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TWO-CATION CORNER- AND EDGE-SHARING INTERLINKED CLUSTERS IN As/Ge-S GLASSES

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Quantum mechanical *ab initio* calculations of corner- and edge-sharing cluster interlinking in binary As/Ge-S glass formers were performed using HyperChem Realise 7,5 program. The average formation energies (AFE) of clusters with respect to single pyramid-like $\text{AsS}_{3/2}$ and tetragon-like $\text{GeS}_{4/2}$ building blocks were calculated. It was shown that AFE associated with the number of Lagrangian constraints per atom would explain the adaptability of chalcogenide glass-forming backbone to structural self organization.

Key words: Chalcogenide glasses, *ab initio* calculations.

The chalcogenide glasses (ChG) derive their name from chalcogen (Ch) elements S, Se or Te but not O as a main component in their chemical composition. They are important materials both for fundamental investigation of particularities in the disordered state and for different applications. Two common chalcogenide systems consist of V-VI elements, i.e. compounds with pnictogen (P) atoms from V group (e.g. As, Sb), where the glass-forming regions are mostly centered around stoichiometric P_2Ch_3 composition, and compounds with group IV elements, i.e. Si, Ge (denoted tetragens, T, in view of the prevalent tetrahedral coordination), where binary glass-forming IV-VI compositions are centered around stoichiometric TCh_2 composition. The atoms in ChG form extended three dimensional networks, they maintaining short-range order by keeping the number of covalent bonds to nearest neighbours in strong dependence on the valence of constituent atoms. Hence group IV elements are four-fold, group V elements are three-fold and group VI elements are two-fold coordinated.

Amorphous chalcogenides of arsenic and germanium are the most characteristic materials. It is well known that at stoichiometric As_2S_3 and GeS_2 compositions (i.e. at the compositions where only heteropolar chemical bonds exist) one As atom is linked to three S atoms and each S atom is linked to two As atoms in As-S glass or each Ge atom is linked to four S atoms and each S atom is linked to two Ge atoms in Ge-S. Experimental data suggest the presence of following structural units in a glass-forming network – pyramidal $\text{As}(\text{S}_{1/2})_3$ with As atom raised above the plane defined by three S atoms and tetrahedral $\text{Ge}(\text{Se}_{1/2})_4$ being a tetrahedron centred on Ge atoms [1].

In dependence on chemical composition the ChG change the number of Lagrangian

constraints per atom n_c forming under- ($n_c < 3$), over- ($n_c > 3$) or optimally-constrained ($n_c = 3$) atomic networks with fully saturated covalent bonding. It was assumed by Phillips [2] that optimal mechanical stability of the network can be achieved when $n_c = 3$, this network being called self-organized phase. The underconstrained (floppy) network with $n_c < 3$ is easily deformed, but in the overconstrained (rigid) networks with $n_c > 3$ any deformation requires stretching or bending bonds. The bonds are not distributed randomly and the network can adapt itself to lower the stress due to overconstrained regions. In general, the n_c number can be calculated according to the known mean-field constraints theory [3, 4]:

$$n_c = \frac{Z}{2} + (2Z - 3) \frac{n_l}{N} - \frac{n^{ring}}{N}, \quad (1)$$

where: $Z = \left(\frac{\sum_r n_r}{\sum_r n_r} \right)$ is coordination number of glass network constructed by n_r atoms having r bonds $\sum_r n_r = N$; n_l and n^{ring} – corrections on dangling bonds and rings, respectively.

