LOCALIZED STATES MODEL OF GeS$_2$ GLASSES BASED ON ELECTRONIC STATES OF Ge$_n$S$_m$ CLUSTERS CALCULATED BY USING TD-DFT METHOD

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The first-principles calculation based on time dependent – density functional theory (TD-DFT) reveals the origin of the molecular electronic structure and its connection to the localized states of the g-GeS$_2$(T$_i$). The band gaps computed for Ge$_n$S$_m$ clusters representing the local structures and their correlation to the experimental band gaps of g-Ge$_x$S$_{100-x}$ together with possible model of band-tail states of g-GeS$_2$ have been discussed. According to the observed results we propose to consider the band-gap states of g-Ge$_x$S$_{100-x}$ as superposition of electronic states of Ge$_n$S$_m$ clusters. The type and concentration of these clusters are compositionally-dependent and influenced by technological conditions used for glass preparation.

1. Introduction

Amorphous and glassy materials have been intensely studied because of their technological importance and fundamental interest. Chalcogenide glasses are excellent sensitive media for optical recording, useful optoelectronic elements and materials for potential applications in different electronic, laser-technology and photonic devices as well as perfect materials for fundamental studies and modelling [1-4]. Past year's and recent investigations of the microscopic structure of chalcogenides shows that the approximation of the simplest structural units (s. u.) only can not explain the realistic nature and properties of glass state. Therefore, further clusters approximation was applied, that being combined with first-principles calculations, is very important both to interpret some features of glasses and predict properties of amorphous materials, too [5,6]. The structure and properties of g-GeS$_2$ were investigated previously both by experimental [7-10] and theoretical [9,11-14] approaches. However, the microscopic origin of possible band-tail states of g-Ge$_x$S$_{100-x}$ is still being discussed.

In this work our attention is centered on localized states of technologically modified g-GeS$_2$. It is known that the band gaps of semiconducting glasses are usually lower compared to the band gaps of their crystalline counterpart [15]. The localized states of crystals are discrete and can occur from different defects in their structure. On the contrary, the localized states of glasses have a quasi-continuous character and form the localized density of states $\rho(E)$ on top of the valence band and on bottom of the conduction band (the so-called band-tail states). These states can significantly influence the properties of chalcogenides. As the localized states of glasses can be related with their structural origin the following important questions can be addressed to researchers: (i) which type of structures in the glass can produce the localized states; (ii) what is the nature of localized states and where the localized state lies in the pseudo band gap of glass; and finally, (iii) can localized states of glasses be modified technologically or compositionally. In this work, the first-principles calculations

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of band gaps of local structures have been used to elucidate the resulting band-gaps of both g-GeS$_2$ prepared under different technological conditions and g-Ge$_x$S$_{100-x}$ by varying the composition. The occupied and unoccupied molecular orbitals energies of Ge$_n$S$_m$ clusters were calculated using DFT/BLYP method. The band gaps of Ge$_n$S$_m$ clusters were also calculated using TD-DFT method.

2. Glass preparation and theoretical details

2.1. Sample preparation

The g-GeS$_2$ samples were synthesized by melt quenching from different temperatures ranging from 1273K (T$_1$) to 1473 K (T$_3$) with cooling rate of 150 K/s. The three different g-GeS$_2$ samples will hereafter be denoted g-GeS$_2$(T$_1$), g-GeS$_2$(T$_2$), and g-GeS$_2$(T$_3$).

