

ON THE PHOTO-DARKENING IN SOME Ge-As-S GLASSES

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In the series of Ge-As-S bulk glasses the maximum in photo-darkening sensitivity was found for the chemical compositions where the mean coordination number lies in the region 2.6-2.7. This result is in agreement with the original result by Tanaka et al. [1]. Far infrared and Raman spectra indicate that these glasses are most probably, in the sense of Boolchand's approach, nano-phase separated. It is suggested that nano-phase separation contributes to the molecular like character of the glasses and it enhances the ability of material to photo-induced changes in intermolecular interaction which assists the photo-darkening.

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1. Introduction

In 1986 Ke. Tanaka et al [1] showed that in certain Ge-As-S, Ge-S and Ge-Se glasses the magnitude of reversible photo-darkening measured as the red shift of the optical gap (dE_g) has a maximum at a chemical composition for which the mean coordination number ($\langle CN \rangle$) is close to 2.65 ($CN_{Ge} = 4$, $CN_{As} = 3$, $CN_S = 2$). This finding could indicate that somewhere in the region $2 < \langle CN \rangle < 3$ the glasses have appropriate intermolecular volume for the occurrence of the photo-induced structural change and simultaneously the structure is sufficiently rigid to conserve photo-induced structural change [1]. Subsequently in the series of papers, see e.g. [2-11] various properties of Ge-As-S amorphous thin films and bulk glasses, inclusive $(Ge_2S_3)_x(As_2S_3)_{1-x}$ system were studied in relation to photo-induced (photo-structural) phenomena. In most of cases the most sensitive materials to illumination were found for chemical compositions where $\langle CN \rangle \approx 2.7$. According to Vateva et al [11] this finding indicates that ...“the structural changes are optimal in compositions around the percolative 2D \rightarrow 3D transition”. Recently, however, Mamedov et al. [12] showed that $(Ge_2S_3)_x(As_2S_3)_{1-x}$ glasses are partially polymerized, and consist of characteristic nano-phases e.g. As_4S_4 , As_4S_3 monomers in the region where $2.4 < \langle CN \rangle < 2.8$. This finding relates to the question whether photo-induced changes in intermolecular interaction between monomers and between monomers and backbone assist to photo-darkening and hence, whether a nano-phase separation enhances photo-induced phenomena.

In this work we have examined some glasses studied by Tanaka et al [1] in order to identify possible indices of nano-phase separation in the region of maximal photosensitivity of these glasses.

2. Experimental

The glasses were prepared by direct synthesis from germanium, sulphur and from pre-synthesised As_2S_3 and As_4S_4 . The components of total mass 7g were placed in quartz ampoules. The ampoules were evacuated to $p \approx 10^{-3}$ Pa, sealed and inserted into a rocking furnace. After annealing at 950 °C for 12 h the ampoules were cooled in water and subsequently they were annealed for 2h at

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the glass-transition temperature (T_g) presented in Ref.[1]. The softening temperature (T_s) was determined from dilatometry measurements using TMA CXO3R system. Both transmission (T) and reflection (R) in the visible region were measured using a Perkin-Elmer Lambda 12 spectrophotometer. The samples for optical transmission measurements were prepared in the form of slides polished to optical quality on both sides. The thickness (d) of these samples was around 0.05 cm. The samples for reflectivity measurements (d = 0.3 cm) were polished on one side only while the opposite side of the samples was roughened and covered by black absorbing paste. Far-infrared reflectivity was measured using an FTIR Nicolet Nexus spectrophotometer. The Raman spectra were measured using an FTIR spectrophotometer IFS 55 (Bruker Germany) provided with an FRA 106 Raman module in back scattering geometry using a Nd:YAG laser beam (90 meV, 1064 nm) as the excitation light. The number of scans was 150, the resolution was 2 cm^{-1} . The samples with thickness $d = 0.05 \text{ cm}$ were illuminated for 6 h at the room temperature by white light using a Hund FLQ 150M light source equipped with a light guide. The incident power density was around 200 mW/cm^2 .

