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RADIATION MODIFICATION OF CHALCOGENIDE NETWORK GLASS FORMERS: COMPARATIVE PREDICTION FOR As-S/Se BINARIES IN NANOCONFINED GEOMETRY

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Abstract. *Radiation-induced modification in network glass formers such as binary arseno-chalcogenides As-X (X=S, Se) is critically reexamined accepted possibility of volume restrictions in their realization. Destruction of covalent bonds in these glasses under above-bandgap exposure or high-energy irradiation is accompanied by relaxation into a new state. When this process occurs via switching of hoteronuclear (As-X) bonds into homonuclear (As-As) and (X-X) ones, like under intrinsic decomposition in* As_2X_3*, an additional volume appears in the glass, resulting in a red shift of the optical absorption edge (darkening effect). Assuming that double-bond-based quasi-tetrahedral* $X{=}As(X_{1/2})_3$ *units are stabilized in a glass due to inner pressure developed in nanoconfined geometry, an opposite blue shift (bleaching effect) is expected. This analysis, based on ab initio quantum-chemical modeling of atomic clusters, critically resolves speculations about quasi-tetrahedral X=As(X1/2)3 units as the principal species facilitating self-organization in arseno-chalcogenide networks.*

Keywords: *radiation, confined geometry, intrinsic pressurization, arseno-chalcogenide, network glass former*

1. INTRODUCTION

Nowadays, network glass formers such as arsenic chalcogenides of the binary As-X system (X = S or Se), also referred to as arseno-chalcogenides, have been in the sphere of intense interest among the glass manufacturers' community due to their unique properties in a variety of applications [1]. Typically, these substances are stabilized by quenching from a high-entropy melt, attaining saturated covalent bonding, in which both elemental constituents retain their main valencies in the polymerized glass network, the anion-type chalcogen X atoms and cation-type As atoms being respectively two-fold x2- and three-fold x3-coordinated. Deviation from this ‘x2-x3’ bonding rule provides a row of modification possibilities for these glassy substances, which could be realized technologically by optimal melt-quenching regimes or post-technologically by processing the quenched alloys with above-bandgap light (photoexposure) or high-energy irradiation [1,2].

That is why, one of the greatest controversies in the arseno-chalcogenides science is related to possibilities of their useful modification, including effects of network optimization due to anomalous covalent bonding, which could be exemplified, in part, by double-bond based quasi-tetrahedral (QT) structural units (s.u.) such as $X{=}As(X_{1/2})_3$. Despite As=X bonds being questioned as network species in As-X compounds [3], there were some reports on these s.u. of sulfide type stabilized as defects. Thus, as reported previously [4], the As-S glass alloy with 28.6 at.% of As compositionally equivalent to arsenic penta-sulfide As_2S_5 or $S{=}As(S_{1/2})_3$ could be crystallized under pressurization at ~70 kbar and 350°C, but under annealing at 190°C these s.u. were dissociated in the As_2S_5 glass on normally coordinated network s.u. like $As(S_{1/2})_3$ pyramids and $(X_{1/2})_2$ bridges. Existence ~3–5 % of these s.u. was also deduced in S-rich glass by Golovchak et al. using high-resolution XPS [5]. The QT s.u. of this type responsible for coordination disordering were found in small amounts as products of intrinsic separation in As_2S_3 glass prepared by quenching in a low-temperature 450–550°C homogenization regime [6,7]. It could be assumed that stabilization of $S{=}As(S_{1/2})_3$ s.u. in the above cases was due to intrinsic pressurization developed technologically in arseno-sulfide As-S alloys obeying locally nanoconfined geometry, whereas such an anomaly was surely hidden in glassy arseno-selenides.

The objective of this work is comparative analysis of structural modification possibilities related to double-bond anomalies in glassy As-S/Se binaries undergoing intrinsic decomposition in a locally confined geometry,

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employing *ab-initio* quantum-chemical modeling route with the known atomic cluster simulation code CINCA (cation interlinked network cluster approach) [8-10].

