

NANOSCALE ARRANGEMENT IN THE $\text{Ge}_x\text{As}(\text{Sb})_{40-x}\text{S}_{60}$ SYSTEMS

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The results on the studies of the structural, optical, mechanical and physicochemical properties as a function of composition and their changes induced by light, electron and γ -irradiation in glasses and/or films of the $\text{Ge}_x\text{As}(\text{Sb})_{40-x}\text{S}_{60}$ systems are reviewed. The found peculiarities are ascribed to the percolative two-to-three dimensional transition or to a chemical transition in connection with the nanoscale arrangement.

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1. Introduction

The present work is a review of our results on complex investigation on $\text{Ge}_x\text{As}(\text{Sb})_{40-x}\text{S}_{60}$ glasses and thin films. The compositional dependences of the structural, optical, mechanical and physicochemical properties of these ternary chalcogenides were studied in detail as well as the changes induced in them by heat, light, electron and γ -irradiation.

The review aims to clarify: (i) the status of the understanding of the short and medium-range order arrangement in these systems where the presence of non-stoichiometric (Ge_2S_3) and stoichiometric (As_2S_3 or Sb_2S_3) components is characteristic; (ii) the influence of the composition, x , and of the average coordination number, Z , on the prevalence of the different nano-structural units, clusters or domains and their connections, and (iii) the influence of the nano-scale structure on the energy induced changes in these materials which reveals possibilities for applications.

The change of x from 0 to 40 at.% Ge increases Z from 2.4 to 2.8. In accordance to the viewpoint of J. C. Phillips [1], two topological transitions exist in this coordination range. In the studied systems the continuous Phillips-Thorpe stiffness transition coincides with a chemical threshold at $Z = 2.4$, while the percolative (fractal) two-to-three dimensional (2D-3D) transition appears around $Z=2.67$. This paper aims to point out the properties of the non-crystalline systems related to the transition across the topological transitions, and the peculiarities of the energy induced changes as a function of composition. An attempt is made to connect them with the respective nano-scale arrangements.

2. Methods and results

2.1. Infrared absorption and Raman scattering

The local atomic order in glasses and films can be established from their vibrational properties. The infrared (IR) spectra of the studied compositions are composed mainly of vibrational modes of the main structural units.

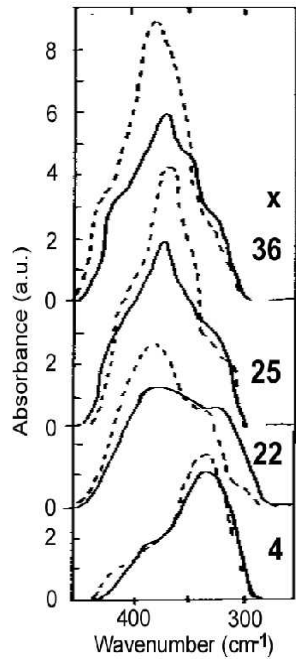


Fig. 1. Infrared absorption spectra of as-deposited (solid curve) and annealed (dashed curve) $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ films ($x = 4, 22, 25, 36$)

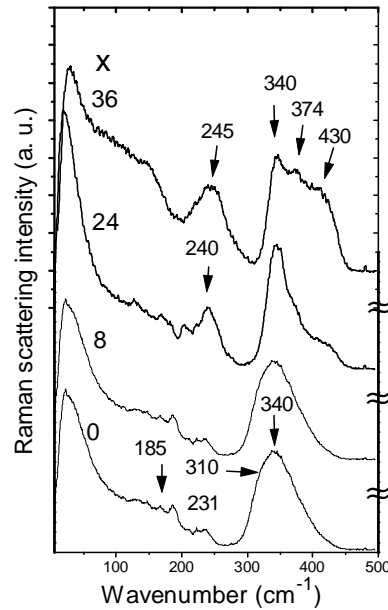


Fig. 2. Raman scattering spectra of $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ glasses ($x = 0, 8, 24, 36$).