3. Results

In Fig. 1 the spectral dependencies of absorption coefficient (α), in the region of Urbach edge are shown. In the Table 1 are summarised both the values of the glass-transition temperatures (T_g) and the optical gaps (E_g) defined as the photon energy for $\log(\alpha) = 3.5$ taken from Ref.[1] and our T_s and E_g values. The differences between T_g and T_s values reflect different origin of both quantities, however, some correspondence is seen between the changes in T_g and T_s values.

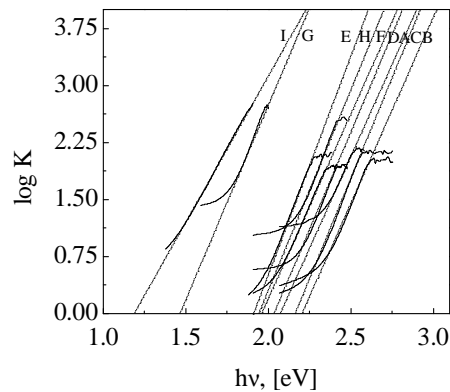


Fig. 1. The spectral dependencies of the absorption coefficient (K) in the Urbach edge region. The full curves are experimental results, the dashed lines are fits to the relation: $K = K_0 \exp(hv/\sigma)$, where σ is the reciprocal slope of Urbach edge. The letters A-I indicate the chemical composition of the glasses, see Table 1.

The differences between E_g values, except of the sample C are acceptable and could be associated to different way of the samples preparation. For a rough estimation of photo-darkening we used illumination by white light only. In this case the whole volume of the illuminated sample can not be homogeneously darkened because most of photons with energy above band gap are absorbed within the thickness much less than the thickness of our samples. Hence for rough estimation of photo-sensitivity we used only the ratio (r) of the sample transmission after illumination to the transmission before illumination ($r = T_{\text{illuminated}}/T_{\text{before}}$). In Fig. 2a are shown spectral dependencies of the ratio r together with the spectral distribution of our white light source. In Fig. 2b are shown normalised values of photo-darkening taken for relevant glasses from Ref.[1] and our normalised r values versus $\langle \text{CN} \rangle$. Except the sample C (the chemical composition $\text{Ge}_{25}\text{As}_{10}\text{S}_{65}$, $\langle \text{CN} \rangle = 2.6$) the general trend in both results is similar, that is the maximum of photo-darkening is observed for the chemical compositions $\text{Ge}_{20}\text{As}_{20}\text{S}_{60}$, $\text{Ge}_{20}\text{As}_{25}\text{S}_{55}$, see Tab.1, that is for $\langle \text{CN} \rangle$ in the region 2.6 - 2.7. Hence we suppose that our results are in reasonable agreement with the results of Ref. [1].

Table 1. Atomic fractions of Ge, As and S in the glasses prepared, the mean coordination number ($\langle CN \rangle = (4[Ge]+3[As]+2[S])/100$, where [] is in at% of Ge,As,S, respectively), the glass-transition temperature ($T_{g,T}$), the optical gap ($E_{g,T}$) taken from Ref.[1] and our values of both the softening temperature (T_s) and the optical gap (E_g).

Symbol	Ge, [at%]	As, [at%]	S, [at%]	$\langle CN \rangle$	$T_{g,T}$, [K]	$E_{g,T}$, [eV]	T_s , [K]	E_g , [eV]
A	10	20	70	2.40	470	2.76	530	2.79
B	20	10	70	2.50	550	2.88	560	2.92
C	25	10	65	2.60	600	3.01	660	2.82
D	20	20	60	2.60	590	2.73	630	2.72
E	20	25	55	2.65	620	2.50	640	2.51
F	30	10	60	2.70	660	2.67	720	2.60
G	20	30	50	2.70	600	2.37	620	2.14
H	30	25	45	2.85	700	2.33	730	2.52
I	40	15	45	2.95	660	2.10	700	2.09