2.2. Calculational methods

The computations consists of first-principles calculations on small atomic Ge$_n$S$_m$ clusters (1<n<3, 1<m<9) as depicted in Fig. 1. These clusters represented the local structures of Ge$_x$S$_{100-x}$ glasses. All clusters were suitably terminated by use of hydrogen atoms.
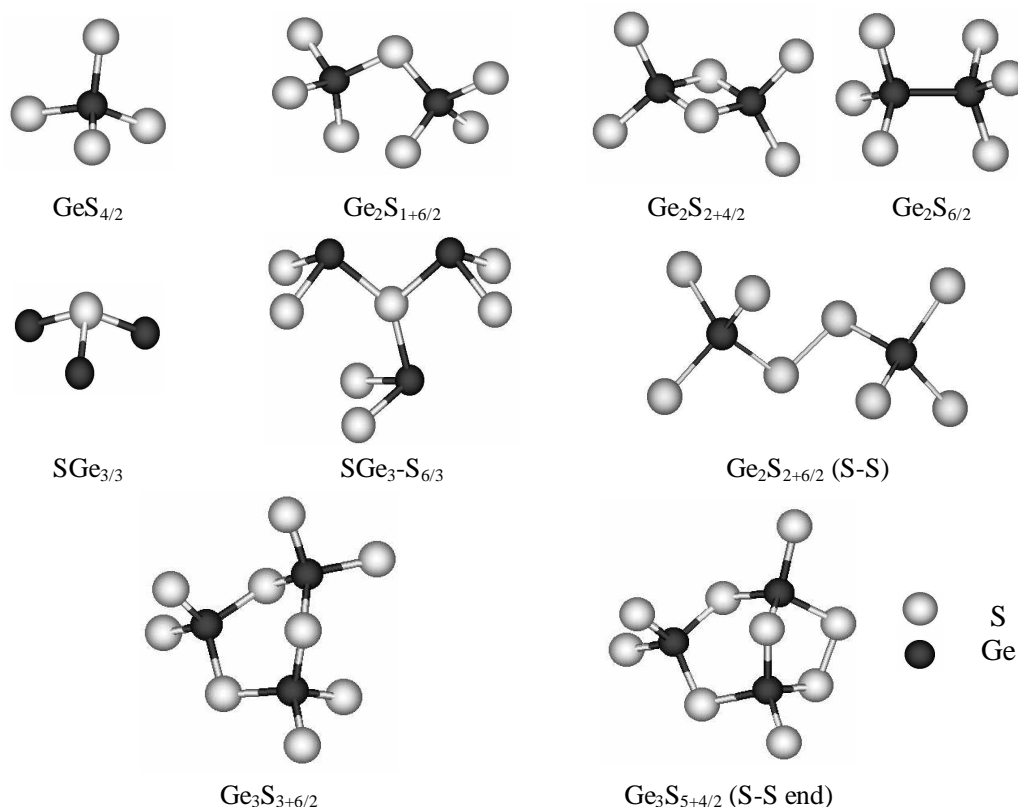

Fig. 1. The structural models of Ge$_n$S$_m$ clusters used for first-principles calculations. Saturating hydrogen atoms and corresponding bonds are not shown for clarity.

All calculations were performed using the Gaussian-03 quantum-chemical program package [16]. The self-consistent field (SCF) and Hartree-Fock (HF) methods were applied initially for geometry optimizations of the clusters using the Berny optimization procedure. The triple-zeta (TZ) valence Pople 6-311G* [17] basis set was used for the Ge and S atoms. For the H atoms the 3-21G

basis set was used. Subsequent second derivative calculations, using the same method and basis set, verified the obtained structures as true energy minimum geometries.

In order to increase the accuracy of the HF calculations either "post-HF" methods or methods based on density functional theory (DFT) can be used, primarily to account for electron correlation. Here we applied DFT methods to obtain more accurate band gaps. The basis sets used were the same as for the HF calculations and used together with the corrected exchange functional proposed by Becke [18] and the gradient-corrected correlation functional of Lee, Yang, and Parr [19] (BLYP). The cluster's geometries were re-optimized and band gaps were estimated in two different ways. The simplest approximation used was the energy difference between the HOMO and LUMO molecular orbital energies (ΔE_{0i}^{H-L}) [20] of Ge$_n$S$_m$ clusters. However, the LUMO is a virtual-type orbital connected only with the ground-state. Therefore, in addition, the low-lying excited states of the clusters were calculated using a time-dependent (TD) approach (TD-DFT) (ΔE_{0i}^{TD}) [21]. Then, the energy positions of all virtual-type orbitals (unoccupied MO's) were corrected for produce the HOMO-LUMO band gaps (ΔE_{0i}^{H-L}) as band gap values calculated using TD-DFT (ΔE_{0i}^{TD}).

