



On radiation modification ability in As–S/Se network glass formers obeying nanoconfined geometry

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Abstract Radiation modification in network glass formers such as arseno-chalcogenide alloys As–X (X = S, Se) is examined accepting possibilities of volume restrictions in their realization. Destruction of covalent chemical bonds in these alloys under above bandgap light exposure or irradiation is accompanied by their relaxation in a new state. When this process occurs via switching of heteronuclear (As–X) bonds into homonuclear (As–As) and (X–X) ones, like under intrinsic decomposition in As₂X₃ glass, an additional volume appears resulting in red shift of optical absorption edge. Assuming that double covalent bond-based X = As(X_{1/2})₃ units are stabilized due to inner pressure in a glass structure caused by nanoconfined geometry, a blue shift in optical absorption edge is expected. This analysis based on quantum-chemical modeling of network-forming atomic clusters clarifies misunderstandings with these X = As(X_{1/2})₃ units as principal species facilitating self-organization in As–X (X = S, Se) glassy networks. Computing the balance of energetic costs needed for hetero-to-homonuclear bond transition in stoichiometric As₂X₃ glasses followed by transformation of single covalent bond-based clusters (As₂X₄) into double covalent bond-based structural units X = As(X_{1/2})₃, it was confirmed the impossibility of such anomaly in glassy arsenoselenides as compared with arsenosulfides.

1 Introduction

Network glass formers such as binary arseno-chalcogenides As–X (X = S or Se) are in favor of contemporary glass science community in view of their uniqueness in a variety of very important practical applications [1]. These alloys are typically stabilized by rapid quenching from a melt attaining completely saturated covalent bonding, when anion-type chalcogen X atoms and cation-type pnictogen atoms (such as As) were respectively two-fold $\times 2$ - and three-fold $\times 3$ -coordinated by neighboring constituents. Deviation from this ‘ $\times 2 \times 3$ ’ bonding rule allows great modification possibilities for these glass-forming alloys, which could be realized technologically due to optimal regimes of their quenching, or post-technologically by processing of melt-quenched alloys by above bandgap light or high-energy irradiation [1, 2]. That is why one of the greatest controversies in chalcogenide materials science is related to modification possibilities of these glassy alloys due to their anomalous covalent bonding, which could be exemplified by double-bond based quasi-tetrahedral (QT) structural units (s.u.) X = As(X_{1/2})₃.

Despite double covalent bonds (As = X) were questioned as principal network-forming species in glassy As–X alloys (see, the notes of Lucovsky et al. [3] on important difference in the bonding chemistry for P–S/Se and As–S/Se systems), there were a few reports on these s.u. appeared rather as specific structural defects in melt-quenched As–S alloys. Thus, as has been reported yet [4], the As–S glasses with 28.6 at.% of As compositionally equivalent to di-arsenic pentasulfide As₂S₅ or QT S = As(S_{1/2})₃ s.u. could be crystallized under pressurization at

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~70 kbar and 350 °C, but under further annealing at 190 °C these s.u. were dissociated on normally coordinated pyramidal $\text{As}(\text{S}_{1/2})_3$ s.u. and chain-like $(\text{X}_{1/2})_2$ bridges. Existence ~3–5% of the QT s.u. was also deduced in S-rich glassy arsenic sulfides As-S by Golovchak et al. [5] using high-resolution XPS technique [5]. The QT s.u. responsible for a so-called coordination disordering as revealed by deviation from canonical “3–2” bonding rule were found as products of intrinsic separation in stoichiometric arsenic tri-sulfide (As_2S_3) glass prepared under homogenization in low-temperature (450–550 °C) regime [6, 7]. Therefore, it was reasonably assumed that stabilization of these double covalent bond-based $\text{S} = \text{As}(\text{S}_{1/2})_3$ s.u. could be initiated by intrinsic pressurization applied to glassy arsenosulfide (As-S) alloys obeying confined geometry, whereas such anomaly was surely hidden in their isoelectronic analogs (glassy arsenoselenides As-Se).

In the early 2000s, the concept of double covalent bond-based QT $\text{X} = \text{As}(\text{X}_{1/2})_3$ s.u. in As-X alloys was in the center of hot controversies related to structural self-organization in network glass formers [8–10]. Indeed, in fully saturated covalent networks obeying mean-field Phillips–Thorpe constraints theory with stretching and bending forces ascribed to intramolecular bonding within principal cation As-centered groups, these s.u. corresponding to mean coordination number $\text{MCN} = 2.286$ and mean count of mechanical constraints equals to space dimensionality ($n_c = 3.0$) facilitate structural self-organization in these alloys. Being stabilized in addition to corner-sharing $\text{As}(\text{X}_{1/2})_3$ pyramids corresponding to di-arsenic tri-chalcogenide As_2X_3 stoichiometry ($\text{MCN} = 2.40$) which is also optimally constrained in view of $n_c = 3.0$, these double covalent bond-based QT $\text{X} = \text{As}(\text{X}_{1/2})_3$ s.u. were announced by Boolchand et al. as most suitable candidates to justify the boundaries of so-called intermediate phase (between onset and rigidity transitions enveloping rigid but stress-free elastic phase), initially, in binary As-Se [11] and, later, in As-S systems [12]. Direct experimental evidence for these QT s.u. stabilized in an amount satisfying formation of optimally constrained networks has been obtained in glassy arsenoselenides, despite sophisticated speculations on crucial role of melt/glass homogenization as necessary conditions for these s.u., which realistically emerged in a very small amount as specific kind of structural defect (not as primary network-forming s.u., as was suggested in [13]), and only in As-S system (not in As-Se alloys, as was inconsistently concluded in [14]). As has been convincingly proved in famous research of Pierre Lucas with coworkers [15], there was no significant contribution of mechanical homogenization of melt finalizing in glass modification as expected in [13, 14].

The objective of this work is comparative analysis of modification possibilities related to double covalent bond anomalies in melt-quenched pnictochalcogenide alloys of two canonical binary glass-forming systems (arsenosulfides, As-S, and arsenoselenides, As-Se) undergoing radiation-induced intrinsic decomposition of primary heteronuclear covalent chemical bonds in nanoconfined geometry, employing ab initio quantum-chemical modeling within developed cluster simulation code CINCA (cation interlinked network cluster approach) [16–18].