The examined glasses can be divided into two groups. In the first group, the samples A-C, the content of the sulphur atoms is sufficient for the coordination of Ge and As atoms by sulphur atoms only. The network of these glasses is formed by AsS_3 pyramids and GeS_4 tetrahedra. In the samples A,B some -S-S- bonds should be present because these samples are sulphur rich. The samples D-I are sulphur poor glasses and some Ge-Ge and As-As bonds should be present in these glasses. We suppose that owing to the well known tendency of Ge atoms to maximise coordination by S atoms, see e.g. [12-15], the density of AsS_3 pyramids in this group of glasses is rather low and most of As-S based network is formed by entities like As_4S_4 and As_4S_3 , while Ge-S based part of the network is composed mainly by (i) GeS_4 tetrahedra, (ii) ethane-like units $S_3Ge-GeS_3$ (Ge_2S_3), depending on the actual chemical composition and (iii) distorted rocksalt-like GeS entities, namely the samples H, I, see e.g.[12].

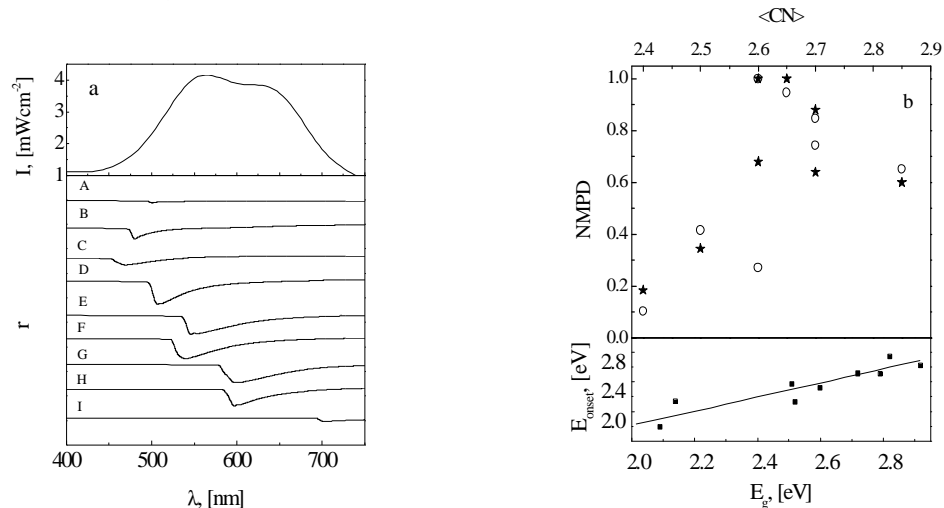


Fig. 2a. Upper part - the spectral distribution of the white light source used for the samples illumination. Lower part - the spectral dependencies of the ratio $r = T_{\text{illuminated}}/T_{\text{before}}$. The letters indicate the chemical composition, see Table 1.

Fig. 2b. Upper part - the open circles show the normalised magnitude of photo-darkening (NMPD) versus $\langle CN \rangle$. NMPD is the amplitude of an "absorption like band" in $r(\lambda)$ dependence divided by the amplitude of the "absorption like band" for the sample D. The asterisks show the normalised magnitude of photo-darkening ($\Delta E_g / \Delta E_g(D)$) taken from the ΔE_g (the red shift of the gap) values in Ref.[1]. Lower part - a correlation between the energy corresponding to the short wavelength onset of the "absorption like band", see Fig. 2a and the optical gap.

