

Structural-topological genesis of network-forming nanoclusters in chalcogenide semiconductor glasses

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New simulation methodology to justify glass-forming trends in covalent-bonded networks like chalcogenide semiconductor glasses known as cation-interlinking network cluster approach (CINCA) was developed. Topological peculiarities of network glass-forming nanoclustering in binary As-S system are illustrated at the example of As₂S₄ base clusters with As_{4/3}S₃ intra-cluster cores interconnected by inter-cluster chalcogen bridges of equal lengths. Numerical criteria to evaluate cluster-forming ability were probed at the example of interlinked tetrahedral GeS(Se)_{4/2}-based clusters typical for binary Ge-S/Se glass formers.

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1. Introduction

Network glass formers constitute an important class of disordered substances, which can be easily prepared in melt-quenched vitreous state with fully saturated covalent bonding [1,2]. The chalcogenide semiconductor glasses (ChSG), the glassy-like alloys of chalcogens (i.e. S, Se or Te but not O) and some chemical elements from IV and V groups of the Periodic table (Si, Ge, As, Sb), can serve as typical representatives of such network-forming disordered solids. Their semiconductor properties extensively studied by N.A. Goryunova and B.T. Kolomiets since the middle of the 20-th century [2-4], have opened a new insight on their unprecedented applicability in optoelectronics and photonics. Numerous achievements in ChSG [5-7] are so important in nowadays civilian developments, that an emergence a new field of knowledge – the *Chalcogenide Photonics* – was claimed at the end of first decade of third millennium [8]. That is why *composition-structure-properties* correlation has attained a significant importance at all stages of ChSG development, from early implementation in optical-electrical memory systems to recent achievements in IR telecommunication, sensing and photonics. An especial role of this problem has been revealed in view of structural-topological organization character for network glass formers governed by bond-related constraints counting algorithms developed within Thorpe-Phillips mean-field rigidity theory [9-11].

In this work, the possibility to understand the driven forces in ChSG evolution will be analyzed from the point of new approach exploring concept of their chemical-topological structural arrangement.

2. Glass structure characterized within CINCA

This model based on total energy calculations for geometrically-optimized atomic nanoclusters of different configurations (CINCA – Cation-Interlinking Network Cluster Approach) [12-14] can be considered as an supplementary to other one developed by M. Micoulaut to explain self-organization tendencies in network glass formers using Boltzmann factor as probability criterion for different structural fragments in ChSG (CICA – Size Increasing Cluster Approximation) [15-19].

2.1 Bond-network probabilistic and main principles of glass formation in ChSG-based systems

It is well known since the earliest stages of ChSG research, that introduction of other polyvalent elements apart from main (As, Ge, S< SE, Te) can contribute to considerable stabilization of their structure and stretch significantly the region of their glass formation ability far beyond simple stoichiometric compositions [1,2]. To a great extend, this remarkable tendency are proper to solids with predominantly covalent-like chemical bonding [20].

In contrast to crystalline counterparts, the elementary components of ChSG can be easily transformed in a system of many atoms chemically bounded within regular network. This network differs from crystalline lattice in that it has no long-range structural order. Atoms in ChSG are known to form extended networks, maintaining short-range order by keeping the number of covalent chemical bonds to the nearest neighbours in strong dependence on the valence state of constituent atoms. It means that, obeying the well-known "8-N" (octet) rule, the chalcogen atoms (acting as potential anions in view of their

electronegativity [21]) are mainly two-fold coordinated, while non-chalcogen atoms (as potential cations) have a higher coordination, e.g. the elements from IV group typically demonstrate four-fold coordination in its nearest neighbouring, while elements from V group are mainly three-fold coordinated. Therefore, in ideal bond-saturated ChSG-based network, there are no surfaces, inner voids, coordination topological defects (locally-charged negative-positive atomic pairs), dangling bonds or atomic rings and every atom has a full set of nearest covalent-bonded neighbours.

Under above circumstances, as it was first noticed by R.L. Myuller in the earliest 1960-s [20], it is relatively simply to represent the glass structure (GS) of ChSG as a superposition of different atomic building blocks or *structural units* (s.u.) in respect to *additive rule*:

$$GS \equiv \Sigma(s.u.)_i + \Sigma(s.u.)_j + \Sigma(s.u.)_k + \dots, \quad (1)$$

where i, j, k indices denote contributions from corresponding s.u. in fully-saturated glassy matrix.

These s.u. including, as much as possible, the number of covalent chemical bonds, are most typical cation- and anion-based atomic groups for different glass forming compositions. In case of ChSG, the maximum number of neighbours for each atom is equal to the number of valence bonds which it can form. Therefore, in terms of R.L. Myuller [20], the glass structure of selenium or sulphur can be presented in the form of simple s.u. like $\text{SeSe}_{2/2}$ or $\text{SS}_{2/2}$, respectively (the super- and subscripts are used to denote number of atoms and linking environment in s.u., respectively). Within this principle, it is quite simply to describe also the structure of binary glassy g-As/Ge-S/Se compounds. For example, the structure of g- As_2Se_3 can be presented by $\text{AsSe}_{3/2}$ pyramidal s.u. with three heteropolar As-Se bonds, while the structure of g-Ge-Se can be presented by $\text{GeSe}_{4/2}$ tetrahedrons with four Ge-Se bonds interconnected via $\text{SeSe}_{2/2}$ s.u. of different lengths. The structure of g- $\text{As}_{50}\text{Se}_{50}$ is formed by interconnecting $\text{As}_2\text{Se}_{4/2}$ s.u. having four heteropolar As-Se and one homopolar As-As bond. These glass-forming s.u. should be taken in a ratio corresponding to the glass composition, their number being easily calculated from atomic density and molar weight of the corresponding ChSG.

