

Compositionally-dependent network-forming tendencies in S-rich As-S glasses

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Structural evolution effects associated with network glass-forming tendencies are examined in As-S system in the concentration range corresponding to S-rich below-stoichiometric compositions. To describe energetically-favorable atomic configurations possible in this archetypal binary As-S system, *ab-initio* quantum chemical modeling routine termed as CINCA (i.e. Cation-Interlinking Network Cluster Approach) with RHF/6-311G* basis set is first employed. Performed energy calculations testify in a favor of geometrically-optimized configurations for As₂S_m network clusters (m=3-9) showing stable glass-forming tendency towards “*chain-crossing*” arrangement within Z=2.40-2.22. But with further increase in S content this system apparently deviates from “*chain-crossing*” model. Thus, the glasses with average atomic coordination of Z=2.40 (As₂S₃) and Z=2.29 (As₂S₅) are most stable against devitrification, while, in contrast, the As₂S₈ glasses (Z=2.20) can be distinguished as inserting the instability onset in As-S system due to abrupt tendency towards both local intrinsic chemical decomposition and global phase separation. These results are in good agreement with known experimental evidences on compositional dependencies of physical-chemical properties of binary As-S glasses.

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1. Introduction

Structurally disordered materials based on arsenic sulfides As-S belong to a wide group of chalcogenide vitreous semiconductors (ChVS), i.e. melt-quenched glassy alloys compounding chalcogens (S, Se or Te, but not O) and some elements from IV-V groups of the Periodic table (typically As, Sb, Bi, Ge, etc.) [1-7]. Because of superior optical transmittance in a wide IR spectral region including both atmospheric windows (3-5 μm and 8-12 μm) and space telecommunication domain (extended to 20-25 μm), the property which has been pointed out by R. Frerichs yet in the earliest 1950-s [8], the ChVS serve as an unprecedented basis for novel promising branch in modern optoelectronics, often termed as *Chalcogenide Photonics* [9-12].

The ChVS of binary As-S system are known to form stable glasses in a wide concentration range covering preferentially S-rich compositions from 44-46 to ~16 at. % of As (in respect to average atomic coordination numbers Z from Z=2.44-2.46 to Z=2.16), including stoichiometric arsenic trisulfide As₂S₃ (Z=2.40) as one of the most studied model network glass former [1-5]. In a glassy state, these compounds can be prepared by conventional melt-quenching (or rapid cooling) from either high (more than 800°C) or reduced temperatures (less than 600°C [3,13,14] or even 500°C [15-17]). Their glass-forming networks are built of trigonal AsS_{3/2} pyramids cross-linked by S_n chains so all constituting atoms saturate covalent chemical bonding obeying the Mott's coordination “8-N” rule [4]. In such a way, the structural network of these ChVS is supposed to be well described by so-called

“*chain-crossing*” model [4,18], where S_n chains are accepted to be more or less homogeneously distributed among trigonal AsS_{3/2} pyramids in dependence on a glass composition.

Nevertheless, these simple network-forming rules do not satisfy necessarily the condition of uniform chemical ordering in this As-S system. Indeed, decomposition on nearest chemical compounds as well as phase separation on more stable terminated products (such as arsenic trisulfide As₂S₃ and S_n chains/rings) are possible (at least, in a vicinity of some defined chemical glass compositions) due to local energetic non-identity in configurational entropies/enthalpies for some network-forming structural units. Thus, in isotypical binary As-Se system, such structural instabilities examined through CINCA (cation-interlinking network cluster approach) employing *ab-initio* quantum chemical cluster modeling with RHF/6-311G* basis set [19,20], demonstrate an obvious oscillating character with most essential deviations near Z=2.25 and Z=2.33 [21]. This conclusion occurred to be in an excellent harmony with known data on compositional anomalies in the physical properties of As-Se ChVS caused by their preparation technologies or prolonged physical aging [22-28]. At the same time, in respect to rich experimental data of Z.U. Borisova [1,2], the binary As-S ChVS also reveal a row of compositional instabilities, which sometimes (under respective glass synthesis conditions) can result in obvious anomalies in many physical properties. Thus, just at the edge of glass-forming region, the AsS_{1.25} glass (Z=2.44) prepared by slow cooling from 800°C (the most explored synthesis regime) represents sub-microdispersive mixture of arsenic monosulfide AsS (As₄S₄) and trisulfide AsS_{1.5} (As₂S₃), which strongly decline optical transmittance of this glass.

Appearance of AsS ($Z=2.50$) along with highly S-enriched AsS_{19} compound ($Z=2.05$) was also detected under phase destabilization in AsS_5 alloy ($Z=2.17$) [1]. In contrast, the most stable As-S glassy specimens were obtained with As_2S_3 ($Z=2.40$) and As_2S_5 ($Z=2.29$) chemical compositions. Stability of the former is expected, since this glass possesses energetically favorable two-dimensional network of covalent chemical bonds forming a so-called layered structure, which block formation of AsS units. Nevertheless, stability of As_2S_5 compound (i.e. $AsS_{2.5}$ with $Z=2.29$) having a more extended three-dimensional covalent network [1] is not too evident. Supposition on quasi-tetrahedral units with double covalent chemical bonding $S=AsS_{3/2}$ in this compositional domain (near $Z=2.29$) has been rejected yet in the 1960-1970s [13,18], when many direct and indirect structural probes clearly demonstrated absence of such structural entities in this As_2S_5 glass, despite successful attempts to stabilize crystalline counterpart of this compound under higher pressures (40-70 kbar) and temperatures (700-1000°C) [1,3].

In this work, we develop further CINCA modeling on binary As-S ChVS to disclose their specificity in respect to computed compositionally-dependent network-forming tendencies.

