

γ -INDUCED CHANGES IN Ge-As-S GLASSES

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γ -irradiation were carried out on Ge-As-S glasses belonging to two different lines of the glass-forming diagram with an equal mol fraction of the As_2S_3 amount. Measurements of some optical properties of the compositions before and after irradiation have been performed. The changes of the optical properties connected with γ -induced structural changes are compared with the photoinduced changes observed in amorphous films evaporated from the same system.

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1. Introduction

It has been pointed in a recent review [1] that the photoinduced structural changes (PSC) are a phenomenon unique to amorphous chalcogenides. A relatively high number of models exist about the possible mechanism of these changes. However, independently of that does either one or several of these mechanisms predominate, the origin of the photostructural changes is supposed to be connected with the presence of many different defects in the amorphous matrix [1]. As a result the structure of the latter is more flexible than that of the crystals and can be easily changed by some energetic treatment. The light that induces the photostructural changes is usually in the range of the semiconductor band-gap or subband-gap energy [2, 3]. The large thickness of the bulk glassy samples, however, leads to complementary experimental difficulties connected with the penetration depth of the light. That is why thin films are preferred as an object of investigation of photoinduced phenomena and only a few works deal with bulk glasses [4].

Changes in the structure of the disordered materials can be also initiated by different kinds of irradiation (neutron, electron, ion, γ -irradiation etc.) [5]. These changes are sometimes supposed to have the same mechanism as the photoinduced ones. The mentioned alternative irradiations may be preferable because of their possibility to penetrate into the volume of the sample thus inducing changes all over it.

The γ -induced changes of the properties of As_2S_3 glasses have been investigated in details [6-8]. A model for γ -induced structural transformations was proposed which coincides with some of the models explaining the photoinduced changes in the same material [9]. Several investigations on γ -irradiated As- and/or Ge-containing ternary chalcogenide glasses are also available in the literature [10, 11].

An opinion exists that with the increase of the As-content in chalcogenides the structural transformations, induced by different type of irradiation, become greater [12, 13]. However, as pointed in [1], PSC have not been observed in amorphous As. The question arises whether the chalcogen-As or another type of bond is more sensitive to the PSC phenomena observed in ternary glasses. As supposed in [3], not only the short-range structure is decisive but also some features of the medium range order can influence the material sensitivity to transformations. That is why

investigation of multinary compositions with different medium range order is advisable. Glasses from the As-Ge-S system meet this requirement.

Our previous investigations on $(As_2S_3)_x(Ge_2S_3)_{1-x}$ thin films [14, 15] have shown that the irreversible PSC are most strongly expressed in the region of the Tanaka's 2D-3D phase transition. Preliminary investigations of γ -irradiated $(As_2S_3)_x(Ge_2S_3)_{1-x}$ glasses showed that the induced changes in 2D (layer-like) and 3D (with cross-linked network) glasses also differ [16, 17]. In these glasses a number of defect bonds exists not only because of their amorphous state but also because of the presence of a non-stoichiometric component in the alloyed glass matrix. A comparative Raman study of $(As_2S_3)_x(GeS_2)_{1-x}$ and $(As_2S_3)_x(Ge_2S_2)_{1-x}$ glasses showed that although their short range order can be approximated as composed by identical structural units, the amount of defect bonds is greater in the latter [18].

The aim of the present work is to compare the induced by γ -irradiation changes of some optical properties of $(As_2S_3)_x(Ge_2S_3)_{1-x}$ and $(As_2S_3)_x(GeS_2)_{1-x}$ glasses with the analogous PSC observed in amorphous films evaporated from the same glassy systems.

2. Experimental details

The group of glasses belonging to the $(As_2S_3)_x(GeS_2)_{1-x}$ line of the As-Ge-S glass-forming system includes only stoichiometric components; the glasses belonging to the $(As_2S_3)_x(Ge_2S_3)_{1-x}$ line of the same system are composed of one stoichiometric and one non-stoichiometric components. For the sake of convenience the first type of glasses will be denoted as ST glasses, the second ones – as NST glasses.

