Journal of Optoelectronics and Advanced Materials Vol. 7, No. 5, October 2005, p. 2299 - 2308

# STRUCTURAL-CHEMICAL APPROACH FOR COMPOSITIONAL DEPENDENCES OF γ-INDUCED OPTICAL EFFECTS IN CHALCOGENIDE GLASSES OF Ge–Sb–S SYSTEM

T. S. Kavetskyy[a,b], O. I. Shpotyuk[b,c*], A. P. Kovalskiy[b,d], V. M. Tsmots[a]

[a]Solid-State Microelectronics Laboratory, Drohobych State Pedagogical University, 24, Franko str., Drohobych, 82100, Ukraine
[b]Institute of Materials, Scientific Research Company "Carat", 202, Stryjska str., Lviv, 79031, Ukraine
[c]Institute of Physics, Jan Dlugosz University of Czestochowa, 13/15, al. Armii Krajowej, Czestochowa, 42201, Poland
[d]Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015, USA

Compositional dependences of γ-induced optical effects in ternary chalcogenide glasses of Ge–Sb–S system within $Sb_2S_3$–$GeS_2$ and $Sb_2S_3$–$Ge_2S_3$ cross-sections have been studied in terms of the average coordination number *Z*. The structural-chemical approach based upon the criterion of structural modification efficiency, covalent bond redistribution and free volume concept has been used for their interpretation. It is found that the most suitable explanation for compositional dependences of γ-induced optical effects can be made in the framework of combination of covalent bond redistribution and free volume content. The microstructural features of the effects observed have been also analysed.

(Received September 1, 2005; accepted September 22, 2005)

*Keywords:* Chalcogenide glasses, Radiation, Optical properties, Ge–Sb–S system

## 1. Introduction

Chalcogenide glasses (ChG) are known to be very sensitive to different external influences, including photoexposure, high-energy ionizing irradiation (γ-quanta, accelerated electrons, protons, neutrons, etc.), light ion flows, etc. [1-4]. This feature predetermines possibilities for their practical application in optoelectronics. However, in respect to radiation-induced optical effects (RIOEs), which reveal themselves through reversible changes in fundamental optical absorption edge [5], there are a number of problems in analytical description of the observed compositional dependences for multicomponent ChG.

This paper is aimed to study compositional features of γ-induced RIOEs (or γ-RIOEs, for simplicity) in ChG of Ge–Sb–S system within $Sb_2S_3$–$GeS_2$ and $Sb_2S_3$–$Ge_2S_3$ cross-sections. Compositional changes will be described in dependence on average coordination number *Z*, calculated as the number of covalent chemical bonds per one atom of formula unit (e.g. for $Ge_xSb_yS_z$: $Z = (4x + 3y + 2z)/(x + y + z)$, where 4, 3, 2 are coordination numbers for Ge, Sb and S atoms, respectively).

We shall try to develop a unique structural-chemical approach to describe adequately compositional features in the observed γ-RIOEs in dependence on so-called criterion for structural modification efficiency (CSME) introduced by Popov A.I. [6], covalent bonds redistribution [7] and free volume content [8,9]. Each of these parameters can be used alone, but their linear combinations will be examined additionally to find the best correlations with experimental data.

* Corresponding author: shpotyuk@novas.lviv.ua

## 2. Experimental

The following ChG samples from $(Sb_2S_3)_x(GeS_2)_{1-x}$ ($x$ = 0.1, $Z$ = 2.63; $x$ = 0.2, $Z$ = 2.59; $x$ = 0.3, $Z$ = 2.55; $x$ = 0.4, $Z$ = 2.53; $x$ = 0.5, $Z$ = 2.50) and $(Sb_2S_3)_y(Ge_2S_3)_{1-y}$ ($y$ = 0.125, $Z$ = 2.75; $y$ = 0.325, $Z$ = 2.67; $y$ = 0.375, $Z$ = 2.65; $y$ = 0.625, $Z$ = 2.55; $y$ = 0.725, $Z$ = 2.45) cut-sections were selected for our research. All ChG were synthesised by melt quenching in evacuated quartz ampoules from high-purity (99.9999 %) constituents. Obtained ingots were cut and polished to 1 mm thickness discs of optical quality.

Radiation treatment of the investigated ChG was performed by γ-quanta in the normal conditions of stationary radiation field, created in the closed cylindrical cavity owing to concentrically established $^{60}Co$ ($E$ = 1.25 MeV) sources. The total value of absorbed dose was equal to 3 MGy. No special measures were used to prevent uncontrolled thermal annealing of the samples, but maximum temperature in the irradiating camera did not exceed 320-330 K during radiation treatment.

Optical transmission measurements were carried out using SPECORD M-40 spectrophotometer (200-900 nm). The special marks by diamond cutter were drifted on the sample surfaces to minimize inaccuracy in the reproduction of measuring conditions before and after irradiation. The maximal deviation in optical transmittance was about ±0.5%.

Difference in optical absorption coefficient $\alpha$ before ($\alpha_0$) and after γ-irradiation $\Delta\alpha/\alpha_0$ calculated at the basis of the obtained optical transmission spectra was chosen as controlled parameter for the observed γ-RIOE. As was shown in our previous work [10], the spectral dependences $\Delta\alpha/\alpha_0(h\nu)$ can be plotted as asymmetric bell-shaped curves with well-defined maximum (peak) $\chi = (\Delta\alpha/\alpha_0)_{max}$ observed at the fixed photon energy $h\nu_{max}$. In fact, this $\chi$ parameter is the most important characteristics for γ-RIOE, reflecting its quantitative magnitude, whereas the peak position $h\nu_{max}$ is only slightly sensitive to irradiation, correlated mainly with optical band gap $E_g$ of ChG [10].