2. COMPUTATIONAL MODELING

The structure of chalcogen X-rich glassy arseno-chalcogenides deviated from As_2X_3 stoichiometry can be imagined as obeying "*chain crossing*" model [1,8-10], when cation-centered polyhedrons such as three-fold x3-coordinated $As(X_{1/2})_3$ pyramids are interlinked by bridging two-fold x2-coordinated $(X_{1/2})_n$ chains. In binary arseno-chalcogenides As-X, this evolution trend is defined compositionally by the *n* parameter, which could be changed from n=1 (corresponding to two atom-shared $As(X_{1/2})_3$ pyramids) to $n \rightarrow \infty$ (corresponding to very long bridging chalcogen chains). In decomposition of stoichiometric As_2X_3 alloy, we should also accept the possibility to stabilize these s.u. without chalcogen links corresponding to $n=0$, meaning $As_2(X_{1/2})_4$ s.u. based on homonuclear As-As covalent bond [9,10].

2.1. *Parameterization of network-forming atomic clusters in arseno-chalcogenides As-X employing quantum-chemical modeling in terms of the CINCA*

To quantify comparison of atomic clusters in binary arseno-chalcogenides, we calculate their mean cluster-forming energies (CFE) using the CINCA algorithm [8]. The quantum-chemical calculations were performed with *HyperChem* program based on restricted Hartree–Fock self-consistent field method using split-valence double-zeta basis set with single polarization function 6-311G* [11,12]. 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 of 0.1 kcal/(Å·mol) was reached. The boundary chalcogen X atoms forming the cluster shell were terminated by the Hydrogen H atoms possessing low energies in network structures (at the level of ~3 kcal/mol [13,14]). In such a way, the network clusters terminated by chalcogen $(–X–X–)_{1/2}=(X_{1/2})_2$ bridges were substituted by respective molecular prototypes having closed self-consistent configurations. Only half-part contributions were considered after subtraction the energies of H atoms and -X-H bonds from the overall CFE of the molecule. In final, the CFE averaged per one atom E_f was accepted as a measure of clustering probability in the examined network [9,10].

The above modeling (CINCA) allows identification of network-forming tendencies in saturated networks characterized by mean coordination number (MCN, number of bonds per atom), thereby parameterizing most favorable network-forming scenarios. To compare atomic clusters composed of small rings or one-fold coordinated atoms, the average number of Lagrangian constraints per atom n_c was calculated using the mean-field Phillips-Thorpe constraint-counting algorithm with stretching and bending forces ascribed to intra-molecular bonds within the examined cluster [15-17].

2.2. *Cluster modelling of decomposition scenarios in stoichiometric As_2X_3 network glass-formers*

Chemical disordering in stoichiometric As_2X_3 glass (X=S, Se) is governed by network disproportionality, which can be parameterized in terms of intrinsic decomposition of main glass-forming s.u.:

$$2\cdot As_2(X_{3/2})_2 \leftrightarrow As_2(X_{1/2})_4 + As_2(X_{4/2})_2. \qquad (1)$$

The above disproportionality (1) means that part of a glass structure composed of heteronuclear As-X bonds within two corner-shared $As(X_{1/2})_3$ pyramidal s.u. (MCN=2.40) is re-transformed in polymerized As- and chalcogen X-rich s.u., based on homonuclear As-As bonds within $As_2(X_{1/2})_4$ clusters (MCN=2.50) and X–X bonds bridging two $As(X_{1/2})_3$ pyramids (MCN=2.33). Realistically, the disproportionality reaction (1) reflects *hetero-to-homonuclear* switching of covalent chemical bonds in As_2X_3 glass, which could be presented *in terms of* bond-changing configurations of respective clusters:

$$2\cdot[(X_{2/2})>As–X–As<(X_{2/2})] \leftrightarrow \\ (X_{2/2})>As–As<(X_{2/2}) + \\ + (X_{2/2})>As–X–X–As<(X_{2/2}). \qquad (2)$$

The above bond-switching reaction was recognized as responsible for reversible radiation-induced effects in amorphous As-X binaries, explaining long-wave shift in their optical absorption edge under above bandgap photoexposure or high-energy irradiation [1,2].

