
On the mechanism of radiation-induced optical effects in vitreous $\text{As}_2\text{S}_3\text{-GeS}_2$

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Abstract

A coordination defects formation model based on the concept of covalent chemical bond switching was developed for the microstructural explanation of γ -induced optical effects in $\text{As}_2\text{S}_3\text{-GeS}_2$ chalcogenide glasses. The whole variety of possible destruction-polymerization transformations was considered separately for the “pure” vitreous $v\text{-As}_2\text{S}_3$ and $v\text{-GeS}_2$, as well as for the mixed $v\text{-As}_2\text{S}_3\text{-GeS}_2$ compositions. The topological schemes of the coordination defect formation were proposed, taking into account results obtained by the IR Fourier spectroscopy method of additional reflectivity in 400-200 cm^{-1} range.

Key words: optical transmittance, chalcogenide vitreous semiconductors, gamma-irradiation

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1. Introduction

Chalcogenide vitreous compounds (ChVC) have been intensely studied in the last years from both theoretical and practical viewpoints, especially owing to their high sensitivity to external influences [1-3]. This remarkable feature is caused mainly by structural flexibility proper to a low-coordinated glass-forming skeleton with a high content of 2-fold coordinated chalcogen atoms and a specific lp -character of electronic states, localized at the top of the valence band [4]. Finally, these features lead to the well-known photo- and radiation-induced effects [1-11].

The photoinduced effects produced by absorbed light exposure are typical, as a rule, for thin films of ChVC obtained by vacuum

deposition [1,2,7]. However, in the bulk glasses prepared by the melt-quenching technique these phenomena are manifested slightly [4,5], while those induced by high-energetic ($E > 1$ MeV) ionizing irradiation (γ -quanta of various radioactive nuclei, reactor neutrons, accelerated electrons, etc.) reveal themselves to a greater extent [3,6,8]. Moreover, the amplitude of radiation-induced changes in ChVC properties sufficiently enhances with the sample thickness owing to a high penetrating ability of ionizing radiation [3,6,9]. This makes the experimental study of radiation-induced effects especially attractive and successful when the microstructural nature of these phenomena is investigated. In consequence, the coordination defect (CD) formation model based on the

concept of covalent chemical bond switching was developed to explain the mechanism of these effects in vitreous $v\text{-As}_2\text{S}_3$ – a typical glass-forming compound with a relatively high radiation sensitivity [9,10]. Unfortunately, such a model has not been applied previously neither for $v\text{-GeS}_2$, nor for more structurally complicated cross-linked ChVC systems which contain two-, three- and four-fold coordinated atoms simultaneously.

In the present paper, we shall try to develop for the first time the CD model for radiation-structural transformations in the ternary As-Ge-S ChVC system, restricted only by simple binary As_2S_3 and GeS_2 components.

2. Experimental procedure

Eight vitreous samples of the pseudobinary $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ system with a parameter x variation from 0.2 to 0.8 were selected for our investigations. These ChVC samples were prepared by a melt-quenching method [11] using a mixture of high purity (99,9999%) Ge, As and S, sealed in quartz ampoules (10^{-3} Pa) and heated gradually up to 1200 K. The furnace was rocked for 24 hours to obtain the most homogeneous melt. Then the obtained ingots were air-quenched at an ambient temperature. All ampoules were annealed additionally at temperatures of 20-30 K below softening point T_g to remove the appeared thermo-mechanical strains. The amorphous state of the glasses was routinely controlled by a visible character conch-like fracture, data of X-ray diffraction analysis and transmission IR microscopy. At the final technological stage, all ingots were sliced into 1 mm parallel-sided plates and polished carefully for precise optical measurements.

The ChVC samples were irradiated by γ -quanta at normal conditions of a stationary radiation field, created in a closed cylindrical cavity owing to a number of concentrically established ^{60}Co ($E=1.25$ MeV) sources. No special procedures were used to prevent the uncontrolled thermal annealing of the irradiated

samples, but the maximum temperature in the irradiating chamber at the dose power of ~ 1 Gy/s did not exceed 320-330 K during the whole period of irradiation. The accumulated dose of $2.2 \cdot 10^6$ Gy was chosen, taking into account the previous radiation experiments on $v\text{-As}_2\text{S}_3$ [3,9,10].

The IR Fourier reflection spectra were vacuum-measured before and three months after γ -irradiation in $400\text{-}200\text{ cm}^{-1}$ region with a LAFS-1000 spectrometer. It has been established that the retention interval of 2-3 months at the ambient conditions allows us to obtain a fully stable post-irradiation effect in the investigated As-Ge-S ChVC [11].