The compositional dependences of the absorption spectra of films from the $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ system, which can be rewritten as $(\text{Ge}_2\text{S}_3)_y(\text{As}_2\text{S}_3)_{1-y}$, have shown [2] the prevalence of the main structural units, either pyramidal $\text{AsS}_{3/2}$ or $\text{GeS}_{4/2}$ tetrahedral, with peaks around 370 (367) cm^{-1} and 320 (310) cm^{-1} . Illumination and annealing near the glass transition temperature, T_g , increases the concentration of these units. Ge-S bonds change more intensively after annealing than the As-S ones (Fig. 1). That is why a conclusion has been drawn [3] that the evaporated films with predominance of the stoichiometric As_2S_3 component are more ordered than the films with predominance of the nonstoichiometric Ge_2S_3 component.

This conclusion is confirmed by the low changes of the optical band gap (E_g^0) in films with low x after annealing [2, 3]. The changes in E_g^0 in the $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ system at $x \rightarrow 0$ are still lower [2, 4]. The importance of this result is that it is in accordance with the assumption (not always accepted) that in these systems chemical ordering appears at $x = 0$, i.e. at the chemical threshold at $Z = 2.4$. However, due to the evaporation procedure, a certain chemical disorder (homopolar bonds) cannot be excluded in all the films. At $x = 0$, As_4S_4 molecular units exist in the as-deposited films, along with two types of pyramidal $\text{AsS}_{3/2}$ units [5]. Their amount decreases after illumination, annealing, and is also less in the bulk glasses. The vibrations of the homopolar bonds (As-As in the As-rich non-stoichiometric units and, at higher x , Ge-Ge in Ge-rich non-stoichiometric polyhedra) influences stronger the Raman spectra than the IR ones. In the Raman scattering spectra of the $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ films the homopolar As-As and Ge-Ge bonds induce overlapping peaks in the 150-300 cm^{-1} range. The vibration modes of the tetrahedral and pyramidal units have still closer locations ($\sim 340 \text{ cm}^{-1}$). The ratio between defects and all structural bonds was estimated [6]. It shows an increase with x which is better expressed at the highest x values, as can be expected, because of the greater chemical disorder in these compositions. Raman spectra of several representative glasses of the $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ system are shown in Fig. 2. The weak bands at ~ 185 and 231 cm^{-1} are ascribed [7], as usually, to vibrations in As-rich (including As_4S_4) molecular units. With the increase of x the 185 cm^{-1} peak disappears and a “blue” shift of the 231 cm^{-1} maximum until 245 cm^{-1} for $x = 36$ is observed.

This is a result of the increase of the ratio of Ge-Ge vs. As-As bond concentration. It is accepted that the Ge-Ge homopolar bonds are located in $\text{Ge-S}_{4-n}\text{Ge}_n$ tetrahedra and/or in $\text{Ge}_2\text{S}_{6/2}$ ethanlike units [7]. For high Ge-content two complementary characteristic bands at 374 and 430 cm^{-1} can be resolved in addition to the main 340 cm^{-1} (A_1 symmetric stretching) mode. The 374 cm^{-1} (companion A_1^c) mode is ascribed to vibrations in edge-shared (ES) tetrahedra or in edges of layer-like clusters that may grow with increasing x . The mentioned clusters include $\text{AsS}_{3/2}$ pyramids at lower x , as well as corner shared (CS) and ES tetrahedra at higher x . They form the two-dimensional patterns (fragments) of the medium range order (MRO). At higher x the largest domains break up in smaller clusters, increasing the number of edges and, as a result, the 374 cm^{-1} band increases (Fig. 2). The 430 cm^{-1} band may be assigned to a S-S stretching mode coming from cluster edge dimers. This band increases simultaneously with the 245 cm^{-1} band from the ethanlike units which may contribute to the cross-linking of the structure at $x > 27$ in accordance with the appearance of the transition to a 3D structure.