3. Computed band-gaps of Ge$_n$S$_m$ clusters and optical pseudo band-gap of g-GeS$_2$

The occupied and unoccupied molecular orbitals for the "normally" coordinated (i.e. Ge is four- and S is two-fold coordinated) Ge$_n$S$_m$ clusters are shown in Fig. 2. However, clusters with tri-coordinated sulfur (SGe$_{3/3}$, SGe$_3$-S$_{6/3}$) representing the local structure of crystalline (c) c-GeS are charged. The charge of these clusters result in shifted MO energies and therefore, their MO values are excluded from Fig. 2. In Table 1 the calculated band gaps of Ge$_n$S$_m$ clusters are shown as differences obtained between ground state and first excited state energies (ΔE_{0i}^{TD}) using TD-DFT. The narrowest band gap is clearly obtained for the Ge$_3$S$_{5+4/2}$ cluster with an S-S connection, while the other ethane-like cluster with Ge-Ge bond (Ge$_2$S$_{6/2}$) has a similarly high HOMO, but a higher energy LUMO results in a significantly, by about 0.7 – 0.8 eV, larger band gap. According to our previous calculations the band gap of edge-shared Ge$_2$S$_{2+4/2}$ cluster can decreased up to 1.74 eV by closing sulfur atoms at the end of cluster (see Ge$_2$S$_6$(S-S end) in ref. [22] for details). According to the Raman spectra [22] this structure is not realized in g-GeS$_2$ in any large content. The narrow band gap has also the cluster with tri-coordinated sulfur (SGe$_{3/3}$) (Table 1).
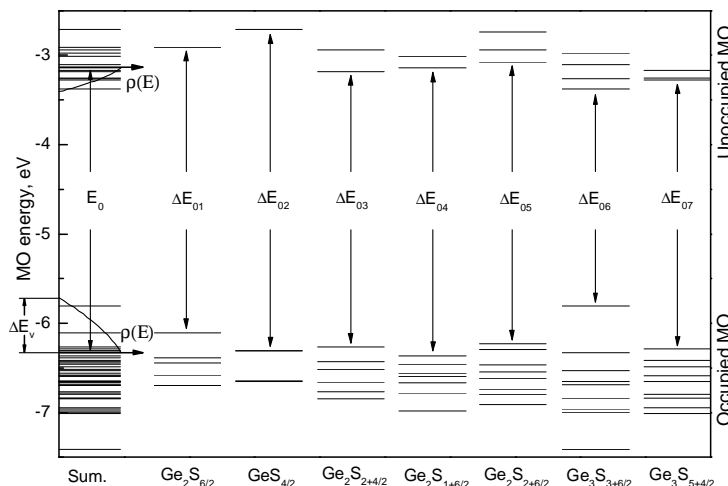

Fig. 2. The electronic energies and HOMO-LUMO band gaps (ΔE_{0i}) for the Ge$_n$S$_m$ clusters (BLYP/6-311G*). The energies of virtual (empty) MO's were corrected using TD-DFT band gaps values. The summarized MO's of Ge$_n$S$_m$ clusters together with the schematic illustrations of pseudo band gap (E$_0 \approx$3.2 eV) and density of localized states ρ(E) of g-GeS$_2$ are shown on the left.

Table 1. Calculated band gaps of the Ge_nS_m clusters by differences in ground and first excited states energies (ΔE_{0i}^{TD}) (TD-BLYP/6-311G*).

Cluster	ΔE_{0i}^{TD}, (eV)	Cluster	ΔE_{0i}^{TD}, (eV)	Cluster	ΔE_{0i}^{TD}, (eV)
$GeS_{4/2}$	3.60	$Ge_2S_{2+4/2}$	3.08	$SGe_{3/3}$	2.89
$Ge_2S_{1+6/2}$	3.23	$Ge_3S_{3+6/2}$	3.01	SGe_3-$S_{6/3}$	3.08
$Ge_2S_{6/2}$	3.20	$Ge_2S_{2+6/2}$	3.16	$Ge_3S_{5+4/2}$ (S-S end)	2.43

4. Discussion

The local structure of GeS_2 glasses prepared by using different technological conditions have been investigated recently [22] by resonant Raman and edge absorption spectroscopy. The short-range order was shown to be different for the samples and consequently we believe that the optical gap of g-GeS_2 can be modified by using different conditions of preparation.