The differences between IR reflection spectra before and after irradiation (so-called additional γ -induced reflectivity $\Delta r(v)$ signal) were used in order to identify the chemical bond-switching reactions associated with the observed radiation-induced CD formation processes. The positive values of $\Delta r > 0$ were attributed to structural complexes (covalent chemical bonds) appearing under irradiation and those of $\Delta r < 0$, the negative ones, were associated with disappearing structural units [10].

3. Results and discussion

The influence of γ -irradiation on the optical properties of the ternary As-Ge-S ChVC was firstly reported in [11]. It was shown that the fundamental optical absorption edge (Urbach tail) of these glasses shifted towards lower photon energies after γ -radiation treatment with accompanying decrease in its slope. It is known that such behavior takes place when the ChVC structure becomes more disordered [12]. The γ -induced disorder, as a rule, is connected with an appearance of stochastic electrical fields created by specific CD in the form of electrically-charged and anomaly-coordinated diamagnetic atomic pairs [13]. They appear in ChVC under external influences as a result of covalent bond switching or, in other words,

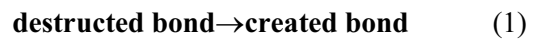
destruction-polymerization transformations (DPT), keeping an average covalent bonding and an electric neutrality of a glassy-like network. It was assumed [11], that these processes in the ternary ChVC are quite similar to those well studied in $v\text{-As}_2\text{S}_3$ previously [9,10], but the correspondent CD formation model has not been developed up to now.

So we suggest that radiation-induced chemical bond switching processes should lead to the CD formation and the alternative variants of non-defect switchings, proposed for explanation of photo-induced structural changes in ChVC [14,15] are presumably of a small probability. The reason is that such non-defect models are based on simultaneous switchings of two chemical bonds (of the same nature) [14] or those switchings, which follow after another through the transient state of CD formation [15]. These switchings are sufficiently limited by strict topological conditions in the initial chemical bonds arrangement - the close co-existence of two heteropolar and homopolar covalent chemical bonds. Possibly, such conditions can be well fulfilled in as-deposited thin-film layers, obtained at non-equilibrium condensation of evaporated substance onto cold substrates. But they are hardly expected in bulk ChVC samples, air-quenched from melt near glass transition temperature. The explanation of the weak-absorption tail in ChVC by means of gap states below the conduction band, which is produced by initially-created wrong homopolar bonds [16], is quite meaningful as an alternative way for such considerations. However, it does not contradict to the concept of induced CD, appearing under non-equilibrium conditions of external influences.

In order to explain the microstructural nature of γ -induced optical effects in the investigated As-Ge-S ChVC, let us consider subsequently the possible bond-switching processes in the "pure" As_2S_3 , GeS_2 and mixed $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$. The following rules and designations were conditionally accepted for the

convenience of such a consideration:

1. The radiation-induced chemical bond switching or destruction-polymerization transformation is denoted by the following scheme:



Only one-bond switching at a time is adopted as an initiated act of the experimentally observed γ -induced changes.

2. The left-side component of the above bond-switching reaction (destroyed bond) attributed with vibrational bands of negative intensities $\Delta r(\nu) < 0$ in the obtained IR Fourier spectra of additional γ -induced reflectivity and, vice versa, the right-side component of the above bond-switching reaction (created bond) attributed with bands of positive intensities $\Delta r(\nu) > 0$.

3. Since high-energetic γ -irradiation introduces an additional disorder in a glassy-like network associated with some deviations in the existing thermally-established distribution of covalent chemical bonds, it can be concluded that the weaker bonds appear instead of the stronger ones as a result of radiation-structural disturbances. This means that only such radiation-induced bond-switching processes should be considered which are accompanied by a negative difference ΔE in dissociation energies for the created E_c and destroyed E_d covalent bonds:

$$\Delta E = E_c - E_d < 0. \quad (2)$$

This condition determines in turn, the low-energy shift of the fundamental optical absorption edge in γ -irradiated ChVC, as a decrease in the character energies of main glass-forming units leads to a narrowing in the band-gap of the correspondent glasses [17]. The greater ΔE , the more essential should be the energetic barrier between the initial and the final metastable states in the structural-configurational diagram of the investigated glassy system and, consequently, the more stable the created CD pair will be.

4. The CD formation, being a part of atomic-dynamic process, is accompanied by

structural changes at the short- and medium-range ordering levels in strong dependence on ChVC compactness. If one has a close-packed glass network with a high atomic compactness, only bond-switching processes with a large $|\Delta E|$ occur. However, this rule is evidently not fulfilled in ChVC of low atomic compactness owing to a high content of intrinsic native microvoids, which prevent the backward annihilation of the created CD.