In this work, we have used new cation-interlinking network cluster approach (CINCA) to build the simplest molecular-like species with fully-saturated covalent bonding within binary As/Ge-S systems: pyramid-like $\text{AsS}_{3/2}$ building blocks having 3 shared S atoms and tetragon-like $\text{GeS}_{4/2}$ building blocks having 4 shared S atoms. These basic structural units having 2 cations (As or Ge) create the whole ChG network. They can be interconnected into two ways, especially as atom-shared clusters (ASC) with shared S atom or as bond-shared clusters (BSC) with shared S-S bond. Figure 1 shows ASC (a) and BSC (b) for two pyramidal units. The ending chalcogen atoms belong to basic unit in the case of BSC cluster, while we should consider only half-part contribution of each terminal chalcogen atom in the case of ASC (because the next half takes part in another unit).

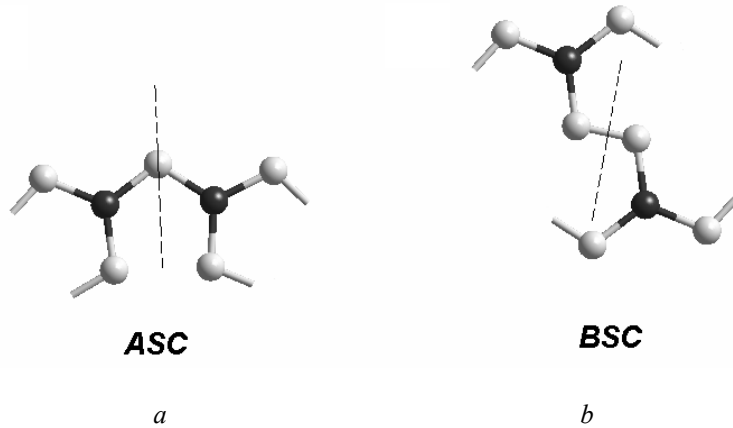


Fig. 1. ASC cluster interlinked with S atom (a) and BSC cluster interlinked with S-S bond (b) for two pyramidal $\text{As}(\text{S}_{1/2})_3$ units (the black color is for S atoms and grey one for As atoms)

The calculations only for ASC structural units were performed. We have studied the formation energy of different type of interconnections between building structural units: corner-sharing CS, edge-sharing ES or face-sharing FC, either pyramidal or

tetrahedral basic units. As a point of reference, energies of single $\text{As}(\text{S}_{1/2})_3$ building blocks having 3 shared chalcogen atoms ($Z = 2,40$) and $\text{Ge}(\text{S}_{1/2})_4$ building blocks having 4 shared chalcogen atoms ($Z = 2,67$). All clusters are shown in fig. 2 and 3.

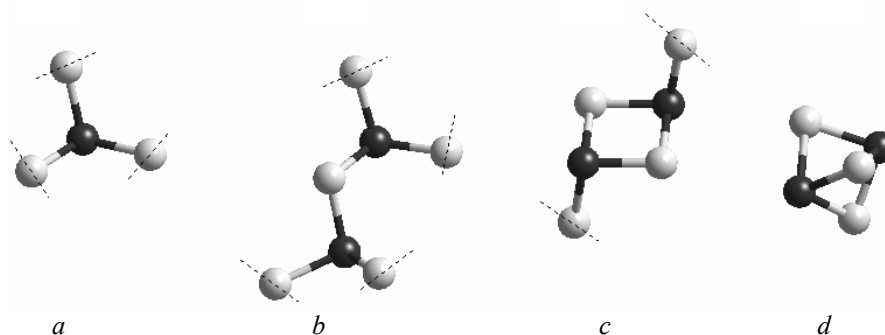


Fig. 2. Schematic view of geometrically optimized single (a), corner- (b), edge- (c) and face-shared (d) $\text{As}(\text{S}_{1/2})_3$ units (the black color is for S atoms and grey one for As atoms)

Recently, the first-principles methods have been very successful to calculate structural properties of materials. In order to study the optimal geometries and calculate formation energy of clusters *ab initio* method based on the Hartree-Fock approximation was used. A few *ab initio* calculations of clusters energy were carried out by R.M. Holomb and co-workers [5–7]. Although the calculations do not allow to drive a conclusion about preferences in connection suitable building units. Then, a new energetic parameter, an average formation energy (AFE), which is defined as formation energy per atom in a cluster, was introduced in our calculations. We have made our conclusions on the base of this parameter. In addition, our analysis was supplemented by mean-field constraints theory.