ST and NST glasses with the same mol fraction of As_2S_3 ($x = 0.1-0.8$) were chosen for the present investigation. Special attention was carried out to maintain identical the technological conditions of preparation for both type of glasses. The glasses were synthesized from constituent elements with 5N purity by a standard melt-quenching method [16, 17]. The ingots have been cut and the 1mm (ST) and 2 mm (NST) thick glassy disks have been polished for optical measurements. The optical measurements were performed in the region of 200-900 nm using spectrophotometer SPECORD M-40.

γ -irradiation with a dose of 4.4×10^6 Gy for NST glasses and 2.2×10^6 Gy for ST ones (the mean energy of γ -flow being $E = 1.25$ MeV) was carried out from a Co^{60} source. Some details of the irradiation treatment were described in previous papers [6-8]. Transmission spectra were taken before and after γ -irradiation. Suitable computer programs were used during the measurements in order to calculate the differences in the optical spectra before and after irradiation. Calculations of the absorption coefficients α were carried out as described previously [16].

3. Results and discussion

The criterion for the optical band-gap E_0 estimation of different investigators is rather different. The energy value obtained by the Tauc plot $(\alpha h\nu)^{1/2} = f(h\nu)$, as well as the value of E_0 defined as an energy at certain value of α in the Urbach's range are used. For that reason the E_0 values vary in different papers but their compositional dependence often is similar. Since we used samples with thickness 1 (or 2) mm we could not obtain the values of the absorption coefficient in the whole Urbach's range and for higher energies. Nevertheless the band-gap shift with the composition can be roughly estimated using some characteristic energy, e.g. E_1 , defined in the beginning of the Urbach's range at $\alpha = 30 \text{ cm}^{-1}$. The E_1 energies are plotted in Fig. 1 and compared with the compositional dependences (towards the amount of As_2S_3) calculated by

$$T_g = 325 + 0.55 (Z - 2) E_0 / 32.2 k, \quad (1)$$

where T_g is the respective glass-transition temperature, Z - the average coordination number and k - the Boltzman's constant [19]. T_g values for both ST and NST glasses are taken from [20]. The shape

of the compositional dependence of the characteristic energy E_I is similar to that of the calculated E_0 , as well to the respective dependences obtained by other authors [21-23].

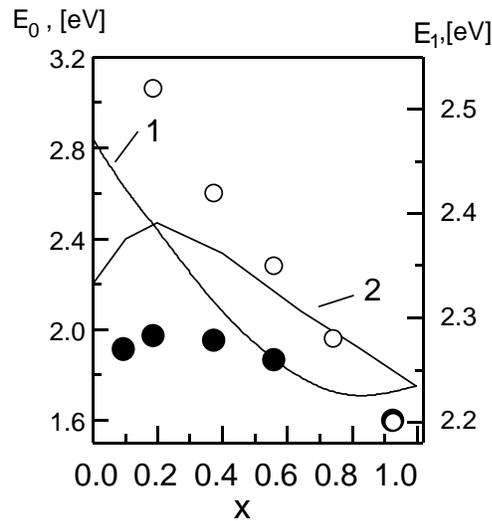


Fig. 1. Curve 1: values of the band-gap energies of ST glasses; Curve 2: values of the band-gap energies of NST glasses. The values are obtained by calculation of E_0 from T_g [19, 20]. The open circles present the characteristic energy $E_I(x)$ for the ST glasses, the solid ones - for the NST ones. Curves 1, 2 are drawn with respect to the left axis, the symbols - with respect to the right one.

Results from the absorption coefficient calculation are shown in Fig. 2. As can be seen, after γ -treatment all of the $\alpha(h\nu)$ curves are shifted towards lower energies (darkening effect), similarly to the reversible photodarkening effect after band-gap illumination of annealed Ge-As-S films [15]. The quantitative and qualitative aspects of the changes depend however not only on the irradiation dose, but also on the composition.