2. Computational approach to network-forming tendencies in ChVS

The network-forming tendencies in binary As-S ChVS will be examined starting from basic structural unit character for this system, i.e. trigonal $AsS_{3/2}$ pyramid with a base outlined by three S atoms and apex As atom [1-5]. Due to differences in the electronegativities, the constituting S and As atoms forming such pyramid can be respectively accepted like anion and cation in a fully-saturated covalent network of this glass. In respect to “chain crossing” model [4,18], whole network of As-S glass can be built of neighboring $AsS_{3/2}$ pyramids interlinked over S_n chains. In general, such structural network is formed by multiply repeated neighboring atomic clusters interconnected into two ways, these being *atom-shared* (AS) links with one common S atom (see Fig. 1a) or *bond-shared* (BS) links with one common S-S bond (see Fig. 1b).

To quantify governing chemical interaction in a system, each two-cation network-forming cluster (outlined by rectangular in Fig. 1) will be structured on *shell* (inner part of the cluster) and *core* (outer part between two neighboring clusters) as it was explained in more details elsewhere [19-21].

Thus, the glass of given chemical composition can be represented by atomic clusters built of shorter $S_{n=0}$ core with longer $S_{n>0}$ shell or longer $S_{n>0}$ core with shorter $S_{n=0}$ shell. The deviation in network-forming tendency from “chain-crossing” model is defined by Δl parameter, i.e. difference in the length of cluster *core* and *shell* determined by the number of S half-atoms (so $\Delta l=0$ corresponds to strong “chain-crossing” arrangement, when all As atoms are interlinked by equivalent S_n chains).

Thus, within this determination, we consider only small atomic clusters with equivalent symmetric inter-cluster legs (*cores*) described by integer Δl values (such simplification allows reliable quantum-chemical calculation for small atomic clusters within CINCA [19]). In general, the fractional Δl values are also possible for asymmetric clusters with non-equivalent inter-cluster legs. But these cases will not be considered in view of essential complications in the calculation procedure.

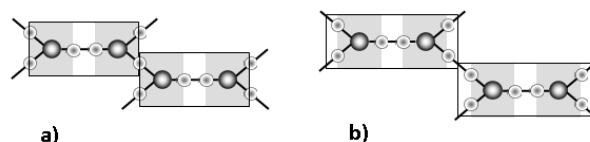


Fig. 1. Schematic ball-and-stick presentation showing AS links ($\Delta l=1$) between network-forming clusters (outlined by rectangular) in As_2S_4 glass (a) and BS links ($\Delta l=0$) in As_2S_6 glass (b)

For As_2S_4 glass with AS intercluster link on Fig. 1a, the Δl parameter reaches 1, while in case of BS link in As_2S_6 glass (shown in Fig. 1b), the Δl equals 0, thus reflecting an ideal “chain-crossing” arrangement.

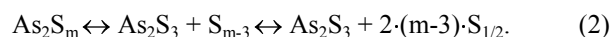
The above *cluster evolution algorithm* enables formation a set of S-rich As_2S_m atomic clusters, from stoichiometric As_2S_3 (two directly linked corner-shared $AsS_{3/2}$ pyramids in a simplest surrounding of $S_{n=0}$ shell) to pure S (chain- or ring-like S_n fragments) in respect to glass composition defined by average coordination number Z (i.e. number of covalent chemical bonds per atom of glass-forming unit).

Two different *intrinsic decomposition processes* will be examined in the studied glassy As-S system, these being *local chemical decomposition* and *global phase separation*.

The first process is decomposition on best energetically-favorable neighboring S-rich (i.e. As_2S_{m+1}) and As-rich (i.e. As_2S_{m-1}) atomic clusters:



The *global phase-separation* is attributed to possibility of glassy network to be separated on two corner-shared $AsS_{3/2}$ pyramids (i.e. As_2S_3 atomic cluster) and “pure” S-chain remainder (i.e. S_{m-3} atomic cluster):



By using CINCA modeling [19,20], we will calculate the averaged cluster-forming energies (CFE) to quantify comparison between different atomic clusters. Simplification made within CINCA allows complicated and time-consuming modeling procedure for real glassy networks usually evolved hundreds or even thousands of atoms, replaced by a more simple simulation route for relatively small atomic clusters using available software (like HyperChem Release 7.5 program). The quantum-chemical *ab initio* calculations based on restricted

Hartree–Fock self-consistent field method using split-valence double-zeta basis set with single polarization function 6-311G* [29,30] will be performed to determine the CFE. The final geometrical optimization and single-point energy calculations will be carried out employing the Fletcher-Reeves conjugate gradient method until root-mean-square gradient of 0.1 kcal/Å·mol is reached.

Formation of molecular-like fragments in accordance to “8-N” rule [4] requires all boundary S atoms in cluster shell to be terminated by hydrogen H atoms (shown by grey-color circles in Fig. 2 and 3). In such a way, the atomic clusters with open covalent chemical bonds will be replaced by clusters of self-closed molecular configurations with fully saturated chemical bonds. Therefore, the calculated total energies of optimized molecular clusters will be corrected on the energies of terminated H atoms and S-H bonds.