Despite apparent simplicity of this approach, the transition to more complicated ternary and multinary ChSG is not always quite meaningful. To build the corresponding s.u. reflecting realistic interatomic correlations in a glassy network evolved a few cations (anions), we should accept a great variety of possible variants. Some of them can be formed from complicated topological interconnections based on small rings, “wrong” covalent chemical bonds and different polyhedrons. Not all of these elements can be strictly evaluated numerically for some ChSG, introducing probabilistic trends in the general estimation procedure. So from a simplicity view, to resolve correctly this controversy, a more preferential seems to be an approach based on finding one unique atomic nanocluster, which

reflect with a necessity all principal covalent-like interactions (both inter- and intra-atomic ones), chemical composition and space topology of ChSG-based network, like as elementary unit cell in a crystalline lattice.

2.2 Network-forming tendencies in ChSG described within CINCA

Thus, in terms of CINCA [12-14], the ChSG can be presented by multiple repetition of one type of mixed cation-anion building blocks, which can be conditionally defined as *network-forming cluster* (NFC):

$$GS \equiv \Sigma(NFC)_i \quad (2)$$

where i corresponds only to one type of building blocks despite their size.

This building block should reflect real glassy network, describing adequately a whole infinite structure. With this in mind, each NFC is composed by *base cluster* (BC) and surrounding *inter-BC bridges* evolved *long chalcogen chains* $m \cdot (\text{S/Se})_{1/2}$, where m is number of chalcogen semi-atoms dependent on ChSG composition:

$$NFC \equiv BC + m \cdot (\text{S/Se})_{1/2}. \quad (3)$$

Main principles of covalent-bonded network forming in ChSG are illustrated conditionally on Fig. 1. The BC itself is formed by *interconnected cations*, which reflects most essential cation-cation interactions typical for chosen network, its being surrounded only by *short chalcogen chains* built of one chalcogen semi-atom $(\text{S/Se})_{1/2}$.

Further, the BC contains both *inner* and *outer* parts, the former being *intra-BC core* created by some number of cations taken in respect to surrounding covalent bonds involved, interconnected by inner links (inter-cation homopolar bonds or chalcogen chains), the latter being *BC shell* containing the rest part of cations linked with chalcogen semi-atoms. So *the intra-BC core* contains, at least, two cations interlinked through *intra-BC bridges* to catch correctly main interactions between closely-neighbouring cations.

To introduce the infinite glassy network with fully-saturated covalent bonding, *the outer part* of BC (*BC shell*) formed by chalcogen semi-atoms around interlinked cations should be further attached to *inter-BC bridges*. These *inter-BC bridges* are linking elements (AS – atom-shared or BS – bond-shared in dependence on the number of chalcogen atoms) between two neighbouring cations belonging to different BC, the latter forming so-called *outer core* or *inter-BC core*. The same type of space interlinking (*inter-BC bridges*) should be throughout a whole glassy network, at least two inter-cluster bridges being attached to each BC.

Thus, the chemical compositions of ChSG and NFC defined in respect to (3) coincide.

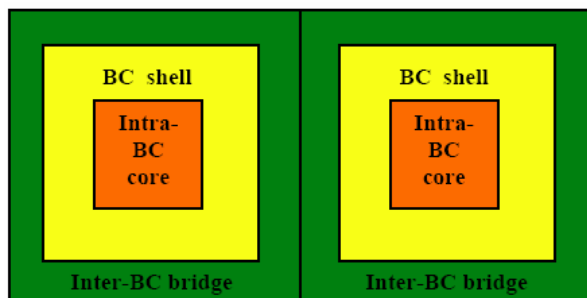


Fig. 1. Schematic illustration showing main principle of covalent-bonded network forming in ChSG with interconnected NFC. Each NFC is attributed to BC composed of intra-BC core (orange rectangle) with surrounding BC shell (yellow rectangle) and attached inter-BC bridge (green rectangle).

So the NFC, as main carrier of basic physical properties of a glass, can be imagined as linking of *intra-BC core*, composed of parts of cations (taken in respect to surrounding chemical bonds), attached *BC shell* and *inter-BC bridge*. The latter is formed by single, double or triple (in dependence on cation coordination) $m \cdot (\text{S}/\text{Se}_{1/2})$ chains between shells in neighboring BC. If $m=2k$, the NFC boundary is bond-sharing BS (includes common covalent bond); if $m=2k+1$, the NFC boundary is atom-sharing AS (includes common chalcogen atom). Thus, direct contact of BC through common chalcogen atom is attributed to *AS-0 inter-BC bridge* (only in this case, the NFC composition fully coincides with BC composition), while different types of BS inter-BC bridges correspond to 2, 6, 10, ... chalcogen semi-atoms and different types of AS inter-BC bridges correspond to 4, 8, 12, ... chalcogen semi-atoms in a chain. Alternatively, by introducing *intra-BC core* as *inter-BC bridge* attached to *BC shell*, it can be easily seen that each NFC can be also composed from linked *inter-BC* and *intra-BC cores*.

