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**CINCA:  
CATION-INTERLINKING NETWORK CLUSTER APPROACH  
IN APPLICATION TO  
BINARY GLASSY CHALCOGENIDES**

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A principally new cation-interlinking network cluster approach was developed to describe glass-forming tendencies in network covalent-bonded solids like to binary chalcogenide glasses. This approach was probed at the example of pyramidal AsS<sub>3/2</sub>-based clusters within As-S system.

*Key words:* Ab initio calculations, chalcogenide glass, glass structure.

Chalcogenide glasses (ChG) are known to be typical representatives of covalent-bonded glass formers having a wide application in photonics [1–3]. However, these disordered materials possess a number of specific features needed a more understanding. This concerns, in part, correlation between glass structure and properties.

In this work, we propose a principally new model, the cation-interlinking network cluster approach (CINCA), to describe these correlations in typical binary glass formers based on layer-type 2D-dimensional AsS<sub>3</sub> and 3D-dimensional GeS<sub>2</sub> building blocks. This model serves as alternative to other one proposed by M. Micoulaut (CICA – the size increasing cluster approximation) to explain self-organization tendencies in ChG [4–8]. The CICA uses the Boltzmann factor as main energetic criterion to estimate probability of different structural fragments within glass-forming backbone. In contrast, we use the total energy of geometrically-optimized atomic clusters to select the most suitable ones to build the real covalent-bonded glassy network.

The basic principle of our approach is grounded on well known chain crossing model [9, 10]. Within this model, the structure of binary ChG can be presented by uniformly distributed non-chalcogen high-coordinated atoms (the cations) mutually interlinked by two-fold coordinated chalcogen atoms forming more or less prolonged chains, the number of chalcogen atoms (conditionally accepted as anions) within each chain corresponding strongly to ChG composition.

In real, the structure of ChG includes some deviations from chain crossing model caused by specific atomic formations in a glassy-like network. Thus, so-called outrigger raft groups having both edge- and corner-shared tetrahedra can be formed in vitreous Ge-Se showing some deviations from homogenous anion/cation distribution [11, 12].

The main working principles of our approach concern atomic clusters and topological variants of their interlinking, which can be introduced to adequately describe structural peculiarities of covalent-bonded glassy networks.

The cluster is accepted to be the aggregate of small and finite number of atoms grouped around other atom. Since chalcogen atoms are two-fold coordinated in ChG, this central atom should be chosen of higher coordination. We can conditionally introduce it as cation-like one taking into account a similarity between ChG and ionic compounds. In such a way, we introduce the cation-centred cluster (CCC) as agglomerate of two-fold coordinated chalcogen atoms (anions), all linking with one cation of higher coordination (elements from IV and V groups of the Periodic table – Ge, Si, P, As, Sb, Bi etc.) through covalent chemical bonds. Thereby, the CCC, in fact, is one-cation-based cluster.

Despite their uniqueness, the CCC themselves do not reflect all peculiarities of glassy network, because of missing types of interlinking between them. Different combinations of such CCC are needed to form the real glassy-like network. In other words, the real structure of ChG should be presented by more stretched atomic clusters, including two or more interlinking CCC (two- or three-cation-based clusters). These individual CCC can be interconnected between each other via shared chalcogen atoms or covalent bonds producing in such a way more stretched network formations – the network-forming clusters (NFC) as it seen on fig. 1, *b* and 1, *c*. Therefore, the NFC is build of two or more mutually interconnected CCC.

Further, the whole glassy network can be formed by infinitely repeated one-type NFC, the type of interlinking between them (intercluster or inter-NFC linking) being not necessary the same as intracluster (intra-NFC) interlinking. In fact, these clusters can be accepted as glass-forming structural units in terms of Muller R.L. [13].

Thus, we put forward two principles in the ground of our approach. The first principle, the cluster uniqueness, can be formulated as follows: one-type CCC with fully-saturated covalent bonding in respect to known 8-N rule can be distinguished as basis forming elements within each glassy network. The second principle concerns cluster interlinking stating that the real glass-forming backbone of ChG can be build by infinitely-repeated NFC, each of them including two or more mutually interlinked CCC.

Since structural network of ChG is built of open NFC having shared atoms or bonds interconnecting them, but not of self-closed molecular clusters (MC), which are most suitable ones for numerical simulation (see fig. 1, *a*), we need an additional algorithm to transform NFC into MC.