The analisis of HOMO and LUMO states of Ge_nS_m clusters allowed us to describe band gap tendency as follows: the largest band gap (ΔE_{02}=3.6 eV) has single GeS_4 tetrahedra. Larger corner-shared $Ge_2S_{1+6/2}$ and ethane-like $Ge_2S_{6/2}$ clusters has band gaps of 3.23 and 3.20 eV, respectively. These two values are in excellent agreement with the pseudo band gap of E_0=3.2 eV determined for g-GeS_2 as Tauc gap at $5*10^4$ cm^{-1} of absorption coefficient $\alpha(E)$. The band gap values of edge-shared cluster $Ge_2S_{2+4/2}$ with "strained" sulfur atoms (ΔE_{03}=3.08 eV) lie in the so-called exponential range of $\alpha(E)$ (~10^3 cm^{-1}). A small part of "outrigger-raft" cluster, $Ge_3S_{5+4/2}$ (S-S end), has ΔE_{06}=2.43 eV which corresponds to the absorption level about ~10 cm^{-1}. The lowest band gap of 1.74 eV and deep centers in the pseudo band gap were obtained [22] for the $Ge_2S_{2+4/2}$ clusters with S-S bonds at the ends (Ge_2S_6 (S-S ends)). Therefore, this cluster can form the band-tail states in the weak absorption range (lower than 1 cm^{-1}). The width of 0.8 eV related to the band-tails near the top of valence band (ΔE_v) (Fig. 2) was estimated from exponential part (Fig. 3) of $\alpha=\alpha(h\nu)$. This value is in excellent agreement with the differences of HOMO states for $Ge_2S_{1+6/2}$ and $Ge_3S_{5+4/2}$ (S-S end):

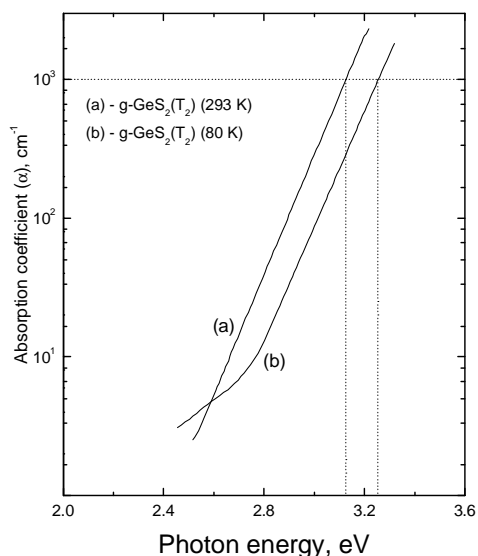$$\Delta E_{64}^H = E_6^{Homo} - E_4^{Homo} \sim 0.8 eV .$$

Fig. 3. Room (293 K) and low (80 K) temperature absorption coefficients (α) of the GeS_2 glass quenched from T_2=1373 K.

Sulfur atoms are known to form the basis of the valence band of germanium disulfide by lone-pair (LP) electron states [15]. The LP-electrons interact through the π-orbitals [20]. In edge-shared tetrahedra the sulfur atoms are in a "strained" state in comparison with corner-shared tetrahedra. The interaction of such sulfur atoms can produce electronic states near the top of the valence band [23]. In Fig. 2 the MO energies of Ge$_n$S$_m$ clusters are shown. Also, the visualized HOMO's structures of such clusters are shown in Fig. 4. The HOMO energy values of most Ge$_n$S$_m$ clusters are all close to –6.3 eV. However, the Ge$_3$S$_{5+4/2}$ cluster has a higher-lying HOMO (–5.8 eV). This is due to the S-S bonds present and LP-electrons interaction. This cluster is, however, in general considered less likely [22]. For the g-GeS$_2$ synthesized from melt temperature of T$_1$=1273 K, however, the observed increase of the 490 cm^{-1} mode with a higher exciting photon energy (see Fig. 3, ref. [22]) supports the existence of the Ge$_3$S$_{5+4/2}$ cluster.