## 3. Results and discussion

### 3.1. Compositional dependences of γ-RIOEs

As was revealed previously [10-12], γ-irradiation of the investigated ChG leads to long-wave shift of their fundamental optical absorption edge (a so-called radiation-induced darkening effect). This effect is unstable and restores gradually to some residual value during a period of 2-3 months after irradiation [10-12]. In other words, the total effect consists of two components – dynamic (dyn), which relaxes after irradiation, and static (st), which remains stable for a long time after irradiation:

$$\chi^{\Sigma} = \chi^{st} + \chi^{dyn} \quad (1)$$

Numerical values of $\chi^{\Sigma}$ and $\chi^{st}$ parameters from Eq. (1) for the investigated ChG as a function of their average coordination number $Z$ are presented in Table 1. In the case of $Sb_2S_3$–$GeS_2$ ChG, these parameters increase with $Z$ or Ge content, beginning approximately from $Z$ = 2.53. At the same time, for $Sb_2S_3$–$Ge_2S_3$ ChG, the absolute values of $\chi^{\Sigma}$ and $\chi^{st}$ parameters reveal strong maxima near $Z \cong 2.7$, decaying completely for composition with $Z$ = 2.45. It should be noted that the relative content of static component $\chi^{st}/\chi^{\Sigma}$ increases with Z for both cross-sections. It means that Sb atoms assist to post-irradiation relaxation in the glass structure independently on the chosen cross-section.

Table 1. The quantitative parameter of γ-RIOEs $\chi$ as a function of the average coordination number $Z$ for the investigated ChG of Ge–Sb–S system.

| $Z$ | Total effect $\chi^{\Sigma}$ (a.u.) | Static component $\chi^{st}$ (a.u.) | (%) | $Z$ | Total effect $\chi^{\Sigma}$ (a.u.) | Static component $\chi^{st}$ (a.u.) | (%) |
|---|---|---|---|---|---|---|---|
| $Sb_2S_3$–$GeS_2$ cross-section | | | | $Sb_2S_3$–$Ge_2S_3$ cross-section | | | |
| 2.50 | 0 | 0 | — | 2.45 | 0 | 0 | — |
| 2.53 | 0.100 | 0.050 | 50 | 2.55 | 0.060 | 0.027 | 45 |
| 2.55 | 0.300 | 0.180 | 60 | 2.65 | 0.135 | 0.080 | 59 |
| 2.59 | 0.440 | 0.270 | 61 | 2.67 | 0.177 | 0.115 | 65 |
| 2.63 | 0.760 | 0.530 | 70 | 2.75 | 0.170 | 0.115 | 68 |

*Footnote*. The relative content of the static (stable) component into the total effect is represented in percent.

### 3.2. γ-RIOEs in terms of CSME

The CSME parameter (the criterion for the structural modification efficiency) was introduced by Popov *et al.* (1983) for the control of ChG properties. A basic idea of CSME was that the degree of possible changes in the structure of the material and, hence, in its properties, can be written as [6]:

$$\Delta \Phi = f\,[\mathrm{CSME}] = f[(N_{0s} - N_c)/(N_c(1 - I_c - M)], \quad (2)$$

where $N_{0s}$ is the average number of electrons in the outermost shells of the atoms, $N_c$ is the average coordination number ($N_c = Z$), $I_c$ is the average coefficient of bond ionicity ($I_c = \Sigma S_m N_m$, $S_m$ is the ionicity of the bond $m$ determined by the electronegativity difference of the atoms and $N_m$ is the fraction of $m$ bonds in the materials), $M$ is the degree of metallization of chemical bonds ($M = (\overline{Z} - Z_{Ch}) \cdot 10^{-2}$, $\overline{Z}$ is the average number of electrons per atom for chosen chemical composition, $Z_{Ch}$ is the overall number of electrons in chalcogen atoms (Ch)).

Firstly, the CSME was used to interpret photoinduced effects in ChG, suggesting that the magnitude of photoinduced changes should depend on the degree of possible changes in structure and therefore should increase with the value of the CSME [6]. It should be noted, however, that the interpretation of photoinduced effects based upon the CSME was controversial from next reasons. On the one hand, it was noted in Ref. [6] that the photoinduced shift of the optical absorption edge in $As_xSe_{1-x}$ increases with increasing $x$, although the rise of As content in the system results in a reduction in CSME. On the other hand, the comparison of photoinduced optical effects in $As_2Se_3$ and $As_3Se_2$ amorphous chalcogenide films indicates that the sensitivity of photodarkening in $As_2Se_3$ sample is greater and $As_2Se_3$ has a grater CSME value than $As_3Se_2$. According to Popov *et al.* [6] this contradiction is permissible, especially when a change in the stability of various structural forms on changing the material composition takes place. Significantly, in the next work [13], Popov *et al.* analyzed the using of CSME for interpretation of the γ-induced changes of mechanical properties in arsenic glassy chalcogenides and concluded that "…the results of measurements confirm the validity of the proposal about the extreme character of the dependence of the structural modification efficiency on the value of the CSME in case when the external influence on the material and its exploitation (examination) is realized at the same temperature". From this point of view, we consider the possibility using of the CSME to interpret the γ-induced changes of optical properties in the investigated ChG in conditions of conducted experimental procedure (see §2).

The compositional dependences of the CSME, calculated from Eq. (2), and the magnitude of the total γ-RIOE $\chi^{\Sigma}$ for the investigated ChG within $Sb_2S_3$–$GeS_2$ and $Sb_2S_3$–$Ge_2S_3$ cross-sections are shown in Figs. 1 and 2, respectively.