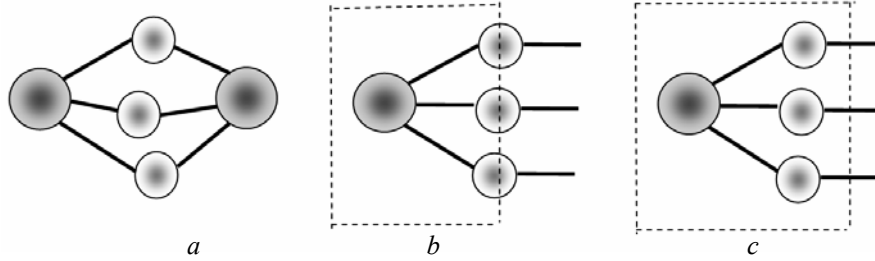


Fig. 1. Types of atomic clusters in network ChG: MC (a), atom-shared NFC (b); bond-shared NFC (c)

The algorithm transforming NFC into MC can be based on saturation procedure for open NFC owing to additional covalent-bonded atoms with known energy. The hydrogen H atom having an extremely low bonding energy in covalent structures is the most suitable ones to be used in this way [14]. By adding these atoms directly to share chalcogen atoms (see fig. 2, a) or through additional S atoms linked with another S atoms (see fig. 2, b) we can transform NSF into MC.

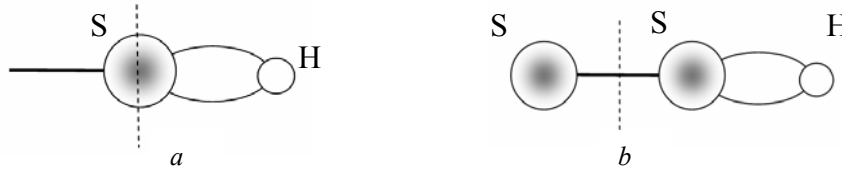


Fig. 2. Schematic illustration showing saturation procedure to form MC from atom-shared (a) and bond-shared NFC (b)

Then, after calculating the full energy of this MC  $E^\Sigma$ , we can easily subtract the energy of added H atoms  $E_H$ , S-H bonds  $E_{S-H}$  and half energy of S atoms  $E_S$  to extract the pure total energy of atom-shared NSF  $E_t$  (fig. 2, a) according to the following expression:

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

In the case of bond-shared NFC (Fig. 2b), the above saturation procedure should be finished with subtracting the energy of H atoms  $E_H$ , energy of S-H bonds  $E_{S-H}$ , energy of S atoms  $E_S$  and half energy of S-S bonds  $E_{S-S}$  from the full energy of MC  $E^\Sigma$ :

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

The numerical criterion of glass-forming tendencies for chosen covalent-bonded networks can be proposed at the basis of energy calculations for different NFC (atom- or bond-shared) forming them.

Having the total energy of NFC  $E_t$ , we can calculate overall cluster formation energy  $E_f^\Sigma$  by subtracting the energy of all atoms within NFC  $E_{at}$  ( $N_{As,Ge,S}$  is number of As, Ge and S atoms in NFC):

$$E_f^\Sigma = E_t - E_{at}, \quad (3)$$

where

$$E_{at} = N_{As}E_{As} + N_{Ge}E_{Ge} + N_S E_S. \quad (4)$$

If we additionally subtract the energy of all covalent bonds within NFC  $E_{bonds}$  (each covalent bond energy is accepted at the basis of corresponding electronegativities of involved atoms in terms of Pauling L. [15]) from overall cluster formation energy  $E_f^\Sigma$ , we shall obtain the pure cluster formation energy  $E_{CFE}$ , which can be treated as cluster-forming energy attained owing to geometrical optimization procedure applied to NFC:

$$E_{CFE} = E_t - E_{at} - E_{bonds} = E_f^\Sigma - E_{bonds}. \quad (5)$$

Since energy is accepted to be negative in computational calculations, the absolute value of  $E_{CFE}$  determined in mean per-atom determination can be conveniently taken into account to compare different NFC formed by N atoms:

$$E_f = \left| \frac{E_{CFE}}{N} \right|. \quad (6)$$

Within this approach, the greater value of mean cluster-forming energy  $E_f$ , the higher probability to form tested cluster in a glassy network.

In a frame of the above approach, let's consider glass-forming tendencies in ChG of binary As-S system near stoichiometric  $As_2S_3$  composition.

To perform energy calculations, the HyperChem Realise 7.5 program was used. Ab initio calculations with RHF/6-311G\* basis set were performed to determine the total energies of clusters in dependence on their intercluster linkaging (corner-, edge or face-shared structural units).

The following clusters were examined by us:

- $AsS_{3/2}$  CCC with atom-sharing interlinking (fig. 3);
- $AsS_3$  CCC with bond-sharing interlinking (fig. 4);
- 2-cation  $As_2S_3$  NFC with corner- ( $As_2S_3$ -CS), edge- ( $As_2S_3$ -ES) and face-sharing ( $As_2S_3$ -FS) itracluster linking (fig. 5).