Further, the products of this disproportionality can be stabilized in a glass structure as network-forming s.u. based on respective atomic clusters, or, alternatively, re-transformed towards more favorable state, if possible. Thus, the $As_2(X_{2/3})_6$ clusters possessing homonuclear (–X–X–) bonding within $(X_{2/2})>As–X–X–As<(X_{2/2})$ s.u. can be transformed to arsenic tri-chalcogenide (As_2X_3) entities related to $(X_{2/2})>As–X–As<(X_{2/2})$ s.u., combined with (i) arsenic penta-chalcogenide (As_2X_5) entities related to $(X_{4/2})>As–X–As<(X_{4/2})$ s.u. or $(X_{2/2})>As–X–X–X–As<(X_{2/2})$ s.u., the both having normally three-fold coordinated cation-type As atoms, or (ii) abnormally coordinated double-bond based QT $S=As(S_{1/2})_3$ s.u. having four-fold coordinated As atoms. It's reasonable the preferential bond-switching scenario in arseno-chalcogenide As-X glass formers (X=S, Se) is defined by energetic barrier ΔE_f of disproportionality scheme corresponding to decomposition of respective network-forming s.u.

3. RESULTS AND DISCUSSION

The geometrically optimized parameters of clusters in arseno-chalcogenide As-X glass networks (X=S, Se) near As_2X_3 stoichiometry participating in intrinsic decomposition governed by disproportionality scheme (1) are presented in [9,10], whereas their CFE calculated within the CINCA [8] for a group of arseno-sulfides (X=S) and arseno-selenides (X=Se) are given in Table 1.

As an example of developed computational models of arseno-sulfide binaries around As_2S_3 stoichiometry, the lengths of heteronuclear As-S covalent bonds are fitted to 2.24÷2.28 Å domain, while homonuclear S-S bond lengths are well fitted from 2.063 to 2.095 Å [10]. 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 fitted to 104.6÷108.6° range, while the angles of heteronuclear S environment are distributed in 98.9÷103.0° range [10]. These bond lengths and angles are well correlated with structural parameterization data for amorphous As-S binaries and some their crystalline counterparts [1]. Thus, according to Morimoto [18], the structure of crystalline As_2S_3 (mineral orpiment) is composed of layers, the As-S spiral intralayer chains being linked by common S atom between two neighboring As atoms, forming interlinked corner-sharing $As(S_{1/2})_3$ pyramidal s.u. The average values of bond angles based on As and S atom in heteronuclear environment are respectively 98.7° and 99.3°, and As-S bond lengths are in 2.21÷2.28 Å range (2.24 Å in average). According to Mullen and Nowacki [19], the average values of bond angles 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 (2.283 Å in average).

Table 1. The forming energies E_f of atomic clusters composing arseno-chalcogenide As-X networks near As_2X_3 stoichiometry

Bonding configuration of arseno-chalcogenide cluster: MCN, n_c	CFE E_f, kcal/mol	
	X=S	X=Se
$As–(X_{1/2})_3$: MCN=2.40, n_c=3.00	-79.404	-72.309
$(X_{2/2})>As–X–As<(X_{2/2})$: MCN=2.40, n_c=3.00	-79.408	-72.619
$(X_{2/2})>As–As<(X_{2/2})$: MCN=2.50, n_c=3.25	-77.682	-72.419
$(X_{2/2})>As–X–X–As<(X_{2/2})$: MCN=2.33, n_c=2.83	-78.342	-71.550
$X=As–(X_{1/2})_3$: MCN=2.286, n_c=3.00	-76.832	-67.484
$(X_{4/2})>As–X–As<(X_{4/2})$: MCN=2.286, n_c=2.71	-78.643	-71.256
$(X_{2/2})>As–X–X–X–As<(X_{2/2})$: MCN=2.286, n_c=2.71	-77.650	-71.359

Consistently and most principally, in the examined As-X binaries (both arsenic sulfides and selenides), the optimally constrained (in view of average number of mechanical constraints per atom n_s corresponding to space dimensionality, D=3.0) network-forming As_2X_3 clusters having intra-cluster configurations based on heteronuclear As–X covalent bonds are most favorable. Under deviation from As_2X_3 stoichiometry towards over-constrained (n_s>3.0) arsenic mono-chalcogenide $AsX=As_2(X_{1/2})_4$ or under-constrained (n_s<3.0) arsenic bi-chalcogenide $AsX_2=As_2(X_{2/3})_6$ compounds, the E_f energies of the clusters get to be substantially worse. This means intrinsic decomposition in stoichiometric As_2X_3 by hetero-to-homonuclear covalent bond switching obeying disproportionality scheme (1) is very unfavorable, and therefore could be realized only under external influences such as high-energy irradiation [1].