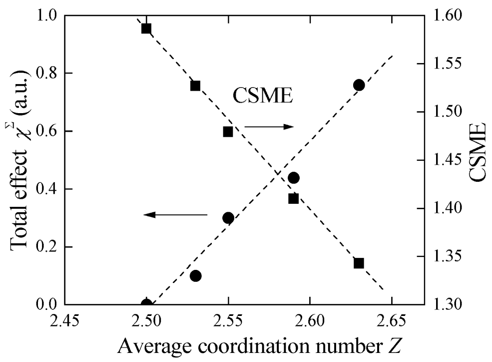


Fig. 1. CSME and magnitude of the total γ-RIOE $\chi^{\Sigma}$ are plotted as a function of $Z$ for $Sb_2S_3$–$GeS_2$ ChG.

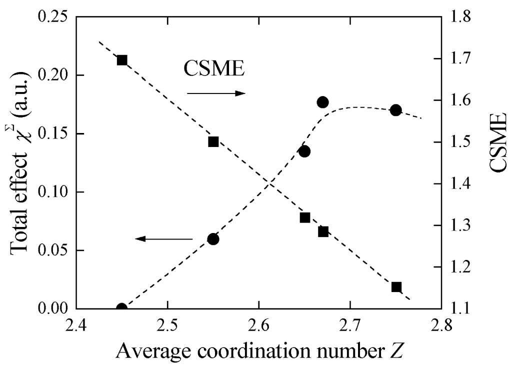


Fig. 2. CSME and magnitude of the total γ-RIOE $\chi^{\Sigma}$ are plotted as a function of $Z$ for $Sb_2S_3$–$Ge_2S_3$ ChG.

It can be seen that dependences of $\chi^{\Sigma} = f(Z)$ and CSME = $f(Z)$ are opposite one to another and their compositional behaviour is essentially different in the case of $Sb_2S_3$–$Ge_2S_3$ ChG. Such compositional trend of γ-RIOE against the CSME is in full contradiction with the main idea of CSME for induced changes in ChG properties [6]. That is, given structural-sensitive parameter in present form is not available to adequate interpretation of compositional features of γ-RIOEs observed. We suppose that the CSME does not include all needed conditions to effective structural modification and it has to be used with some corrections.

### 3.3. γ-RIOEs in terms of covalent bond redistribution

The idea of radiation-induced covalent bond redistribution model is based on the presentation of the magnitude of effect as summa of products of the concentration of covalent bonds and coefficients, reflecting their contribution into the magnitude of effect. In the case of bulk glasses, the ordered bond network model (OBNM) [7] is recommended to determine the concentration of main covalent bonds.

According to OBNM, the main covalent bonds in $Sb_2S_3$–$GeS_2$ cross-section are heteropolar Sb–S and Ge–S bonds. Thus, the magnitude of γ-RIOEs $\chi^k$ can be presented as:

$$\chi^k = \xi_k^{Sb\text{-}S} \cdot x^{Sb\text{-}S} + \xi_k^{Ge\text{-}S} \cdot x^{Ge\text{-}S}, \qquad (3)$$

where index "$k$" stands for total (Σ), static (*st*) and/or dynamic (*dyn*) effects (see Eq. (3)), $\xi_k^{Sb\text{-}S}$ stands for the coefficient that reflects the contribution of Sb–S bonds into the magnitude of effect $\chi^k$, $x^{Sb\text{-}S}$ stands for the concentration of Sb–S bonds, $\xi_k^{Ge\text{-}S}$ stands for the coefficient that reflects the contribution of Ge–S bonds into the magnitude of effect $\chi^k$, $x^{Ge\text{-}S}$ stands for the concentration of Ge–S bonds (according to OBNM $x^{Sb\text{-}S} + x^{Ge\text{-}S} = 1$).

The positive values of coefficients mean that the corresponded to them covalent bonds assist for radiation-induced changes to be appeared, while their negative values testify on the contrary (the absolute values of coefficients determine the magnitude of this influence).

In the framework of OBNM for $Sb_2S_3$–$Ge_2S_3$ cross-section, the main covalent bonds are heteropolar Sb–S, Ge–S and homopolar Sb–Sb, Ge–Ge bonds. Therefore, analogically to the Eq. (3), the magnitude of effect $\chi^k$ can be written as:

$$\chi^k = \xi_k^{Sb\text{-}S} \cdot x^{Sb\text{-}S} + \xi_k^{Ge\text{-}S} \cdot x^{Ge\text{-}S} + \xi_k^{Sb\text{-}Sb} \cdot x^{Sb\text{-}Sb} + \xi_k^{Ge\text{-}Ge} \cdot x^{Ge\text{-}Ge}. \qquad (4)$$

The values of coefficients (calculated from Eqs. (3) and (4)), reflecting the contribution of respective chemical bonds into the magnitude of γ-RIOEs, are summarized in Table 2. We can see that only Ge–S heteropolar bonds give the positive contribution into γ-RIOEs. It is significant that among of the homopolar bonds the Sb–Sb bonds make the most negative contribution into the effects.

