

Non-linear optical properties and structure of wide band gap non-crystalline semiconductors

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Received 3 October 2010, accepted 4 February 2011

Published online 11 May 2011

Keywords Raman scattering, chalcogenide glasses, nonlinearities, XPS spectra

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The non-linear two-photon absorption coefficient (TPA) of ternary Ge-As-S glasses of different sections (As_2S_3 - GeS_2 , As_2S_3 - Ge_2S_3 , As-GeS_2 , $\text{As-Ge}_2\text{S}_3$) was measured at 690 nm. The obtained data were interpreted based on the evolution of the glass structure and mean coordination number with the composition. Raman spectroscopy was used to investigate the bonding configuration of the

glasses and the structural interpretation of the vibrational bands was performed based on DFT calculations of vibrational spectra of different types of $\text{As}(\text{Ge})_n\text{S}_m$ clusters and XPS measurements. It was found that the TPA is decreasing near the magic coordination numbers of 2.4 and 2.67. Relationship between TPA and nanophase separation in ternary glasses is discussed.

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1 Introduction Due to their outstanding optical properties nowadays chalcogenide glassy semiconductors (ChGS) are widely used in optoelectronics. The field of their application can be extended further by utilization of non-linear optical properties. Earlier non-linear optical properties of binary ChGS glasses with small additives were studied using short pulse laser illumination [1-3]. At the beginning of this century new data have been published on unique combination of non-linear characteristics in ChGS: large ultrafast non-linear refractive index (n_2) and low two-photon absorption (TPA) coefficient (β), which are connected through the figure of merit ($\text{FOM} = n_2/\beta\lambda$, where λ is the wavelength of the coherent illumination), a geometry-independent criteria, widely used to classify different non-linear materials. Non-linearities in ChGS were found to be as high as 900x that of fused silica and can be applied to all-optical switching [4-7].

In isotropic non-linear optical media major contribution to n_2 comes from one and two-photon resonant processes [8]. It is expected that, when added to binary sulphide glasses, germanium and selenium, being heavier than sulphur, will raise the linear index of refraction and so enhance the nonlinearity in multinary glasses [5, 8].

In $\text{Ge}_x\text{As}_y\text{S}_{1-x-y}$ type ternary glasses with coordination numbers of 4, 3, 2 for Ge, As, S respectively, the dependence of optical properties on mean coordination number $z = 4x + 3y + 2(1-x-y)$ manifests extrema at $z = 2.4$ and 2.67 [2, 3, 7]. According to the Thorpe-Philips model at $z = 2.4$ the structure of glass becomes rigid [9]; in the $2.4 < z < 2.8$ region stressed-rigid structure can be obtained [10]; in the frames of Tanaka model [11] at $z = 2.67$ topological phase transition occurs in network connectivity from two dimensional to three dimensional structure.

Earlier it was suggested [12] that the concentration of lone-pair electrons plays key role in ultrafast nonlinear optical responses. In ChGS the chalcogen atoms are twofold coordinated [2, 9, 11]. So only two of their four p electrons form covalent bonds; the remaining two will be lone pair electrons [9, 11]. On the other hand, in Ge-rich glasses one of the identified phases was containing threefold coordinated Ge and threefold coordinated S atoms, similarly to the crystalline c-GeS [3, 13], in which there are no lone-pair electrons.

So in order to improve non-linear properties of ChGS new compositions have to be found based on a strategy that takes into account also the evolution of the structure in glasses during modification of glass matrix. Here we report

on our results obtained in systematic study of the relationship between the structure, TPA and linear optical properties in wide band gap chalcogenide glasses of Ge-As-S system along different sections.