The calculated from the transmission spectra $\alpha(h\nu)$ curves are characterized by two different slopes: (i) δ , which corresponds to the high energetic range of the curve and (ii) η , corresponding to the low-energetic one (Fig. 2). After γ -irradiation the slope δ decreases in both systems. However, while in the ST glasses the relative slope change $\Delta\delta/\delta$ is almost constant (~10-15 %) for all of the compositions, in the NST ones $\Delta\delta/\delta$ decreases (34.5-11.5 %) with increasing x . Our investigations on PSC in thin Ge-As-S films have shown that the change in the slope of the $\alpha(h\nu)$ dependences after band-gap illumination is qualitatively similar. As known [24], the decrease of this slope takes place when the structure of the amorphous chalcogenides becomes more disordered. It can be supposed that, similarly to the case of photoinduced changes, the increased disorder induced by γ -irradiation is connected with an increase of the amount of homopolar defect bonds at the expense of that of the heteropolar one's. The formation of defect bonds is probably accompanied by formation of new charged centers [25].

The second slope (η) of the $\alpha(h\nu)$ dependence may be connected with different types of defects and inhomogeneities in the glass matrix. After γ -irradiation its value increases in all of the spectra. This fact is connected with the creation of new defects. Structural defects, which increase with the γ -dose rate, were also found in a-As-Se-Te glasses [10].