Table 2. The values of coefficients obtained on the basis of proposed model of radiation-induced redistribution of covalent bonds for the investigated ChG of Ge–Sb–S system.

| $Sb_2S_3$–$GeS_2$ cross-section | | | $Sb_2S_3$–$Ge_2S_3$ cross-section | | | |
|---|---|---|---|---|---|---|
| Chemical bond coefficients | $\xi_k^{Sb\text{-}S}$ | $\xi_k^{Ge\text{-}S}$ | $\xi_k^{Sb\text{-}S}$ | $\xi_k^{Ge\text{-}S}$ | $\xi_k^{Sb\text{-}Sb}$ | $\xi_k^{Ge\text{-}Ge}$ |
| Total effect: $\chi^{\Sigma}$ | -0.79 | 0.96 | -0.26 | 4.67 | -33.61 | -26.68 |
| Static effect: $\chi^{st}$ | -0.63 | 0.68 | -0.18 | 3.83 | -28.40 | -21.99 |
| Contribution of covalent bonds into the effects ( *n* – negative; *p* – positive) | | | | | | |
| Total effect: $\chi^{\Sigma}$ | Sb–S (*n*); Ge–S (*p*) | | Sb–S (*n*); Ge–S (*p*); Sb–Sb (*n*); Ge–Ge (*n*) | | | |
| Static effect: $\chi^{st}$ | Sb–S (*n*); Ge–S (*p*) | | Sb–S (*n*); Ge–S (*p*); Sb–Sb (*n*); Ge–Ge (*n*) | | | |

The compositional dependences of the concentration of Ge–S heteropolar covalent bonds (determined according to OBNM [7]) and the magnitude of total γ-RIOE $\chi^{\Sigma}$ for the investigated ChG within $Sb_2S_3$–$GeS_2$ and $Sb_2S_3$–$Ge_2S_3$ cross-sections are shown in Figs. 3 and 4, respectively.

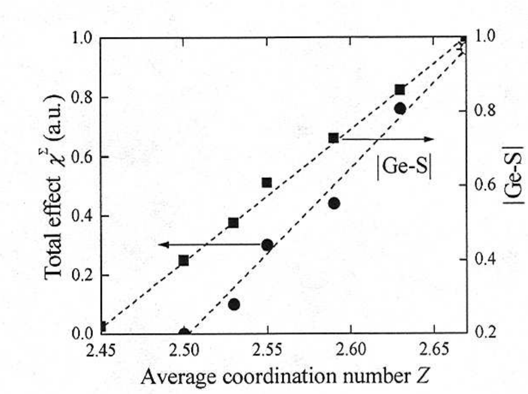


Fig. 3. Concentration of Ge–S covalent bonds (determined according to OBNM [7]) and magnitude of the total γ-RIOE $\chi^{\Sigma}$ are plotted as a function of *Z* for $Sb_2S_3$–$GeS_2$ ChG (☼ – theoretically calculated value of $\chi^{\Sigma}$ from Eq. (3), using data of Table 2).

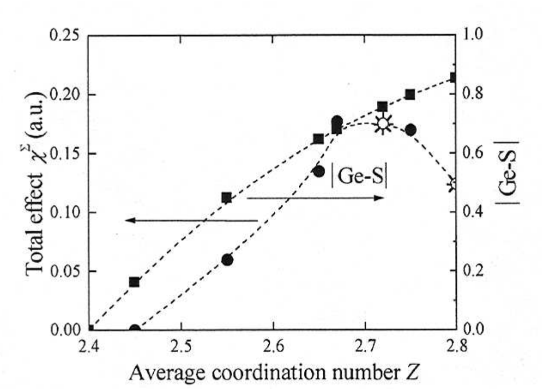


Fig. 4. Concentration of Ge–S covalent bonds (determined according to OBNM [7]) and magnitude of the total γ-RIOE $\chi^{\Sigma}$ are plotted as a function of *Z* for $Sb_2S_3$–$Ge_2S_3$ ChG (☼ – theoretically calculated values of $\chi^{\Sigma}$ from Eq. (4), using data of Table 2).

As it will be expected, the values of effect increase with (Ge–S) and low concentration of Ge–S bonds in Sb-rich samples with the smallest *Z* values can be a reason for absence of radiation-induced changes in such glass compositions. However, in this case of $Sb_2S_3$–$Ge_2S_3$ cross-section from dependence of $\chi^{\Sigma} = f(Z)$ the clear maximum in the region of $Z \cong 2.7$ is obtained, whereas from dependence of (Ge–S) = $f(Z)$ such feature is absent. In other words, the compositional behaviour of Ge–S bonds does not explain fully the compositional trend of γ-RIOEs for $Sb_2S_3$–$Ge_2S_3$ ChG. Therefore, the proposed model of radiation-induced covalent bond redistribution is not enough for adequate interpretation of radiation-induced phenomena in whole Ge–Sb–S system.

### 3.4. γ-RIOEs in terms of free volume concept

The free volume concept has successfully been applied to interpret photoinduced phenomena in amorphous solids [8,9]. Let’s consider the role of this concept for interpretation of γ-RIOEs observed.

A measure of free volume is the compactness of structure $\delta$ calculated according to the well-known formula [8,9]:

$$\delta = (\Sigma V_i - V_a)/V_a = \rho\,[\Sigma A_i x_i/\rho_i - \Sigma A_i x_i/\rho]/\Sigma A_i x_i, \qquad (5)$$

where $V_i$ is the volume occupied by the atoms of $i$-th chemical element of glass; $V_a$ is the experimentally measured volume of glass (the mean atomic volume); $Ai$, $x_i$ and $\rho_i$ are the atomic weight, the atomic fraction and the atomic density of $i$-th chemical element, respectively; $\rho$ is the measured density of glass. The quantities $\delta$ can take the negative values, corresponding to larger free volume [9].

The compositional dependences of the compactness of structure $\delta$ and the magnitude of total γ-RIOE $\chi^{\Sigma}$ for the investigated ChG within $Sb_2S_3$–$GeS_2$ and $Sb_2S_3$–$Ge_2S_3$ cross-sections are shown in Figs. 5 and 6, respectively. According to formula (5), it is clear that increasing of free volume in glass network will be conditioned by increasing of the mean atomic volume $V_a$. That is, the compactness of structure is also a measure of the normalized change of the mean atomic volume [14]. Therefore, compositional dependences of $V_a$ for the investigated ChG are also shown in Figs. 5 and 6 (insets).