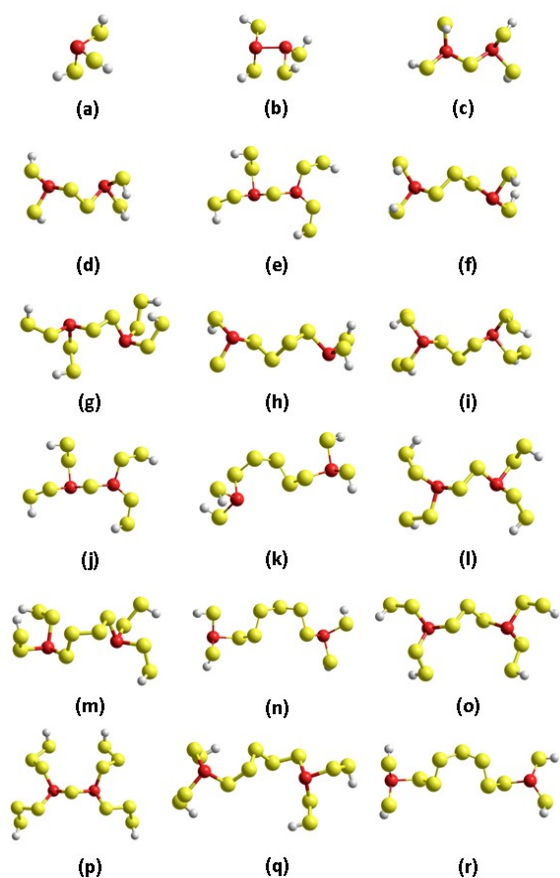


Fig. 2. Geometrically-optimized configurations of As_2S_m atomic clusters terminated by H atoms: single trigonal $AsS_{3/2}$ pyramid (a); $As_2S_{4/2}$ (b); As_2S_3 , $\Delta l=0$ (c); As_2S_4 , $\Delta l=1$ (d); As_2S_5 , $\Delta l=1$ (e); As_2S_5 , $\Delta l=2$ (f); As_2S_6 , $\Delta l=0$ (g); As_2S_6 , $\Delta l=3$ (h); As_2S_7 , $\Delta l=1$ (i); As_2S_7 , $\Delta l=2$ (j); As_2S_7 , $\Delta l=4$ (k); As_2S_8 , $\Delta l=1$ (l); As_2S_8 , $\Delta l=2$ (m); As_2S_8 , $\Delta l=5$ (n); As_2S_9 , $\Delta l=0$ (o); As_2S_9 , $\Delta l=3$ (p); As_2S_9 , $\Delta l=3$ (q); As_2S_9 , $\Delta l=6$ (r)

After all, the CFE (obtained by subtracting the energy of all atoms within cluster, where only half-part contribution from boundary S atoms are considered) averaged per one atom will be taken as a probabilistic measure for cluster formation.

Finally, the *respective* CFE E_f for each chosen atomic cluster will be given in comparison to the energy of single geometrically-optimized $AsS_{3/2}$ trigonal pyramid shown in Fig. 2a (with CFE $E_f=-79.404$ kcal/mol), serving as a reference point in the comparison of different computed cluster configurations.

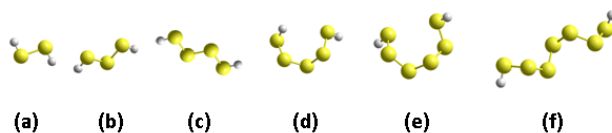


Fig. 3. Geometrically-optimized configurations of S_n chains terminated by H atoms: S_1 (a), S_2 (b), S_3 (c), S_4 (d), S_5 (e), S_6 (f)

3. Results and discussion

The computed geometrically optimized configurations of As_2S_m atomic clusters ($m=2\div 9$) with fully-saturated covalent chemical bonding along with single $AsS_{3/2}$ trigonal pyramid and $As_2S_{4/2}$ cluster built of two such pyramids linked through homonuclear As-As covalent chemical bond are shown in Fig. 2, the corresponding values of chemical bond distances and angles being presented in Table 1 and 2 (the averaged values of these geometrically optimized parameters are *italic*-font distinguished)

Table 1. Geometrical parameters of optimized single $AsS_{3/2}$ trigonal pyramid and $As_2S_{4/2}$ ($m=2$) cluster

Cluster	Bond distance [$\cdot 10^{-4}$ nm]		Bond angle [deg]	
	As-S	As-As	$\angle S-As-S$	$\angle S-As-As$
$AsS_{3/2}$	2252	-	101.9	-
	2254	-	102.9	-
	2256	-	92.7	-
<i>average</i>	<i>2254</i>	-	<i>99.2</i>	-
$As_2S_{4/2}$	2252	2464	100.7	103.0
	2256	-	101.0	95.08
	2253	-	-	102.9
	2254	-	-	94.9
<i>average</i>	<i>2254</i>	<i>2464</i>	<i>100.9</i>	<i>99.0</i>

In our modeling, the lengths of heteronuclear As-S chemical bonds in all simulated network-forming clusters of As_2S_m chemical compositions are well fitted to 2.244÷2.280 Å domain, thus giving in average 2.261 Å. The lengths of homonuclear S-S covalent chemical bonds occur to be from 2.063 Å to 2.095 Å, thus giving in average 2.076 Å.

The values of bond angle centered on As atom neighboring with two S atoms $\angle S-As-S$ change from 90.7° to 107.5° (so giving 99.2° in average).

Other angles in As_2S_m clusters are based on S atom. Thus, the angles for homonuclear S environment $\angle S-S-S$ are fitted to 104.6÷108.6° range (giving 106.7° in average). The angles of heteronuclear S environment $\angle As-S-As$ are distributed to be in 98.9÷103.0° range (giving 100.6° in average). The angles of mixed S environment $\angle S-S-As$ occur to be in 99.5÷110.1° range with an averaged value reaching 101.9°.