2.3 Glass-forming networks in binary As-S system composed of S-interlinked As_2S_4 BC

Let's consider, for example, the glassy networks formed by As_2S_4 BC having $\text{As}_{4/3}\text{S}_3$ intra-BC core interconnected by different inter-BC bridges of equal lengths. In the simplest case of directly linked BC contacting through common S atom (i.e. AS-0 inter-BC bridge) as it shown in Fig. 2, this backbone reflects the structure of *g-As₂S₄*. The corresponding NFC can be defined as As_2S_4 too, it being built of $\text{As}_{4/3}\text{S}_3$ intra-BC and $\text{As}_{2/3}\text{S}_1$ inter-BC cores. This structural element can also be formed from one $\text{As}_{4/3}\text{S}_3$ intra-BC core surrounded by two $\text{As}_{1/3}\text{S}_{1/2}$ shells.

At higher chalcogen content corresponding to *g-As₂S₅* (Fig. 3), the As_2S_4 BC is interlinked by $\text{As}_{2/3}\text{S}_2$ bridges having two S semi-atoms. The NFC defined in this case as As_2S_5 is composed by $\text{As}_{4/3}\text{S}_3$ intra-BC and $\text{As}_{2/3}\text{S}_2$ inter-BC cores with the same as in Fig. 2 composition of BC (As_2S_4).

In case of *g-As₂S₆* shown in Fig. 4, the same As_2S_4 BC are interlinked by $\text{As}_{2/3}\text{S}_3$ inter-BC bridges having four S semi-atoms.

Other glass structures in binary As-S system can be easily built in a like way by composing As_2S_4 BC interlinked with S chains of variable length. So six S semi-atoms appear in *g-As₂S₇*, eight S semi-atoms appear in *g-As₂S₈*, ten S semi-atoms appear in *g-As₂S₈* and so on with the same BC.

One very important advantage is seen from this consideration. To build the possible glass-forming structures, we should chose correctly all corresponding BC and examine different ways of its incorporation in a chalcogen-rich environment. The preferential structure can be identified numerically by using energy counting algorithm like as in [15-19, 22-24].

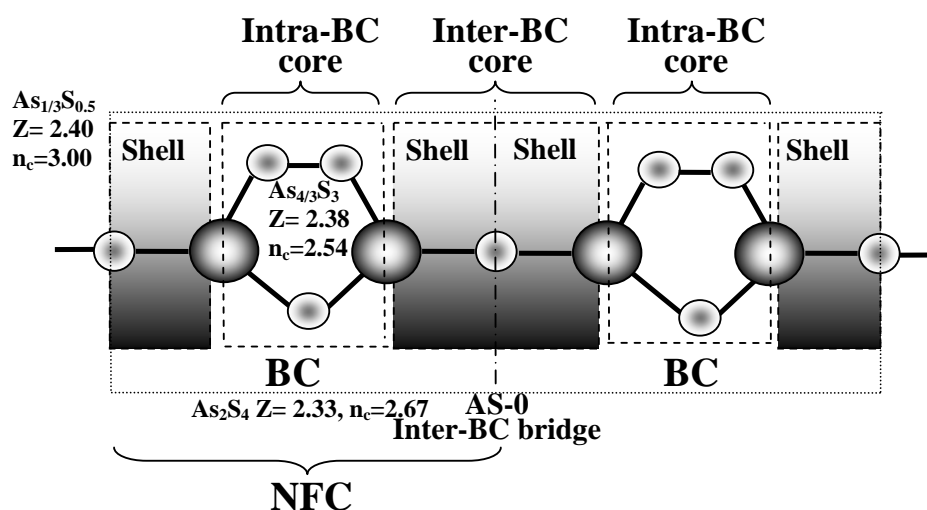


Fig. 2. Structural network of *g-As₂S₄* composed by AS-0 inter-BC and $\text{As}_{2/3}\text{S}_1$ inter-BC core.