The most typical infrared active feature (IRF) of AsS_3 pyramids in e.g. As_2S_3 lies at around 310 cm^{-1} (i.r. ν_3) [16] and the most typical IRF of As_4S_4 and As_4S_3 lie at around 340 cm^{-1} and 370 cm^{-1} , see e.g. [17]. The most typical stretching frequency of Ge-S bonds lies at around 370 cm^{-1} [16]. In Fig. 3 far-infrared (IR) spectra after Kramers-Kronig transformation are shown in the region of bond stretching frequencies. The spectra for the samples A-H indicate a two-mode behaviour (Fig. 3). The first broad infrared feature (IRF) at around 330 cm^{-1} we assign to a combination of the stretching motion of As and S atoms, see e.g. [18]. Broadening of this IRF and its shift to high frequency region we associate with inter-cluster coupling between Ge-S network and As-S network realized e.g. by $\equiv\text{Ge}-\text{S}-\text{As}=\text{}$ bridges, and also with appearance of As_4S_4 and As_4S_3 entities, namely for the samples D-G. The second broad IRF at around $370\text{-}380 \text{ cm}^{-1}$ we assign to stretching frequency of Ge-S bonds combined, however, with IRF of As_4S_4 and As_4S_3 , namely for the samples D-G. Of interest is high frequency broadening of this IRF. This broadening, for the samples A-F we associate to edge shared GeS_4 tetrahedra [19]. The single broad IRF for the samples H,I we suppose is due to combination of As,Ge and S stretching motion in various entities like e.g. As_4S_4 , As_4S_3 , $\text{Ge}_x\text{S}_{3-x}\text{Ge-GeS}_{3-x}\text{Ge}_x$ ($x = 0,1,2$) and GeS .

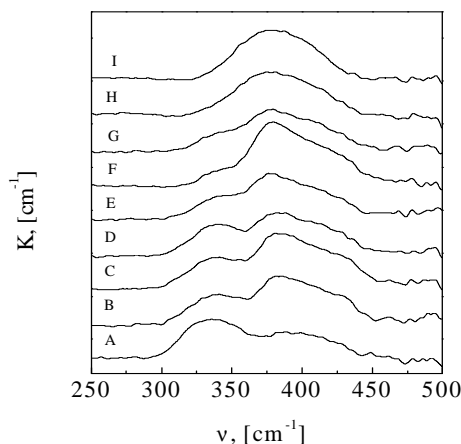


Fig. 3. The spectral dependencies of absorption coefficient calculated from far infrared reflectivity spectra. The letters indicate the chemical composition, see Table 1.

The most typical Raman active (R) stretching frequencies of As-S bond in e.g. AsS_3 pyramids lie at around 345 cm^{-1} (R, ν_1) and 310 cm^{-1} (R, ν_3), Raman active stretching frequencies of Ge-S bond lie at around 345 cm^{-1} (R, ν_1) and 367 cm^{-1} (R, ν_3), respectively [16]. The most intensive Raman features (RF) due to As-S stretching in As_4S_4 are in the region $330\text{-}370 \text{ cm}^{-1}$ and the other intensive RF of As_4S_4 are observed in the region $170 \text{ cm}^{-1} - 240 \text{ cm}^{-1}$ [20]. In the region around 250 cm^{-1} and below 250 cm^{-1} symmetric Raman modes are observed in Ge-rich Ge-S glasses due to tetrahedra with fewer than four sulphur atoms [18]. In Fig. 4 Raman spectra are shown for some most typical studied glasses together with Raman spectra of As_4S_3 . The first broad RF at around 350 cm^{-1} for the A,C,E,F,G samples we assign to a combination of As-S and Ge-S stretching. The very weak but resolved RF at around 475 cm^{-1} , the sample A, we assign to presence of S_8 rings [21]. It means that within the network of this glass, (formed by AsS_3 pyramids and GeS_4 tetrahedra), the S_8 rings or “meandering” like S_8 rings are dispersed. For the sample A and for the stoichiometric glass, the sample C, there are no other RF observed below 300 cm^{-1} , hence, one can assume that density of structural entities composed by homo bonds (As_4S_4 , As_4S_3 , $\text{Ge}_x\text{S}_{3-x}\text{Ge-GeS}_{3-x}\text{Ge}_x$) is very weak in this case. For the S-poor glasses, the samples E,F,G,H, however, significant RF are seen below 300 cm^{-1} . The broad features below 270 cm^{-1} we suppose indicate a presence of As_4S_4 , As_4S_3 , and $\text{Ge}_x\text{S}_{3-x}\text{Ge-GeS}_{3-x}\text{Ge}_x$ entities where $0 < x < 3$. The well distinct RF at around 270 cm^{-1} , the samples E,G is a clear indication of presence of As_4S_3 molecular entities in the matrix of this glasses. Consequently the S-poor glasses are formed by various structural entities of which at least As_4S_4 and As_4S_3 can be present in the form of monomers, see e.g. [12]. We suppose that formation of As-As bonds and hence the formation of As_4S_4 and As_4S_3 entities is enhanced by a tendency of Ge atoms to be four fold coordinated by S atoms. This means that the network around the Ge atoms could be rather well ordered. This suggestion seems to be supported by the high frequency broadening of the

first RF at around 350 cm^{-1} , where for the samples C,E,F,G the shoulder around 435 cm^{-1} indicates the presence of edge shared GeS_4 tetrahedra [19].