2 Computational cluster modeling

2.1 General approach to intrinsic phase separation in glassy pnictochalcogenides

The network structure of under-stoichiometric glassy arsenic chalcogenides As-X (where X = S or Se) obeying “chain crossing” model [1, 4] is known to be defined to a great extent by two-cation (di-arsenic) multi-chalcogenide As_2X_n clusters ($n \geq 3$) formed by some cation-centered polyhedrons such as trigonal $\text{As}(\text{X}_{1/2})_3$ pyramids based on three-fold $\times 3$ -coordinated pnictogen atoms (As) interlinked by $(\text{X}_{1/2})_n$ bridges of two-fold $\times 2$ -coordinated chalcogen (X) atoms [16–18]. Thereby, for under-stoichiometric binary As-X glassy alloys deviated from As_2X_3 stoichiometry in chalcogen X-rich side, the governing evolution trend is defined by the n parameter, which could be changed from $n = 1$ (corresponding to two corner-sharing trigonal $\text{As}(\text{X}_{1/2})_3$ pyramids in stoichiometric As_2X_3), to $n \rightarrow \infty$ (corresponding to very long chains composed of chalcogen half-atoms $(-\text{X}_{1/2}-)_n = \text{X}_{n/2}$ bridging almost uncorrelated single $\text{As}(\text{X}_{1/2})_3$ pyramids). Owing to intrinsic phase separation proper to As_2X_3 glass [17–19], we expect possible decomposition of heteronuclear (As-X) covalent bonds within trigonal $\text{As}(\text{X}_{1/2})_3$ pyramids into chalcogen X-rich clusters based on homonuclear (X-X) bonds and pnictogen As-rich clusters composed of two corner-sharing $\text{As}(\text{X}_{1/2})_3$ pyramids without bridging chalcogen link, the latter meaning $\text{As}_2(\text{X}_{1/2})_4$ s.u. possessing homonuclear bonding configuration of $(\text{X}_{2/2}) > \text{As} - \text{As} < (\text{X}_{2/2})$ type (see Table 1).

2.2 Atomic clusters in glass-forming chalcogenide networks parameterized within quantum-chemical modeling CINCA

To quantify comparison of atomic clusters in arsenic chalcogenides As-X (where X = S or Se), we calculate their mean cluster-forming energies (CFE) using ab initio quantum-chemical modeling in terms of CINCA [16–18]. The CFE calculations were performed with the *HyperChem* program based on the restricted Hartree–Fock self-consistent field method using split-valence double-zeta basis set with single polarization function 6-311G* [20, 21].

Table 1 Nomenclature and optimized geometrical parameterization of atomic clusters composing saturated arseno-chalcogenide As-X covalent networks in a vicinity of As₂X₃ and As₂X₅ compositions

Network-forming arsenic chalcogenide clusters				CFE E_f , kcal/mol	
Atomic cluster nomenclature in terms of network-forming s.u	MCN	Local bonding configuration	n_c	X = S	X = Se
Mono-arsenic tri-chalcogenide As ₂ X ₃ , single As(X _{1/2}) ₃ pyramid	2.40	As-(X _{1/2}) ₃	3.00	– 79.404	– 72.309
Di-arsenic tri-chalcogenide As ₂ X ₃ = As ₂ (X _{1/2}) ₆ , two corner-sharing As(X _{1/2}) ₃ pyramids	2.40	(X _{2/2})>As–X–As<(X _{2/2})	3.00	– 79.408	– 72.619
Di-arsenic di-chalcogenide AsX = As ₂ (X _{1/2}) ₄ , two As-As bonded single pyramids As ₂ (X _{1/2}) ₄	2.50	(X _{2/2})>As–As<(X _{2/2})	3.25	– 77.682	– 72.419
Di-arsenic tetra-chalcogenide As ₂ X ₄ = As ₂ (X _{1/2}) ₈ two (X _{1/2}) ₂ bonded single As(X _{1/2}) ₃ pyramids	2.33	(X _{2/2})>As–X–X–As<(X _{2/2})	2.83	– 78.342	– 71.550
Di-arsenic penta-chalcogenide As ₂ X ₅ -I two (X _{1/2}) ₂ bonded As(X _{1/2}) ₄ s.u	2.286	(X _{4/2})>As–X–As<(X _{4/2})	2.71	– 78.643	– 71.256
Di-arsenic penta-chalcogenide As ₂ X ₅ -II two (X _{1/2}) ₄ bonded single As(X _{1/2}) ₃ pyramids	2.286	(X _{2/2})>As–X–X–X–As<(X _{2/2})	2.71	– 77.650	– 71.359
Di-arsenic penta-chalcogenide As ₂ X ₅ -QT double-bond based QT X = As(X _{1/2}) ₃ s.u	2.286	X = As–(X _{1/2}) ₃	3.00	– 76.832	– 67.484

The final geometrical optimization and single-point energy calculations were carried out with the Fletcher-Reeves conjugate gradient method until the root-mean-square gradient approaching 0.1 kcal/(Å·mol) was reached.

The network glass structure of arsenic chalcogenides As–X (X = S or Se), can be imagined as multiple repetitions of some mixed pnictogen-chalcogen ‘building’ blocks known as network-forming clusters (NFC) [16]. These clusters are carriers of basic properties of a glass, reflecting the most essential interactions in their networks. In terms of CINCA, the connectivity of glassy network is reflected in a so-called base NFC represented two (or more) interconnected As atoms surrounded by short chalcogen chains (inner base NFC core) and inter-cluster bridges forming outer base NFC shell (long m·(S/Se)_{1/2} chains, where m is a number of chalcogen half-atoms). Thereby, the short-range ordering in a glass is defined mainly in the inner cores of respective base NFC, whereas small medium-range ordering (only within a few coordination spheres) is reflected in the outer base NFC cores.

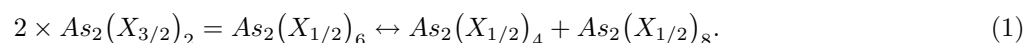
To parameterize network-forming tendencies in a glass, the boundary chalcogen X atoms forming NFC shell (half-atom –X_{1/2}– link) are terminated by the hydrogen atoms (H) possessing low energies in the known covalent-type structures (at the level of ~3 kcal/mol [22, 23]). Thereby, the NFC terminated by open chalcogen bridges such as (–X–) = (–X_{1/2}–X_{1/2}–) = (X_{1/2})₂ are substituted by their molecular prototypes terminated by –H atoms possessing closed self-consistent bonding configurations. Only half-part contributions were considered after subtraction the energies of terminated H atoms and –X–H bonds from the overall CFE of the molecule. The CFE averaged per one atom (E_f) is accepted as the measure of clustering probability in the examined networks [16–18]. Noteworthy, for

double cation-centered NFC such as As_2X_n , stability of a glassy network is defined by base NFC cores $\text{As}(\text{X}_{1/2})_3$, which are deterministic in short-range ordering, surrounded by H-terminated shells $-\text{X}_{1/2}-\text{H}$, which are decisive in small medium-range ordering in a glass [16]. Diversity of such NFC based on single covalent bonding in As/Ge-S/Se glasses are analyzed in [17, 18], testifying that difference in the CFE for some NFC which can be introduced under external influences can serve as a criterion for preferential network-forming tendency, irrespective to actual thermodynamic and/or kinetic preferences in melt-quenching derived glass system.