3.1. Intrinsic decomposition in stoichiometric optimally-constrained arsenic tri-chalcogenides As_2X_3 associated with hetero-to-homonuclear covalent bond switching

The ball-and-stick presentation of network-forming atomic clusters participating in hetero-to-homonuclear bond switching in arsenic tri-chalcogenide As_2X_3 via disproportionality reaction (1) under external influence is exemplified in Figure 1 for a group of sulfides (X=S). It's obvious that locally inhomogeneous network having homonuclear As-As and S-S covalent bonds appear instead of initial network based on the energetically favorable heteronuclear As-S covalent chemical bonds.

As can be also inferred from visual inspection of Figure 1, the inhomogeneous network composed of homonuclear As-As and X-X covalent chemical bonds appear instead of some part of initial network having exceptionally heteronuclear As-X covalent chemical bonding. Using the forming energies (E_f) for these atomic clusters taken from 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 arseno-sulfides of stoichiometric As_2S_3 composition and +0.72 kcal/mol for arseno-selenides of As_2Se_3 composition.

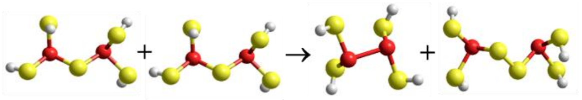

Figure 1. The ball-and-stick presentation of atomic clusters corresponding to intrinsic decomposition reaction (1) changing hetero-homonuclear covalent bond balance in stoichiometric As_2S_3. The optimized geometrical configurations of network-forming clusters are reproduced in terms of their H-saturated molecular prototypes with As, S and H atoms labeled by red, yellow and grey balls, respectively.

Thereby, the much higher energy is to be transferred to stabilize local inhomogeneities in covalent chemical bond network of glassy arseno-sulfides as compared with glassy arseno-selenides. This finding corresponds well to the difference in the optical bandgap energies (Eg) for these stoichiometric compounds approaching ~2.4 eV for $As2S_3$ and ~1.8 eV for As_2Se_3 [1,2].

3.2. Local decomposition in chalcogen-rich under-constrained arseno-chalcogenides As-X activated in normal and volume-confined conditions

The products of bond-switching disproportionality reaction (1) can be re-transformed in a more favorable state, provided such state is possible.

Thus, as was first reported by Shpotyuk et al. [9,10], the two-cation As_2X_m clusters enriched in chalcogen (X) content below As_2X_3 stoichiometry (corresponding to X-rich under-constrained arseno-chalcogenides having MCN<2.4, n_s<3.00) could undergo *local* decomposition on two compositionally asymmetric parts, these being (i) chalcogen X-deficient As_2X_{m-1} clusters, and (ii) chalcogen X-enriched As_2X_{m+1} clusters, in respect to the disproportionality scheme presented as follows:

$$As_2X_m \leftrightarrow As_2X_{m+1} + As_2X_{m-1}. \qquad (3)$$

As to As_2X_4 atomic clusters (which are under-stoichiometric and under-constrained in view of MCN=2.33 and n_c=2.83) as one of the products of network disproportionality reaction (1) activated in arsenic tri-chalcogenide glass As_2X_3, the *local* chemical decomposition (3) justifies stabilization possibilities for two types of network-forming atomic clusters, such as (i) chalcogen X-deficient $As_2X_{4-1}=As_2X_3$ ones, which are compositionally stoichiometric (in view of MCN=3.00) and topologically optimally constrained (n_c=3.00), and (ii) chalcogen X-rich $As_2X_{4+1}=As_2X_5$ atomic clusters, which are under-stoichiometric (with MCN=2.286), but possess different topology of covalent chemical bonding in view of cation-centered As atoms occupying normal (three-fold x3-coordination) or abnormal (four-fold x3-coordination) state.

In case of normal state (corresponding to three-fold x3-coordinated cation-centered As atoms), we deal with two *local* decomposition scenarios for As_2X_4 s.u. of under-constrained $(X_{2/2})>As–X–X–As<(X_{2/2})$ covalent bonding topology (n_c=2.83, see Table 1), leading to stabilization of arsenic tri-chalcogenide As_2X_3 clusters having optimally-constrained $(X_{2/2})>As-X-As<(X_{2/2})$ bonding topology, along with more X-enriched As_2X_5-I atomic clusters possessing $(X_{4/2})>As-X-As<(X_{4/2})$ bonding configuration (see Figure 2) or As_2X_5-II atomic clusters possessing $(X_{2/2})>As-X-X-X-As<(X_{2/2})$ bonding configuration (see Figure 3), the both latter being topologically under-constrained (in view of n_c=2.71, see Table 1).