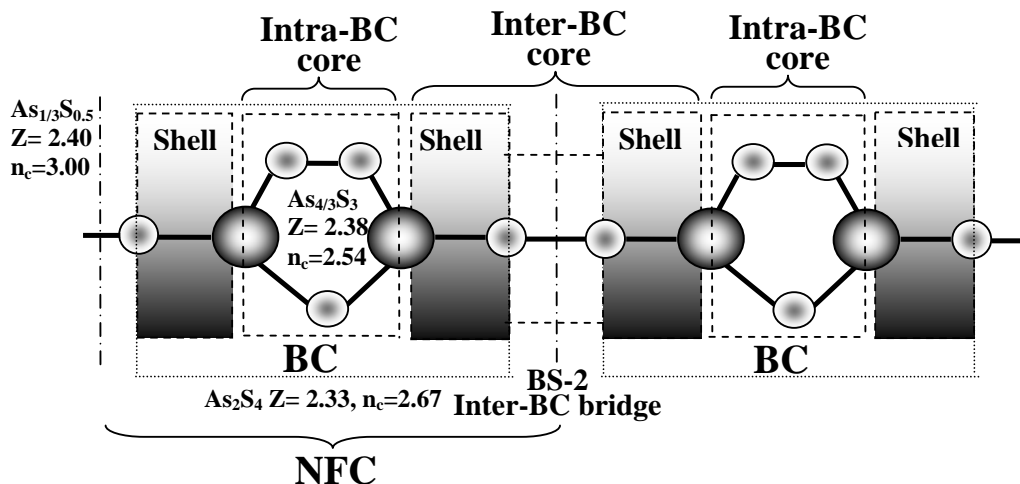


Fig. 3. Structural network of $g\text{-As}_2\text{S}_5$ composed by BS-2 inter-BC and $\text{As}_{2/3}\text{S}_2$ inter-BC core.

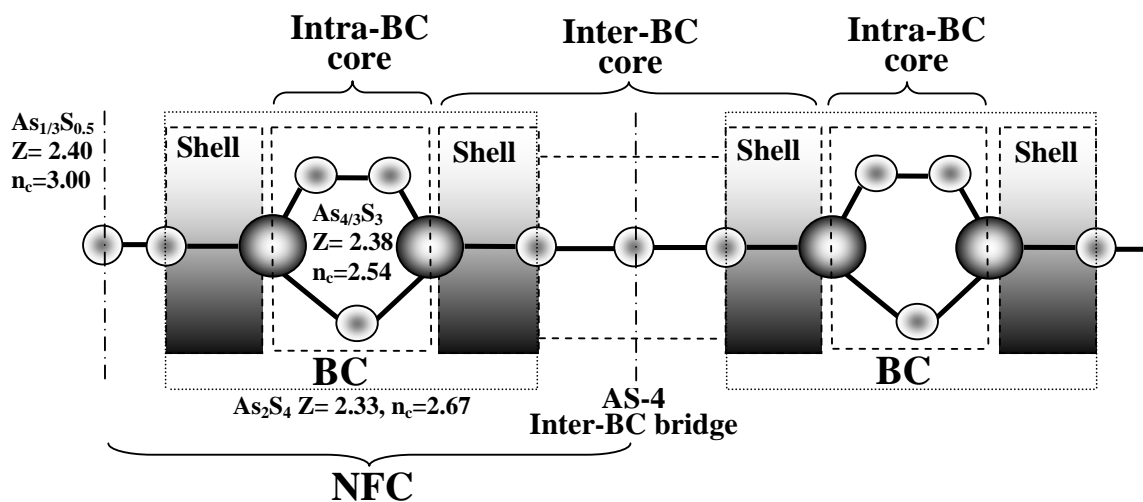


Fig. 4. Structural network of $g\text{-As}_2\text{S}_6$ composed by AS-4 inter-BC and $\text{As}_{2/3}\text{S}_3$ inter-BC core.

3.4 Energy calculations for possible glassy structures within CINCA [12-14]

Since structural network of ChSG is built of open NFC having shared atoms and/or covalent chemical bonds interconnecting them, but not of self-terminated molecular clusters (MC), which are most suitable for numerical simulation (see Fig. 5), we need an additional algorithm to transform NFC into MC. This algorithm can be based on bond saturation procedure owing to additional atoms with known energy [25]. The hydrogen H atom having low bonding energy in covalent-like structures is most suitable candidate for this purpose. The termination procedure is quite reasonable since electronegativity of H (2.20) is close to ones of other atoms forming glassy backbone of typical ChSG, being intermediate between electronegativities of cation-like (As – 2.18, Ge – 2.01) and anion-like atoms (S – 2.58, Se – 2.55) [21]. Apart from, owing to relative weakness of interaction with chalcogen environment, the H bonding energies in covalent structures are rather

negligible (approximately ~ 3 kcal/mol [26]) in comparison with dissociation energies of main bonds forming glassy networks, which are typically as high as tens of kcal/mol [21]. So no strong disturbances are expected in the electron density distribution within main glass-forming s.u. of ChSG due to additional H atoms terminated dangling bonds. By adding H atom directly to shared chalcogen atoms (Fig. 6a) or through additional chalcogen atoms linked with another ones (Fig. 6b) we can transform NFC into MC.

Then, after calculating the full energy E^Σ of this MC, we can easily subtract the energy E_H of added H atoms, S-H bonds (E_{S-H}) and half energy of S atoms (E_S) to extract the pure total energy of atom-shared NFC E_t (Fig. 6a):

$$E_t = E^\Sigma - E_H - E_{S-H} - \frac{1}{2}E_S \quad (4)$$

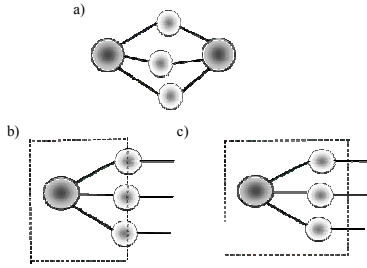


Fig. 5. Different types of atomic nanoclusters possible in ChSG: molecular-forming MC (a), NFC ending by shared atoms (b); NFC ending by shared bonds (c).