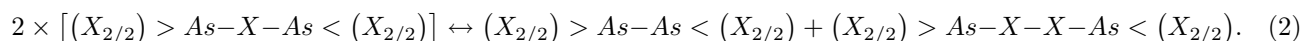
The CINCA approach allows reliable identification of network tendencies in the examined chalcogenide glasses characterized by different MCN (equivalent to the count of covalent chemical bonds per atom), thereby parameterizing most favorable bond-changing decomposition scenarios in these substances including those based on NFC possessing single and double covalent bonding. Finally, to compare plausibility of the reconstructed topological configurations for the respective NFC, the mean number of the Lagrangian constraints (n_c) is calculated following the known Phillips-Thorp constraint-counting algorithm [8–10].

2.3 Cluster modeling of intrinsic decomposition scenarios in As_2X_3 glass networks

Chemical disordering in stoichiometric glasses As_2X_3 (where $\text{X} = \text{S}, \text{Se}$) possessing heteronuclear As-X bonding is governed by network disproportionality, which can be defined in terms of intrinsic decomposition of principal NFC corresponding to main As-rich and chalcogen X-rich glass-forming s.u. (gathered in Table 1):



The above disproportionality scenario (1) means that part of a glass structure composed exclusively of heteronuclear (As-X) covalent chemical bonds stabilized within two corner-sharing pyramidal $\text{As}(\text{X}_{1/2})_3$ s.u. (MCN = 2.40) is transformed in completely polymerized network built of pnictogen As-rich and chalcogen X-rich s.u., which are respectively based on homonuclear As-As covalent bonds within $\text{As}_2(\text{X}_{1/2})_4$ clusters (MCN = 2.50) and homonuclear X-X bonds within $\text{As}_2(\text{X}_{1/2})_8$ clusters bridging two single $\text{As}(\text{X}_{1/2})_3$ pyramids (MCN = 2.33). Realistically, the above disproportionality scheme (1) reflects hetero-to-homonuclear covalent bond switching in stoichiometric di-arsenic tri-chalcogenide As_2X_3 glass, which could be presented in terms of decomposition of atomic configurations based on the respective NFC gathered in Table 1:



The above single covalent bond-switching reaction (2) is energy-consuming in both arsenoselenide and arsenosulfide glasses, and can be recognized as responsible for reversible radiation-induced effects in these As-X binaries explaining reversible long-wave shift in their optical absorption edge under above bandgap photoexposure or high-energy irradiation [1, 2].

Further, the products of the above intrinsic decomposition (2) can be stabilized as network-forming s.u. based on respective NFC or, alternatively, retransformed in more favorable state, provided such state is possible. The di-arsenic tetra-chalcogenide As_2X_4 NFC possessing homonuclear $(X_{2/2}) > \text{As}-\text{X}-\text{X}-\text{As} < (X_{2/2})$ bonding configuration can be transferred to di-arsenic tri-chalcogenide s.u. (compositionally corresponding to As_2X_3) possessing only heteronuclear $(X_{2/2}) > \text{As}-\text{X}-\text{As} < (X_{2/2})$ bonding configuration, combined with two di-arsenic penta-chalcogenide As_2X_5 -I and As_2X_5 -II entities based on $\times 3$ -coordinated As atoms, which respectively possess normally coordinated $(X_{4/2}) > \text{As}-\text{X}-\text{As} < (X_{4/2})$ and $(X_{2/2}) > \text{As}-\text{X}-\text{X}-\text{X}-\text{As} < (X_{2/2})$ bonding configurations or abnormally coordinated QT $\text{S} = \text{As}(\text{S}_{1/2})_3$ s.u. having $\times 4$ -coordinated pnictogen As atoms due to double covalent bond with terminated chalcogen X atom. The preferential bond-switching scenario in the examined glassy As-X ($\text{X} = \text{S}, \text{Se}$) alloys is defined by energetic barrier ΔE_f corresponding to decomposition of the respective s.u.

Thus, the mapping of these ΔE_f values serves as testable hypothesis to choose the most energetically favorable atomic configurations stabilized in these stoichiometric glassy pnictochalcogenides As_2X_3 ($\text{X} = \text{S}, \text{Se}$) under decomposition scenario (1), but not clarify specificity of covalent chemical bond-transformation pathways corresponding to such transformations at a nanoscale level.

3 Results and discussion

3.1 General characterization of network-forming clustering in glassy arsenic chalcogenides around As_2X_3 stoichiometry

The geometrically optimized parameters of glass-forming NFC in binary arseno-chalcogenide As-X networks ($\text{X} = \text{S}, \text{Se}$) in the vicinity of As_2X_3 stoichiometry participating in intrinsic decomposition scenarios with respect to

network disproportionality scheme (1) are presented in our preliminary research for glassy arsenosulfides ($X = S$) [17] and arsenoselenides ($X = Se$) [18], whereas the CFE (E_f) for these pnictochalcogenides calculated within the CINCA modeling approach are gathered in Table 1. The geometrically optimized parameters of molecular prototypes reconstructed by CINCA modeling from single pyramidal normally $\times 3$ -coordinated $As(S_{1/2})_3$ and double-bond based anomalously $\times 4$ -coordinated $S = As(S_{1/2})_3$ clusters are presented in Table 2.

As an example of successful computational models developed for amorphous arsenosulfides in a vicinity of As_2S_3 stoichiometry, the lengths of heteronuclear As-S covalent bonds are fitted to be within $2.24 \div 2.28$ Å domain, while homonuclear S-S bond lengths are well fitted in a range from 2.063 Å to 2.095 Å [18]. The values of bond angle based on As atom neighboring with two S atoms change from 90.7° to 107.5° , the bond angles of homonuclear S environment are well fitted within $104.6 \div 108.6^\circ$ domain, while the angles of heteronuclear S environment are distributed within $98.9 \div 103.0^\circ$ domain.

