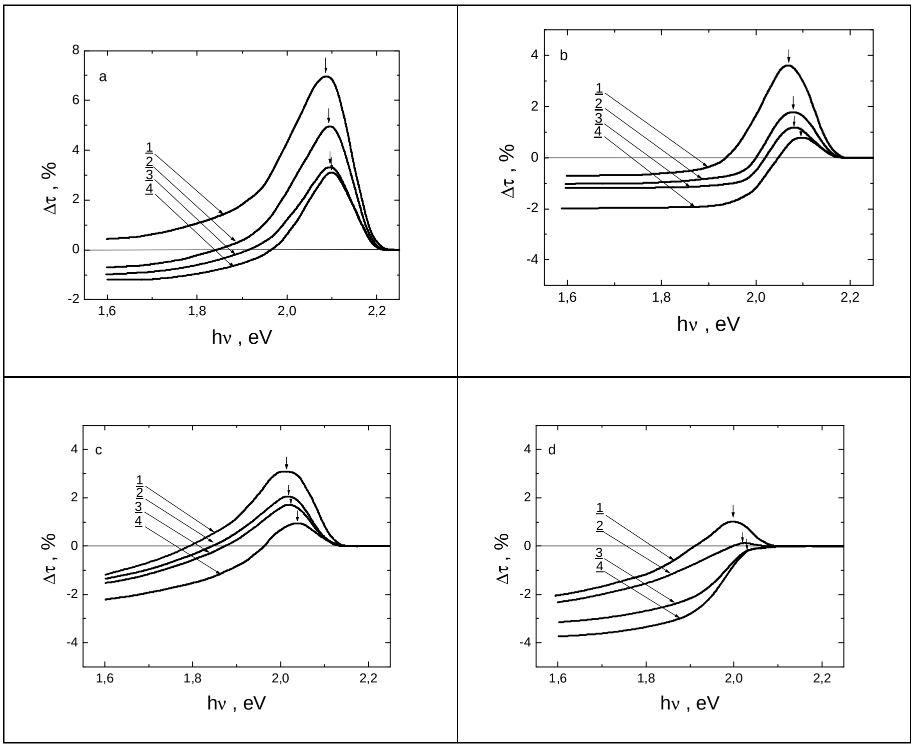

Fig. 4. Spectral dependences of optical transmission differences Δτ in the v-$(As_2S_3)_x(Sb_2S_3)_{1-x}$ glasses (d=0.7 mm) measured 1 (curve 1), 3 (curve 2), 5 (curve 3) and 40 (curve 4) days after γ-irradiation (Φ=1.66 MGy, P~1 Gy/s): a – x=1.0; b – x=0.9; c – x=0.8; d – x=0.7.

The similar γ-induced changes are observed in another quasibinary ChVS system formed by structurally different glass-forming units – layer-like $AsS_{3/2}$ pyramids and cross-linked $GeS_{4/2}$ tetrahedra (Fig. 5a, Table 1) [41]. The radiation-optical effects increase smoothly with $GeS_{4/2}$ concentration in these ChVSs, the most considerable changes occurring only in the fundamental optical absorption edge region similar to v-As_2S_3.

The ChVS samples of non-stoichiometric sulphide systems also typically demonstrate a well-pronounced γ-induced long-wave shift of their fundamental optical absorption edge. Let's consider the quantitative features of this shift at the example of $(As_2S_3)_x(Ge_2S_3)_{1-x}$ ChVSs characterized by a wide range of average coordination number Z from Z = 2.4 (v-As_2S_3, x = 1.0) to Z = 2.8 (v-Ge_2S_3, x = 0) [40,41]. The ChVS compositions with Z<2.67 can be conditionally accepted as those having 2D-dimensional layer-like structure, while the ChVS compositions with Z>2.67 are considered as 3D-dimensional cross-linked glasses.