In general, the edge-shared Ge$_2$S$_{2+4/2}$ cluster is considered more likely to contribute to the resonant Raman spectra [22], but has a much larger band gap than 2.48 eV (3.08 eV, Table 2). However, by closing the structure, modifying the Ge$_2$S$_{2+4/2}$ cluster (S-S distance ~3.43 Å) to the Ge$_2$S$_6$(S-S ends) cluster (~2.31 Å), both the HOMO change upward (–5.8 eV) and the band gap becomes much smaller than 2.48 eV (1.74 eV) [22]. Thus small variations in the local structure seem to be able to be responsible for the formations of band-tail states of g-GeS$_2$. Therefore, we conclude that S-S bonds form the band-tail states of g-GeS$_2$, a result in accordance with the results of electronic density of states (DOS) calculated by Louie [25] for g-GeSe$_2$. However, it is important to note here that not every S-S bond can be responsible for the formation of localized states. Indeed, as shown in Fig. 2 the calculated electronic states of Ge$_2$S$_{2+6/2}$ cluster formed by S-S connection between two GeS$_4$ tetrahedra have no significant influence on the band-tail states of g-GeS$_2$. Moreover, variations of geometrical configuration (*i. e.* variations of dihedral angle of chains with an S-S bond) influence on the location of π-orbitals (Fig. 4) and, therefore on interaction between LP-electrons of neighbor chalcogen atoms. According to the calculations, the existence and energy level of a localized state depend from geometrical configuration of -Ge-S-S-Ge- chains (Ge$_3$S$_{5+4/2}$ (S-S end) and Ge$_2$S$_{2+6/2}$ (S-S) clusters, Fig. 2 and Fig. 4). Therefore, the slow decrease in pseudo band gap of sulfur-rich Ge$_x$S$_{100-x}$ glasses (Fig. 5) with increasing sulfur content occurred not only from intense formation of S-S bonds but also from -Ge-S-S-Ge- geometrical configuration.
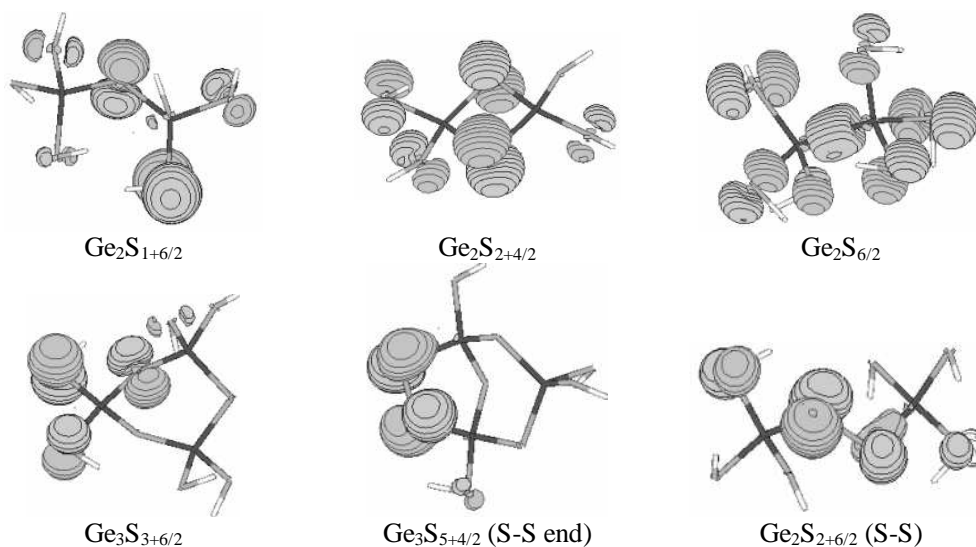

Fig. 4. Calculated and visualized HOMO's of Ge$_n$S$_m$ clusters. Contours shows that all HOMO's (except Ge$_2$S$_{6/2}$ cluster with Ge-Ge bond) represents the antibonding (*) π*-orbitals.

Calculated gaps of Ge$_2$S$_{1+6/2}$ and Ge$_2$S$_{2+4/2}$ are 3.23 eV and 3.08 eV, respectively. On the other hand, if the Ge$_3$S$_{5+4/2}$ cluster contributed, the band gap should be much lower (calc. 2.43 eV). This hardly indicates that this cluster is realized in the structure of g-GeS$_2$ to any large extent, as also