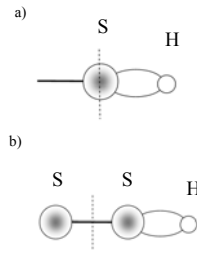


Fig. 6. Schematic illustration showing saturation procedure to form MC from atom-shared (a) and bond-shared NFC (b).

In case of bond-shared NFC (Fig. 6b), the above saturation procedure should be finished with subtracting the energies of H atoms E_H , S-H bonds E_{S-H} , S atoms E_S and half energy of homopolar S-S bonds E_{S-S} from total energy of MC E_t^Σ :

$$E_t = E_t^\Sigma - E_S - E_H - E_{S-H} - \frac{1}{2} E_{S-S}. \quad (5)$$

The numerical criterion of glass-forming tendencies for chosen covalent-bonded networks can be developed at the basis of energy calculations for different NFC forming them. Having the total energy of NFC E_t , we can calculate the overall cluster formation energy E_f^Σ by subtracting the energy of all atoms within NFC E_{at} :

$$E_f^\Sigma = E_t - E_{at}. \quad (6)$$

Since energy is accepted to be negative in computational calculations, the absolute value of E_f^Σ determined in mean per-atom determination can be conveniently taken as a criterion to compare different NFC formed by N atoms:

$$E_f = \left| \frac{E_f^\Sigma}{N} \right|. \quad (7)$$

Finally, this mean cluster formation energy E_f determined by expression (7) can be normalized in respect to the energy of principal cation-centered network-forming s.u., such as single As(S/Se)_{3/2} pyramids in g-As-S/Se or Ge(S/Se)_{4/2} tetrahedrons in g-Ge-S(Se). Within this approach, the greater E_f , the higher probability to form this cluster in a glassy network.

Other advantage of the developed approach (CINCA) consists in a principal possibility to compare the calculated energetic criteria with structural-topological features of tested NFC and their constituting s.u. (inter- and intra-cluster bridges, shells, cores, etc.).

3.5 Structural-topological genesis of glass networks within mean-field rigidity formalism [9-11,27]

According to mean-field rigidity approach of M.F. Thorpe and J.C. Phillips [2,19], the mean coordination number of glass Z possessing an ideal N -atoms ($N \rightarrow \infty$) covalent-bonded network constructed by n_r atoms each having r bonds, can be calculated as average number of covalent bonds per atom:

$$Z = \left(\frac{\sum_r r n_r}{\sum_r n_r} \right) \quad (8)$$

where $N = \sum_r n_r$.

Since the number of degrees of freedom for an atom is constrained by covalent bonds, as it was assumed by J.C. Phillips [1], the optimal mechanical stability of covalent-bonded glassy network can be achieved, when the number of Lagrangian constraints per atom n_c is equal to space dimensionality D (in case of three-dimensional networks $n_c=3$). In dependence on the average number of Lagrangian constraints per atom n_c , the glass structures can be characterized as under-constrained (floppy with $n_c < 3$), over-constrained (rigid and stressed with $n_c > 3$) or optimally-constrained (rigid but not stressed with $n_c=3$).

The total number of Lagrangian constraints N_c of the network can be estimated as:

$$N_c = \sum_r n_r (n_\alpha + n_\beta) = \sum_r n_r \left[\frac{r}{2} + (2r - 3) \right] \quad (9)$$

where $n_\alpha = \frac{r}{2}$ and $n_\beta = \frac{(D-1)(2r-D)}{2}$ are numbers of bond-stretching and bond-bending forces for r -coordinated atom (for 3D networks $n_\beta = 2r - 3$).

So the number of Lagrangian constraints per atom of a whole network can be defined in respect to the expression below:

$$n_c = \frac{Z}{2} + (2Z - 3), \quad (10)$$

and fraction of floppy modes f can be calculated as:

$$f = (3N - N_c) / 3N = 2 - \frac{5}{6} Z. \quad (11)$$

Two types of possible deviations from ideal covalent-bonded network can be considered, they being dangling bonds and ring-like fragments. So the above formula (9) for total number of Lagrangian constraints N_c should be finally corrected. In case of dangling bonds in the structure of ChSG, the number of bond-bending forces $n_\beta = -1$ instead of 0 for $r = 1$, and

$$N_c = \sum_r n_r \left[\frac{r}{2} + (2r - 3) \right] + n_1, \quad (12)$$

where n_1 is number of singly-coordinated atoms.

The second case is associated with inner network-forming processes resulting in appearance of ring-like structural fragments, when some constraints attain linear dependence. The 6-sided ring is just rigid, while triangles, quadrilaterals and pentagons are also rigid, but the number of constraints calculated due to above formula is overcounted by 3, 2 and 1, respectively. Other isolated rings having 7 or more sides are floppy. The corrected formula for N_c is as below:

$$N_c = \sum_r n_r \left[\frac{r}{2} + (2r - 3) \right] - n^{ring}, \quad (13)$$

where n^{ring} is ring-correction parameter dependent on ring number and type.