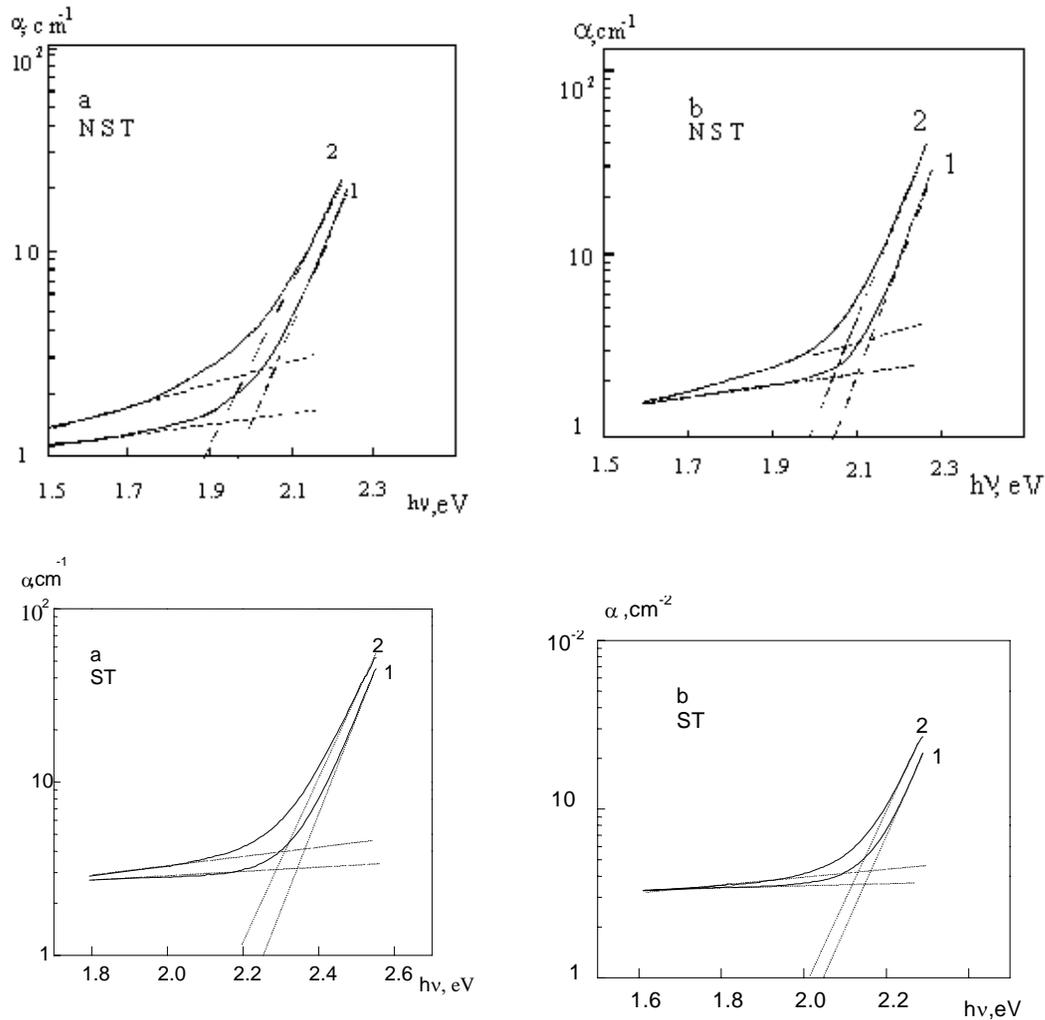


Fig. 2. $\alpha(h\nu)$ curves before (1) and after (2) γ -irradiation; a: $x = 0.2$, b: $x = 0.6$.

The level of influence of γ -irradiation on the optical properties of ST and NST glasses and the stability of the induced changes can be described by the spectral dependence of $\Delta\tau$. $\Delta\tau(h\nu)$ is defined as the difference between the respective values of the transmission spectra before and after irradiation. Several representative $\Delta\tau(h\nu)$ curves are shown in Fig. 3. All $\Delta\tau(h\nu)$ curves have an asymmetric form. It was obtained that: *i*) a tendency to saturation of the effect is present. Saturation is achieved approximately after ~ 3 months; *ii*) there is a well-expressed partial self-restoration of the radiation-induced optical changes in the course of time. It should be noted that the effect of the PSC diminishes in a similar way even when the samples are maintained at room temperature. This effect however is very small. *iii*) Two components are composing the self-restoration effect of the γ -induced optical changes. The first is a dynamic one. It gradually decreases after irradiation. The decrease of the dynamic component is related to the restoration of the optical transmittance and, hence, to the increase of $\Delta\tau$. The other component is the static one (constant in the time); *iv*) the restoration effect leads to greater changes in the low-energetic side of the $\Delta\tau(h\nu)$ curves.

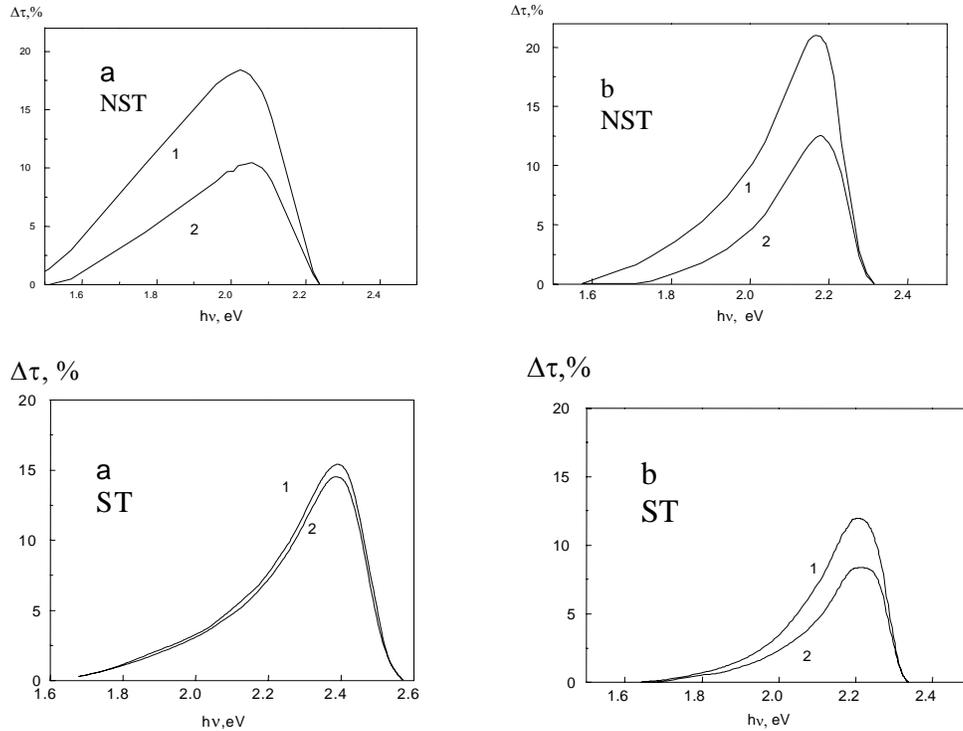


Fig. 3. $\Delta\tau(h\nu)$ curves for glasses from both investigated systems; a: $x = 0.2$, b: $x = 0.6$. Curves (1) are measured a day after the irradiation, curves (2) - 4 months later.