seen by the very weak intensity of the 490 cm^{-1} band in experimental Raman spectra [22]. The optical gap (determined at $\alpha=10^3$ cm^{-1}) shifts from 3.05 to 3.15 eV for g-GeS$_2$ quenched from melt temperature of $T_1=1273$ and $T_2=1373$ K respectively [22]. This value is still possible to ascribe to Ge$_2$S$_{1+6/2}$ or Ge$_2$S$_{2+4/2}$ clusters. The corner- and edge-shared clusters have a delicate balance as previously calculated from formation energies of Ge$_2$S$_{1+6/2}$ and Ge$_2$S$_{2+4/2}$ clusters [26], and the up-shifted absorption edge is possibly due to concentration differences amongst the two clusters. This shift can also be related to the absence of S-S bonds in the structure of g-GeS$_2$(T$_2$) sample in comparison with g-GeS$_2$(T$_1$) [22]. The role of three-fold coordinated SGe$_3$ cluster (2.89 eV) is still negligible here.
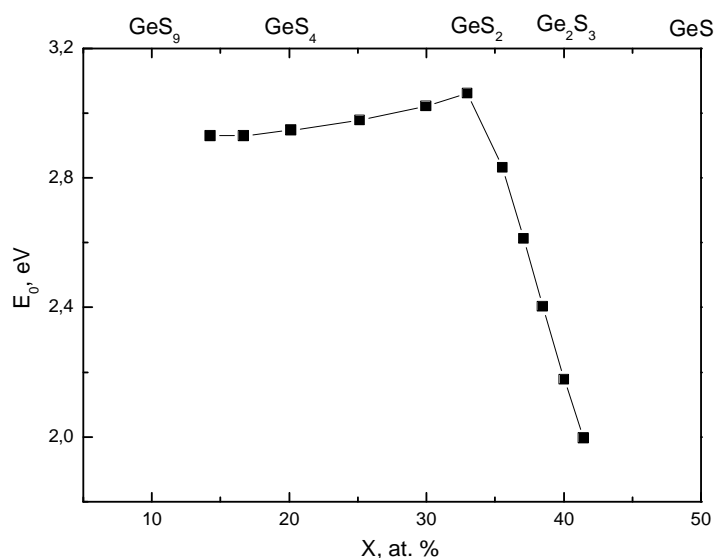

Fig. 5. The concentration dependence of optical pseudo band gap of Ge$_x$S$_{100-x}$ glasses [24] determined by results of absorption edge spectroscopy at $\alpha \sim 10^3$ cm^{-1}.

The absorption edge of g-GeS$_2$ sample prepared by quenching from melt temperature of $T_3=1473$ K is red-shifted and corresponds an optical gap less than 3.05 eV. The sharp decrease of pseudo band gap for Ge-rich Ge$_x$S$_{100-x}$ glasses with increasing Ge content is shown in Fig. 5. According to the calculations the Ge-rich ethane-like cluster with an Ge-Ge bond (Ge$_2$S$_{6/2}$) has a similarly high HOMO and can form the localized state at the top of valence band of g-GeS$_2$, but a higher energy LUMO results in band gap of 3.2 eV. Therefore, the decreased gap can only occur by association of three-fold coordinated SGe$_{3/3}$ clusters and formation of c-GeS micro-phases. Fig. 5 demonstrates an optical gap of g-Ge$_2$S$_3$ about 2.0 eV. Also, the room temperature optical energy gap of 1.57 eV was measured for the $\vec{b}$ axis of c-GeS [27]. The formation of c-GeS micro-phases in the structure of g-GeS$_2$ prepared by quenching from melt temperature of T_3 is well supported by Raman spectra at 200-300 cm^{-1} [22].

Comparison of the calculated band gaps and electronic states of Ge$_n$S$_m$ clusters with the experimental pseudo band gap of technologically modified g-GeS$_2$ allowed us to consider that the local structure and experimental pseudo band gap of g-GeS$_2$ can be modulated by the synthesis procedure (melt temperature). The localized density of states $\rho(E)$ of g-GeS$_2$ got from the electronic states of Ge$_n$S$_m$ clusters illustrates the local structures of g-GeS$_2$. The number and energies of localized states depend on the type and concentration of Ge$_n$S$_m$ clusters in the glass structure.

5. Conclusions

The origin of the band gaps of technologically modified g-GeS$_2$ is very complex, but nevertheless the results allow us to conclude that the formation of such S-S bond(s) leads to the

creation of localized states. Both a delicate balance of different S-S distances and variations of dihedral angles of –Ge-S-S-Ge- chains within the glasses seem to decrease the optical gap of g-GeS$_2$ and S-rich Ge$_x$S$_{100-x}$ glasses.

Rapidly decreased band gaps obtained for the g-GeS$_2$ quenched from T$_3$=1473 K and Ge-rich Ge$_x$S$_{100-x}$ glasses result from the extensive formation of tri-coordinate structures, which can be similar to an c-GeS micro-phase. Though ethane-like structures yield the localized states near the top of the valence band, a high-lying first excited electronic state does not correspond to the decrease of the band gap.

It is thus possible to modulate the band gaps by the synthesis procedure both by melt temperature used for glass preparation and by composition variations. As pseudo band gap of g-GeS$_2$ is correlate with the ground and excited electronic states of Ge$_n$S$_m$ clusters we propose to consider the band gap values as superposition of basic clusters. The types and concentrations of basic clusters depend on the glass composition and on technological condition used for glass preparing procedure.

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