3.1. Radiation-induced chemical bond switching in $v\text{-As}_2\text{S}_3$

Two schemes of radiation-induced bonds switching with negative differences in bond energies before and after γ -irradiation ΔE , were experimentally identified in $v\text{-As}_2\text{S}_3$ with IR Fourier spectroscopy measurements (see Fig.1) [9,10]:



The first scheme gives $\Delta E = -0.62$ eV, and the second one $-\Delta E = -0.2$ eV (the dissociation energies for different covalent chemical bonds in ChVC are taken from [18]).

The spectra of additional IR reflectivity induced by γ -irradiation in the $v\text{-As}_2\text{S}_3$ revealed a sharp increase of 379, 231, 168 and 140 cm^{-1} vibrational bands corresponded to As-As homopolar chemical bonds. At the same time, the band intensities of homopolar S-S (243 and 188 cm^{-1}) and heteropolar As-S (~ 310 cm^{-1}) bonds decreased. The above mentioned

vibrational bands were identified, based on the well-known experimental data [19-22] and theoretical group analysis [23].

The pairs of over-coordinated As_4^+ and under-coordinated S_1^- CD were proved to be formed as the results of the above schemes (3) and (4) [10]. The superscript in the defect signature means the electrical charge of the atom, and the subscript – the number of the nearest covalent-bonded atoms. It is quite understandable that statistical weight of the scheme (4) is accepted to be significantly less than those of the scheme (3) because of the negligible S-S bond concentration in the investigated bulk ChVC samples of stoichiometric As_2S_3 composition.

3.2. Specific features of radiation-induced CD formation in $v\text{-GeS}_2$

The bulk samples of germanium disulfide $v\text{-GeS}_2$ of a high optical quality cannot be obtained at conventional conditions of ChVC preparation, because this composition lies too close to the border of the glass-forming region in As-Ge-S system [24]. So we shall try to restrict our analysis only to topological consideration of statistically possible bond switching processes in this specimen. Let us apply the topological-mathematical approach developed for $v\text{-As}_2\text{S}_3$ previously [10] to describe the possible radiation-structural transformations in $v\text{-GeS}_2$. Since maximum local atomic coordination in covalent-bonded

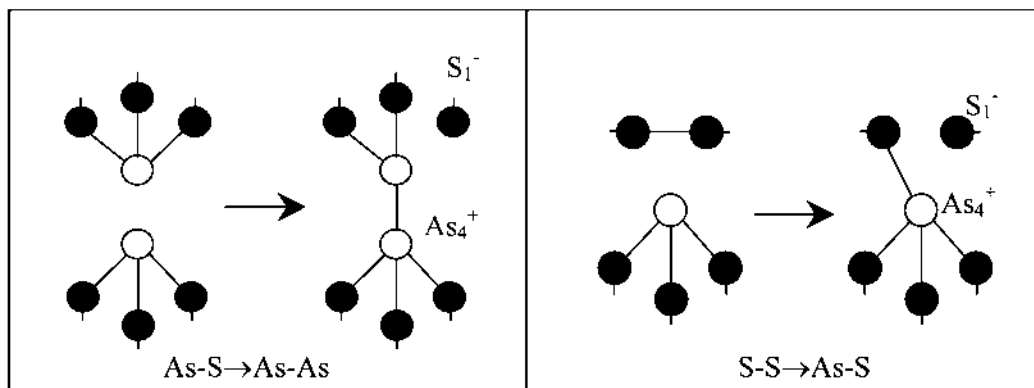


Fig.1. Experimentally-proved topological variants of γ -induced destruction-polymerization transformations in $v\text{-As}_2\text{S}_3$ [10].

materials does not exceed four, the Ge_5^+ CD should be ignored in such consideration.

The detailed analysis (according to the rules 2-4) testifies that only one topological variant of radiation-induced destruction-polymerization transformation, shown in Fig.2, is possible in $v-GeS_2$. It is connected with the formation of heteroatomic (Ge_3^- , S_3^+) CD pair owing to the bond-switching scheme given below:



This scheme is described by a negative ΔE value close to -0.2 eV.

The topological bond-switching variants, which do not change the bond type (shown in Fig.3), are excluded from our analysis in both $v-As_2S_3$, and $v-GeS_2$, because they are experimentally undetectable. We suppose that these CD can be responsible for the origin of the so-called dynamic radiation effects, recently discovered in some ternary ChVC [11]. The reason is that the energetic difference between the created and destroyed bonds ΔE is negligible (close to 0), so the backward bond-switching reaction of CD annihilation can be easily activated in the irradiated samples under ambient temperature conditions. It is interesting to state, that contrary to the bond-switching schemes (3)-(5), only homoatomic CD (involving one-type atoms) appear as a result of such dynamic transformations (Fig.3).