The calculated values of covalent bond lengths and angles are well correlated with the known structural parameters experimentally derived for realistic amorphous As-S binaries and their crystalline prototypes [1, 24, 25]. Thus, according to Morimoto [24], the structure of crystalline di-arsenic tri-sulfide As_2S_3 (corresponding to mineral orpiment) is composed of some 2D layers, the heteronuclear As-S spiral intralayer chains being linked by common S atom between two neighboring pnictogen atoms (As), thus forming interlinked corner-sharing trigonal $As(S_{1/2})_3$ pyramidal s.u. based on single covalent bonding. The average values of covalent bond angles on As and S atoms in heteronuclear atomic environment in these alloys respectively approach 98.7° and 99.3° , the As-S bond lengths being in $2.21 \div 2.28$ Å range (approaching 2.24 Å in average). According to Mullen and Nowacki [25], the average values of single covalent bond angles respectively based on As and S atoms in heteronuclear environment are 99° and 97.5° , and heteronuclear As-S bond lengths are ranged from 2.243 Å to 2.308 Å (thereby approaching 2.283 Å in average).

Consistently and most principally, in binary arseno-chalcogenide As-X glassy alloys (both arsenosulfides and arsenoselenides, As-S and As-Se), the optimally constrained (in view of the n_s value corresponding to space dimensionality, $D = 3.0$) stoichiometric di-arsenic tri-chalcogenide As_2X_3 NFC having intra-cluster configurations based on heteronuclear As-X covalent chemical bonds are the most energetically favorable ones.

Under deviation from this As_2X_3 stoichiometry ($MCN = 2.40$, $n_s = 3.00$) towards As-rich over-constrained ($MCN > 2.4$, $n_s > 3.00$) di-arsenic di-chalcogenide $As_2X_2 = As_2(X_{1/2})_4$ NFC or Se-rich under-constrained ($MCN < 2.40$, $n_s < 3.00$) di-arsenic tetra-chalcogenide $As_2X_4 = As_2(X_{1/2})_8$ NFC, the calculated CFE E_f gets to be substantially worse (as this follows from Table 1).

These findings mean that intrinsic phase decomposition scenario in stoichiometric As_2X_3 glass by hetero-to-homonuclear covalent chemical bond switching obeying the above disproportionality scheme (1) is unfavorable (needs additional energy costs for realization), and can be realized only under some external influences such as absorbed light exposure or high-energy irradiation [1, 2]. Comparison of geometrical parameters of molecular prototypes reconstructed from the respective NFC by the H atom saturation of external -S- bridges within = $As-(S_{1/2})_3$ configuration of cation-centered $As(S_{1/2})_3$ s.u. obeying pyramidal $\times 3$ -coordination (in respect to normally $\times 3$ -coordinated As atom) and double-bond based QT $S = As(S_{1/2})_3$ s.u. obeying abnormal $\times 4$ -coordinated As atom shows more shortened heteronuclear As-S bonding in the latter (see Table 2).

Therefore, it should be expected that under double covalent bond $S = As$ distance reduced by ~ 0.2 Å with respect to single covalent bond As-S distance, the volume occupied by two $S = As(S_{1/2})_3$ s.u. (As_2X_5 -QT NFC in Table 1) appears to be much smaller than that corresponding to isocompositional di-arsenic penta-sulfide s.u.

Table 2 Geometrically optimized parameters of molecular clusters reconstructed from single pyramidal normally $\times 3$ -coordinated $As(S_{1/2})_3$ and double-bond based anomalously $\times 4$ -coordinated $S = As(S_{1/2})_3$ clusters

Cation-centered atomic cluster			Bond distances (Å)		Bond angles ($^\circ$)	
Molecular prototype	Network-forming s.u.	Bonding configuration	As = S	As-S	$\angle(S-As-S)$	$\angle(S-As = S)$
AsS_3H_3	$AsS_{3/2}$	Pyramidal $As-(S_{1/2})_3$	—	2.252	101.9	—
				2.254	102.9	
				2.256	92.7	
				av. 2.254 Å	av. 99.2	
				—	—	
$S = AsS_3H_3$	$S = As(S_{1/2})_3$	Quasi-tetrahedral S $= As-(S_{1/2})_3$	2.056	2.217	102.5	115.9
				2.216	102.4	115.7
				2.217	102.2	116.0
				av. 2.056 Å	av. 102.4°	av. 115.8°
				av. 2.217 Å	av. 102.4°	av. 115.8°

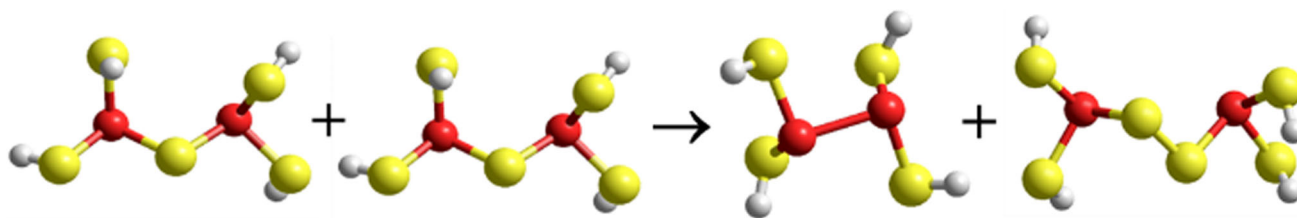


Fig. 1 The ball-and-stick presentation of NFC corresponding to intrinsic decomposition reaction (1) changing hetero-homonuclear covalent bond balance in glassy As_2S_3 . The optimized configurations of atomic clusters are given in terms of H-saturated molecular prototypes with As, S and H atoms labeled by red, yellow and gray balls, respectively

formed by chalcogen -S- linking between two normally coordinated pyramidal $\text{As}(\text{S}_{1/2})_3$ s.u. within As_2X_5 -I and/or As_2X_5 -II NFC, as denoted in Table 1).