2 Experimental and theoretical details The glasses for investigation were synthesized by ampoule method with further purification of elementary components before being melted, in accordance with procedure described in [2, 3]. Band gap (E_0) was determined from absorption spectroscopic data by estimating E_0 for $\alpha=1000\text{ cm}^{-1}$. Refractive index was measured by prism method. Raman spectra were recorded using a Renishaw System 1000 Raman spectrometer. A diode laser operating at 785 nm was used as excitation source. Investigation of two photon absorption was made by experimental measurement of transmittance of pulsed coherent illumination of ruby laser at 690 nm ($E=1.8\text{ eV}$) and $\tau=40\text{ ns}$ [2]. The TPA coefficient (β) was obtained from the intensity dependence of light transmission. The binding energies of core electrons were determined using a Vacuum Generators ESCA spectrometer with Mg-K α X-ray source (1253.6 eV). The computational procedure consisted of geometry optimization and ab initio calculation of vibrational modes of different As_nS_m and Ge_nS_m nanoclusters, as it was described earlier [14, 15].

Table 1 Vibrational mode frequencies (ν , cm^{-1}) and Raman intensities (I^R , $\text{\AA}^4/\text{a.m.u.}$) of Ge_nS_m clusters (HF/6-311G*).

Cluster	ν^*	I^R	Cluster	ν^*	I^R
$\text{Ge}_2\text{S}_{1+6/2}$	342	49.3	$\text{Ge}_3\text{S}_{3+6/2}$	347	52.6
	399	11.1		399	9.7
	408	16.5		406	6.7
	411	5.2		408	17.2
	411	14.4		411	5.7
	415	5.3		414	22.4
	419	15.1		417	8.5
$\text{Ge}_2\text{S}_{2+4/2}$	348	6.3	$\text{Ge}_3\text{-S}_{6/3}$	211	12.4
	381	59.9		212	11.0
	413	25.4		217	6.3
	441	19.1		223	10.9
				246	9.9
$\text{Ge}_2\text{S}_{6/2}$	250	25.4	274	5.8	
	391	35.0			
	396	18.9			
	402	20.9			
	407	5.8			
	409	11.6			

* The empirical scaling factor of 0.940 was used.

3 Results and discussion Optical edge of the absorption spectra of different $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses are shown in Fig. 1. It can be seen that the absorption edge continuously shifts to higher energies with increasing GeS_2 content. All samples exhibit an exponential (Urbach) tail in their absorption edge in range of $1 < \alpha < 10^3\text{ cm}^{-1}$. Starting

from $x=0.4$ the sharpness of the absorption edge decreases and the slope of the Urbach tail is monotonically increases with GeS_2 content and reaches maximum for the binary

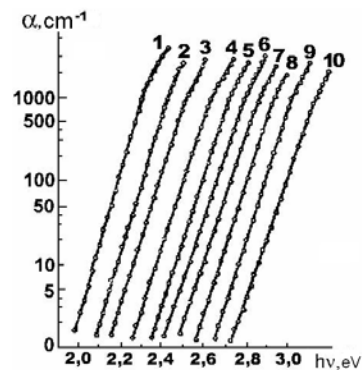


Figure 1 Edge absorption spectra of $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses: (1) $x=1.0$; (2) $x=0.9$; (3) $x=0.7$; (4) $x=0.6$; (5) $x=0.5$; (6) $x=0.4$; (7) $x=0.3$; (8) $x=0.2$; (9) $x=0.1$; (10) $x=0.0$.

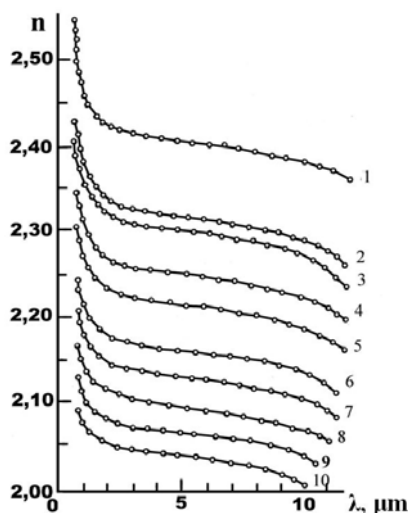


Figure 2 Dispersion of the refractive index of $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses. (1) $x=1.0$; (2) $x=0.9$; (3) $x=0.7$; (4) $x=0.6$; (5) $x=0.5$; (6) $x=0.4$; (7) $x=0.3$; (8) $x=0.2$; (9) $x=0.1$; (10) $x=0.0$.