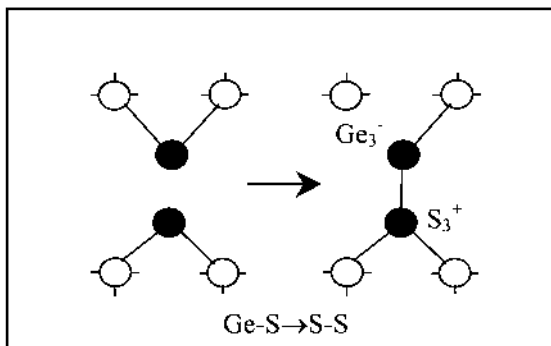


Fig.2. Possible topological variant of γ -induced destruction-polymerization transformations in $v-GeS_2$.

3.3. Topological variants of chemical bond switching in mixed $v-As_2S_3-GeS_2$

The above considerations lead to the conclusion that heteropolar $=As-S-$ and $\equiv Ge-S-$ structural fragments are responsible for the observed radiation-induced effects in binary $v-As_2S_3$ and $v-GeS_2$, respectively, to the bond-switching reactions (3) and (5). However, due to the chemically ordered bond network model [25], the real structure of mixed $(As_2S_3)_x(GeS_2)_{1-x}$ is preferentially composed of neighboring $=As-S-$ and $\equiv Ge-S-$ fragments. So the CD formation processes occurring in this ChVC system embrace these two fragments simultaneously. The correspondent topological variants of chemical bond switchings can be simulated as in the case of binary ChVC, replacing one of the $=As-S-$ or $\equiv Ge-S-$ complexes by another and taking into account the impossibility of Ge_5^+ CD formation. As a result, the following bond-switching schemes can be distinguished according to the above-introduced rules 2-4 (see Fig.4):



The ΔE values are negative in each of these schemes (-0.2, -0.4 and -0.86 eV, respectively). Besides (As_4^+, S_1^-) and (Ge_3^-, S_3^+) CD pairs proper to the boundary As_2S_3 and GeS_2 compositions respectively, the additional heteroatomic (Ge_3^-, As_4^+) CD pair can be formed owing to the bond-switching scheme (7) in mixed $(As_2S_3)_x(GeS_2)_{1-x}$ ChVC (Fig.4).

Thus, the overall variety of the possible DPT in the investigated ChVC is restricted by the above-considered bond-switching topological schemes. The probability of the scheme (4) is small because of the low concentration of the initial "wrong" S-S bonds (according to the chemically ordered bond network model [25]) in $(As_2S_3)_x(GeS_2)_{1-x}$ glasses. But this scheme is supposed to be a logical continuation of the processes shown in Fig.2 (scheme 5) and Fig.4a (scheme 6), because their final products