Table 2. Geometrical parameters of optimized As_2S_m ($m=3\div 9$) clusters

Cluster, Δl	Bond distance [$\cdot 10^{-4}$ nm]		Bond angle [deg]			
	As-S	S-S	$\angle S-As-S$	$\angle S-S-As$	$\angle S-S-S$	$\angle As-S-As$
As_2S_3 , $\Delta l=0$	2249	-	102.6	-	-	98.9
	2252		103.2			
	2264		92.4			
	2264		96.9			
	2252		99.6			
	2253		97.1			
<i>average</i>	2256	-	98.6	-	-	98.9
As_2S_4 , $\Delta l=1$	2252	2081	97.7	100.4	-	-
	2249		98.8	101.4		
	2269		95.9			
	2248		103.2			
	2248		100.9			
	2275		95.7			
<i>average</i>	2257	2081	98.7	100.9	-	-
As_2S_5 , $\Delta l=1$	2267	-	102.8	-	-	103.0
	2261		104.6			
	2265		91.0			
	2253		107.5			
	2266		105.3			
	2259		97.7			
<i>average</i>	2262	-	101.5	-	-	103.0
As_2S_5 , $\Delta l=2$	2248	2076	103.3	101.5	106.6	-
	2247	2076	101.5	101.3		
	2277		96.0			
	2248		102.0			
	2255		97.5			
	2270		96.6			
<i>average</i>	2257	2076	99.5	101.4	106.6	-
As_2S_6 , $\Delta l=0$	2264	2086	102.9	99.6	-	-
	2262		103.7	99.7		
	2267		93.1			
	2261		105.9			
	2263		102.5			
	2262		100.1			
<i>average</i>	2263	2086	101.3	99.7	-	-
As_2S_6 , $\Delta l=3$	2245	2072	103.3	101.9	106.7	-
	2277	2073	101.5	101.9	106.7	
	2248	2072	95.6			
	2273		96.1			
	2246		98.1			
	2253		102.1			
<i>average</i>	2257	2072	99.5	101.9	106.7	-
As_2S_7 , $\Delta l=1$	2257	2079	106.9	100.1	107.4	-
	2262	2076	103.1	99.5		
	2264		100.0			
	2256		102.7			
	2264		96.6			
	2266		99.0			
<i>average</i>	2262	2077	101.4	99.8	107.4	-
As_2S_7 , $\Delta l=2$	2267	2077	101.6	101.0	-	100.1
	2269	2080	98.3	100.7		
	2259	2080	91.6	100.7		
	2259	2077	91.7	100.9		
	2269		98.3			
	2266		101.5			

Table 2. continued

<i>Average</i>	2265	2078	97.2	100.8	-	100.1
As₂S₇, $\Delta l=4$	2258	2079	101.7	101.2	106.3	-
	2250	2069	97.2	102.0	107.1	
	2271	2072	96.2		107.5	
	2272	2076	96.1			
	2252		97.7			
	2249		97.6			
<i>average</i>	2259	2074	97.7	101.6	106.9	
As₂S₈, $\Delta l=1$	2265	2078	100.0	101.0	-	-
	2269	2078	99.8	101.2		
	2270	2084	90.7	102.2		
	2266	2079	103.0	99.6		
	2262	2079	99.0	100.3		
	2259		97.0	109.4		
<i>average</i>	2265	2080	98.3	102.3	-	-
As₂S₈, $\Delta l=2$	2257	2095	102.1	110.1	104.6	-
	2268	2063	101.5	99.7	108.6	
	2267	2078	103.2			
	2257		96.9			
	2269		102.9			
	2263		98.6			
<i>average</i>	2263	2079	100.9	104.9	106.6	-
As₂S₈, $\Delta l=5$	2249	2077	98.1	109.6	106.1	-
	2251	2070	99.3	101.0	106.7	
	2266	2071	103.7		106.3	
	2276	2074	102.2		107.4	
	2245	2073	93.1			
	2252		98.0			
<i>average</i>	2256	2073	99.1	105.3	106.6	-
As₂S₉, $\Delta l=0$	2263	2079	95.7	100.3	107.3	-
	2266	2080	95.9	101.5		
	2271	2078	96.2	101.7		
	2271	2078	96.4	101.4		
	2262	2080	95.8	101.6		
	2266	2079	95.9	101.2		
<i>average</i>	2266	2079	96.0	101.3	107.3	-
As₂S₉, $\Delta l=3$	2275	2075	91.3	101.0	-	100.5
	2269	2078	101.6	101.9		
	2260	2078	97.3	101.8		
	2261	2075	91.3	100.9		
	2268		97.6			
	2275		101.6			
<i>average</i>	2268	2076	96.8	101.4	-	100.5
As₂S₉, $\Delta l=3$	2255	2078	98.8	100.9	106.3	-
	2265	2072	106.5	102.9	105.8	
	2263	2074	104.6		107.3	
	2272	2075	102.7			
	2261		97.6			
	2259		97.6			
<i>average</i>	2263	2075	101.3	101.9	106.5	-
As₂S₉, $\Delta l=6$	2244	2073	93.5	108.8	105.9	-
	2244	2071	103.0	100.9	106.6	
	2280	2072	104.0		106.5	
	2273	2071	101.4		107.1	
	2252	2071	94.0		107.1	
	2254	2072	97.4			
<i>average</i>	2258	2072	98.8	104.9	106.6	-

The above values of calculated covalent chemical bond lengths and angles for different As_2S_m atomic clusters correlate well with known experimental data on structural parameterization in S-rich glasses of binary As-S system as well as their crystalline counterparts.

Thus, the structure of crystalline As_2S_3 known as mineral orpiment [4] was refined from X-ray diffraction patterns by Morimoto [31], and Mullen and Nowacki [32]. These authors showed that orpiment was composed of layers, the As-S spiral intralayer chains being bridged through S atom between As atoms creating interlinked corner-sharing $AsS_{3/2}$ pyramids. The values of bond angles $\angle S-As-S$ and $\angle As-S-As$ determined by Morimoto [31] are in $92.7\div 106.5^\circ$ and $94.4\div 102.8^\circ$ range, respectively, the average values of bond angles based on As and S atom are respectively 98.7° and 99.3° , and As-S bond lengths are in $2.21\div 2.28$ Å range (i.e. 2.24 Å in average). According to Mullen and Nowacki [32], the values of covalent chemical bond angles $\angle S-As-S$ and $\angle As-S-As$ are respectively ranged from 92.8° to 105.0° and from 87.9° to 103.7° , the average values of bond angles based on As and S atom are 99° and 97.5° , and As-S bond lengths are ranged from 2.243 Å to 2.308 Å (giving 2.283 Å in average).