It can be seen the correlation between the character in dependences of $\chi^{\Sigma} = f(Z)$ and $\delta = f(Z)$ or $V_a = f(Z)$ takes place, and the maximum of the radiation-induced darkening effect at $Z \cong 2.7$ for $Sb_2S_3$–$Ge_2S_3$ ChG corresponds to minimum of $\delta$ and/or maximum of $V_a$, i.e. to larger free volume.

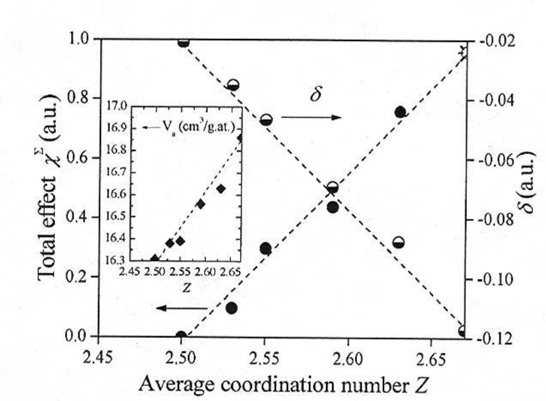


Fig. 5. Compactness of structure $\delta$ and magnitude of the total γ-RIOE $\chi^{\Sigma}$ are plotted as a function of $Z$ for $Sb_2S_3$–$GeS_2$ ChG (☼ – theoretically calculated value of $\chi^{\Sigma}$ from Eq. (3), using data of Table 2). Inset indicates $Z$-dependence of mean atomic volume $V_a$.

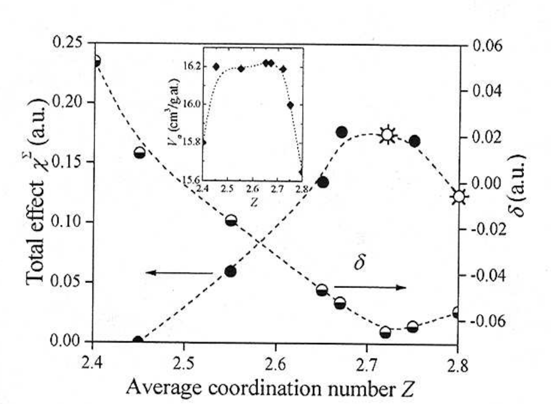


Fig. 6. Compactness of structure $\delta$ and magnitude of the total γ-RIOE $\chi^{\Sigma}$ are plotted as a function of $Z$ for $Sb_2S_3$–$Ge_2S_3$ ChG (☼ – theoretically calculated values of $\chi^{\Sigma}$ from Eq. (4), using data of Table 2). Inset indicates $Z$-dependence of mean atomic volume $V_a$.

### 3.5. γ-RIOEs in terms of combination of covalent bond redistribution and free volume concept

On the basis of above mentioned explanation of the radiation-induced changes observed, we suppose that covalent bond redistribution and free volume concept should be additionally tested in combination to find the most adequate parameter to be well correlated with γ-RIOEs. Similar approach has also been made in the case of photoinduced effects in ChG through $\omega$ parameter expressed by formula $\omega = (M\text{–}X)\cdot\delta$, where (M–X) are the concentrations of heteropolar bonds which might be changed by incident light, and $\delta$ is the compactness of glass structure [15,16]. However, in our case, according to the developed radiation-induced covalent bond redistribution model, the parameter $\omega$ should be represented as $\omega$ = (Ge–S)·$\delta$.

The compositional dependences of the parameter $\omega$ and the magnitude of total γ-RIOE $\chi^{\Sigma}$ for the investigated ChG within $Sb_2S_3$–$GeS_2$ and $Sb_2S_3$–$Ge_2S_3$ cross-sections are shown in Figs. 7 and 8.

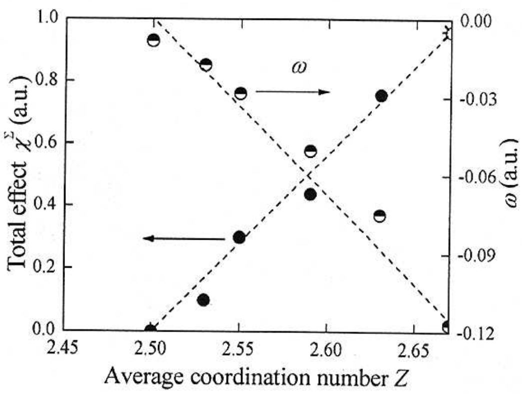


Fig. 7. Parameter $\omega$ and magnitude of the total γ-RIOE $\chi^{\Sigma}$ are plotted as a function of $Z$ for $Sb_2S_3$–$GeS_2$ ChG (☼ – theoretically calculated value of $\chi^{\Sigma}$ from Eq. (3), using data of Table 2).

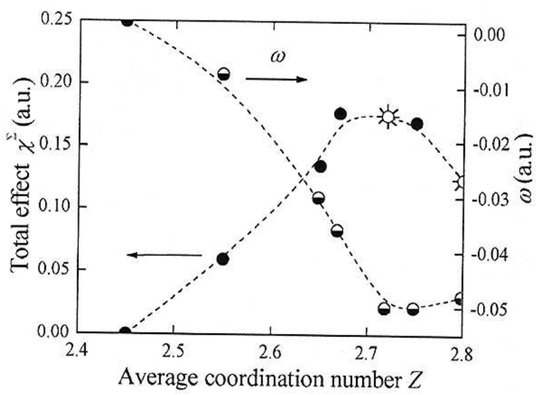


Fig. 8. Parameter $\omega$ and magnitude of the total γ-RIOE $\chi^{\Sigma}$ are plotted as a function of $Z$ for $Sb_2S_3$–$Ge_2S_3$ ChG (☼ – theoretically calculated values of $\chi^{\Sigma}$ from Eq. (4), using data of Table 2).