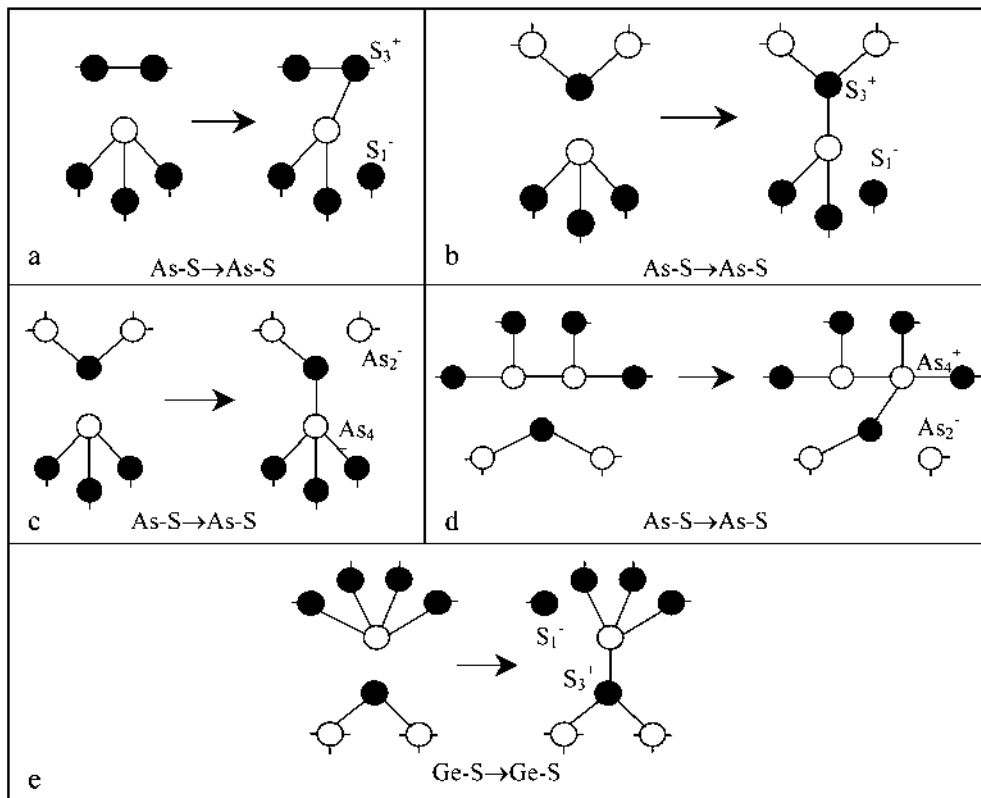


Fig.3. Possible topological variants of γ -induced destruction-polymerization transformations in $v\text{-As}_2\text{S}_3$ (a-d) and $v\text{-GeS}_2$ (e) without changes in bond type owing to bond-switching schemes 6 (a), 7 (b) and 8 (c).

(homopolar S-S bonds) can be the initial ones for the scheme (4). In such a way, the unique row of DPT in $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ ChVC should be supplemented with the bond-switching schemes (5,6)-(4) (see Fig.5), being the additional source for $(\text{Ge}_3^-, \text{As}_4^+)$ CD pairs.

3.4. Experimental results

The IR Fourier spectra of additional γ -induced reflectivity $\Delta r(\nu)$ for two investigated glass compositions with most GeS_2 and As_2S_3 content ($x=0.2$ and $x=0.8$, respectively) are presented in Fig.6. Similar spectra with intermediate $\Delta r(\nu)$ band intensities were obtained for all the other samples. Apart from the considered vibrational bands proper to As-based structural fragments (containing As-S (310 cm^{-1}), As-As (379 and 231 cm^{-1}) and S-S (243 cm^{-1}) covalent chemical bonds) [19-22], the other vibrational bands associated with Ge-based Ge-S (370 cm^{-1}) [21] and Ge-As bonds (274 cm^{-1}) [7] are observable in these spectra.

It is clearly seen that the strongest γ -induced changes in the reflection vibrational bands are due to the heteropolar As-S chemical bonds (310 cm^{-1}) of $\text{AsS}_{3/2}$ pyramids and Ge-S bonds (370 cm^{-1}) of $\text{GeS}_{4/2}$ tetrahedra, while the others reveal themselves as slight features on the background of these bands. This fact is not surprising, since As-S and Ge-S heteropolar chemical bonds are predominant in the investigated ChVC obtained by melt-quenching [24,25].

The qualitative distribution of positive and negative peak intensities in the obtained IR Fourier spectra of additional γ -induced reflectivity $\Delta r(\nu)$, as well as their relationship to the discussed DPT, presented in sections 3.1, 3.2 and 3.3, are given in Table 1.

The strong negative band at 370 cm^{-1} corresponds to Ge-S bonds disappearing under the influence of γ -irradiation. Due to the above topological analysis, this feature is caused by