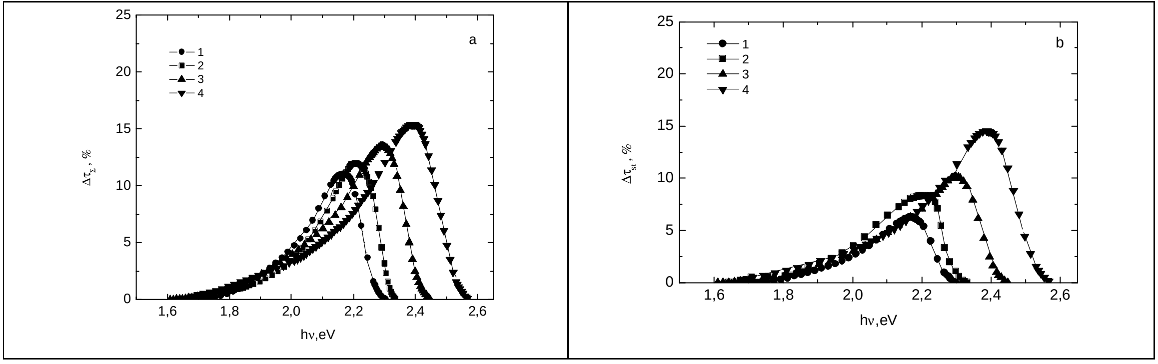

Fig. 5. Spectral dependences of optical transmission differences Δτ in the v-$(As_2S_3)_x(GeS_2)_{1-x}$ glasses (d=1 mm) measured 1 day (a) and 2 months (b) after γ-irradiation (Φ=2.2 MGy, P~1 Gy/s): curve 1 – x=0.2; curve 2 – x=0.4; curve 3 – x=0.6; curve 4 – x=0.8.

Table 1. Quantitative characteristics of γ-induced darkening effects (Φ=2.2 MGy, P~1 Gy/s) for quasibinary $(As_2S_3)_x(GeS_2)_{1-x}$ ChVSs.

Glass composition		The total RIE		The static RIE		The dynamic RIE
x	Z	$(h\nu_{max})_\Sigma$, eV	$(\Delta\tau_{max})_\Sigma$, a.u.	$(h\nu_{max})_{st}$, eV	$(\Delta\tau_{max})_{st}$ a.u.	$(\Delta\tau_{max})_{dyn}$ a.u.
0.8	2.43	2.16	0.110	2.18	0.065	0.045
0.6	2.48	2.21	0.120	2.22	0.080	0.040
0.4	2.52	2.30	0.135	2.31	0.100	0.035
0.2	2.59	2.39	0.155	2.40	0.145	0.010

It is shown that the value and character of the above long-wave shift of the fundamental optical absorption edge of these glasses depend strongly on their structural dimensionality and γ-irradiation parameters. Thus, for non-stoichiometric 2D-like ChVS samples ($Z < 2.67$), the parallel shift of optical transmission $\tau(h\nu)$ edge is observed. However, in the case of 3D-like glasses ($Z > 2.67$), this edge shifts with an additional decrease in a slope.

The above peculiarity is clearly expressed in recalculated $\Delta\tau(h\nu)$ dependences (Fig. 6). The more extended low-energetic tail is observed for 3D-like ChVS samples. Similar behaviour is revealed also in γ-induced relative changes of optical absorption $(\Delta\alpha/\alpha_o)_{max}$.

In general, the $\Delta\tau_{max}$ or $(\Delta\alpha/\alpha_o)_{max}$ values achieve a local maximum with glass composition near the “magic” point of Z = 2.67. However, at the prolonged γ-irradiation accompanied with more essential uncontrolled thermal annealing of the investigated glasses, this effect can be changed by the opposite one. This feature is illustrated by the typical concentration dependences of $(\Delta\alpha/\alpha_o)_{max}$ parameter of these glasses for 1.0 and 4.4 MGy doses (Fig. 7). At the small dose (1.0 MGy) accompanied with non-essential thermal heating ($T<310$ K), the sharply expressed maximum is visible in the above concentration dependence (Fig. 7a, curve 1). At the higher doses (4.4 MGy), the temperature in the irradiating chamber rises more essentially and, as a result, the slight minimum is revealed in the above concentration dependence (Fig. 7b, curve 1).