A well-resolved Boson peak (BP) has been observed in the low-frequency region in the spectra of all the samples. The BP intensity increases with Ge-content up to $x = 27$. Recently, the BP intensity, which is related to the disorder of the structure, was accepted to be proportional to the amplitudes of the medium range scale fluctuations of the cohesion of the distinct nanodomains [8]. In Fig. 3 a “master” curve of the BP of glasses from the Ge-As-S system can be seen (the curves are normalized to the BP height of the reduced intensity spectra, as well as to the frequency of the respective intensity maximum) [9]. Almost all of the normalized spectra overlap in the range 5-100 cm^{-1} . The only deviations from the common shape of the curve are in the spectra of the samples with $x > 2.67$. These deviations are an evidence for changes in the structure at the dimensionality transition (similar deviations are seen and connected with changes in the microstructure in other investigations; in [10] an overlapping of the BP frequencies with a polarized mode, suggests changes in the network dimensionality). The position of the BP peak, ω_0 , is inversely proportional to the size of the domains that defines the BP form, as stated in Ref. [8], or, to the correlation length of the MRO. The changes in the position of ω_0 (shown in the insert in Fig. 3) confirm the supposition about the fragmentation of the structural domains near $Z = 2.67$.

2.2. Neutron and X-ray diffraction results

The results obtained from the neutron and X-ray diffraction studies [11, 12] are in accordance with the conclusions drawn from the vibrational spectra. The analysis of the neutron structural factors $S(Q)$ and the radial distribution function (RDF) shows [11] that the short range order (SRO) of the glasses can be approximated by a pseudo-binary model, despite of the presence of the non-stoichiometric component in the compositions. The main structural units are the $\text{GeS}_{4/2}$ tetrahedra and the $\text{AsS}_{3/2}$ (or $\text{SbS}_{3/2}$) pyramids. The first coordination peak in Ge-As-S glasses is situated at 0.221 nm. The comparison of this value with the respective ones for As-S (0.229 - 0.23 nm) and Ge-S (0.224 - 0.248 nm) in binary crystals leads to the conclusion that a shortening of the heteropolar bonds appears in the glassy state. The well expressed first sharp diffraction peak (FSDP), regarded as a MRO feature, is related to elements of pyramid bands and of chains of tetrahedra [11] which may be clusterized. At higher x they can interconnect with with the ethanlike units. The FSDP increases with x as the X-ray diffraction studies of the Ge-Sb-S system have shown [12]. The repetitive characteristic distance R , calculated from the position Q of FSDP, increases with x with a slight change in the slope at $x \approx 27$ (Fig. 4). The values of R in the films are higher than in the glasses. After annealing they change but do not reach the lower values specific to bulk glass. The values of the repetitive distances in the As- and Sb-containing glasses are almost the same. In the compositions in which R may be connected with an interlayer distance, the interlayer correlation length $D \approx 2\pi/\Delta Q$, where ΔQ is the FSDP width, extents to about 4 layers. Peculiarities in D around $x = 27$ can be seen. In the Ge-Sb-S system D decreases at $x > 27$ from 2.3 to 1.9 nm [12]. In glasses of this system a new pre-FSDP was observed (with $R \approx 1.3$ nm) which was attributed to higher structural organization in the MRO than that defined by the FSDP only.

Light exposure of the fresh films induces photobleaching (PB) in Ge-As(Sb)-S films (a shift of the absorption edge to higher energies, i.e. to shorter wavelengths). A strongly expressed maximum around $Z = 2.67$ has been obtained for ΔE_g^0 [2]. It was established [27, 28] that not only irreversible