The experimental data on structural parameters of binary As-S glasses have been also reported (see, for example, [33-36]). The value of heteronuclear As-S bond length obtained from high-resolution time-of-flight neutron-diffraction experiments carried out on stoichiometric As_2S_3 glass is 2.27 Å [33]. The pulsed neutron diffraction study performed on this As_2S_3 glass gave the As-S bond length as 2.29 Å [34]. Lead better and Apling [35] using X-ray and neutron diffraction experimental techniques on some compositions of vitreous As-S close to As_2S_3 found that distribution of As-S bond lengths is centered about 2.24 Å. Yang *et al.* [36] examined structural changes associated with chemical composition using X-ray-absorption spectroscopy and found that As-S bond length is ~ 2.27 Å for S-rich As-S glasses.

Good coincidence in the computed values of covalent chemical bond lengths and angles in our model for two-cation As_2S_m atomic clusters with realistic experimental bond lengths and angles determined for glassy As-S specimens justifies a reasonable ground for further conclusions.

The calculated values of respective CFE E_f for As_2S_m atomic clusters ($m=3\div 9$) are given in Table 3.

To validate eq. (1) for these network-forming clusters at $m=3$ ($Z=2.40$), we parameterize the $As_2S_{4/2}$ atomic cluster corresponding to $m=2$ (see Fig. 2b), the results being listed in Table 1. This $As_2S_{4/2}$ cluster built on direct covalent bridging between two neighboring $AsS_{3/2}$ pyramids (see Fig. 2a) through homonuclear As-As bond possesses the CFE $E_f=-77.683$ kcal/mol, so it is less favored than single trigonal $AsS_{3/2}$ pyramid possessing $E_f=-79.404$ kcal/mol.

There is only one geometrical configuration for As_2S_m cluster with $m=3$ satisfying the condition of ideal “*chain-crossing*” arrangement with $\Delta l=0$ under accepted cluster-evolution algorithm.

Thus, in fact, we deal with two corner-sharing $AsS_{3/2}$ pyramids forming stoichiometric As_2S_3 glass with $Z=2.40$ (Fig. 2c). This cluster possesses CFE $E_f=-79.408$ kcal/mol (which corresponds to respective energy 0.004 kcal/mol, i.e. CFE recalculated in respect to forming energy of single $AsS_{3/2}$ trigonal pyramid). Other linking between $AsS_{3/2}$ pyramids through two common S atoms (edge-sharing) or three S atoms (face-sharing) are unlikely in view of unfavorable CFE [37,38]. Two corner-sharing $AsS_{3/2}$ pyramids (e.g. glass-forming As_2S_3 cluster) are transformed by additional S atom in As_2S_4 cluster with $m=4$ and $Z=2.33$ (see Fig. 2d), which is also alone on this level of compositional row. This atomic cluster with respective CFE reduced to $E_f=-1.06$ kcal/mol has inner *shell*, which is two S half-atoms longer than inter-cluster *core* ($\Delta l=1$), thus resulting only in slight deviation from “*chain-crossing*” model.

Two types of network-forming clusters of the same As_2S_5 composition ($m=5$) but of different topological configurations can be formed in binary As-S system at $Z=2.29$ (Fig. 2e, 2f). The first of them possessing short core and long shell (thus giving $\Delta l=1$) has an obvious preference, the respective CFE being $E_f=-0.76$ kcal/mol, which is the best CFE among all character for S-rich As_2S_m atomic clusters ($m>3$).

With further increase in S content, the modeled As_2S_m clusters keep stable tendency towards “*chain-crossing*”.

Thus, among two different configurations of As_2S_6 clusters ($m=6$, $Z=2.25$) shown in Fig. 2g and 2h, the first one with $\Delta l=0$ has preference ($E_f=-1.43$ kcal/mol).

This tendency is still proper for next step including three types of As_2S_7 atomic clusters ($m=7$, $Z=2.22$) shown in Fig. 2i, 2j and 2k, the cluster with smallest core-shell lengths deviation ($\Delta l=1$, Fig. 2i) having best CFE reaching $E_f=-1.84$ kcal/mol.

Three topological configurations of As_2S_8 atomic clusters ($m=8$, $Z=2.20$) are presented on Fig. 2l, 2m, 2n. But at this level of structural evolution, the “*chain-crossing*” trend does not dominate, since cluster with $\Delta l=2$ (Fig. 2m) has an obvious preference over two others with $\Delta l=1$ (Fig. 2l) and $\Delta l=5$ (Fig. 2n).

In final, we turn to As_2S_9 atomic clusters ($m=9$, $Z=2.18$) allowing four topological configurations under accepted evolution algorithm: one for $\Delta l=0$ (see Fig. 2o), two for $\Delta l=3$ having either short (see Fig. 2p) or long (see Fig. 2q) inter-cluster core, and one for $\Delta l=6$ (see Fig. 2r). From Table 3, it follows that the best respective CFE (i.e. $E_f=-2.30$ kcal/mol) is obtained for atomic cluster with $\Delta l=3$ comprising short core and long shell (shown in Fig. 2p).

Thus, concluding on the above computed CFE values (gathered in Table 3), we can claim that stable glass-forming tendency towards “*chain-crossing*” structural arrangement in binary As-S system is well kept within $Z=2.40\div 2.22$ compositional domain, but with further increase in the S content this system apparently deviates from “*chain-crossing*” model.