So the ChVS samples with Z = 2.67 are the most sensitive to the influence of both γ-irradiation and accompanying thermal annealing.

There has been no exact explanation for the above concentration feature in ChVS up to now. The origin of this «magic» point at Z = 2.67 is sometimes connected with topological phase transition from 2D to 3D glassy-like network [56] as in the case of floppy-rigid on-set at Z = 2.4 [57,58]. Another microstructural explanation is related to the specific redistribution of covalent chemical bonds [59] or possible phase segregation [60]. Whatever the case, the described RIOEs in non-stoichiometric ChVS systems show the evident sharp anomalies in the vicinity of this point (Z = 2.67) similar to the analogous concentration behaviour of other physical-chemical parameters [61-64]. However, taking into account the fact that atomic compactness drops to the minimum in this range of average coordination numbers Z [5,64], we suppose the origin of this anomaly is linked with a high stability of created radiation defects owing to effective blocking of backward transformations in conditions of a more sparse atomic network.

As to v-As_2Se_3 and quasibinary As_2Se_3-based ChVSs, their optical properties are more sensitive to thermal conditions of γ-irradiation and absorbed dose Φ [65,66]. The γ-induced darkening effect is observed only at relatively low doses of $\Phi<1.5\text{-}2.0$ MGy, the maximal magnitude of this effect being nearly four times smaller as in v-As_2S_3. The greatest changes in v-As_2Se_3 optical properties are observed at $\Phi \approx 0.5\text{-}0.7$ MGy. At more prolonged γ-irradiation ($\Phi>3\text{-}5$ MGy), this γ-induced darkening effect decays fully and transfers subsequently into the γ-induced bleaching one. The above transition takes place owing to uncontrolled thermal annealing of the irradiated samples. The critical absorbed dose of γ-irradiation for this transition can be replaced towards higher Φ values by keeping the relatively low temperature in γ-source chamber or by accumulating the total absorbed dose in small separate cycles with prolonged pauses between them. It should be noted that the described short-wave shift of fundamental optical absorption edge in v-As_2Se_3 at high γ-irradiation doses is in a good agreement with the same behavior of spectral position of radiative recombination maximum observed in this glass after γ-irradiation previously [9].

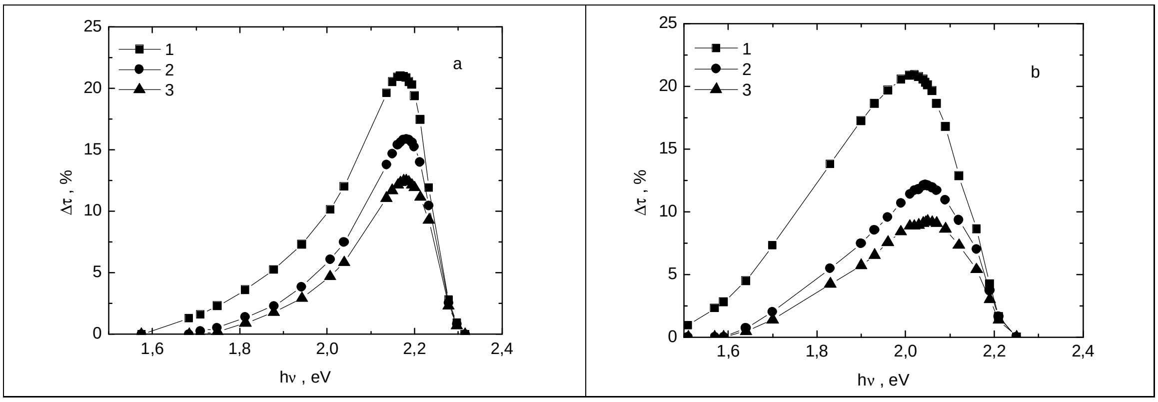

Fig. 6. Spectral dependences of optical transmission differences Δτ in the v-$(As_2S_3)_x(Ge_2S_3)_{1-x}$ glasses (d=2 mm) with typical 2D (x=0.6; a) and 3D (x=0.1; b) structure measured 1 day (1), 1 month (2) and 2 months (3) after γ-irradiation (Φ=4.4 MGy, P~1 Gy/s).