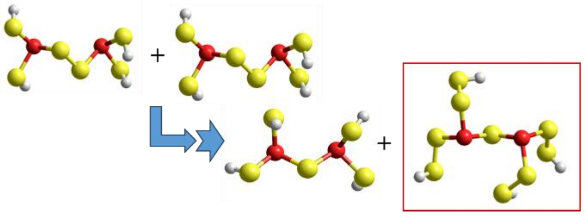

Figure 2. The ball-and-stick presentation of bond-switching scenario for two neighboring As_2S_4 clusters re-transformed in corner-sharing $AsS_{3/2}$ pyramids and size-extended As_2S_5-I s.u. The optimized geometrical configurations of network-forming clusters are reproduced in terms of H-saturated molecular prototypes with As, S and H atoms labeled by red, yellow and grey balls, respectively.

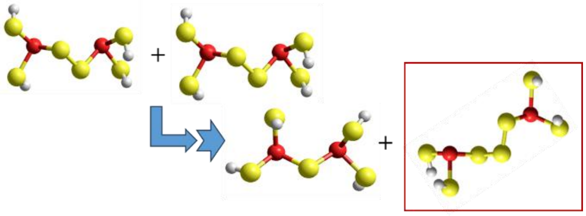

Figure 3. The ball-and-stick presentation of bond-switching scenario for two neighboring As_2S_4 clusters re-transformed in corner-sharing $AsS_{3/2}$ pyramids and size-extended As_2S_5-II s.u. The optimized geometrical configurations of network-forming clusters are reproduced in terms of H-saturated molecular prototypes with As, S and H atoms labeled by red, yellow and grey balls, respectively.

The both reactions for As-X binaries in Figure 2 corresponding to local decomposition scheme (4):

$$\begin{aligned}&2\cdot[(X_{2/2})>As-X-X-As<(X_{2/2})] \leftrightarrow\\&(X_{2/2})>As-X-As<(X_{2/2}) +\\&+ (X_{4/2})>As-X-As<(X_{4/2}),\end{aligned}\tag{4}$$

and Figure 3 corresponding to local decomposition scheme (5):

$$\begin{aligned}&2\cdot[(X_{2/2})>As-X-X-As<(X_{2/2})] \leftrightarrow\\&(X_{2/2})>As-X-As<(X_{2/2}) +\\&+ (X_{2/2})>As-X-X-X-As<(X_{2/2}),\end{aligned}\tag{5}$$

are *spontaneous*, meaning the possibility to be realized in normal conditions (without any external activation), because of negative energetic barrier of respective bond-switching scenario ΔE_f approaching only -0.62 kcal/mol and -0.04 kcal/mol for local decompositions scenarios (4) and (5) activated in a group of arseno-sulfides (X=S), and -0.27 kcal/mol and -0.33 kcal/mol for these local decomposition scenarios (4) and (5) activated in a group of arseno-selenides (X=Se).

The above finding means that under-constrained chalcogen-rich As_2X_4 clusters (MCN=2.33, n_c=2.83), which appear from intrinsic decomposition in As_2X_3 in respect to disproportionality reaction (1), are stabilized in this stoichiometric glass keeping under-constrained $(X_{2/2})>As-X-X-As<(X_{2/2})$ covalent bonding topology, or, alternatively, could be spontaneously transformed to more X-rich state (typical for As_2X_5-I and As_2X_5-II clusters with MCN=2.286) possessing more under-constrained bonding topology in view of n_c=2.71.

Specifically, the both bond transferring scenarios resulting in As_2X_5-I and As_2X_5-II atomic clusters are more-or-less equally possible in the examined arseno-selenides (X=Se) because of the ΔE_f barrier approaching -0.3 kcal/mol, while transition to more homogeneous structure based on As_2X_5-I clusters prevails in arseno-sulfides (X=S) because of the ΔE_{f}=-0.62 kcal/mol.