PB, but also irreversible photodarkening (PD) appears in the $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ films, depending on the prevalence of the As- or Ge- content (Fig. 9, curve 1). PB in Ge-containing films was explained [29, 30] by the assumption that E_g^0 increases when Ge-Ge homopolar bonds are transformed by photo- or thermoinduced changes to heteropolar Ge-S bonds. The homo- to heteropolar changes in As-containing films lead not to an increase but to a decrease of the optical band gap. Recent results [28] have shown that the appearance of PB with increasing x in these films depends not only on the composition, but, also, on the characteristics of the irradiation source. Further studies using pulsed and CW laser irradiation will be useful for specifying the structural rearrangements and the sign and values of ΔE_g^0 connected with them. The irreversible photostructural changes in the thin films have greater effect on the optical properties than the reversible ones, which are connected only with PD. The physico-chemical properties are also highly affected. High selective solubility has been established, especially in Ge-As-S films, with a well expressed maximum at $Z = 2.67$ [2]. This behaviour is of great importance for the nanometer photolithography and other applications. The maximal photostructural changes around $Z = 2.67$ are usually connected with: (i) the lowest density ρ and negative compactness δ which ensures free spaces for structural rearrangements and, (ii) the greater interlayer distances R at the fully evolved layer-like structure of the Ge-As-S films. The light induced structural changes in the Ge-As-S lead to a photoexpansion, which is nearly “giant” around $Z = 2.67$ as can be concluded from Ref. [31]. The Z dependence of the film thickness change, Δd , (obtained by averaging the values from both methods used in [31]) is shown in Fig. 9, curve 2. The maximal reported relative change of $\sim 8\%$ is at $Z = 2.7$. It should be pointed that the films are not obliquely but normally deposited. Nevertheless, the high irreversible volume expansion may be explained within a supposition similar to that accepted in [32, 33] for obliquely deposited As-based films. It results from a repelling motion of layered clusters, charged after excitation, which are surrounded with a lot of free space, large enough to ensure high changes in thickness. It is interesting to point that in the system the irreversible photoexpansion do not correlate with a band gap decrease as expected in [32, 34]. Moreover, similarly to the large irreversible contraction in obliquely deposited Ge-chalcogenide thin films, a contraction of the films is observed around $x = 10$. The change from photoexpansion to photocontraction appears near the compositions in which a change from PB to PD appears. Here the competition between the chemical ordering transition and the 2D-3D transition is the strongest. The chemical disorder increases towards $x = 10$ -15 where the still little layer-like cluster fragments have not yet evolved to the layer-like structure. The mentioned disorder may ensure a collapse of voids between fragments moving after excitation because of the electrostatic forces similar to those supposed in obliquely deposited films. The contraction which appears in normally deposited Ge-As-S films can be characterized by $\Delta d/d$ which is $\approx 3\%$ at $Z = 2.5$. The electron bombardment also induces compositional dependent changes [16]. The refractive index n reveals a minimum around $x = 27$ and an increase towards $x = 0$. The refractive index of the light exposed films [31] shows a very highly expressed decrease for $x > 10$. It should be mentioned that an electron induced expansion has also been observed [16]. At a dose of $1.5 \cdot 10^{-2} \text{ C/cm}^2$ the thickness increment was 20 to 30 nm in the 0.1 to 1.0 μm thick films. More detailed experiments have started with the aim to elucidate the compositional dependence of the last phenomena and their connection with the optical parameter dependences.

γ -darkening effect has been observed in Ge-As-S glasses [14, 35]. It is better expressed in glasses with higher Ge-content. It has been found that the γ -induced changes of the optical band gap relax in time. The self-restoration is also compositional dependent. It is more pronounced in the region with high Ge-content. The γ -induced changes of the absorption spectra can be connected with formation of defects and bond rearrangements. Raman scattering spectra measured before and after γ -darkening [14, 36] have demonstrated that in glasses with low Ge-content (e.g. in $\text{Ge}_8\text{As}_{32}\text{S}_{60}$) the vibrational bands of the main structural units have the same form. Only a slight increase in the bands connected with the As-As bonds vibrational modes can be hardly seen. The observed changes are in accordance with the expected ones by reversible PD in As-based chalcogenides. In the Ge-rich glasses (e.g. $\text{Ge}_{32}\text{As}_8\text{S}_{60}$) the increase and the broadening of the 230-250 cm^{-1} bands are better expressed because of the higher increase of the homopolar Ge-Ge bonds (in the ethanlike units) after γ -irradiation. Moreover, a stronger increase of the 374 and 430 cm^{-1} bands is established. As pointed above, the increase of these bands is connected with a break up of the largest nanodomains to smaller clusters. As a result, the number of their edges (connected with the 374 cm^{-1} band) and of the edge