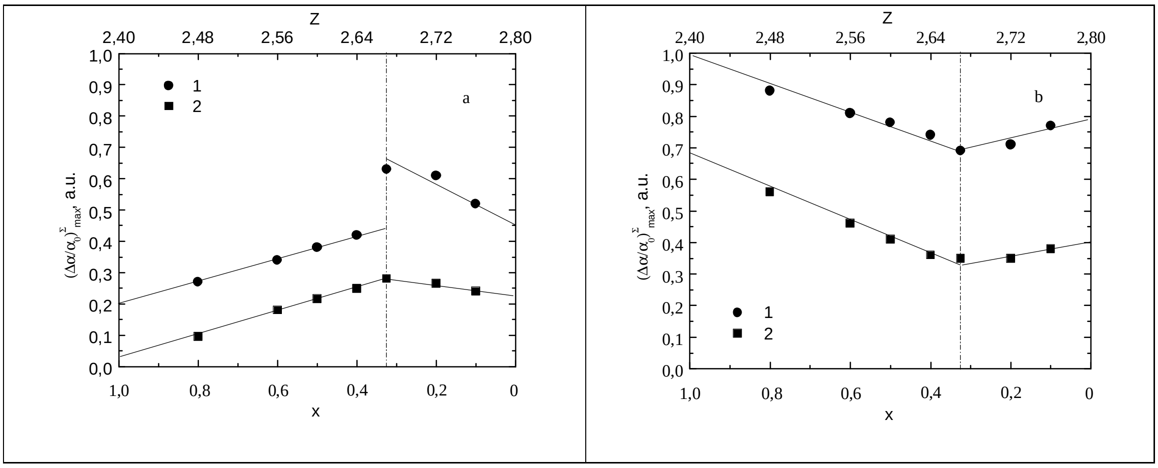

Fig. 7. Compositional dependences of the maximum value of relative absorption coefficient increase $(\Delta\alpha/\alpha)_{max}$ in the v-$(As_2S_3)_x(Ge_2S_3)_{1-x}$ glasses for total (1) and static (2) RIEs at absorbed dose Φ of 1.0 (a) and 4.4 MGy (b).

The long-wave shift of the fundamental optical absorption edge of v-As_2Se_3 after γ-irradiation with Φ = 1.0 MGy dose is accompanied by relative slope decrease of Δσ/σ = 15 %. This value falls down to only 4.6 % after γ-irradiation with Φ = 5.0 MGy dose, which causes the opposite γ-induced bleaching effect. The subsequent thermal annealing at T = 423 K (Δt= 2-3 h) enhances the σ value additionally by 2.5 %. However, after these treatments, the spectral position of the fundamental optical absorption edge of v-As_2Se_3 becomes non-sensitive to the next cycles of γ-irradiation and thermal annealing.

These anomalies reveal themselves yet more distinguishably in ChVS samples of quasibinary $(As_2Se_3)_x(Sb_2Se_3)_{1-x}$ system characterized by smaller T_g values [66].

It has been pointed out in one of the first papers of I. A. Domoryad [67] that the observed changes in ChVSs' mechanical properties caused by ^{60}Co γ-quanta are fully unchangeable for a long time after radiation treatment of up to 5-7 months, provided the irradiated samples are kept at the normal temperature conditions (T ≈ 290-310 K). In other words, any post-irradiation effects have been accounted as negligible ones in γ-irradiated ChVSs at the room temperature independently on glass composition. Thermal annealing of γ-irradiated samples at the temperatures of 20-30 K below glass transition point T_g has been accepted as the only way to restore partially their initial physical properties. However, the accuracy of this statement has not been experimentally verified since the end of the 60-s.