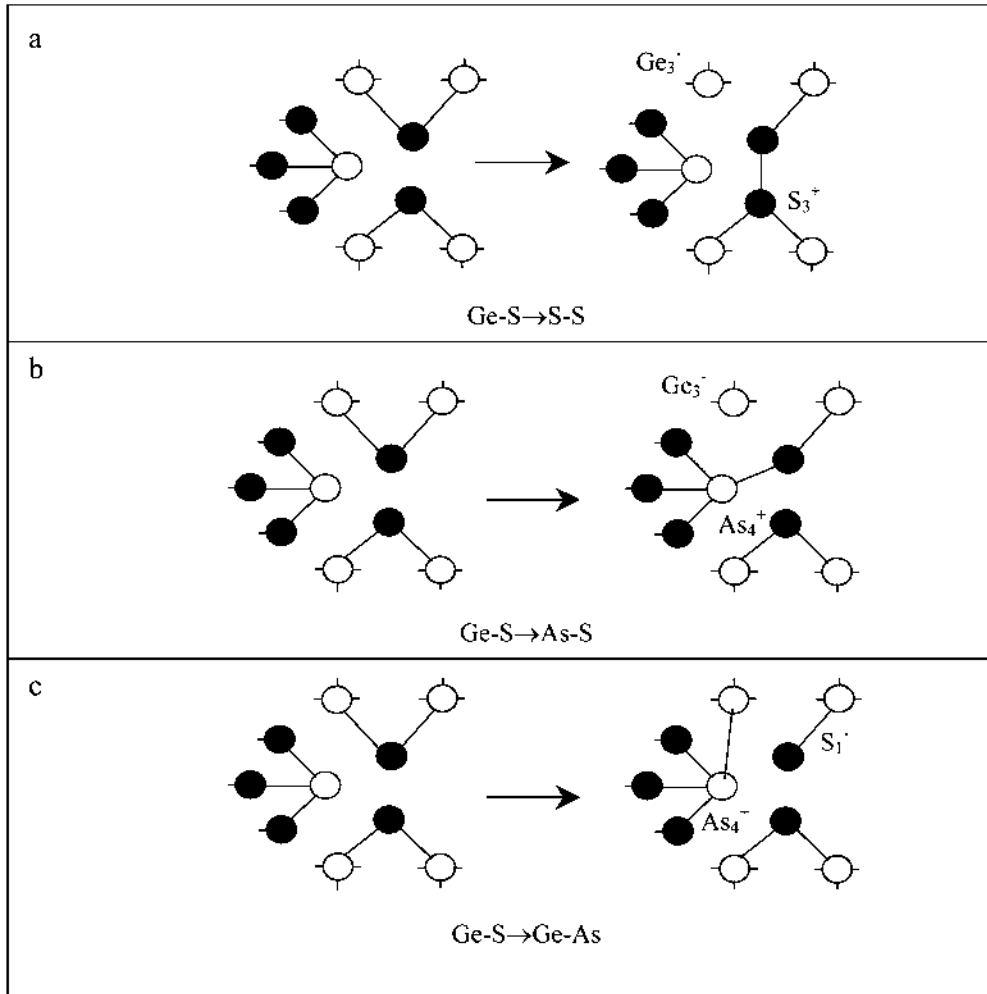


Fig.4. Possible topological variants of γ -induced destruction-polymerization transformations in mixed $(As_2S_3)_x(GeS_2)_{1-x}$ ChVC with changes in bond type.

the bond-switching schemes (5), (6), (7) and (8). The heteropolar Ge-S chemical bonds are the initial ones for all of these topological reactions, but their results are of different nature (compare Fig.2 and Fig.4). The first two schemes lead to the appearance of homopolar S-S chemical

bonds and the next two – to the appearance of heteropolar As-S and Ge-As chemical bonds, respectively.

The increase in the amount of S-S chemical bonds, caused by the schemes (5) and (6), should result in the intensification of the

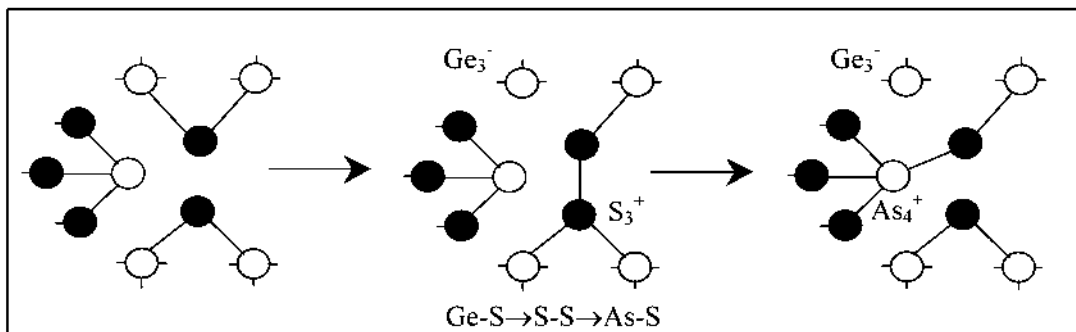


Fig.5. The unique row of γ -induced DPT in $(As_2S_3)_x(GeS_2)_{1-x}$ ChVC including subsequent (5,6) and (4) bond-switching schemes.