Under these conditions, we can introduce a more generalized form for total number of Lagrangian constraints of a glassy network:

$$N_c = \sum_r n_r \left[\frac{r}{2} + (2r - 3) \right] + n_1 - n^{ring}, \quad (14)$$

So the number of Lagrangian constraints n_c and fraction of floppy modes per atom f can be calculated respectively as:

$$n_c = \frac{Z}{2} + (2Z - 3) + \frac{n_1}{N} - \frac{n^{ring}}{N}, \quad (15)$$

$$f = 2 - \frac{5}{6}Z - \frac{n_1}{3N} + \frac{n^{ring}}{3N}, \quad (16)$$

The onset from floppy ($n_c < 3.00$) to stressed-rigid ($n_c > 3.00$) networks predicted to be solitary within mean-field rigidity theory [9-11], but it can split into two points with accepting that bonds are not distributed randomly revealing a tendency to self-organization [27]. Thus, the second-order transition occurs from floppy to unstressed-rigid phase and first-order transition occurs from unstressed-rigid to stressed-rigid phase. So the stressed-free intermediate phase having just $n_c = 3.00$ Lagrangian constrains per atom appears so as to avoid stress, forming a so-called *reversibility window*. In device application, the self-organized intermediate-phase glasses are most attractive since they reveal unique non-aging ability under

natural conditions. In contrast, the under-constrained glasses exhibit the pronounced drift in their properties caused by thermodynamically-driven forces to achieve a more favorable energetic state, this effect being known as physical ageing [28-30]. The over-constrained glasses were supposed can be affected by ageing too but only at higher temperatures [28]. However, in [31], it was shown this thermally-induced ageing differs significantly from natural one affected at room temperatures.

By using above constraints counting algorithm, we can calculate the n_c values for different types of NFC possible in the tested glass-forming system as well as for other constituting s.u. being under consideration, including inter- and intra-cluster bridges, shells, cores, etc. This allows us also to introduce *the self-organization* definition (an alternative and more correct is *the self-adaptability* definition [32]) for covalent-bonded network in terms of *BC cores connectivity*.

If all cores of BC are optimally-constrained possessing $n_c^{Intra-BC} = n_c^{Inter-BC} = 3.00$, this network can be recognized as *global optimally-constrained network with intermediate phase window*. In contrast, *the local optimally-constrained covalent-linked network with pseudo-intermediate phase window* corresponds to $n_c^{Intra-BC} > 3.00$, but $n_c^{Inter-BC} = 3.00$. In all other cases, when one of $n_c^{Intra-BC}$ or $n_c^{Inter-BC}$ is less than 3.00, the network is *under-constrained one* (floppy).

4. Nanoclustering evolution in ChSG exemplified by canonical Ge-S/Se systems

In terms of CINCA, let's consider structural-topological diversity of NFC based on $\text{GeS}_{4/2}$ and $\text{GeSe}_{4/2}$ tetrahedrons, justifying favorable atomic configurations possible in binary Ge-S and Ge-Se systems, respectively.

The quantum-chemical *ab initio* calculations were performed using *HyperChem* program package based on restricted Hartree-Fock self-consistent field method using split-valence double-zeta basis set with single polarization function 6-311G* [33,34]. The final geometrical optimization was carried out employing the Fletcher-Reeves conjugate gradient method until root-mean-square gradient of 0.1 kcal/(Å·mol) was reached. All boundary S (Se) atoms belonging to two clusters were terminated by H atoms to be two-fold coordinated. Only half-part contributions from these atoms were considered after subtraction both energies of H atoms and -S(Se)-H bonds from the total cluster-forming energy. This value averaged per one atom of cluster E_f was taken as a *measure for NFC formation probability*.

We have examined E_f of NFC formed by possible interconnections between two single $\text{Ge(S/Se)}_{4/2}$ tetrahedrons having different amount of common elements: corner-sharing CS based on one common chalcogen atom, edge-sharing ES with two common chalcogen atoms (or one common edge) or face-sharing FS with three common chalcogen atoms (or one common plane). So in respect to Fig. 1 we deals, in turn, with three types of $\text{Ge}_2\text{S(Se)}_4$ NFC, each being formed by two-cation BC based on CS-, ES- and FC- $\text{Ge(S/Se)}_{4/2}$ tetrahedrons having the same BC shell and inter-BC bridge (AS-0 type), but different configurations of intra-BC cores, as it reflected in Table 1.

Table 1. Types of tested NFC in Ge-S(Se) ChSG based on $\text{GeS(Se)}_{4/2}$ tetrahedrons

NFC	BC	Intra-BC core	BC shell	Inter-BC bridge
I- $\text{Ge}_2\text{S(Se)}_4$, $Z=3.67$	$\text{Ge}_2\text{S(Se)}_4$ -CS, $Z=3.67$	$\text{Ge}_{1/2}\text{S(Se)}$, $Z=2.67$	$\text{S(Se)}_{1/2}$	AS-0
II- $\text{Ge}_2\text{S(Se)}_4$, $Z=3.67$	$\text{Ge}_2\text{S(Se)}_4$ -ES, $Z=3.67$	GeS(Se)_2 , $Z=2.67$	$\text{S(Se)}_{1/2}$	AS-0
III- $\text{Ge}_2\text{S(Se)}_4$, $Z=3.67$	$\text{Ge}_2\text{S(Se)}_4$ -FS, $Z=3.67$	$\text{Ge}_{3/2}\text{S(Se)}_3$, $Z=2.67$	$\text{S(Se)}_{1/2}$	AS-0

The geometrically-optimized configurations of these nanoclusters are shown in Fig. 7 (the terminated H atoms are not shown), while their energetic characteristics and corresponding optimized bond distances and bond angles are gathered in Tables 2-4.