3.2 Intrinsic decomposition in optimally-constrained glassy di-arsenic tri-chalcogenides As_2X_3 (X = S, Se) by hetero-to-homonuclear covalent bond switching

The ball-and-stick presentation of network-forming atomic clusters participating in hetero-to-homonuclear covalent bond switching in stoichiometric di-arsenic tri-chalcogenide (As_2X_3) via disproportionality reaction (1) initiated under an external influence is reproduced in Fig. 1 for binary arsenic sulfides As-S. It is obvious that locally inhomogeneous saturated covalent bond network having homonuclear As-As and S-S bonds appears instead of initial homogeneous network based on energetically favorable heteronuclear As-S covalent chemical bonds. As can be inferred from visual inspection of Fig. 1, the inhomogeneous network composed of homonuclear As-As and X-X covalent bonds appears instead of some part of initial network having exceptionally heteronuclear As-X bonds.

Using the forming energies for these clusters (E_f) as presented in Table 1, the energetic barrier (ΔE_f) of hetero-to-homonuclear covalent-bond-switching scenario (2) was estimated to approach as high as +1.33 kcal/mol for glassy arsenosulfides of stoichiometric di-arsenic tri-sulfide As_2S_3 and +0.72 kcal/mol for glassy arsenoselenides of stoichiometric di-arsenic tri-selenide As_2Se_3 composition.

Thus, the much higher energy is to be transferred to stabilize local inhomogeneities in covalent network of glassy arsenosulfides (As-S) as compared with glassy arsenoselenides (As-Se). This finding corresponds well to difference in the optical bandgap energies (E_g) for these glassy pnictochalcogenides, approaching ~2.4 eV for As_2S_3 and ~1.8 eV for As_2Se_3 [1, 2].

3.3 Chemical decomposition in chalcogen-rich under-constrained glassy arsenic chalcogenides activated in normal and volume-confined conditions

The products of covalent-bond-switching disproportionality (1) can be transferred in more favorable state. Thus, as was reported by Shpotyuk et al. [17, 18], two-cation di-arsenic multichalcogenide As_2X_m clusters enriched in chalcogen (X) over As_2X_3 stoichiometry (corresponding to X-rich As-X alloys with $\text{MCN} < 2.40$) could undergo local chemical decomposition into two compositionally asymmetric parts: these being (i) chalcogen X-deficient $\text{As}_2\text{X}_{m-1}$ atomic clusters and (ii) chalcogen X-enriched $\text{As}_2\text{X}_{m+1}$ clusters, determined in respect to decomposition scheme that can be presented as follows:

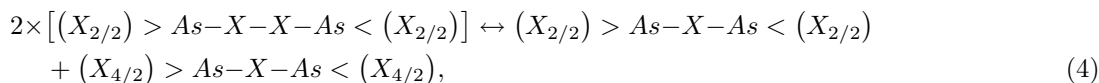


As to X-enriched di-arsenic tetra-chalcogenide $\text{As}_2\text{X}_4 = \text{As}_2(\text{X}_{1/2})_8$ clusters (which are under-stoichiometric and under-constrained in view of $\text{MCN} = 2.33$ and $n_c = 2.83$, see Table 1) as one of the products of intrinsic network disproportionality scheme (1) activated in di-arsenic tri-chalcogenide (As_2X_3) network, the local chemical decomposition via scheme (3) justifies possibilities for two types of the network-forming atomic clusters, such as (i) chalcogen X-deficient $\text{As}_2\text{X}_{4-1} = \text{As}_2\text{X}_3$ ones, which are compositionally stoichiometric (corresponding to di-arsenic tri-chalcogenide with $\text{MCN} = 2.40$) and topologically optimally constrained (in view of $n_c = 3.00$), as well as (ii) chalcogen X-enriched clusters corresponding to di-arsenic penta-chalcogenide $\text{As}_2\text{X}_{4+1} = \text{As}_2\text{X}_5$, which are under-stoichiometric ($\text{MCN} = 2.286 < 3.00$), but comprise different topology of covalent bonding in view of cation-centered As atoms occupying normal (three-fold $\times 3$ -coordination) or abnormal (four-fold $\times 4$ -coordination) state.

In case of normal state corresponding to $\times 3$ -coordinated As atoms within single $\text{As}(\text{X}_{1/2})_3$ pyramidal s.u., two local decomposition scenarios can be activated for the aforementioned di-arsenic tetra-chalcogenide As_2X_4 clusters of under-constrained $(\text{X}_{2/2}) > \text{As-X-X-As} < (\text{X}_{2/2})$ covalent bonding topology, leading to stabilization of

di-arsenic tri-chalcogenide As_2X_3 clusters having optimally-constrained $(\text{X}_{2/2}) > \text{As}-\text{X}-\text{As} < (\text{X}_{2/2})$ topology ($n_c = 3.00$), along with X-enriched $\text{As}_2\text{X}_5\text{-I}$ clusters of $(\text{X}_{4/2}) > \text{As}-\text{X}-\text{As} < (\text{X}_{4/2})$ bonding configuration (reproduced in Fig. 2) and/or $\text{As}_2\text{X}_5\text{-II}$ clusters of $(\text{X}_{2/2}) > \text{As}-\text{X}-\text{X}-\text{X}-\text{As} < (\text{X}_{2/2})$ bonding configuration (reproduced in Fig. 3), the both latter being topologically under-constrained in view of $n_c = 2.71$ (see also Table 1).

The first reaction corresponding to the local chemical decomposition scheme (4) presented as



and the second reaction corresponding to the local chemical decomposition scheme (5) presented as

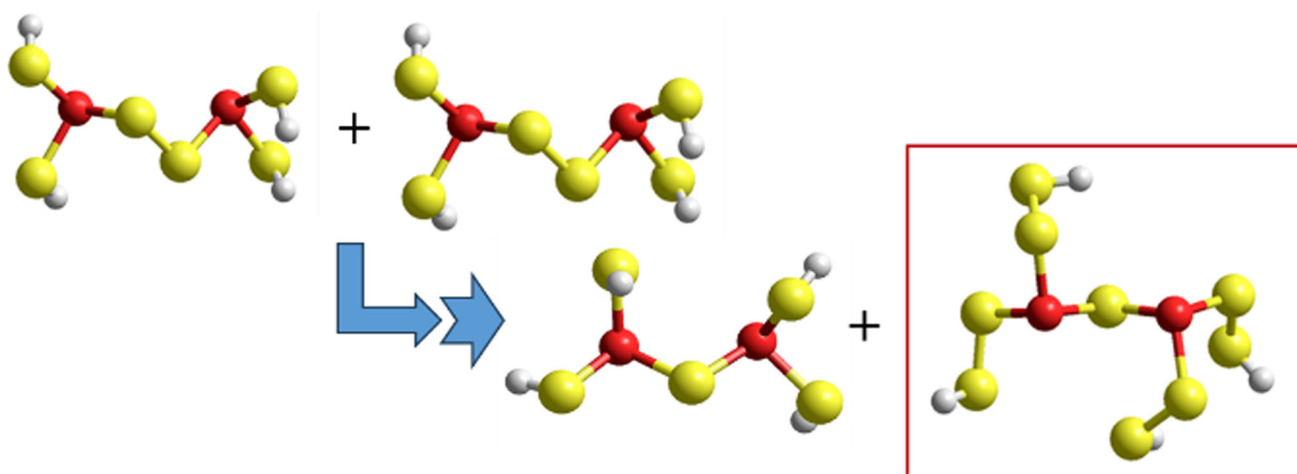
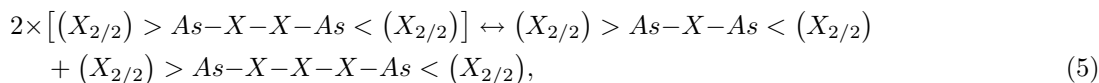