Fig. 3. Geometrically-optimized  $AsS_{3/2}$  CCC with atom-sharing interlinking

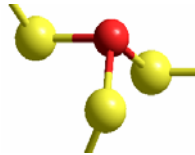


Fig. 4. Geometrically-optimized  $AsS_3$  CCC with bond-sharing interlinking

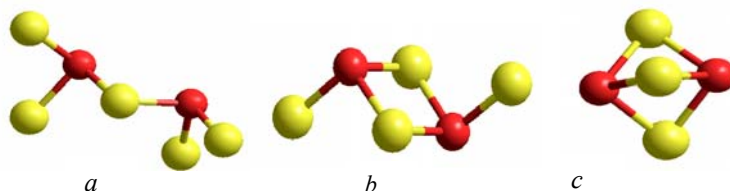


Fig. 5. Geometrically-optimized 2-cation  $\text{As}_2\text{S}_3$  NFC with corner-(a), edge-(b) and face-sharing (c) intracluster linking

The results of our modelling ( $E_f$  values) along with numerical characteristics of clusters (number of atoms within cluster  $N$ , average coordination number  $Z$ , mean number of Lagrangian constraints per atom within cluster  $n_c$  calculated in terms of mean-field constraints theory [16, 17] and overall energy of all covalent bonds within cluster  $E_{bonds}$ ) are gathered in table.

Table

Main characteristics of different clusters within binary As-S glassy system

Cluster type/ characteristics	$\text{AsS}_{3/2}$ CCC	$\text{AsS}_3$ CCC	$\text{As}_2\text{S}_3$ -CS NFC	$\text{As}_2\text{S}_3$ -ES NFC	$\text{As}_2\text{S}_3$ -FS NFC
$N$	2,5	4	5	5	5
$Z$	2,40	2,25	2,40	2,40	2,40
$n_c$	3,00	2,625	3,00	2,60	2,20
$E_{bonds}$ , kcal/mol*	58,7	60,6	58,7	58,7	58,7
$E_f$ , kcal/mol	20,7	18,5	20,7	19,6	15,6

Note:  $E_{bonds}$  were calculated by accepting the bond strength energies  $E_{\text{As-S}}=48,9$  kcal/mol and  $E_{\text{S-S}}=48,9$  kcal/mol [15].

It is obvious that single (1-cation)  $\text{AsS}_{3/2}$  CCC is equivalent, in fact, with  $\text{As}_2\text{S}_3$ -CS 2-cation NFC because of the same cluster-forming energy in mean per-atom determination  $E_f = 20,7$  kcal/mol. These clusters are optimally-constrained in terms of mean-field constraints theory [16, 17] since  $n_c = 3,00$ . However, other clusters both 1- or 2-cation based with  $n_c < 3,00$  are less energetically favourable in spite of their  $Z$ .

These conclusions are in good agreement with known experimental data on glass-forming tendency in binary As-S system as well as previous conclusions made of Holomb R. with co-workers on quantum-chemical program package Gaussian (US) [18–21].

The new approach, namely CINCA – the cation-interlinking network cluster approach, to simulate glass-forming tendencies in chalcogenide glassy-like systems was developed at the basis of the HyperChem 7,5 program package. Within this approach, the probabilities of different glass-forming structural fragments are estimated via cluster-forming energy in mean per-atom determination.

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**CINCA:**

**МОДЕЛЬ ВЗАЄМОПОВ'ЯЗАНИХ СІТКОВИХ КАТІОННИХ КЛАСТЕРІВ У  
ЗАСТОСУВАННІ ДО  
БІНАРНИХ СКЛУВАТИХ ХАЛЬКОГЕНІДІВ**

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Запропоновано новий підхід до моделювання катіонних сіткових кластерів в ковалентно-пов'язаних бінарних халькогенідних стеклах бінарної системи As-S.

*Ключові слова:* ab initio обрахунки, халькогенідне скло, структура скла.

**CINCA:**

**МОДЕЛЬ ВЗАИМОСВЯЗАННЫХ СЕТОЧНЫХ КАТИОННЫХ  
КЛАСТЕРОВ В ПРИМЕНЕНИИ К  
БИНАРНЫМ СТЕКЛИСТЫМ ХАЛЬКОГЕНИДАМ**

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Предложен новый подход к моделированию катионных сеточных кластеров в ковалентно-связанных бинарных халькогенидных стеклах бинарной системы AS-S.

*Ключевые слова:* ab initio расчет, халькогенидное стекло, структура стекла.

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