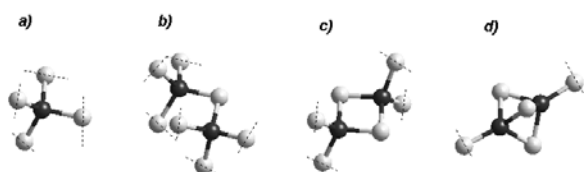


Fig. 7. Schematic view of geometrically optimized single (a), CS (b), ES (c) and FC (d) $\text{Ge(S/Se)}_{4/2}$ tetrahedrons (the black and grey colours are for Ge and S(Se) atoms, respectively).

The energetic characteristics of geometrically optimized $\text{Ge}_2\text{S(Se)}_4$ NFC based on different types of two-cation BC (ES, CS and FC) along with corresponding values of Lagrangian constraints per atom, n_c , and mean cluster formation energy determined in respect to single $\text{GeS(Se)}_{4/2}$ tetrahedron, $\Delta(E_f)^{\text{single}}$, are given in Table 2 (the optimally-constrained NFC and intra-BC cores having $n_c=3.00$ are bold-distinguished).

As it follows from Table 2, the most energetically favorable (the lowest) value of E_f is character for single $\text{GeS}_{4/2}$ and $\text{GeSe}_{4/2}$ clusters, while the highest ones are achieved for FS interlinking between tetrahedrons despite its optimal topology ($n_c = 3.00$) in both Ge-S and Ge-Se systems. It means that FS structural fragments apparently do not occur in these glass-forming networks at all.

In contrast, the NFC including BC built of CS and ES

tetrahedrons having comparative mean cluster-forming energies are in evident preference in Ge-S(Se) glasses.

In case of Ge-Se system, the energetic difference between Ge_2Se_4 -CS and Ge_2Se_4 -ES clusters is only negligible being quite close to mean energy of single $\text{GeSe}_{4/2}$ tetrahedron. As it follows from Table 2, this feature is probably caused by similarity in mean forming energies for intra-BC cores corresponding to these BC. Thus, both types of these clusters play an approximately equivalent role in the glass-forming ability of binary Ge-Se network. By changing glass composition within binary Ge-Se system, the tight interconnection between CS and ES structural blocks serves as main network-forming tendency determining deviation from “chain-crossing” model of uniformly-distributed cation-centered units towards molecular clustering. Because of geometrical restrictions typical for spatially-stretched structure of $\text{GeSe}_{4/2}$ tetrahedrons [1], the whole glassy network cannot be built by only CS and/or ES clusters, but rather by interconnecting ES-CS complexes. The CS units are needed to close ES tetrahedrons within a more stretched formation known as *outrigger raft structural motif* [35], consisting of two ES $\text{GeSe}_{4/2}$ tetrahedrons surrounded by four CS ones from each side. This conclusion is argued by good agreement with known experimental data on chemical ordering in binary Ge-Se through high-resolution XPS [36] and similarity in the structural parameters of geometrically-optimized clusters given in Table 4 and derived from previous research [37-44]. The above over-constrained *outrigger raft motives* ($n_c > 3.00$) can be interlinked via optimally-constrained =Ge-Se-Se-Ge= bridges ($n_c = 3.00$), forming a compositional range of *topological pseudo-self-organization* within $2.43 < Z < 2.545$, as it shown in [45-47].

Table 2. A comparison of energetic characteristics for geometrically optimized $\text{Ge}_2\text{S(Se)}_4$ NFC based on different types of two-cation BC

NFC				Intra-BC core			
BC composition	n_c	E_f	$\Delta(E_f)^{\text{single}}$	Chemical composition	n_c	E_f	$\Delta(E_f)^{\text{single}}$
		kcal/mol	kcal/mol			kcal/mol	kcal/mol
$\text{GeS}_{4/2}$ - single		-96.38	0	-	-	-	-
Ge_2S_4 -CS	3.67	-94.34	-2.04	$\text{Ge}_{1/2}\text{S}$	3.67	-88.22	-8.16
Ge_2S_4 -ES	3.33	-95.97	-0.40	GeS_2	3.00	-95.57	-0.81
Ge_2S_4 -FS	3.00	-89.06	-7.32	$\text{Ge}_{3/2}\text{S}_3$	2.78	-86.62	-9.76
$\text{GeSe}_{4/2}$ - single		-87.03					
Ge_2Se_4 -CS	3.67	-86.79	-0.24	$\text{Ge}_{1/2}\text{S}$	3.67	-86.05	-0.98
Ge_2Se_4 -ES	3.33	-86.66	-0.37	GeSe_2	3.00	-86.28	-0.75
Ge_2Se_4 -FS	3.00	-80.72	-6.31	$\text{Ge}_{3/2}\text{Se}_3$	2.78	-78.61	-8.42

Table 3. Geometric parameters of optimized NFC based on $\text{GeS}_{4/2}$ tetrahedrons