Quantum mechanical calculations were performed using HyperChem Realise 7,5 PC program [8]. The RHF *ab initio* level was taken as a ground for mathematical calculating procedure, either geometry optimization or single point energy, the 6–311G* basis set, being employed. All ending S atoms within clusters were additionally terminated by H atoms to be two-fold coordinated in full respect to their saturated covalent bonding. As a result of single point energy calculations, the total energy E_t for each molecule was obtained. Since all clusters were of ASC type, the $\frac{1}{2}$ energy of S atom along with energy of H atoms and bonds between them were subtracted from total energy E_t . The ASC energy was calculated as half of total energy of *H-S-H* molecule giving $E_{ASC} = -125091,0876$ kcal/mol. The energy of single As, Ge and S atoms was accepted to be $E_{As} = -140190,133$ kcal/mol, $E_{Ge} = -1302219,833$ kcal/mol and $E_S = -249381,9706$ kcal/mol, respectively. The overall energy of atoms within cluster E_{at} was equal to:

$$E_{at} = n_{As} \cdot E_{As} + n_{Ge} \cdot E_{Ge} + n_S \cdot E_S, \quad (2)$$

where n_{As} , n_{Ge} and n_S are the number of As, Ge and S atoms, respectively.

The cluster formation energy, E_f , was calculated as:

$$E_f = E_c - E_{at}, \quad (3)$$

where E_c was total energy of the cluster, E_{at} was overall energy of atoms forming the cluster.

To estimate the glass-forming tendency within cation-interlinked clusters, the average formation energy AFE defined as cluster formation energy per atom was introduced:

$$E_f^{av} = E_f / N, \quad (4)$$

where E_f was cluster formation energy in respect to (3), N was total number of atoms in the cluster ($N = n_{As} + n_{Ge} + n_S$).

The structures of clusters studied displayed in fig. 2 and 3 (the terminated H atoms are not shown).

The optimized bond distances and bond angles for all clusters are given in table 1 and 2. These values are quite close to known experimental data proper to crystalline As_2S_3 and GeS_2 . We calculated the number of Lagrangian constraints per atom, n_c , too. The results of both constraints and energetic calculations for both binary systems (As-S and Ge-S) are presented in Table 3 and 4, respectively.

Table 1

Geometric parameters of optimized $As(S_{1/2})_3$ -based clusters

Type	Bond distance [10^{-4} nm]	Bond angle [deg]	
	As-S	S-As-S	As-S-As
As(S_{1/2})₃-single	2251,5	101,94	-
	2254,0	102,94	
	2256,1	92,67	
As(S_{1/2})₃-CS	2248,6	102,62	98,9
	2252,3	103,17	
	2263,5	92,35	
	2264,3	96,98	
	2252,4	99,57	
	2253,1	97,14	
As(S_{1/2})₃-ES	2252,2	101,00	91,18
	2266,7	101,60	91,16
	2266,3	88,83	
	2267,4	101,46	
	2267,0	100,89	
	2250,6	88,80	
As(S_{1/2})₃-FS	2284,8	86,99	74,74
	2284,9	86,98	74,74
	2284,6	86,99	74,74
	2284,8	86,99	
	2284,8	86,98	
	2284,7	86,99	