dimers (connected mostly with the S-S stretching mode at the 430 cm^{-1} band) increases. These results allow to advance the explanation of the γ -darkening within the framework of the model of photodarkening where the change in the lone pair (LP) interactions of the electrons of the S-atom after excitation plays a substantial role [34]. The formation of dynamic bonds, distortion and bond-breaking leads to new structural arrangement (better expressed in compositions with larger volumes). The changes of the chalcogen atomic positions and the LP repulsive interactions decrease the band gap through an upward shift of the valence band. In accordance to [10], the S-S defect bonds can be related to an increase of the band tails in the band gap leading also to a darkening effect. Besides the scalar energy induced effects, vectoral effects induced by polarized light have been observed [30]. They also are dependent on composition. In $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ films the linearly polarized light induces both linear dichroism and linear birefringence. The dichroism sign is always the same as in the binary chalcogenide films which show PD and not PB when illuminated in an as-prepared state. The inducing polarized light always decreases the absorption of the probing light polarized parallel to the inducing one. This fact can be understood if the polarized light is absorbed preferentially by defects (native or generated) having the axes parallel to the electrical vector of the inducing light and destroys these defects, creating new randomly oriented defects. The defect rearrangement will be more effective if there are larger free spaces. That is why in the compositions around the 2D-3D threshold the highest values of the photoinduced dichroism (10-15%) are reached while at $x = 36$ they are only 3-4%. Thus, the compositional dependences of the vectoral effects correlate with those of the scalar photoinduced effects.

3. Trends for applications

The compositional dependences of the energy induces changes of the structural related properties of the $\text{Ge}_x\text{As}(\text{Sb})_{40-x}\text{S}_{60}$ systems, related to structure, have shown that these changes are maximal in the compositions situated around the percolative 2D-3D transition. In the $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ system As is replaced by the heavier element Sb. The density is higher and the compactness does not fall to values low enough to allow structural changes of the type observed in the $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ compositions. The higher free spaces in the As-containing system facilitate the nanoscale arrangement and trends for applications in this system could be emphasized.

Up to now we have proved the possibilities of the Ge-As-S films as positive photoresists using the high selective solubility in fresh films with compositions around the 2D-3D transition. The dissolution process depends both on the photostructural changes and the interaction with the solvent. A suitable alkaline solvent has been found [37] with surface active substances. The solvent interacts with the weak bonds in the Ge-based chalcogenides which structure can be maximally changed (in compositions with maximal free volumes). The highest sensitivity for non-silver inorganic photoresists has been obtained [38] at an exposure $H \approx 0.1\text{ J.cm}^{-2}$. Images with submicron dimensions have been obtained. The same films have been examined as antireflective coatings for GaAlAs light diodes [39]. Their self photolithography can be used for opening the contacts during preparation of the coated diodes. The parameters of the coated light diodes have been checked up in production conditions. They have stood up to the technological tests, showing good perspectives for practical applications. There are also other unproved trends for applications. The electron- or photoinduced expansion (3-8%) is interesting for microlens production. The induced changes of the refractive index give possibilities for direct formation of phase gratings. The large values of the photoinduced dichroism in as-prepared Ge-As-S films (up to 15%) can be used in holographic or other optoelectronic applications.

4. Conclusions

The review of the property-composition dependences and the energy induced changes in glasses and/or films of the $\text{Ge}_x\text{As}(\text{Sb})_{40-x}\text{S}_{60}$ systems has shown that the structural changes are optimal

in compositions around the percolative 2D-3D transition. The higher free spaces in the As-containing system facilitates the nanoscale arrangement and trends for applications in this system could be emphasized.

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