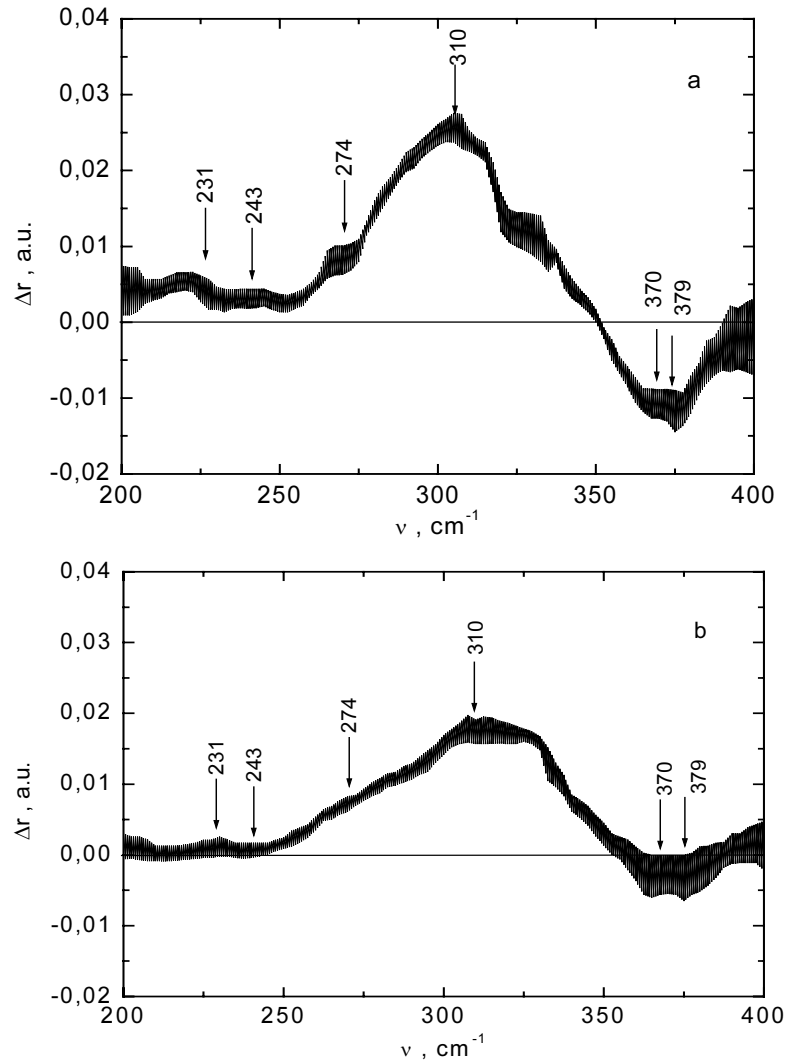


Fig.6. IR Fourier spectra of additional γ -induced reflectivity in $v\text{-(As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ for GeS_2 -enriched ($x=0.2$, a) and As_2S_3 -enriched chemical compositions ($x=0.8$, b).

243 cm^{-1} vibrational band in $\Delta r(\nu)$ spectra (see Table 1). However, this positive band is of low intensity (very weak), because the created S-S chemical bonds can be effectively switched into As-S bonds due to scheme (4). The correspondent unique bonds switching scheme is shown in Fig.5. The final products of this scheme are the heteropolar As-S chemical bonds (see Table 1), resulting from the intensification of the correspondent vibrational band at 310 cm^{-1} in $\Delta r(\nu)$ spectra (Fig.6). Besides thus it, the decreasing of the Ge-S bond concentration according to the switching scheme (7) (see Table 1) leads to the same tendency in the $\Delta r(\nu)$ spectra. A very strong positive vibrational band

at 310 cm^{-1} (Fig.6), which is associated with As-S chemical bonds confirms such consideration.

The positive band of medium intensity at 274 cm^{-1} reveals itself as a shoulder in the vicinity of the 310 cm^{-1} band (see Fig.6) and corresponds to the increasing of Ge-As bond concentration, predicted by (8) bond-switching scheme.

Since the heteropolar Ge-S chemical bonds are the initial ones for all of the above discussed bond-switching schemes, we expect the intensification of the related processes with Ge content in the investigated ChVC. In other words, when the increase of GeS_2 content takes place, the statistical weight of the topological

Table 1.

Vibrational bands in IR Fourier spectra of additional γ -induced reflectivity $\Delta r(\nu)$ and their relationship with the proposed bond-switching schemes.

Band position (cm ⁻¹)	Band intensity (peak type)	Bond-switching scheme responsible for:		Type of associated covalent chemical bond
		positive contribution in $\Delta r(\nu)$	negative contribution in $\Delta r(\nu)$	
370	vs (negative)	-	(5),(6),(7),(8)	Ge-S
310	vs (positive)	(4), (7)	(3)	As-S
274	m (positive)	(8)	-	Ge-As
243	vw (positive)	(5), (6)	(4)	S-S
231	w (positive)	(3)	-	As-As

Note: The following classification of band intensities was used in the table:

“vs”- very strong; “s” – strong; “m” – medium; “w” – weak; “vw” – very weak.

schemes (5)-(8) increases drastically in accordance with the obtained experimental results (compare Fig.6a and Fig.6b).

In contrast, the role of these topological bond-switching schemes in As₂S₃-enriched ChVC is of less importance. However, the statistical weight of the scheme (3) increases in these glasses being the source for additional reduction of As-S bonds. As a result, the band intensities of both As-S (310 cm⁻¹) and Ge-S (370 cm⁻¹) chemical bonds in $\Delta r(\nu)$ spectrum decrease with As₂S₃ content.