This is why the first announcement on self-restoration effect for γ-induced changes in optical properties of the ternary As-Ge-S ChVSs at the end of the 90-s [68] has been accepted as a real surprise. It has been shown, in part, that the experimentally studied RIEs observed just after γ-irradiation are unstable in time at room temperature, gradually restoring to some residual value (associated with the static RIE component) during a certain period of up to 2-3 months [40-42,68]. Hence, the total RIE in as-irradiated ChVS samples consists of two components – the static one, remaining constant for a long time after γ-irradiation, and the dynamic one, gradually decaying with time after γ-irradiation.

The "dynamic component" definition is not appropriate in respect to the observed post-irradiation instability. Sometimes it concerns the RIEs measured directly in the stationary radiation field, such as γ-induced electrical conductivity [21] or structural relaxation [31]. But we shall use this definition in the above context, taking into account only its close relation to the decaying behavior of the investigated RIEs.

The post-irradiation instability effects are sharply determined in γ-induced changes of ChVSs' optical properties shown in Fig. 11 a-d (curves 1-3), Fig. 12 a-b (curves 1-4) and Fig. 13 a-b [40-42, 68]. It should be emphasized that $\Delta\tau(h\nu)$ dependences obtained 6 months after irradiation are very similar to those denoted by curve 3 in Fig. 4, curves 1-4 in Fig. 5b and curve 3 in Fig. 6. The following conclusions can be drawn from a detailed inspection of these figures:

- the effect of post-irradiation instability reveals itself most sharply in the fundamental optical absorption edge region of the investigated ChVSs, but sometimes, as in the case of quasibinary As_2S_3-Sb_2S_3 glasses (Fig. 4), it stretches in the low-energetic spectral region of optical transmittance;
- the observed self-restoration effect (or the dynamic RIE component) is described by time-dependent decrease of $\Delta\tau_{max}$ value with simultaneous high-energetic shift of its spectral position $h\nu_{max}$;
- this effect embraces only part of the total RIE;
- the tendency towards saturation of this effect with time is present;
- the $\Delta\tau(h\nu)$ curves take more symmetric shape after restoration (the greatest changes take place in the low-energetic spectral region).

Therefore, in terms of the spectral dependence of γ-induced optical transmission decrease in the fundamental optical absorption edge region $\Delta\tau(h\nu)$, the observed total RIEs in ChVSs $\Delta\tau_\Sigma(h\nu)$ can be decomposed in two components owing to the following expression:

$$\Delta\tau_\Sigma(h\nu) = \Delta\tau_{dyn}(h\nu) + \Delta\tau_{st}(h\nu), \qquad (1)$$

where the subscript denotes total (Σ), static (st) and dynamic (dyn) RIEs, respectively.

The quantitative characteristics of γ-induced darkening (Φ = 2.2 MGy, P~1 Gy/s) in quasibinary As_2S_3-GeS_2 ChVSs (see Fig. 5) in dependence on their chemical composition, determined by x parameter and average coordination number Z, are presented in Table 1. It is obvious that amplitude of total $(\Delta\tau_{max})_\Sigma$ and static $(\Delta\tau_{max})_{st}$ RIEs enhances with GeS_2 content, while amplitude of dynamic RIE $(\Delta\tau_{max})_{dyn}$ decreases. These features correspond entirely to well-known compositional dependence of free volume in this ChVS system [5]. The larger the free volume fraction (which is proper to GeS_2-enriched ChVS compositions because of high concentration of native topologically inconsistent structural units [69,70]), the more sharply defined the total and static RIEs. The opposite statement for dynamic RIEs in these glasses is obvious, too. The more compact a glassy-like network is (which is proper to As_2S_3-enriched ChVSs), the greater post-irradiation relaxation and, as a consequence, the amplitude of dynamic RIEs. The similar compositional dependence was observed in the changes of v-As_2S_3-GeS_2 optical properties caused by hydrostatic pressure [71].

4. Conclusions

The analysis of radiation-induced effects in chalcogenide glasses shows that the magnitude and compositional behaviour of controlled changes depends on the nature of constituent atoms, structural dimensionality, stoichiometry of the glass system, concentration of main chemical bonds and free volume parameters.

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