Fig. 2 The ball-and-stick presentation of bond-switching scenario for two As_2S_4 NFC re-transformed in two corner-sharing $\text{AsS}_{3/2}$ and volume confined $\text{As}_2\text{S}_5\text{-I}$ s.u. enveloped by red rectangular. The optimized configurations of the reconstructed atomic clusters are shown in terms of their H-saturated molecular prototypes with As, S and H atoms respectively labeled by red, yellow and gray balls

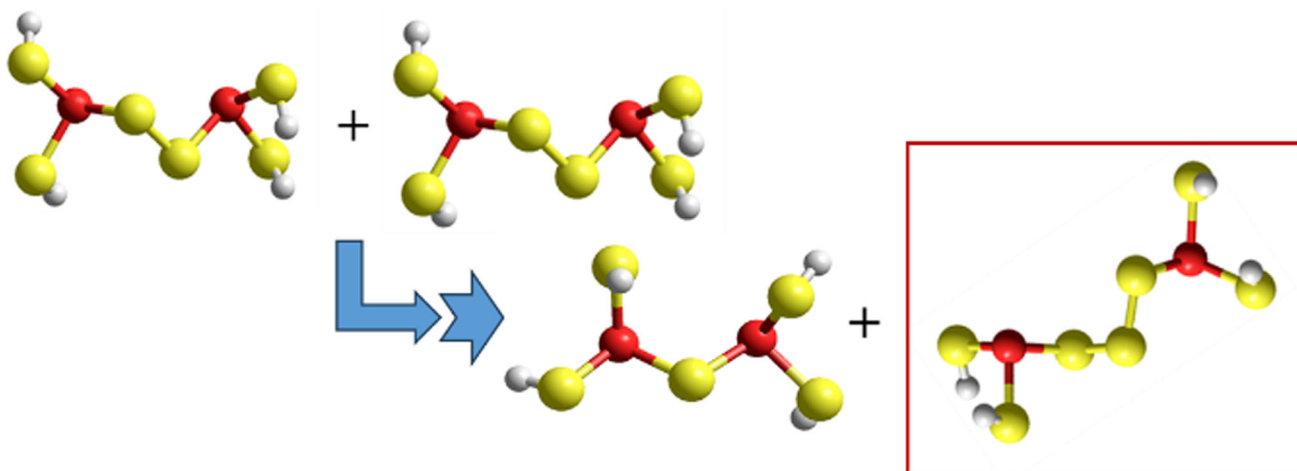


Fig. 3 The ball-and-stick presentation of covalent bond-switching scenario for two As_2S_4 NFC re-transformed in two corner-sharing $\text{AsS}_{3/2}$ and volume-extended $\text{As}_2\text{S}_5\text{-II}$ s.u. enveloped by red rectangular. The optimized configurations of the reconstructed atomic clusters are shown in terms of their H-saturated molecular prototypes with As, S and H atoms respectively labeled by red, yellow and gray balls

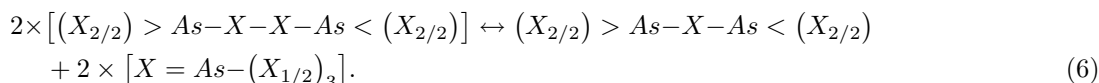
are *spontaneous*, meaning possibility to be realized in normal conditions (without any external activation), because of negative barrier of respective covalent bond switching scenario ΔE_f approaching -0.62 kcal/mol and -0.04 kcal/mol for both scenarios corresponding to local decompositions schemes (4) and (5) activated in glassy arsenic sulfides, and -0.27 kcal/mol and -0.33 kcal/mol for these scenarios activated in arsenic selenides. Both bond switching scenarios are reproduced in Figs. 2 and 3 for arsenic sulfide As-S glassy alloys.

The above finding means that chalcogen X-rich As_2X_4 clusters (MCN = 2.33), which appear from intrinsic decomposition in optimally-constrained As_2X_3 glass in respect to disproportionality scheme (1), are most probably stabilized in this glass keeping under-constrained $(\text{X}_{2/2}) > \text{As}-\text{X}-\text{X}-\text{As} < (\text{X}_{2/2})$ topology ($n_c = 2.83$), or, alternatively, spontaneously re-transformed to chalcogen X-enriched state of As_2X_5 -I and/or As_2X_5 -II NFC (MCN = 2.286) possessing more under-constrained covalent bonding topology corresponding to $n_c = 2.71$.

Specifically, both bond-changing scenarios (4) and (5) resulting in di-arsenic penta-chalcogenide As_2X_5 -I and As_2X_5 -II network-forming clusters based on $\times 3$ -coordinated As atoms are equally possible in glassy arsenoselenides (X = Se) because of the energetic barrier (ΔE_f) approaching -0.3 kcal/mol, while transition via bond-changing scenario (4) to more homogeneous glass structure composed of As_2X_5 -I clusters (which demonstrate under-constrained $(\text{X}_{4/2}) > \text{As}-\text{X}-\text{As} < (\text{X}_{4/2})$ bonding topology with $n_c = 2.71$) prevails in glassy arsenosulfides (X = S) in view of the ΔE_f approaching -0.62 kcal/mol.