The numerous data on glass-forming ability in ChVS of As-S system are in good agreement with these findings. Indeed, as it follows from comprehensive and systematic

research performed yet in the 1960-1970s [1-4], the As-S glasses containing 21-30 at. % of As were most stable against crystallization, while those enriched on S occurred to be quickly affected by spontaneous crystallization even at relatively low room temperature. It was also shown that

As-S ChVS built of trigonal $AsS_{3/2}$ pyramidal structural units linked via S_n chain-like or ring-like formations became unstable with lower average atomic coordination at $Z < 2.20$ [13,14,18, 39,40].

Table 3. Computed values of respective CFE for geometrically-optimized As_2S_m clusters (the preferential energies are bold-distinguished)

As_2S_m cluster, Z	E_f [kcal/mol]						
	$\Delta l=0$	$\Delta l=1$	$\Delta l=2$	$\Delta l=3$	$\Delta l=4$	$\Delta l=5$	$\Delta l=6$
As_2S_3 , Z=2.40	0.004						
As_2S_4 , Z=2.33		-1.06					
As_2S_5 , Z=2.29		-0.76	-1.75				
As_2S_6 , Z=2.25	-1.43			-2.25			
As_2S_7 , Z=2.22		-1.84	-3.39		-2.64		
As_2S_8 , Z=2.20		-3.68	-2.46			-3.14	
As_2S_9 , Z=2.18	-3.57			-2.30 -2.72			-3.34

Table 4 Parameterization of cluster-decomposition reactions (1) and (2) for binary As-S glasses

Initial cluster characteristics			Final cluster characteristics				
As_2S_m	Z	Δl	$\Delta E(1)$ in eq. (1), [kcal/mol]	$S_{1/2}$ number in eq. (2), 2-(m-3)	E_f for S_{m-3} [kcal/mol]	CFE for $As_2S_3 + S_{m-3}$ [kcal/mol]	$\Delta E(2)$ in eq. (2), [kcal/mol]
As_2S_3	2.40	0	-1.330	0	-	-79.408	0
As_2S_4	2.33	1	0.620	2	-65.720	-77.127	-1.22
As_2S_5	2.29	1	-0.508	4	-65.676	-75.485	-3.16
As_2S_6	2.25	0	0.056	6	-65.639	-74.245	-3.73
As_2S_7	2.22	1	-0.156	8	-73.251	-76.672	-0.89
As_2S_8	2.20	2	0.363	10	-73.148	-76.278	-0.67
As_2S_9	2.18	3	-	12	-73.415	-76.139	-0.97

Similar glass-stability region identified due to diminishing non-reversing heat flow in temperature-modulated calorimetric measurements (22.5-29 at. % of As) [23,41], was ascribed to the reversibility window in this system, e.g. the glass compositions, which are optimally constrained (rigid, but stress-free) being inserted between under-constrained floppy and over-constrained stress-rigid phases [42].

Despite this criterion is not satisfied to determine unambiguously the boundaries of optimally constrained phases for compositionally-variable glassy systems (mainly, due to artefacts of experimental measuring technique, employing only one-frequency heat-flow signal to teste different glassy samples at significantly different distance from glass transition temperature) [43-45], these data testify on close similarity with against-crystallization compositional range in As-S system [1-4].

Let's examine intrinsic decomposition processes in As-S glasses described by reaction (1) to verify which types of As_2S_m atomic clusters with characteristic respective CFE listed in Table 3 are most stable in their network-forming ability, the result of such examination being gathered in Table 4.

We can see that decomposition of As_2S_3 network-forming clusters represented themselves as geometrically-optimized configurations of two corner-shared $AsS_{3/2}$ trigonal pyramids (Fig. 2c) is unlikely due to high negative energetic barrier $\Delta E(1)$ for decomposition reaction (1) reaching -1.33 kcal/mol. These atomic clusters are surely dominated among near-stoichiometric glass compositions in binary As-S system. The same concerns As_2S_5 clusters (Z=2.29) with $\Delta E(1)=-0.508$ kcal/mol, as well as As_2S_7 clusters (Z=2.22) with lower but still negative barrier $\Delta E(1)$ close to -0.156 kcal/mol. Oppositely, the decomposition in respect to reaction (1) becomes favorable for As-S glasses near Z=2.33, 2.25 and 2.20, where structural response in glass-forming ability is respectively defined by preferential behavior of As_2S_4 , As_2S_6 and As_2S_8 clusters. Noteworthy, the strong positive decomposition barrier of $\Delta E(1)=0.620$ kcal/mol for As_2S_4 clusters is well distinguished as contrast to $\Delta E(1)=-1.330$ kcal/mol for neighboring As_2S_3 clusters (Z=2.40).

Intrinsic local chemical decomposition of As_2S_m atomic clusters on the best energetically-favorable As_2S_{m+1} and As_2S_{m-1} clusters in respect to reaction (1) can be experimentally revealed, provided it will be accompanied by essential global phase-separation [46] due to reaction

(2). This reaction is to estimate most expected phase-separation products composed of corner-shared $\text{AsS}_{3/2}$ pyramids (e.g. As_2S_3 clusters shown in Fig. 2c) and S_{m-3} chain remainders among the same set of As_2S_m clusters.

Let's examine these decomposition variants.

Preliminary, we computed S_{m-3} chains in dependence on their length defined by number of S half-atoms [47]. The geometrically-optimized configurations of such atomic clusters are shown in Fig. 3, their parameters including CFE E_f being presented in Table 4.

Then, the energetic barrier $\Delta E(2)$ of reaction (2) was calculated for geometrically optimized As_2S_m clusters from Table 3 with boundary counterparts of these phases (such as As_2S_3 and S_{m-3} clusters). In general, the $\Delta E(2) < 0$ is indicative of stable As_2S_m clusters (blocked global phase separation), while $\Delta E(2)$ approaching 0 and tending towards positive side testifies on possible phase separation in a system.