Assuming the possibility of abnormal x4-fold coordination for cation-type As atoms, we come to very controversial bond-switching scenario related to decomposition of two As_2X_4 clusters possessing under-constrained $(X_{2/2})>As-X-X-As<(X_{2/2})$ covalent bond topology (in view of MCN=2.33, and n_c=2.83) into stoichiometric As_2X_3 cluster (MCN=2.40) possessing optimally-constrained $(X_{2/2})>As-X-As<(X_{2/2})$ bonding topology (n_c=3.00), along with two double-bond As=X based $X=As(X_{1/2})_3$ clusters (with MCN=2.286) showing the optimally-constrained QT $X=As-(X_{1/2})_3$ bonding topology (n_c=3.00). The ball-and-stick presentation of this covalent bond-switching scenario for glassy arseno-sulfides (X=S) is shown in Figure 4.

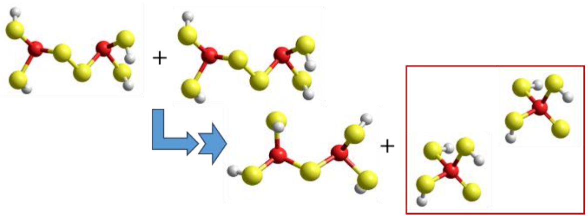

Figure 4. The ball-and-stick presentation of covalent bond-switching scenario for two neighboring As_2S_4 clusters re-transformed in two corner-sharing $AsS_{3/2}$ pyramids and two double-bond based QT $S=As(S_{1/2})_3$ s.u. expected for volume-confined conditions. The optimized configurations of atomic clusters are reproduced in terms of H-saturated molecular prototypes with As, S and H atoms labeled by red, yellow and grey balls, respectively.

The above bond-switching reaction shown in Figure 4 corresponds to local decomposition scheme (6) which can be presented in terms of covalent bonding configurations undergoing changes as follows:

$$\begin{aligned}&2\cdot[(X_{2/2})>As-X-X-As<(X_{2/2})] \leftrightarrow\\&(X_{2/2})>As-X-As<(X_{2/2}) +\\&+ X=As-(X_{1/2})_3\end{aligned}\tag{6}$$

Because of very unfavorable CFE for such double-bond based QT $X=As(X_{1/2})_3$ clusters (as can be inferred from Table 1), the energetic barrier ΔE_f of bond-switching scenario reproduced in Figure 4 is positive, approaching +0.44 kcal/mol for arseno-sulfide (X=S) and +1.93 kcal/mol for arseno-selenide (X=Se) binaries.

In general, this finding means that additional energy should be injected in the arseno-chalcogenide network to stabilize such anomaly in covalent chemical bonding as optimally-constrained (n_c=3.00) double-bond based $X=As(X_{1/2})_3$ s.u. with MCN=2.286. Such effect can be caused, in part, by *local* network pressurization in a glass due to inner pressure developed in volume-confined conditions (like those hosting the pressure-induced polyamorphism in chalcogenides [20-22]).

Coordination disordering in binary As-X networks causes inhomogeneities in atomic density distribution around As atoms obeying 'abnormal' x4-coordination due to QT topology of cation-centered $X{=}As(X_{1/2})_3$ s.u. in addition to these As atoms obeying 'normal' x3-coordination due to pyramidal topology of $As(X_{1/2})_3$ s.u. The experimental conditions stabilizing such covalent chemical bonding anomalies in arseno-tri-chalcogenide compounds are defined by the energetic barriers which should be overcome for successful *intrinsic* hetero-to-homonuclear covalent chemical bond decomposition in stoichiometric As_2X_3 glass and *local* decomposition of chalcogen X-rich under-constrained As_2X_4 atomic clusters resulted from this intrinsic decomposition scenario.

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

Thus, disbalance in the energetic barriers which should be overcome for successful intrinsic hetero-to-homonuclear covalent chemical bond decomposition resulting in the QT bonding in arseno-sulfide binaries is promising approaching as high as (+1.33)/(+0.44)=3.0. Of course, spontaneous decomposition of S-rich under-constrained As_2S_4 clusters (possessing MCN=2.33 and n_c=2.83) into stoichiometric optimally-constrained As_2X_3 clusters (possessing MCN=2.40 and n_c=3.00) and more under-constrained S-rich clusters such as As_2S_5-I and As_2S_5-II (both possessing MCN=2.286 and n_c=2.71) as depicted in Figure 2 and 3, prevails reliable identification of such structural anomalies, which could be detected rather as defective ones.