The high values of $\omega$ in Sb-rich ChG explain the absence of γ-RIOEs in these samples. The correlation between dependences of $\chi^{\Sigma} = f(Z)$ and $\omega = f(Z)$ takes place. The well agreement between numerical values of effect and $\omega$ in the ChG of Ge–Sb–S system has also been detected. So, the minimum values of $\omega$ for the glasses of $Sb_2S_3$–$Ge_2S_3$ and $Sb_2S_3$–$GeS_2$ cross-sections differ about in three times, whereas the maximum values of total effect differ about in four times (see Figs. 7 and 8). It means that free volume in the glass structure defines not only the compositional trend of γ-RIOEs in the both investigated cross-sections of Ge–Sb–S system, but also influences on their magnitude. Moreover, in the case of $Sb_2S_3$–$Ge_2S_3$ compositions it can be seen that the shapes of $\omega = f(Z)$ and $\chi^{\Sigma} = f(Z)$ are agreed better than respective shapes of $\delta = f(Z)$ and $\chi^{\Sigma} = f(Z)$ (see Figs. 6 and 8).

Therefore, among the probes proposed to interpret the compositional dependences of γ-RIOEs observed in the ChG of Ge–Sb–S system the structural-chemical approach based upon combination of covalent bond redistribution and free volume concept, describing by $\omega$ parameter, is the most suitable and adequate. Besides, successful using of such type model for explanation of photoinduced optical phenomena in ternary Ge–Sb–S ChG [15,16] allows us to foresee that this approach can be universal for interpretation of induced phenomena in Ge–Sb–S glassy system, in general.

### 3.6. Microstructural features of γ-RIOEs

In order to understand better the role of free volume in the appearance of the static (stable) component of γ-RIOEs, let's consider the radiation-induced darkening effects in $Sb_2S_3$–$GeS_2$ and $Sb_2S_3$–$Ge_2S_3$ ChG on the microstructural level. So, the microstructural origin of the observed phenomena is connected with radiation-induced defect formation processes. This statement confirms by the decreasing of the slope of Urbach tail Γ after γ-irradiation (Fig. 9), where parameter Γ is a measure of the defectiveness of structure [17]. It is clear that the relationship between the slope of Urbach tail and the concentration of defects should be existed.

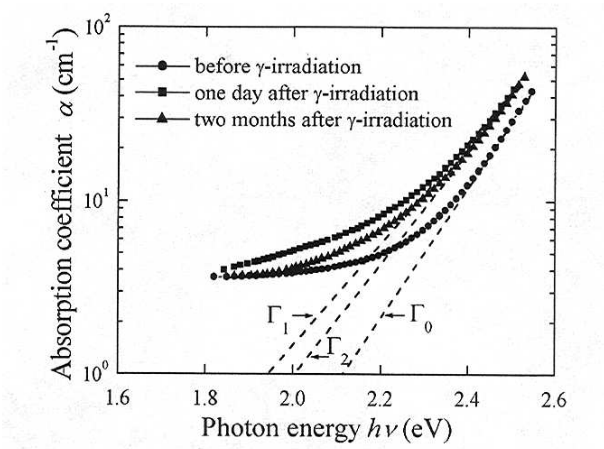


Fig. 9. The typical spectral dependence of the optical absorption coefficient $\alpha(h\nu)$ before and after γ-irradiation for the ChG of $Sb_2S_3$–$GeS_2$ cross-section at $Z$ = 2.63 ($Ge_{28.125}Sb_{6.25}S_{65.625}$). The parameters $\Gamma_0$, $\Gamma_1$ and $\Gamma_2$ correspond to the slope of Urbach tail before, one day and two months after γ-irradiation, respectively.

According to [18] some characteristic energy $\overline{E}$ (where $\overline{E} \sim 1/\Gamma$), determined from Urbach role ($\alpha \sim \exp\{(h\nu - E_g)/\overline{E}\}$), can be written as:

$$\overline{E} = 2.2\, W_B \,(n_t^* a_B^3)^{2/5}, \qquad (6)$$

where $W_B = e^2/2\varepsilon a_B$, $a_B$ is the boron radius, $\varepsilon$ is the dielectric constant, $n_t^*$ is the concentration of charge defect centres. Hence, the relative radiation-induced change in concentration of charge defect centres $\Delta n_t^* / n_{t_o}^*$ can be simply estimated through expression:

$$\frac{\Delta n_t^*}{n_{t_0}^*} = \left(\frac{\Gamma_0}{\Gamma_i}\right)^{5/2} - 1, \qquad (7)$$

where $\Gamma_0$ and $\Gamma_i$ stand for the slope of Urbach tail before and after γ-irradiation, respectively ($i \neq 0$). In our case, if $i$ = 1 or $\Gamma_1$ takes place (one day after γ-irradiation), we will have $(\Delta n_t^*/n_{t_0}^*)^{\Sigma}$ **(**total effect**)** and if $i$ = 2 or $\Gamma_2$ takes place (two months after γ-irradiation), we will have $(\Delta n_t^*/n_{t_0}^*)^{st}$ (static effect).