As it follows from Table 4, the energetic barriers $\Delta E(2)$ of phase-separation reaction (2) are gradually negative in binary As-S system within $2.25 < Z < 2.40$ (for As_2S_m atomic clusters with $m=3-6$), strong maximum $\Delta E(2) = -3.73$ kcal/mol being character for As_2S_6 glass ($Z=2.25$). This glass seems to be most stable against devitrification due to competitive input of different glass-forming structural blocks [1,2]. In these ChVS, only anomalies caused by oscillation character of local chemical decomposition due to reaction (1) are possible, i.e. intrinsic decomposition near As_2S_4 ($Z=2.33$) and As_2S_6 ($Z=2.25$). With transition to As_2S_7 composition ($Z=2.22$), the $\Delta E(2)$ barrier shows abrupt change to -0.89 kcal/mol (so jump in the barrier height reaches 2.8 kcal/mol), this effect being quite stable in all further S-rich glasses with slight deviations around $-(0.8-0.9)$ kcal/mol (see Table 4). Such behavior can be attributed to global phase separation due to reaction (2), despite positive $\Delta E(2)$ values are not achieved in this compositional row, which can be presumably caused by difference in the procedure of chalcogen chains termination for As_2S_m and S_{m-3} clusters. The As_2S_7 glass ($Z=2.22$) does not correspond to full coincidence in the glass-forming tendencies due to (1) and (2) reactions, since unfavorable barrier for local chemical decomposition $\Delta E(1)$ is accompanied by favorable one for global phase separation $\Delta E(2)$, as it follows from Table 4. This is proper for ChVS of next S-rich composition As_2S_8 ($Z=2.20$), where both trends coincide by energetic directionality, inserting *the instability onset* in binary As-S system due to approaching region of intrinsically decomposed and phase separated glasses.

Noteworthy, in other archetypal binary As-Se system, which can be accepted as electronic counterpart for current As-S system [1-5], this instability onset is more shifted towards stoichiometry (As_2Se_6 , $Z=2.25$), thus defining some technological fluctuations in the densities of these ChVS [21]. At the same time, the inhibited phase-separation tendencies in As-Se glasses can be obviously associated with more depressed energetic barriers of global phase-separation in this system. Thus, the character jump in the $\Delta E(2)$ barrier heights of the global phase-separation reaction (2) reaches only ~ 0.6 kcal/mol [21], so

being essentially lower than in the binary As-S system where this jump overcomes ~ 3 kcal/mol (as estimated from the corresponding barrier heights for As_2Se_6 and As_2Se_8 glasses given in Table 4). This conclusion on global phase-separation in As-S glass-forming system for highly S-rich chemical compositions ($Z < 2.22$) is in an excellent respect to great amount of experimental evidences [1-4,13,40,41].

4. Conclusions

The compositionally-dependent network-forming tendencies in ChVS of archetypal As-S system are examined within $2.18 < Z < 2.40$ domain using *ab-initio* quantum chemical modeling routine termed as CINCA (cation-interlinking network cluster approach). Different possible configurations of As_2S_m clusters ($m=3-9$) are considered. On the basis of computed energies for more than 20 clusters, we conclude that stable glass-forming tendency towards "chain-crossing" arrangement is well kept within $Z=2.40-2.22$ range, but with further increase in S content this glassy system apparently deviates from "chain-crossing" model. The As-S glasses with mean coordination of $Z=2.40$ (corresponding to stoichiometric As_2S_3) and $Z=2.29$ (corresponding to As_2S_5 glass) are expected to be most stable in this binary As-S system. Some instabilities are character for glasses with $Z=2.33$, 2.25 and 2.20 because of their preference to intrinsic local chemical decomposition on As- and S-rich structural fragments. The As-S glasses within $2.25 < Z < 2.40$ domain are quite stable against separation on As_2S_3 and "pure" S_n phases, while those expending in S-rich side beyond this composition ($Z < 2.22$) are most sensitive to global phase separation. The As_2S_8 glass ($Z=2.20$) is distinguished as introducing instability onset in As-S system due to abrupt tendency towards both local intrinsic chemical decomposition and global phase separation.

References

- [1] Z. U. Borisova, Chemistry of glassy semiconductors (in Rus.), Ed. Leningrad. Univ. Leningrad (1972).
- [2] Z. U. Borisova, Glassy semiconductors, Plenum Press, New York-London (1981).
- [3] G. Z. Vinogradova, Glass formation and phase equilibria in chalcogenide systems. Binary and ternary systems (in Rus.), Nauka, Moscow, (1984).
- [4] A. Feltz, Amorphous Inorganic Materials and Glasses, VCH Verlagsgesellschaft, Weinheim / VCH Publishers, New York (1993).
- [5] M. Popescu, Non-crystalline chalcogenides, Kluwer Academic Publ., Dordrecht-Boston-London (2000).