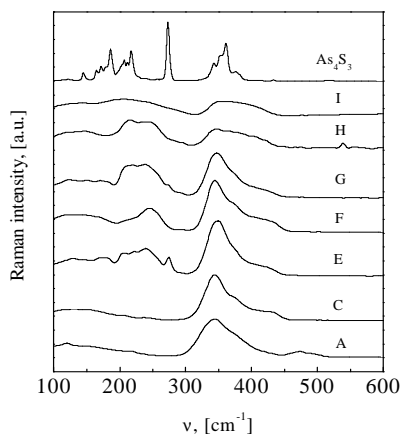


Fig. 4. Raman spectra for some most typical samples. The letters indicate the chemical composition, see Table 1. Upper part - Raman scattering from As_4S_3 polycrystalline sample.

4. Discussion

The results of infrared and Raman spectroscopy support the assumption that studied photo-sensitive S-poor glasses are composed by several structural entities of which As_4S_3 molecular entities were unambiguously identified in the glasses E,G. We note that the presence of As_4S_3 has been observed also in the glass D [13,22]. In Fig. 5 the glass forming region in the Ge-As-S system is shown [12], where the studied glasses are marked by open circles. It is evident that the most photo-sensitive glasses, see Fig. 2b, lie in the region where nano-scale phase separation appears associated with precipitation of As_4S_4 and As_4S_3 monomers, see e.g. [12]. According to Elliott [23] photo-darkening results from photo-induced intra-molecular and/or inter-molecular bond scission. In the present glasses pronounced nano-phase separation significantly contributes to the molecular like character of the glasses, hence, the probability of photo-induced changes in intermolecular interaction between monomers and between monomers and backbone increases and photo-sensitivity increases too. This seems to be in correspondence with the statement given by Skordeva et al [24] "... that Ge-As-S films and glasses are more sensitive to structural changes on illumination, heating and pressure than Ge-As-Se films and glasses...". In selenium poor Ge-As-Se glasses Ge-Ge and As-As bonds nucleate as part of the backbone [25]. In such case nano-scale phase separation is much less pronounced in Ge-As-Se glasses contrary to Ge-As-S glasses and consequently less photo-sensitivity of Ge-As-Se glasses is observed.

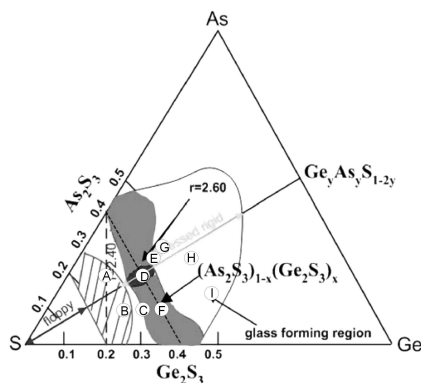


Fig. 5. The glass forming region in Ge-As-S system taken from Ref. [12]. The green region indicates the intermediate phase, the brown red area indicates the region where nano-phase separation is suggested and the deeper brown red region indicates the area where As_4S_4 and As_4S_3 monomers are pervasive which results into nano-scale phase separated networks [12]. The letters indicate the position of studied samples in the diagram.

5. Conclusion

In the As-rich glasses where $\langle \text{CN} \rangle$ is around 2.6-2.7 the formation of As-As bonds associated with a strong tendency of Ge atoms to be maximally coordinated by the sulphur atoms enhances nano-phase separation due to formation of molecular entities like As_4S_4 and As_4S_3 monomers. The molecular like character of a glass network increases and simultaneously the density of strained homo As-As bonds increases too. Hence, the probability of photo-induced intra-molecular and inter-molecular bond scission increases and the magnitude of photo-darkening is enhanced. This suggestion could be an alternative to that one based on the idea that the high photo-darkening sensitivity of the chemical compositions where $\langle \text{CN} \rangle \approx 2.7$ is associated with the percolative 2D \rightarrow 3D transition.