The compositional features of the slope of Urbach tail (before and after γ-irradiation) and, respectively, the relative radiation-induced change in concentration of charge defect centres $\Delta n_t^* / n_{t_0}^*$ (determined from Eq. (7)) for the ChG of $Sb_2S_3$–$GeS_2$ and $Sb_2S_3$–$Ge_2S_3$ cross-sections are presented in Table 3. It can be seen that in the non-irradiated samples the magnitude of $\Gamma_0$ is decreased with increasing of $Z$. According to Eq. (6), we can conclude that the degree of defectiveness of structure rises into side of Ge-rich ChG. Immediately (one day) after γ-irradiation, $\Gamma_1$ is reduced with increasing of $Z$. It means that γ-irradiation leads to the increasing of defect centres in the glass structure, concentration of which should be the largest in Ge-rich compositions. For the period of two months after γ-irradiation the parameter $\Gamma_2$ some redacts. The $\Delta n_t^* / n_{t_0}^*$ data were obtained on the basis of $\Gamma_0$, $\Gamma_1$ and $\Gamma_2$ one (see Table 3). It is significant that $(\Delta n_t^*/n_{t_0}^*)^{\Sigma}$ and $(\Delta n_t^*/n_{t_0}^*)^{st}$ are characterized by the same compositional features as $\chi^{\Sigma}$ and $\chi^{st}$ in the investigated glasses (see Tables 1 and 3).

The dependences of $\chi^{\Sigma}$ against $(\Delta n_t^*/n_{t_0}^*)^{\Sigma}$ and $\chi^{st}$ against $(\Delta n_t^*/n_{t_0}^*)^{st}$ for $Sb_2S_3$–$GeS_2$ and $Sb_2S_3$–$Ge_2S_3$ cross-sections at various values of $Z$ are shown in Fig. 10. It can be seen the well correlation between $\chi$ and $\Delta n_t^*/n_{t_0}^*$. Because of $\chi = f(Z)$ agrees with $\delta = f(Z)$, the dependences of $\Delta n_t^*/n_{t_0}^* = f(Z)$ and $\delta = f(Z)$ should be also correlated. It means that free volume in the glass structure assists to the stabilisation of radiation-induced defects results in the appearance of the static (stable) component of γ-RIOEs.

The origin of defects, created by γ-irradiation, is an objective of individual research. From this point of view we have used method of far IR spectroscopy and positron annihilation technique. The results obtained in this field will be compared to the former ones [19,20] and will be the subject of our next work presented in our next work.

Table 3. Compositional dependences of the slope of Urbach tail before ($\Gamma_0$), one day ($\Gamma_1$) and two months ($\Gamma_2$) after γ-irradiation and the relative radiation-induced change in concentration of charge defect centres $\Delta n_t^*/n_{t_0}^*$ (for total effect (Σ) and its static component (*st*)) for the investigated ChG of Ge–Sb–S system.

| $Z$ | $\Gamma_0$ (eV$^{-1}$) | $\Gamma_1$ (eV$^{-1}$) | $\Gamma_2$ (eV$^{-1}$) | $(\Delta n_t^*/n_{t_0}^*)^{\Sigma}$ a. u. | $(\Delta n_t^*/n_{t_0}^*)^{st}$ | |
|---|---|---|---|---|---|---|
| | | | | | a. u. | % |
| $Sb_2S_3$–$GeS_2$ cross-section | | | | | | |
| 2.50 | 10.9 | 10.9 | 10.9 | 0 | 0 | — |
| 2.53 | 10.8 | 10.25 | 10.55 | 0.14 | 0.07 | 50 |
| 2.55 | 11.1 | 10.1 | 10.5 | 0.27 | 0.15 | 56 |
| 2.59 | 9.75 | 8.5 | 8.9 | 0.41 | 0.26 | 63 |
| 2.63 | 8.35 | 6.65 | 7.1 | 0.77 | 0.50 | 65 |
| $Sb_2S_3$–$Ge_2S_3$ cross-section | | | | | | |
| 2.45 | 11.4 | 11.4 | 11.4 | 0 | 0 | — |
| 2.55 | 11.4 | 11.25 | 11.35 | 0.03 | 0.01 | 33 |
| 2.65 | 11.1 | 10.7 | 10.9 | 0.10 | 0.05 | 50 |
| 2.67 | 11.0 | 10.4 | 10.65 | 0.15 | 0.08 | 53 |
| 2.75 | 9.95 | 9.45 | 9.65 | 0.14 | 0.08 | 57 |

*Footnote.* The relative content of the static (stable) component into the total effect is represented in percent.

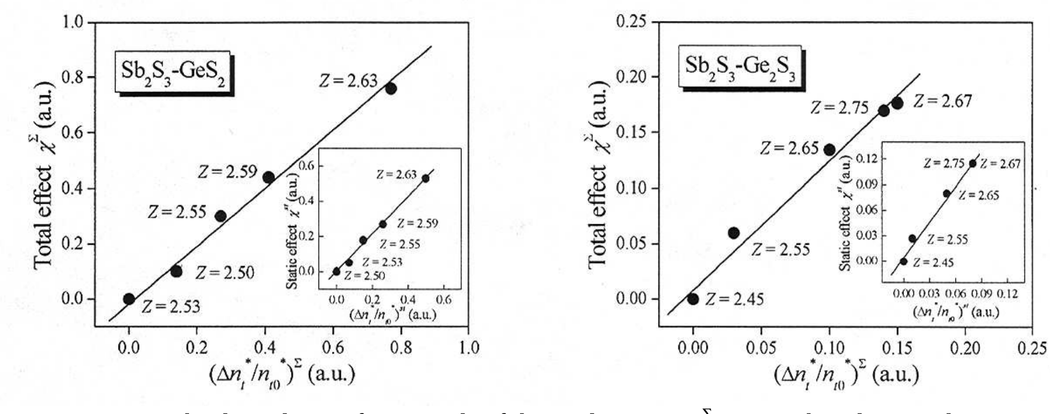


Fig. 10. The dependence of magnitude of the total γ-RIOE $\chi^{\Sigma}$ against the relative radiation-induced change in concentration of charge defect centres $(\Delta n_t^*/n_{t_0}^*)^{\Sigma}$ (estimated from Eq. (7), using data of Table 3) for the investigated ChG at various values of $Z$. Insets demonstrate the same dependences for the static γ-RIOE $\chi^{st}$.