Table 2

Geometric parameters of optimized $\text{Ge}(\text{S}_{1/2})_4$ -based clusters

Type	Bond distance	Bond angle	
	$[10^{-4} \text{ nm}]$	[deg]	
	Ge-S	S-Ge-S	Ge-S-Ge
$\text{Ge}(\text{S}_{1/2})_4$-single	2224,9	112,67	-
	2236,6	109,62	
	2236,6	109,42	
	2215,1	102,80	
		112,67	
	109,42		
$\text{Ge}(\text{S}_{1/2})_4$-CS	2238,5	108,56	98,42
	2238,7	107,88	
	2238,5	110,67	
	2242,7	108,28	
	2238,5	109,53	
	2238,6	111,82	
	2238,5	110,67	
	2242,8	111,83	
		108,55	
	107,88		
	109,53		
	108,28		
$\text{Ge}(\text{S}_{1/2})_4$-ES	2224,0	111,88	83,79
	2223,9	113,88	
	2231,5	110,06	84,30
	2242,4	110,05	
	2224,0	113,88	
	2223,9	95,96	
	2242,4	110,05	
	2231,4	113,88	
		111,88	
	110,05		
	113,88		
	95,96		
$\text{Ge}(\text{S}_{1/2})_4$-FS	2194,9	124,80	67,62
	2274,9	124,80	
	2274,9	121,89	67,81
	2269,7	91,76	
	2194,9	92,13	
	2275,6	92,13	
	2275,6	124,91	
	2269,7	124,91	
		121,71	
		92,11	
		92,11	
	91,72		

Table 3

Results of calculated the number of Lagrangian constraints per atom, n_c , and energetic calculations for both binary system As-S; $Z=2,40$

Cluster characterization			Energetic parameters			
Type	N	n_c	As _n S _m H _p total energy, E _t	As _n S _m cluster energy, E _c	Forma- tion energy, E _f = E _c - E _{at}	AFE average formation energy, E _f ^{av} = E _f /N
			kcal/mol	kcal/mol	kcal/mol	kcal/mol
As(S _{1/2}) ₃ -single	2,5	3,00	-2151444,860	-1776171,598	-198,509	-79,404
As(S _{1/2}) ₃ -CS	5	3,00	-4052707,566	-3552343,215	-397,038	-79,408
As(S _{1/2}) ₃ -ES	5	2,60	-3802519,623	-3552337,448	-391,271	-78,254
As(S _{1/2}) ₃ -FS	5	2,20	-3552319,113	-3552319,113	-372,936	-74,587

Table 4

Results of calculated the number of Lagrangian constraints per atom, n_c , and energetic calculations for both binary system Ge-S; $Z=2,67$

Cluster characterization			Energetic parameters			
Type	N	n_c	Ge _n S _m H _p total energy, E _t	Ge _n S _m cluster energy, E _c	Forma- tion energy, E _f = E _c - E _{at}	AFE average formation energy, E _f ^{av} = E _f /N
			kcal/mol	kcal/mol	kcal/mol	kcal/mol
Ge(S _{1/2}) ₄ -single	3	3,67	-2301637,257	-1801272,907	-289,133	-96,378
Ge(S _{1/2}) ₄ -CS	6	3,67	-4353080,104	-3602533,578	-566,029	-94,338
Ge(S _{1/2}) ₄ -ES	6	3,00	-4102907,744	-3602543,394	-575,845	-95,974
Ge(S _{1/2}) ₄ -FS	6	3,00	-3852684,078	-3602501,903	-534,354	-89,059

In the case of pyramidal As(S_{1/2})₃-based clusters, the highest AFE value (-74,587 kcal/mol) is achieved for face-sharing interlinking (table 3). It means that these structural units are unprofitable in ChG from energetic point of view. The AFE either of single As(S_{1/2})₃ pyramid or two corner-sharing As(S_{1/2})₃ pyramids are the lowest ones being as high as -79,404 kcal/mol and -79,408 kcal/mol, respectively. Hence the structure of binary As-S system prefers units built of corner-sharing As(S_{1/2})₃ pyramids.

These corner-sharing pyramids form the optimally-constrained atomic network ($n_c=3$), while the edge-sharing pyramids form only under-constrained glassy network ($n_c<3$).