glass g- GeS_2 . The increase of the band gap E_0 from 2.35 eV (g- As_2S_3) to 3.2 eV (g- GeS_2) is accompanied by the decrease of the refractive index at 690 nm from 2.57 to 2.12 (Fig. 2). It can be seen also (Fig. 1) that the level of linear absorption at 690 nm (1.8 eV) is less than 1 cm^{-1} for all samples.

For $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses with increasing GeS_2 content a monotonic decrease in β can be observed from 0.1 cm^2/MW for $x=1$ to $\beta=0.01\text{ cm}^2/\text{MW}$ for $x=0.3$ ($z=2.47$) (Fig. 3). It may be connected with growing connectivity of the structure and the decreasing number of states in the band gap, which was considered as main factor responsible for TPA in amorphous materials [4, 8]. Figure 4 shows the dependence of the band gap on the mean coordination

number in ternary $\text{Ge}_x\text{As}_y\text{S}_{1-x-y}$ glasses. We have shown earlier that during technological modification of binary arsenic tri-sulphide the nanophase inclusions of realgar type $r\text{-As}_4\text{S}_4$ molecules modify the optical properties and change the level of TPA in $g\text{-As}_2\text{S}_3$ [16].

Our recent analysis has shown that orpiment-like rings are energetically favorable among different As_nS_m nanoclusters and so they may be present in the matrix of $g\text{-As}_2\text{S}_3$ [17] too. If we subtract the Raman spectrum of $g\text{-As}_2\text{S}_3$ with broad band at 342 cm^{-1} from Raman spectra of $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses, the differential Raman spectra clearly show the decreasing intensity of As-As vibration of realgar type (r) $r\text{-As}_4\text{S}_4$ molecules at 185 cm^{-1} [14] (see Fig. 5).

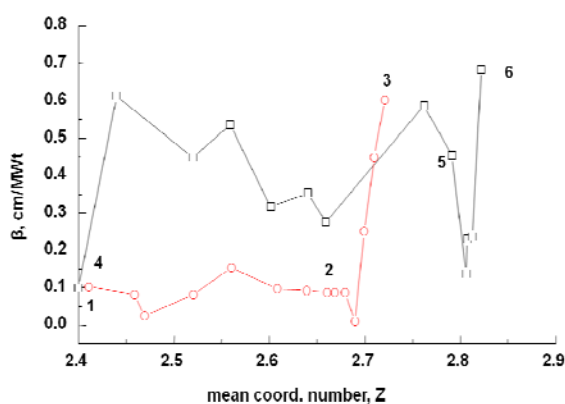


Figure 3 Dependence of the TPA coefficient (β) on the mean coordination number (Z) in $\text{Ge}_x\text{As}_y\text{S}_{1-x-y}$ glasses along different sections: (1-2) $\text{As}_2\text{S}_3\text{-GeS}_2$; (2-3) As-GeS_2 ; (4-5) $\text{As}_2\text{S}_3\text{-Ge}_2\text{S}_3$; (5-6) $\text{As-Ge}_2\text{S}_3$.

In addition new small bands appear at 347 and 416 cm^{-1} . First candidates for their assignment are $\text{Ge}_3\text{S}_{3+6/2}$ rings composed of $\text{GeS}_{4/2}$ tetrahedrons connected by corners and having main intensive vibrational frequencies at $347, 408, 414$ and 422 cm^{-1} (see Table 1).