Type of cluster	$\text{GeS}_{4/2}$ -single	$\text{Ge}_2\text{S}_{4/2}$ -CS	$\text{Ge}_2\text{S}_{4/2}$ -ES	$\text{Ge}_2\text{S}_{4/2}$ -FS
Bond distance [10^{-4} nm]	Ge-S			
	2224.9	2238.5	2224.0	2194.9
	2236.6	2238.7	2223.9	2274.9
	2236.6	2238.5	2231.5	2274.9
	2215.1	2242.7	2242.4	2269.7
		2238.5	2224.0	2194.9
		2238.6	2223.9	2275.6
		2238.5	2242.4	2275.6
		2242.8	2231.4	2269.7
Bond angle [deg.]	S-Ge-S			
	112.67	108.56	111.88	124.80
	109.62	107.88	113.88	124.80
	109.42	110.67	110.06	121.89
	102.80	108.28	110.05	91.76
	112.67	109.53	113.88	92.13
	109.42	111.82	95.96	92.13
		110.67	110.05	124.91
		111.83	113.88	124.91
		108.55	111.88	121.71
		107.88	110.05	92.11
		109.53	113.88	92.11
		108.28	95.96	91.72
	Ge-S-Ge			
	-	98.42	83.79 84.30	67.62 67.62 67.81

In case of Ge-S system, the network-forming entities based on ES interlinking (both having BC and intra-BC cores) are in obvious domination upon CS structural blocks. Interestingly, the optimally-constrained intra-BC cores ($n_c = 3.00$) having closed four-fold rings occur the best in their network-forming abilities. These structural entities are more important in network-forming tendencies of this binary glassy system than CS clusters. It means that deviations from “chain-crossing” model in Ge-S glasses will result in a more complex structure of partially destroyed *outrigger raft* formations mixed with separate S-rich clusters (chain-like and ring-like ones such as S_8 and/or S_6), as well as ES and CS entities as it was demonstrated in [48-50].

It should be noted that face-shared FC inter-tetrahedral structural units are practically impossible in both Ge-S and Ge-Se glassy systems in view of their unfavorable cluster-forming energies as it presented in Table 2. The geometrical optimization procedures for these clusters (see Table 3 and 4) show that this is caused probably by strong deviations from typical tetrahedral angle on Ge atoms.

In contrast to ES and CS configurations having S(Se)-Ge-S(Se) bond angles of mainly around 109 deg., the FC-interlinked $\text{Ge}_2\text{S}(\text{Se})_4$ nanoclusters contain in nearly equal proportions two kinds of bond angles, which are grouped near 92-93 deg. and 122-125 deg.

Table 4. Geometric parameters of optimized NFC based on $\text{GeSe}_{4/2}$ tetrahedrons

Type of cluster	$\text{GeSe}_{4/2}$ -single	$\text{Ge}_2\text{Se}_{4/2}$ -CS	$\text{Ge}_2\text{Se}_{4/2}$ -ES	$\text{Ge}_2\text{Se}_{4/2}$ -FS
Bond distance [10^{-4} nm]	Ge-Se			
	2375.2	2378.8	2371.0	2342.9
	2379.0	2381.8	2371.0	2416.0
	2378.9	2381.7	2376.1	2424.1
	2365.5	2366.6	2385.3	2403.7
		2395.5	2376.2	2423.8
		2371.3	2385.8	2404.0
		2371.3	2371.3	2415.6
		2367.0	2371.3	2342.8
Bond angle [deg.]	Se-Ge-Se			
	102.75	111.93	114.21	120.85
	108.57	111.93	114.20	123.92
	108.57	110.61	111.96	124.60
	110.39	100.60	109.17	93.16
	113.06	110.71	109.17	93.09
	113.06	110.71	96.94	92.67
		107.28	114.21	123.84
		112.47	114.21	120.94
		107.28	111.96	124.59
		114.74	109.17	92.66
		114.85	109.17	93.09
		98.83	96.92	93.18
	Ge-Se-Ge			
	-	109.23	83.27 82.87	66.23 66.29 66.28

5. Conclusions

Glass-forming tendencies in fully-saturated covalent-bonded networks can be quantitatively justified with specific energies for typical nanoclusters composed by base parts of interconnected cations, which reflects most essential cation-cation interactions for a chosen system, with surrounding inter-cluster chalcogen bridges. Topological peculiarities of network clustering in binary As-S system are illustrated at the example of As_2S_4 base clusters with $\text{As}_{4/3}\text{S}_3$ intra-cluster cores interconnected by inter-cluster chalcogen bridges of equal lengths.

Within this cation-interlinking network cluster approach (CINCA) developed for binary Ge-S and Ge-Se systems, directly linked corner-, edge- and face-shared $\text{GeS}(\text{Se})_{4/2}$ tetrahedrons were examined as possible glass-forming structural entities. It was shown that only corner- and edge-shared clusters were essential in these binary systems testifying in a favor of deviations from “chain-crossing” model towards specific *outrigger raft* structural motives consisting of two edge-shared tetrahedrons surrounded by four corner-shared ones. Because of more pronounced difference in mean formation energies for intra-cluster cores corresponding to corner- and edge-shared tetrahedrons, these structural entities are expected to be unstable in Ge-S glasses provoking possible phase separation under compositional variations in this system.

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