The appearance of homopolar As-As bonds, predicted by the (3) bond-switching scheme (3), is difficult to verify experimentally, since the correspondent stretching vibrational band (379 cm⁻¹) is overlapped with an intense broad band of Ge-S bonds (370 cm⁻¹). On the other hand, the bending mode of As-As vibrations observed at 231 cm⁻¹ is of relatively small sensitivity to the described DPT in comparison with the first one (379 cm⁻¹) [10].

4. Conclusion

The covalent chemical bond-switching processes in v-As₂S₃, v-GeS₂ and mixed (As₂S₃)_x(GeS₂)_{1-x} compositions were considered separately in order to explain the microstructural mechanism of γ -induced optical effects in the ternary As-Ge-S ChVC. The physically possible schemes of DPT were adopted as model ones in

accordance with the experimental results, obtained by the IR Fourier spectroscopy technique. The heteroatomic (Ge₃⁻, S₃⁺), (Ge₃⁻, As₄⁺) and (As₄⁺, S₁⁻) CD pairs are shown to be responsible for the observed radiation effects. In contrast to them, the homoatomic (S₁⁻, S₃⁺) and (As₂⁻, As₄⁺) CD pairs are supposed to be a reason for the dynamic post-irradiation changes in these glasses.

References

1. Shimakawa K., Kolobov A., Elliott S.R., *Adv. in Physics* **44**, 6 (1995) 475.
2. Tanaka K., *Current Opinion in Solid State & Materials Science* **1** (1996) 567.
3. Shpotyuk O.I., Matkovskii A.O., Kovalskiy A.P., Vakiv M.M., *Rad. Effects and Defects in Solids* **133**, 1 (1995) 1.
4. Elliott S.R., *J.Non-Cryst.Solids* **81** (1986) 71.
5. Lyubin V., Kolobov A.V., Yasuda T., Klebanov M., Boehm L., Tanaka K., *J.Non-Cryst. Solids* **227-230** (1998) 677.
6. Shpotyuk O.I., Balitska V.O., *Phys. Stat. Sol. A* **165**, 8 (1998) 295.
7. Vateva E., Skordeva E., Arsova D., *Phil.Mag.* **B 67**, 2 (1993) 225.
8. Konorova L.F., Zhdanovich N.S., *Fiz. i techn. poluprovodn.* **27**, 3 (1993) 470 (in rus.).
9. Balitska V.O., Shpotyuk O.I., *J.Non-Cryst. Solids* **227-230** (1998) 723.

10. Shpotyuk O.I., Phys. Stat. Sol. **A 145**, 1 (1994) 69.
11. Shpotyuk O.I., Kovalskiy A.P., Skordeva E., Vateva E., Arsova D., Golovchak R.Ya., Vakiv M.M., Physica B. Condensed Matter **271** (1999) 242.
12. Mott N.F. and Davis E.A., Electronic Processes in Non-Crystalline Materials, Clarendon Press, Oxford, 1971 (p.374).
13. Mott N.F., Davis E.A., Street R.A., Phil. Mag. **32**, 5, 961 (1975).
14. Frumar M., Firth A.P., Owen A.E., J. Non-Cryst. Solids **59-60** (1983) 921.
15. Fritzsche H., Phil. Mag. **B 68** (1993) 561.
16. Tanaka Ke., J. of Optoelectronics and Advanced Matter. **3**, 2 (2001) 189.
17. Kastner M., Phys. Rev. B **7**, 12 (1973) 5237.
18. Tichy L., Ticha H., J. Non-Cryst. Solids **189** (1995) 141.
19. Strom U., Martin T.P., Solid State Commun. **29** (1979) 527.
20. Scott D.W., McCullough J.P., Kruse F.H., J. Molec. Spectroscopy **13** (1964) 313.
21. Lucovsky G., Keezer R.C., Six H.A. and Geils R.H., Proc. of the Sixth Intern. Conf. on Amorphous and Liquid Semiconductors, Leningrad, Nauka, 1975, p.296-299.
22. Lucovsky G., Galeener F.L., Keezer R.C., Six H.A. and Geils R.H., Phys. Rev. **B 10** (1974) 5134.
23. Mori T., Matsuishi K., Arai T., J. Non-Cryst. Solids **65** (1984) 269.
24. Feltz A., Amorphous and vitreous inorganic solids. Moscow, Mir, 1986, (p.556) (in Rus.).
25. Arsova D., J. Phys. Chem. Solids **57**, 9 (1996) 1279.