Starting from $x=0.4$ a new broad band appears in differential Raman spectra of ternary glasses with GeS_2 at 240 cm^{-1} which can be assigned to valence vibration of Ge-S bonds in $\text{SGe}_3\text{-S}_{6/3}$ minority nanoclusters with 3-fold coordinated Ge and S (Table 1). For higher x values the intensity of the band slightly increases and it shifts to 250 cm^{-1} (Fig. 3). According to Table 1 peak with maximum at 250 cm^{-1} can be assigned to ethane-like vibration of $\text{Ge}_2\text{S}_{6/2}$ nanoclusters connected with Ge-Ge bonds. So the broad band around 250 cm^{-1} having shoulders at $211, 220$ and 270 cm^{-1} is formed probably by overlapping valence vibration bands of minority-type $\text{SGe}_3\text{-S}_{6/3}$ and $\text{Ge}_2\text{S}_{6/2}$ nanoclusters. This conclusion is in good agreement with earlier structural interpretation of vibrational spectra of Ge-containing sulphide glasses [18-23].

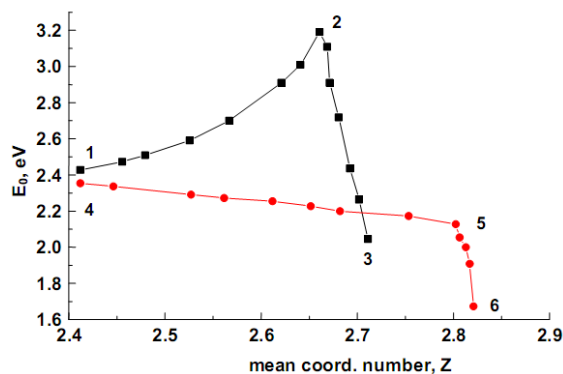


Figure 4 Dependence of the band gap (E_0) on the mean coordination number (Z) in $\text{Ge}_x\text{As}_y\text{S}_{1-x-y}$ glasses along different sections: (1-2) $\text{As}_2\text{S}_3\text{-GeS}_2$; (2-3) As-GeS_2 ; (4-5) $\text{As}_2\text{S}_3\text{-Ge}_2\text{S}_3$; (5-6) $\text{As-Ge}_2\text{S}_3$.

For compositions with $x > 0.4$ another three bands appear in the Raman spectra of $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses at $342, 375$ and 435 cm^{-1} (Fig. 5) the intensity of which increases with the GeS_2 content. The first band can be related to valence vibration of $\text{GeS}_{4/2}$ tetrahedrons connected by corners in $\text{Ge}_2\text{S}_{1+6/2}$ clusters (Table 1) and the next two - to vibrations of $\text{GeS}_{4/2}$ clusters connected by edges. A more detailed description of structural interpretation of these three bands is given in [14, 15].

Comparison of vibrational frequencies of major nanoclusters presented in Table 1 and the Raman spectra of glasses with $x > 0.4$ (Fig. 3) shows that the band at 416 cm^{-1} (appearing as a shoulder in Raman spectrum of $g\text{-GeS}_2$) is an overlapping band arising from vibrations of ring type $\text{Ge}_3\text{S}_{3+6/2}, \text{Ge}_2\text{S}_{1+6/2}$ and $\text{Ge}_3\text{S}_{3+6/2}$ clusters.

Based on our previous calculations on the band-gap of different Ge_nS_m clusters, the appearance of $\text{Ge}_2\text{S}_{1+6/2}$ and $\text{Ge}_2\text{S}_{2+4/2}$ nanoclusters in the matrix of ternary glasses will lead to broadening of the absorption edge, which is in good agreement with experimental investigations (Fig. 1, Fig. 4). Nanophase inclusion with threefold coordinated Ge and S, ethane-like clusters, etc. can form new states in the band gap of ternary glasses, which will decrease the sharpness of the Urbach tail. The increase of E_0 and formation of extra states in the band gap could cause the enhancement of TPA, what is clearly seen for wide band gap ternary glasses $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ at $x > 0.3$ ($z > 2.47$) (Fig. 3).