The shapes, the positions of the maxima, the width and the area S_1 under the $\Delta\tau(h\nu)$ curves (which can be used as an estimation of the integral induced change) depend on the composition. The area S_1 under the curves were calculated by the Monte-Carlo method as the integral

$$S = \int_{E1}^{E2} \Delta\tau(E)d(E). \quad (2)$$

In Fig. 4a the area S_1 , (obtained from a measurement carried out a day after irradiation) are plotted as a function of x . Note that the used irradiation doses are different for both glassy systems; that is why any comparison based on their values should be incorrect.

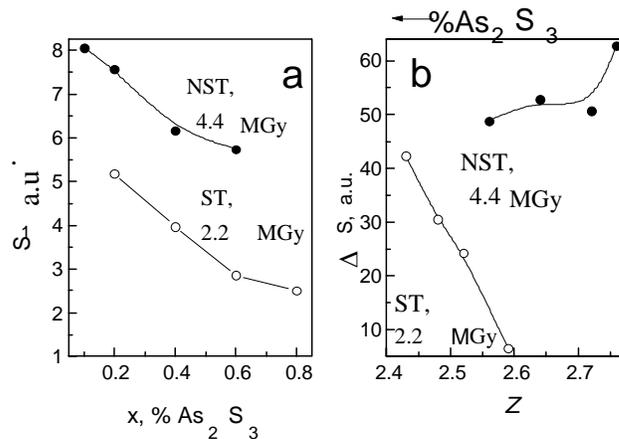


Fig. 4. (a) - The calculated area $S_1(x)$ under the $\Delta\tau$ curves, measured a day after the irradiation. (b) - The measure of an optical transmittance restoration $\Delta S = (S_1 - S_2) / S_1$.

In both systems greater changes have been induced not in the As- but in the Ge-rich compositions. A reason for this behavior can be found in the features of their local medium range order. The matrix of these ternary glasses is composed by As-S pyramids and Ge-S tetrahedra forming different clusters interconnected one to another through the chalcogen atoms. In [21] the presence of voids in the structure, appropriate to GeS_2 crystals, is supposed to take place in the $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses as well. Elliott [26] has proposed the cluster/voids model for both As_2S_3 and GeS_2 structures. In the ST system the increase of GeS_2 should increase the amount (or the dimension) of voids because of its possibility to form bigger clusters than As_2S_3 . This conclusion follows from investigations of the position of their first sharp diffraction peaks. The mean atomic volume of the $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses also increases sternly with the decrease of x [20]. That is why glasses with more GeS_2 are easily influenced by γ -irradiation (Fig. 4a) because of their looser structure.

As concerning the NST glasses, although they have almost the same structural units as the ST ones [18], they exhibit two essential structural differences: *i*) short range structure differences (many defect homopolar bonds) and *ii*) medium range differences (2D structure for $x = 0.4$ and 0.6 ; 3D structure for $x = 0.1$ and 0.2). The greater γ -induced changes in the NST glasses with higher Ge-content are due to their higher degree of chemical disorder and to their 3D fragile structure [16].

In Fig. 4 (b) the curves illustrate the degree of optical transmission restoration in both systems after 4 months. The relative change $\Delta S = (S_1 - S_2)/S_1$ is plotted vs. Z (the average coordination number of the compositions). S_1 are the area, calculated oneday after the irradiation, S_2 - 4 months later. The smaller is ΔS , the smaller is the dynamic component, i.e. the greater are self-restored the induced optical (and structural) changes. It is seen that the Ge-rich ST glasses recover easier, while the NST glasses have a greater static component. It should be stressed once more that the glasses with $Z < 2.67$ have 2D structure, which is more flexible than the 3D one. May be this is the reason for the peculiarities of the restoration effect.