Assuming possibility of abnormal four-fold $\times 4$ -coordination for cation-type pnictogen atom (such as As), one can come to very controversial covalent-bond-switching scenario related to local decomposition of two neighboring As_2X_4 clusters having under-constrained $(\text{X}_{2/2}) > \text{As}-\text{X}-\text{X}-\text{As} < (\text{X}_{2/2})$ covalent bonding topology (MCN = 2.33, $n_c = 2.83$) into stoichiometric As_2X_3 cluster (MCN = 2.40) possessing optimally-constrained $(\text{X}_{2/2}) > \text{As}-\text{X}-\text{As} < (\text{X}_{2/2})$ topology (MCN = 2.40, $n_c = 3.00$), along with two double-bond As = X based X = $\text{As}(\text{X}_{1/2})_3$ clusters (MCN = 2.286) showing optimally-constrained QT X = $\text{As}-(\text{X}_{1/2})_3$ bonding topology (with $n_c = 3.00$). The ball-and-stick presentation of this bond-switching scenario for glassy arsenic sulfides (X = S) is reproduced in Fig. 4.

The bond-switching reaction depicted in Fig. 4 corresponds to local chemical decomposition scheme (6) which can be presented in terms of covalent bonding configurations of the clusters undergoing changes as follows:



Because of very unfavorable CFE for such double-bond based QT X = $\text{As}(\text{X}_{1/2})_3$ clusters (as can be inferred from Table 1), the energetic barrier ΔE_f of bond-switching scenario reproduced in Fig. 4 occurs to be positive, approaching $+0.44$ kcal/mol for glassy arsenic sulfides (X = S) and $+1.93$ kcal/mol for arsenic selenides (X = Se).

This finding means that additional energy should be injected into binary As-X network to stabilize such local anomaly in covalent bonding as optimally-constrained ($n_c = 3.00$) X = $\text{As}(\text{X}_{1/2})_3$ s.u. with MCN = 2.286. Such effect can be caused by intrinsic network pressurization in a glass due to inner pressure developed in volume-confined conditions like those hosting pressure-induced polyamorphism in chalcogenides [26–28].

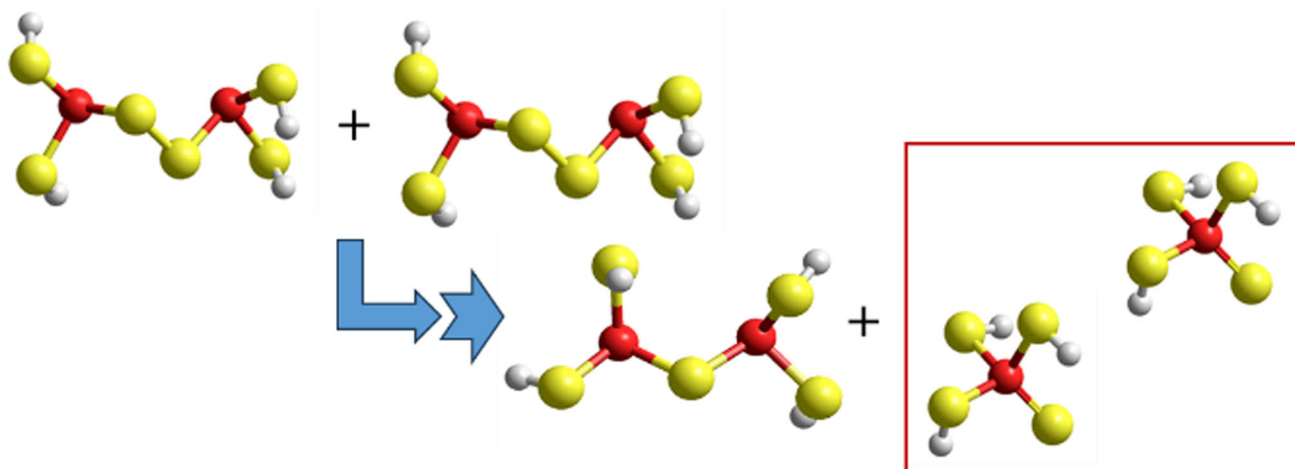


Fig. 4 The ball-and-stick presentation of bond-switching scenario for two As_2S_4 NFC re-transformed in two corner-sharing $\text{AsS}_{3/2}$ and two double-bond based QT S = $\text{As}(\text{S}_{1/2})_3$ s.u. enveloped by red rectangular. The optimized configurations of the reconstructed atomic clusters are reproduced in terms of their H-saturated molecular prototypes with As, S and H atoms labeled by red, yellow and gray balls, respectively

Coordination disordering in binary As-X networks causes inhomogeneities in atomic density distribution around As atoms obeying abnormal $\times 4$ -coordination due to QT topology of cation-centered $X = \text{As}(\text{X}_{1/2})_3$ s.u. in addition to these As atoms obeying normal $\times 3$ -coordination due to simple pyramidal topology of $\text{As}(\text{X}_{1/2})_3$ s.u. Experimental conditions stabilizing such covalent chemical bonding anomalies in glassy As-X alloys compositionally corresponding to di-arsenic tri-chalcogenide As_2X_3 stoichiometry are defined by the energetic barriers which should be overcome for successful *intrinsic* hetero-to-homonuclear bond switching followed by local decomposition of chalcogen rich As_2X_4 clusters in respect to above decomposition scenario (6).

In arsenic sulfide glass-formers based on stoichiometric As_2S_3 , where intrinsic decomposition via hetero-to-homonuclear covalent bond-switching scheme (2) is realized as over-barrier transition with ΔE_f approaching as high as +1.33 kcal/mol, the local decomposition of S-rich As_2S_4 clusters (MCN = 2.33 and $n_c = 2.83$) in double-bond based QT S = $\text{As}(\text{S}_{1/2})_3$ s.u. needs an additional energy transfer above +0.44 kcal/mol, which seems quite realistic as resultant of respective covalent chemical bond-switching processes developed in volume confined conditions.

Disbalance in energetic barriers which should be overcome for successful intrinsic hetero-to-homonuclear covalent bond switching followed by double-bond clustering due to QT S = $\text{As}(\text{S}_{1/2})_3$ s.u. seems quite plausible in arsenic sulfide alloys approaching $(+1.33)/(+0.44) = 3.0$. Of course, spontaneous decomposition of S-rich under-constrained As_2S_4 clusters (MCN = 2.33, $n_c = 2.83$) into optimally-constrained stoichiometric As_2X_3 clusters (MCN = 2.40, $n_c = 3.00$) and more under-constrained S-rich clusters such as As_2S_5 -I and As_2S_5 -II (both having MCN = 2.286 and $n_c = 2.71$) as illustrated in Fig. 2 and 3 fails reliable identification of such structural anomalies (double-bond clustering), which could be detected rather as some defective entities.