The increasing content of As_4S_4 and As_4S_3 cage-like clusters in As-rich compositions of the $(\text{Ge}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ section ternary glass system ($x=0.3$ and $x=0.5$) [10] leads to higher TPA values and decreasing band gap E_0 (Fig. 4) in the range of $2.4 < z < 2.55$ compare to β and E_0 values of $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses in same range (Fig. 3). Similarly to the latter section, $(\text{Ge}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ glasses with $2.46 < z < 2.66$ also contain Raman active modes of $\text{Ge}_2\text{S}_{1+6/2}$ and $\text{Ge}_3\text{S}_{3+6/2}$ clusters in their Raman spectra [10,22] (the spectra are not provided here). We suggest that their presence can lead to the increase of the band gap (Fig. 4) and could

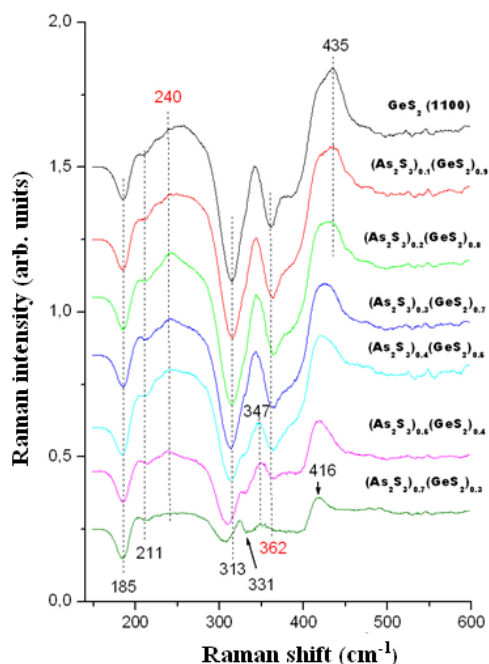


Figure 5 Differential Raman spectra of $(As_2S_3)_x(GeS_2)_{1-x}$ glasses excited with $\lambda_{exc}=785$ nm. The spectra were obtained by subtraction of the Raman spectrum of As_2S_3 from the measured spectra.

be a structural origin for the lowering of the TPA (Fig. 3). Similar peculiarities for stressed rigid network at $z=2.6$ [10] can be observed on compositional dependences of other physical properties (thermal, optical, sound velocity [10,21] in $(Ge_2S_3)_x(As_2S_3)_{1-x}$ glasses. When the composition of the ternary glass approaches to g- Ge_2S_3 ($z>2.75$) the intensity of As_4S_4 and As_4S_3 vibrations in the Raman spectrum decreases [10, 21]. This is accompanied by the decrease of TPA to the value of $\beta=0.15$ cm/MW for binary g- Ge_2S_3 ($z=2.8$).

For structural interpretation of the Raman spectrum of Ge-rich ternary glasses $Ge_2S_{1+6/2}$ chain and $Ge_3S_{3+6/2}$ ring with $GeS_{4/2}$ corner sharing tetrahedrons were considered (Table 1). In the case of g- Ge_2S_3 the $SGe_3-S_{6/3}$ and ethane-like $Ge_2S_{6/2}$ nanoclusters could contribute to the Raman spectrum in the 250-300 cm^{-1} region. (It is known that peaks at 375 and 435 are not present in the Raman spectrum of g- Ge_2S_3 so edge sharing tetrahedrons in the $Ge_2S_{2+4/2}$ chain can be excluded from the Raman interpretation (Table 1)). This conclusion is confirmed by the results of XPS measurements performed on g- Ge_2S_3 (Fig.6). Ge_{3d} electrons have a maximum at $E_b=33.0$ eV, which is slightly shifted to lower energies compare to Ge_{3d} electrons of g- GeS_2 ($E_b=33.8$ eV) [3]. This shift can be due to overlapping of XPS band of major cluster group based on four-fold coordinated Ge with the band of minority clusters containing 3-fold coordinated Ge atoms. In crystalline c- GeS , where Ge atoms are 3-fold coordinated, the maximum of Ge_{3d} peak is at 31.4 eV [3].