## 4. Conclusions

On the basis of experimental results obtained we have proposed an adequate phenomenological description of compositional dependences of γ-RIOEs ("radiation-induced darkening") for the ChG of Ge–Sb–S system within $Sb_2S_3$–$GeS_2$ and $Sb_2S_3$–$Ge_2S_3$ cross-sections in the framework of structural-chemical approach based upon criterion for the structural modification efficiency (CSME), covalent bond redistribution and free volume concept.

It has been established that: (i) CSME is unfit to interpret γ-RIOEs observed for the ChG of Ge–Sb–S system; (ii) radiation-induced covalent bond redistribution model proposed allows to determine the chemical bonds supporting the occurrence of radiation-induced changes; (iii) combination of covalent bond redistribution along with free volume concept, taking into account the concentration of covalent bonds which assist the appearance of radiation-induced changes, is the most adequate and suitable for interpretation and quality description of compositional dependences of γ-RIOEs for the ChG of Ge–Sb–S system.

On the microstructural level the radiation-induced darkening effect observed is connected with radiation-induced defect formation processes. The relative radiation-induced change in concentration of charge defect centres $\Delta n_t^* / n_{t_o}^*$ correlates with the qualitative parameters of the effects ($\chi^{\Sigma}$ and $\chi^{st}$) and free volume ones ($\delta$ and $\omega$) for the investigated ChG. It can be supposed that free volume in the glass structure assists to the stabilisation of radiation-induced defects results in the appearance of the static (stable) component of γ-RIOEs.

Structural-chemical approach proposed to interpret the compositional features of γ-RIOEs for the ChG of Ge–Sb–S system is recommended to be used for explanation of induced phenomena in other such type of amorphous chalcogenide materials.

**Acknowledgements**

This work was partially supported by a grant from the Fund of Fundamental Researches of Ministry of Education and Science of Ukraine (Project No 02.07/0042). The authors thank Dr. V. Pamukchieva from the Institute of Solid State Physics of Bulgarian Academy of Sciences for useful discussions and preparation of investigated samples.

## References

[1] A. Feltz, Amorphous and Vitreous Inorganic Solids, Mir, Moscow, 1986 (in Russian).
[2] S. Onari, T. Inokuma, H. Kataura, T. Arai, Phys. Rev. **B 35** (9), 4373 (1987).
[3] S. Kokenyesi, J. Csikai, P. Raics, I. A. Szabo, S. Szegedi, A. Vitez, J. Non-Cryst. Solids **326&327**, 209 (2003).
[4] Semiconducting Chalcogenide Glass. 1: Glass Formation Structure and Simulated Transformations in Chalcogenide Glasses. Edited by R. Fairman & B. Ushkov, Academic Press, 2004.
[5] O. I. Shpotyuk, A. O. Matkovskii, J. Non-Cryst. Solids **176,** 45 (1994).
[6] A. I. Popov, N. I. Michalev, V. K. Shemetova, Phil. Mag. **B 47**, 73 (1983).
[7] D. Arsova, J. Phys. Chem. Solids **57**, 1279 (1996).
[8] Ya. A. Teteris, M. Ya. Rejnfelde, Izv. AN SSSR. Neorgan. Mater. **22**(4), 584 (1986) (in Russian).
[9] I. P. Kotsalas, D. Papadimitriou, C. Raptis, M. Vlcek, M. Frumar, J. Non-Cryst. Solids **226**, 85 (1998).
[10] O. I. Shpotyuk, T. S. Kavetskyy, A. P. Kovalskiy, V. Pamukchieva, Proc. SPIE **4415**, 278 (2001).
[11] O. Shpotyuk, T. Kavetskyy, J. Filipecki, A. Kovalskiy, V. Pamukchieva, Wyższa Szkoła Pedagogiczna w Częstochowie. Prace Naukowe. Chemia **5**, 189 (2001).
[12] O. I. Shpotyuk, R. Ya. Golovchak, T. S. Kavetsky, A. P. Kovalskiy, M. M. Vakiv, Nucl. Instrum. Methods Phys. Res., Sect. **B 166-167**, 517 (2000).
[13] A. I. Popov, I. A. Domoryad, N. I. Michalev, Phys. Stat. Sol. (a) **106**, 333 (1988).
[14] L. Tichy, H. Ticha, Mater. Lett. **21**, 313 (1994).
[15] M. Vlcek, M. Frumar, A. Vidourek, J. Non-Cryst. Solids **90,** 513 (1987).
[16] M. Vlcek, M. Frumar, J. Non-Cryst. Solids **97&98,** 1223 (1987).
[17] N. F. Mott, E. A. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon Press, Oxford, 1971.
[18] Ya. G. Klyava, Fiz. Tverd. Tela **27**, 1350 (1985) (in Russian).
[19] O. Shpotyuk, A. Kovalskiy, T. Kavetskyy, R. Golovchak, J. Optoelectron. Adv. Mater. **5**(5), 1169 (2003).
[20] O. Shpotyuk, A. Kovalskiy, T. Kavetskyy, R. Golovchak, M. Popescu, J. Optoelectron. Adv. Mater. **5**(5), 1181 (2003).