As can be inferred from visual inspection of red-contoured rectangular spaces around As_2S_5 -I, As_2S_5 -II and S = $\text{As}(\text{S}_{1/2})_3$ clusters stabilized by local decomposition scenarios (4), (5) and (6) respectively reproduced in Fig. 2, 3 and 4, the double-bond based QT S = $\text{As}(\text{S}_{1/2})_3$ clusters occupy minimum volume in a glass structure. So, it can be reasonably suggested that stabilization of such clusters in these As-S alloys is substantially facilitated by inner pressure due to artificial nanoconfined geometry developed under hetero-to-homonuclear bond switching.

On the contrary, such structural anomalies are principally inaccessible in arsenic selenide As-Se alloys, where intrinsic decomposition by hetero-to-homonuclear covalent bond-switching scheme (1) is activated through over-barrier transitions with ΔE_f value approaching +0.72 kcal/mol. Indeed, the greater energy transfer above +1.93 kcal/mol is needed to stabilize double-bond based QT Se = $\text{As}(\text{Se}_{1/2})_3$ s.u. in these glassy alloys. Disbalance in the calculated values of energetic barriers which should be overcome for successful intrinsic hetero-to-homonuclear covalent bond switching by decomposition scheme (1) followed by double-bond clustering in As-Se alloys occurs to be unrealistically low approaching only $(+0.72)/(+1.93) = 0.4$. It seems impossible to develop such colossal local pressurization in these As-Se alloys creating volume confinement conditions under inner pressure accompanying irradiation induced bond switching in respect to disproportionality scheme (1).

Noteworthy, when such transformations are finished by local decomposition in the $\times 3$ -fold coordinated As species (such as di-arsenic penta-sulfide As_2S_5 -I and As_2S_5 -II clusters), the long-wave (red) shift is expected in optical absorption edge of these alloys (a so-called darkening effect), as this can be exemplified by the known photodarkening effect in arsenic chalcogenide films [1, 2] or high-energy irradiation-induced darkening in stoichiometric and S-rich melt-quenched As-S glasses [29–34]. However, when these intrinsic bond-changing decomposition scenarios are realized in the volume confined conditions (because of restricted inner space available to accommodate the products of such structural transformations) followed by local decomposition into stable $\times 4$ -glass-forming networks of As-X binaries, $\times 4$ -coordinated As species such as double-bond based QT S = $\text{As}(\text{S}_{1/2})_3$ s.u., an opposite short-wave (blue) shift is expected in optical absorption edge of these alloys (this is a so-called bleaching effect), as has been convincingly exemplified by changes observed under coordination disordering in near-stoichiometric As_2S_3 glasses [5, 6].

Returning to difference in ability to accommodate the double-bond based QT X = $\text{As}(\text{X}_{1/2})_3$ s.u. in networks of As-X binaries built mainly of chalcogen-interlinked pyramidal $\text{As}(\text{X}_{1/2})_3$ s.u., it's reasonable to explain this phenomenon by difference in the ratio of respective CFE (E_f) of these entities $\kappa = E_f(X = \text{As}(\text{X}_{1/2})_3)/E_f(\text{As}(\text{X}_{1/2})_3)$. This ratio approaches unity (1.0) if the E_f value for QT X = $\text{As}(\text{X}_{1/2})_3$ s.u. tends to this energy for $\text{As}(\text{X}_{1/2})_3$ pyramids. For binary As-S system where such anomaly is possible, the calculated κ value occurs to be 0.97, while for As-Se system where such anomaly is impossible, the κ value is only 0.93. At the basis of these calculations, we come to conclusion that double-bond based clustering is possible in binary phosphorus sulfides P-S ($\kappa = 0.99$) and selenides P-Se ($\kappa = 0.95$), but evidently impossible in both antimony sulfides (Sb-S) and selenides (Sb-Se) where $\kappa \sim 0.91$. Therefore, it should be concluded the energetic barrier to overcome for anomalous double-bond clustering in pnictochalcogenide alloys is close to $\kappa^{\text{cr}} = E_f(\text{QT})/E_f(\text{Pyr.}) = \sim 0.94$.

4 Conclusions

Radiation modification effect in network glass formers such as binary arseno-chalcogenides As-X (where X = S, Se) is reexamined accepted the possibility of some volume restrictions in their realization.

Destruction of covalent chemical bonds in these glassy pnictochalcogenides under above bandgap light exposure or high-energy irradiation is accompanied by relaxation in a new metastable state. When this process occurs via switching of heteronuclear (As-S) covalent chemical bonds into homonuclear (As-As) and (S-S) ones, like under intrinsic decomposition in stoichiometric di-arsenic trichalcogenide As_2X_3 alloy, an additional volume appears in a glass resulting in the red shift of optical absorption edge (the known darkening effect). Assuming that cation-centered double-bond X = As based quasi-tetrahedral $\text{X} = \text{As}(\text{X}_{1/2})_3$ structural units are stabilized in a glass due to inner pressure developed in the volume restricted nanoconfined geometry, an opposite the blue shift (the bleaching effect) is expected.

Computing the balance of energetic costs needed for intrinsic hetero-to-homonuclear bond decomposition in stoichiometric As_2X_3 glassy alloy followed by decomposition of chalcogen-rich di-arsenic tetra-chalcogenide As_2X_4 clusters into double covalent bond-based $\text{X} = \text{As}(\text{X}_{1/2})_3$ structural units, it was confirmed impossibility of such anomalies in As-Se network in comparison with As-S one. The double covalent bond-based clustering is possible in pnictochalcogenide networks possessing the ratio of respective forming energies for double covalent bond-based $\text{X} = \text{As}(\text{X}_{1/2})_3$ units and single covalent bond-based $\text{As}(\text{X}_{1/2})_3$ pyramidal units above ~ 0.94 .

This analysis based on quantum-chemical modeling of atomic clusters in arsenochalcogenide binaries (As-X) critically resolves misunderstandings with quasi-tetrahedral double covalent bond-based $\text{X} = \text{As}(\text{X}_{1/2})_3$ units as principal structural species facilitating self-organization in these network glass formers.

Author contributions

The manuscript was written through contributions of all authors.

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Data availability Data will be made available on reasonable request.

Declarations

Conflict of interest The authors declare no conflict of interest regarding this article.

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