Some Raman scattering spectra of the investigated glasses must be used in order to explain the observed radiation-structural transformations [27]. The dose of γ -irradiation in this case was about 1 MGy and the curves were obtained 8 months after the irradiation. Changes in the Raman spectra of the ST glasses could not be seen. Some differences between the non-irradiated and γ -irradiated NST glasses were registered. In Fig. 5 the spectra of two representative NST glasses are shown. It should be mentioned that the vibrational modes of the main structural fragments of the Ge-As-S glasses have similar Raman activities. The band at 340 cm^{-1} is due to As-S vibrational modes in $\text{AsS}_{3/2}$ pyramids and the Ge-S vibrational band of the $\text{GeS}_{4/2}$ tetrahedra is situated very near - at 344 cm^{-1} . In the glass with $x = 0.8$ (curve 2, 2') the vibrational band of the main structural units retains its form after γ -irradiation. A change in the bands $\sim 185, 230\text{ cm}^{-1}$ that are connected with As-As bonds vibrational modes is hardly seen. In the Ge-rich glass (curve 1, 1') an increase and broadening in the $230 - 250\text{ cm}^{-1}$ region are better expressed because the amount of defect homopolar As-As and Ge-Ge bonds increases after γ -irradiation. In this spectrum the Raman scattering at 430 cm^{-1} is strongly changed after irradiation (curve 1, 1'). This band can be related to the increase of homopolar S-S bonds [18, 28, 29]. Thus the Raman spectra give another prove for the defect bonds augmentation in the Ge-rich NST glasses after γ -irradiation. According to [29] these defect bonds can be related to the increase of the band tails in the band-gap and to the darkening effect.

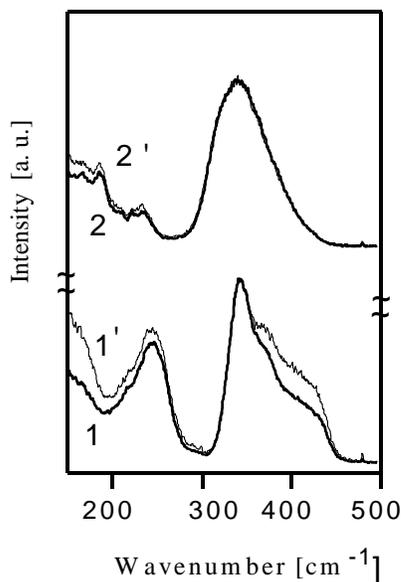


Fig. 5. Raman spectra of non-irradiated (1, 2) and γ -irradiated (1', 2') $(\text{As}_2\text{S}_3)_x(\text{Ge}_2\text{S}_5)_{1-x}$ glasses with $x = 0.2$ (1, 1') and $x = 0.8$ (2, 2') [27]. Each pair of curves (1 and 1', 2 and 2') is normalized with respect to the peak intensity of the main structural units ($\sim 340 \text{ cm}^{-1}$).

As concerning the possibility of checking the γ -induced changes in the main structural units other experiments will be carried out. They could be proved by IR Fourier spectroscopy method where the main structural fragments have relatively separated spectral activities. The results of IR Fourier spectroscopy measurements of Ge-As-S glasses will be published later.

4. Conclusions

The investigation of γ -irradiation of Ge-As-S glasses has shown that the induced optical (and structural) changes are similar to the reversible photoinduced ones and can be explained by the same phenomenological models. The presence of defect bonds in the structure and the possibility of bond rearrangements are the main reasons for the occurrence of these changes.

When the relative amount of As_2S_3 in the glasses increases, the observed γ -darkening effect in both ST and NST glasses decreases.

The γ -induced changes in the optical properties of Ge-As-S glasses consist of two components: dynamic component and a static component. The dynamic component is time dependent.

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