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References

- [1] Ke. Tanaka, T. Nakawa, A. Odajima, *Philos. Mag. Lett.* **54**, 23 (1980).
- [2] E. Vateva, E. Skordeva, D. Arsova, *Philos. Mag.* **B 67**, 225 (1993).
- [3] K. Petkov, B. Dinev, *J. Mat. Sci.* **29**, 468 (1994).
- [4] E. Skordeva, D. Arsova, *J. Non-Cryst. Solids* **192&193**, 665 (1995).
- [5] R. Ston, M. Vlček, H. Jain, *J. Non-Cryst. Solids* **326&327**, 220 (2003).
- [6] M. Popescu, F. Sava, A. Lorinczi, E. Skordeva, P. J. Koch, H. Bradaczek, *J. Non-Cryst. Solids* **230 (B)**, 719 (1998).
- [7] K. Christova, Z. Dimitrova, E. Skordeva, *Thin Solid Films* **396**, 174 (1997).
- [8] E. Skordeva, K. Christova, M. Tzolov, Z. Dimitrova, *Appl. Phys.* **A 66**, 103 (1998).
- [9] E. Vateva, M. Nikoforova, E. Skordeva, *J. Non-Cryst. Solids* **77&78**, 1133 (1985).
- [10] O. I. Shpotyuk, A. P. Kovalskiy, E. Skordeva, E. Vateva, D. Arsova, R. Ya. Golovchak, M. M. Vakiv, *Physica B* **271**, 242 (1999).
- [11] E. Vateva, E. Skordeva, *J. Optoelectron. Adv. Mater.* **4**, 3 (2002).
- [12] S. Mamedov, D. G. Georgijev, Tao Qu, P. Boolchand, *J. Phys.: Condens. Matter* **15**, S2397 (2003).
- [13] B. G. Aitken, C. W. Ponader, *J. Non-Cryst. Solids* **256&257**, 143 (1999).
- [14] R. Vahalová, L. Tichý, M. Vlček, H. Tichá, *phys. stat. sol. (a)* **181**, 199 (2000).
- [15] M. Munzar, L. Tichý, *J. Phys. Chem. Solids* **61**, 1647 (2000).
- [16] G. Lucovsky, R. J. Nemanich, S. A. Solin, R. C. Keezer, *Solid State Commun.* **17**, 1567 (1975).
- [17] M. D. Mikhailov, I. I. Kryzhanowski, I. M. Petcherizin, *J. Non-Cryst. Solids* **265**, 1 (2000).
- [18] G. Lucovsky *Vibrational properties of amorphous solids in Physical Properties of Amorphous Materials* (eds. D. Adler, B. B. Schwartz and M. C. Steele), Plenum Press, New York, 1985.
- [19] K. Jackson, A. Briley, S. Grossman, D. V. Prezag, M. R. Pederson, *Phys. Rev.* **B60**, R14985 (1999).
- [20] M. Muniz-Miranda, G. Sbrana, P. Bonazzi, S. Menchetti, G. Pratesi, *Spectrochimica Acta A* **52**, 1391 (1996).
- [21] G. Lucovsky, F. L. Galeener, R. C. Keezer, R. H. Geils, H. A. Six, *Phys. Rev.* **B 10**, 5134 (1974).
- [22] M. Kincl, L. Tichý, to be published.
- [23] S. R. Elliott, *J. Non-Cryst Solids* **81**, 71 (1986).
- [24] E. R. Skordeva, D. D. Arsova, *J. Non-Cryst Solids* **192&193**, 665 (1995).
- [25] T. Qu, D. G. Georgiev, P. Boolchand, M. Micoulaut, *Mat. Res. Soc. Symp. Proc. Vol.* **754**, CC8.1.1 (2003).