Therefore, on the basis of our calculations, we can expect the corner-sharing pyramidal-like interlinking in stoichiometric As_2S_3 ChG in full respect to known structural model given by Zachariasen yet in the 1930-s [9].

In the case tetrahedral $\text{Ge}(\text{S}_{1/2})_4$ -based clusters, the highest AFE value (-89,059 kcal/mol) is achieved for face-sharing interlinking too (see table 4). So these structural units apparently do not occur in the real glass-forming networks. The lowest AFE value (-96,378 kcal/mol) is character for single $\text{Ge}(\text{S}_{1/2})_4$ cluster and two-cation interlinking edge-sharing cluster (-95,974 kcal/mol), while the corner-sharing tetrahedrons have AFE=-94,338 kcal/mol.

Therefore, the edge-sharing tetrahedral-like units form the optimally-constrained glassy network ($n_c=3$), while the corner-sharing units form the over-constrained one ($n_c>3$). In general, this conclusion appears to be consistent with outrigger raft model proposed by Phillips [10].

On the basis of calculations performed with HyperChem Realise 7,5 program, it is shown that corner-shared $\text{As}(\text{S}_{1/2})_3$ pyramids form the optimally-constrained atomic network ($n_c=3$) with the lowest AFE value, while the edge-sharing interlinking of $\text{Ge}(\text{S}_{1/2})_4$ tetrahedrons is the most preferential one for optimally-constrained Ge-S glassy network.

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**ДВОКАТИОННЕ ПОЄДНАННЯ ЧЕРЕЗ КУТ ТА ЧЕРЕЗ РЕБРО
СКЛОФОРМУЮЧІ КЛАСТЕРИ У СТЕКЛАХ СИСТЕМИ As/Ge-S****М. Хиля¹, В. Бойко², О. Шпотюк², Я.Філіпецький¹**¹*Інститут Фізики, Університет Яна Длугоша**ал. Армії Крайової 3/15, 42 201 Ченстохова, Республіка Польща*²*Інститут Матеріалів, Науково-виробниче підприємство "Карат"**вул. Стрийська 202, Львів 79031, Україна*

Проведено квантово-механічні *ab initio* обчислення поєднаних через кут та через ребро склоформуючих кластерів бінарних систем As/Ge-S за допомогою програми HyperChem 7,5. Обчислено середню енергію утворення кластера по відношенню до піраміди AsS_{3/2} та тетраедра GeS_{4/2}. Показано, що ця енергія разом з числом обмежень ступенів вільності Лагранжа пояснює адаптивність халькогенідного склоутворювального каркасу до структурної самоорганізації.

Ключові слова: халькогенідні стекла, *ab initio* обчислення.

**ДВОКАТИОННЫЕ ОБЪЕДИНЕННЫЕ ЧЕРЕЗ УГОЛ И ЧЕРЕЗ РЕБРО
СТЕКЛОФОРМИРУЮЩИЕ КЛАСТЕРЫ В СТЕКЛАХ СИСТЕМЫ As/Ge-S****М. Хиля¹, В. Бойко², О. Шпотюк², Я.Филипецкий¹**¹*Інститут Фізики, Університет Яна Длугоша**ал. Армії Крайової 3/15, 42 201 Ченстохова, Республіка Польща*²*Інститут Матеріалів, Научно-виробниче підприємство "Карат"**ул. Стрийська 202, Львів 79031, Україна*

Проведены квантово-механические *ab initio* расчеты объединенных через угол и через ребро стеклоформирующих кластеров бинарных систем As/Ge-S с помощью программы HyperChem 7,5. Вычислена средняя энергия образования кластера по отношению к пирамиде AsS_{3/2} и тетраэдру GeS_{4/2}. Показано, что эта энергия вместе с числом ограничений степеней свободы Лагранжа объясняет адаптивность халькогенидного стеклообразующего каркаса к структурной самоорганизации.

Ключевые слова: халькогенидные стекла, *ab initio* вычисления.

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