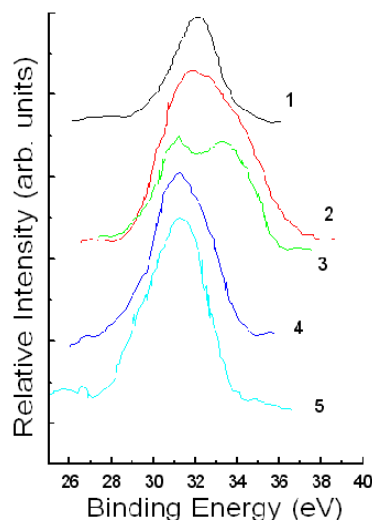


Figure 6 XPS Ge_{3d} spectra of $As_x(Ge_2S_3)_{1-x}$ glasses: (1) $x=0$; (2) $x=0.05$; (3) $x=0.10$; (4) $x=0.15$; (5) $x=0.3$.

For $x=0.05$ the width of XPS peak of $As_x(Ge_2S_3)_{1-x}$ glasses broadens and the maximum shifts to 32 eV (Fig. 6). If the As content reaches $x=0.1$, two separate bands can be distinguished in the XPS spectrum at 31.4 and 33.8 eV. This is a clear evidence of the existence of 3- and 4-fold coordinated Ge atoms in nanoclusters of Ge-As-S glasses and supports structural interpretation of Raman spectra based on the DFT calculations. For $x=0.15$ the width of the XPS peak decreases and the maximum appears at 31.4 eV, similarly to the case of $x=0.3$.

In both $As_x(Ge_2S_3)_{1-x}$ and $As_x(GeS_2)_{1-x}$ glasses for compositions with $x>0.10$ a main intense complex band at 210 cm^{-1} , typical for c- GeS , dominates the Raman spectrum. It means that optical properties of glasses of these sections are governed by clusters based on pyramidal $SGe_{3/3}$ structural units. In the frames of the concept of the influence of lone-pair electrons on non-linear properties of ChGS it means that the concentration of threefold coordinated sulphur atoms (that have no lone-pair electrons) increases. With increasing As content the band gap (Fig. 4) for glasses of both sections shifts to the value of c- GeS ($E_g=1.6$ eV) and linear absorption and TPA increase for $z>2.7$ and $z>2.8$ respectively (Fig. 3).

TPA measurements showed one exception for the $(As)_x(GeS_2)_{1-x}$ section at $0<x<0.1$ ($z \sim 2.7$). In this As concentration range the TPA value decreases to $\beta=0.01$ cm/MW at $x=0.07$, which composition has mean coordination number close to the magic value of $z=2.67$ corresponding to change in the network connectivity. It is possible that the addition of small amount of As to g- GeS_2 decrease the concentration of structural defects in the glassy network.

4 Conclusions Dependence of two-photon absorption coefficient on structure and mean coordination number in ternary Ge-As-S chalcogenide glasses of different sections

was investigated. Ternary $\text{Ge}_x\text{As}_y\text{S}_{1-x-y}$ glasses with the same mean coordination number but different composition have different properties and structure. It was found that the level of TPA is connected with the value of the band gap. The clusters with three-fold coordinated sulphur and germanium and/or ethane-like $\text{Ge}_2\text{S}_{6/2}$ cluster in the structure of ternary germanium rich glasses decrease the band gap what results in increased β value.

Acknowledgements The authors are grateful to Dr. M. Mitkova and Dr. S. Yannopoulos for helpful discussion.

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