- [6] Semiconducting Chalcogenide Glass 1: Glass Formation, Structure, and Simulated Transformations in Chalcogenide Glasses. – Semiconductors and Semimetals, vol. 78, R. Fairman, B. Ushkov (Eds.). Elsevier Academic Press, Amsterdam-Boston-London-New York-Oxford-Paris-San Diego-San Francisco-Singapore-Sydney-Tokyo (2004).
- [7] Chalcogenide glasses: Preparation, properties and applications. Woodhead Publishing Series in Electronics and Optical Materials, J.-L. Adam, X. Zhang (Eds.) Philadelphia-New Delhi (2013).
- [8] R. Frerichs, *J. Opt. Soc. Am.* **43**, 1153 (1953).
- [9] X. Zhang, B. Bureau, C. Boussard-Pledel, J. Lucas, P. Lucas, *Chem. Europ. J.* **14**, 432 (2008).
- [10] K. Richardson, D. Krol, K. Hirao, *Intern. J. Appl. Glass Sci.* **1**, 74 (2010).
- [11] B. J. Eggleton, B. Luther-Davies, K. Richardson, *Nature Photonics* **5**, 141 (2011).
- [12] J.-L. Adam, L. Calvez, J. Troles, V. Nazabal, *Intern. J. Appl. Glass Sci.* **6**, 287 (2015).
- [13] S. Tsuchihashi, Y. Kawamoto, *J. Non-Cryst. Sol.* **5**, 286 (1971).
- [14] S. Maruno, M. Noda, *J. Non-Cryst. Sol.* **7**, 1 (1972).
- [15] J. S. McCloy, B. J. Riley, S. K. Sundaram, H. A. Qiao, J. V. Crum, B. R. Johnson, *J. Non-Cryst. Sol.* **356**, 1288 (2010).
- [16] R. Golovchak, O. Shpotyuk, J. S. McCloy, B. J. Roley, C. F. Windisch, S. K. Sundaram, A. Kovalskiy, H. Jain, *Phil. Mag.* **90**, 4489 (2010).
- [17] S. K. Sundaram, J. S. McCloy, B. J. Riley, M. K. Murphy, H. A. Qiao, C. F. Windisch, E. D. Walter, J. V. Crum, R. Golovchak, O. Shpotyuk, *J. Am. Ceram. Soc.* **95**, 1048 (2011).
- [18] M. B. Myers, E. J. Felty, *Mat. Res. Bull.* **2**, 535 (1967).
- [19] O. Shpotyuk, M. Hyla, V. Boyko, *J. Optoelectron. Adv. M.* **15**, 1429 (2013).
- [20] O. Shpotyuk, V. Boyko, M. Hyla, *Phys. Status Solidi C* **6**, 1882 (2009).
- [21] O. Shpotyuk, M. Hyla, V. Boyko, *Comp. Mater. Sci.* **110**, 144 (2015).
- [22] D. G. Georgiev, P. Boolchand, M. Micoulaut, *Phys. Rev. B* **62**, 9228 (2000).
- [23] P. Boolchand, P. Chen, U. Vempati, *J. Non-Cryst. Sol.* **355**, 1773 (2009).
- [24] P. Chen, P. Boolchand, D.G. Georgiev, *J. Phys.: Condens. Matter* **22**, 065104 (2010).
- [25] O. Shpotyuk, M. Hyla, V. Boyko, R. Golovchak, *Physica B* **403**, 3830 (2008).
- [26] R. Golovchak, O. Shpotyuk, A. Kozdras, B. Bureau, M. Vlcek, A. Ganjoo, H. Jain, *Phil. Mag.* **67**, 4323 (2007).
- [27] R. Golovchak, H. Jain, O. Shpotyuk, A. Kozdras, A. Saiter, J.-M. Saiter, *Phys. Rev. B*, **78**, 014202 (2008).
- [28] O. Shpotyuk, R. Golovchak, A. Kozdras, Physical aging of chalcogenide glasses, in: J.-L. Adam and X. Zhang (Eds.), *Chalcogenide glasses: Preparation, properties and applications*, Woodhead Publ. Ser. in Electronics and Optical Materials, Philadelphia-New Delhi (2013).
- [29] W. J. Hehre, R. F. Stewart, J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969).
- [30] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **72**, 5639 (1980).
- [31] I. Morimoto, *Miner. J.* **1**, 160 (1954).
- [32] D. J. E. Mullen, W. Nowacki, *Z. Kristallogr.* **136**, 48 (1972).
- [33] J. H. Lee, A. C. Hannon, S. R. Elliott, arXiv preprint cond-mat/0402587 (2004).
- [34] Y. Iwadate, T. Hattori, S. Nishivama, K. Fukushima, Y. Mochizuki, M. Misawa, T. Fukunaga, *J. Phys. Chem. Solids*, **60**, 1447 (1999).
- [35] A. J. Leadbetter, A. J. Apling, *J. Non-Cryst. Sol.* **15**, 250 (1974).
- [36] C. Y. Yang, M. A. Paesler, D. E. Sayers, *Phys. Rev. B*, **39**, 10342 (1989).
- [37] M. Hyla, V. Boyko, O. Shpotyuk, *J. Filipecki, Visnyk Lviv. Univ. Ser. Physics*, **43**, 118 (2009).
- [38] O. Shpotyuk, V. Boyko, Ya. Shpotyuk, M. Hyla, *Visnyk Lviv. Univ. Ser. Physics*, **43**, 226 (2009).
- [39] A. Bertoluzza, C. Fagnano, P. Monti, G. Semerano, *J. Non-Cryst. Sol.* **29**, 49 (1978).
- [40] L. Busse, *Phys. Rev. B*, **29**, 3639 (1984).
- [41] P. Chen, Ch. Holbrook, P. Boolchand, D. G. Georgiev, K. A. Jackson, M. Micoulaut, *Phys. Rev. B*, **78**, 224208 (2008).
- [42] M. F. Thorpe, D. J. Jacobs, M. V. Chubynsky, J. C. Phillips, *J. Non-Cryst. Sol.* **266-269**, 859 (2001).
- [43] P. Lucas, E. A. King, O. Gulbiten, J. L. Yarger, E. Soignard, B. Bureau, *Phys. Rev. B* **80**, 2141140 (2009).
- [44] H. Y. Zhao, Y. P. Koh, M. Pyda, S. Sen, S. L. Simon, *J. Non-Cryst. Sol.* 2013, **368**, 63.
- [45] O. Shpotyuk, A. Kozdras, R. Golovchak, M. Iovu, *Phys. Stat. Solidi C*, **8**(11-12), 3043 (2011).
- [46] M. B. Myers, J. S. Berkes, *J. Non-Cryst. Sol.* **8-10**, 804 (1972).
- [47] V. Boyko, M. Hyla, O. Shpotyuk, *Visnyk Lviv. Univ. Ser. Physics*, **43**, 233 (2009).

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