On the contrary, such network-forming structural anomalies are principally inaccessible in the arseno-selenide binaries, where *intrinsic* decomposition by hetero-to-homonuclear bond-switching scheme (1) can be activated as over-barrier transition with ΔE_f close to +0.72 kcal/mol. Indeed, the greater energy transfer approaching as high as +1.93 kcal/mol is needed to stabilize the double-bond based QT s.u. in the arseno-selenide network, which seems too unrealistic as compared with the barrier of *intrinsic* decomposition in this glass.

Thereby, disbalance of the calculated energetic barriers which should be overcome for successful intrinsic hetero-to-homonuclear bond decomposition resulting in QT covalent bonding in arseno-selenide binaries occurs to be unrealistically low approaching (+0.72/(+1.93) = 0.4.

As can be inferred from visual inspection of red- countered rectangular spaces filled with As_2S_5-I, As_2S_5-II and $S{=}As(S_{1/2})_3$ s.u., stabilized by local decomposition bond-switching scenarios (4), (5) and (6) respectively reproduced in Figures 2, 3 and 4, the double-bond based QT $S{=}As(S_{1/2})_3$ atomic clusters occupy the minimum volume in a glass-forming backbone. Therefore, it could be reasonably assumed that stabilization of such network-forming clusters in these arseno-chalcogenide glassy substances is substantially facilitated by inner pressure developed in the nanoconfined geometry.

It worth mentioning, when such transformations are finished by local decomposition into 'normal' x3-fold coordinated As species (such as As2S5-I/II clusters), the long-wave (the red) shift is expected in the optical absorption edge in these chalcogenide glasses (a so-called darkening effect), as this can be exemplified by the well-known reversible photodarkening phenomena in arseno-chalcogenide films [1,2], or radiation-induced darkening in stoichiometric and S-rich bulky glass arseno-sulfides [23-28].

However, when the above intrinsic bond-changing decomposition scenarios occur in the volume confined conditions (because of restricted inner spaces available to accommodate products of such transformations) finished by local decomposition into stable abnormal four-fold x4-coordinated cation-centered As species such as cation-centered double-bond X=As based QT $X{=}As(X_{1/2})_3$ s.u., an opposite short-wave (the blue) shift is expected in the optical absorption edge in these network-forming glassy substances (bleaching effect), as was recently exemplified by coordination disordering in the near-stoichiometric arseno-tri-sulfide As_2S_3 glasses [5,6].

4. CONCLUSION

Radiation-induced modification effects in network glass formers, such as binary arseno-chalcogenides As-X (X=S, Se), are critically reexamined in light of the accepted possibility of volume restrictions in their realization. Destruction of covalent chemical bonds in these glasses under photoexposure above the bandgap or high-energy irradiation is accompanied by relaxation into a new metastable state. When this process occurs via switching of hoteronuclear (As-S) bonds into homonuclear (As-As) and (S-S) ones, like under intrinsic decomposition in stoichiometric arseno-tri-chalcogenide As_2X_3, an additional volume appears in a glass network, resulting in red shift of optical absorption edge (the known darkening effect). Assuming that cation-centered double-bond X=As based quasi-tetrahedral $X{=}As(X_{1/2})_3$ structural units are stabilized in a glass network due to inner pressure developed in nanoconfined geometry, an opposite blue shift (the bleaching effect) is expected. Computing the balance of energetic costs needed for intrinsic hetero-to-homonuclear decomposition in stoichiometric arseno-tri-chalcogenides As_2X_3 and local decomposition of chalcogen-rich arseno-bi-chalcogenides As_2X_4, resulting in quasi-tetrahedral X=As(X1/2)3 units, it was confirmed that the principal impossibility of such structural anomalies in arseno-selenide glass networks in comparison with arseno-sulfide ones.

This analysis, based on ab-initio quantum-chemical modeling of atomic clusters in the arseno-chalcogenide binaries, critically resolves speculations with cation-centered double-bond X=As based quasi-tetrahedral $X{=}As(X_{1/2})_3$ units as principal structural species facilitating self-organization in arseno-chalcogenide glass-forming networks.

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