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Radiation-induced bond switching in chalcogenide semiconductor glasses from *first-principles* quantum-chemical calculations: On the role of dipole-type charged coordination defects

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ABSTRACT

The probabilities of radiation-induced charged coordination defects in the form of dipole-type valence alteration pairs were estimated for glass-forming chalcogenide networks built of edge-shared $GeS_{4/2}$ tetrahedrons, $AsS_{3/2}$ trigonal pyramids and S_n chains. Geometrical optimization and single-point energy calculation was performed for selected atomic clusters utilizing *ab-initio* quantum-chemical modeling with CINCA (cation-interlinking network cluster approach) algorithm, the computed atomic configurations being compared by corresponding cluster-forming energies accepting inner distortions in coordination polyhedrons with miscoordinated atoms.

It was concluded such dipole-type defective configurations could be unlikely realized in Ge–S and As–S glasses, because of unrealistically high energetic gains needed to accommodate lateral and angular distortions connected with three-fold closed rings and homopolar S–S bonds. Defect formation energy was minimal in chain-like glassy structures built by only S atoms, but corresponding energetic barrier left still high to activate such transformations under thermodynamically stabilized conditions.

1. Introduction

Structural study on chalcogenide semiconductor glasses (ChSG) has still been an actual due to rich diversity of corresponding atomic clusters serving as glass-forming building blocks to reproduce their fully-saturated covalent backbone [1]. In addition, the ChSG can accommodate some defective irregular states occurring under photo- or radiation-induced redistribution of covalent chemical bonds (changes in bond type and concentration) [1–4]. An elementary precursor of such defect-related state can be imagined as a result of destruction–polymerization transformation, e.g. destruction of one covalent bond followed by formation of new one, these newly coordinated atoms not obeying bond-saturation *8-N* rule and thus forming valence alteration pair (VAP) [5]. In an alternative terminology, the VAP represents diamagnetic pair of over- and under-coordinated charged defects (in full respect to known Anderson's principle of negative electron correlation energy [6]). In addition to "wrong" local coordination, these miscoordinated atoms possess opposite electrical charges (positive and negative for over- and under-coordinated configuration, respectively). Non-defect destruction–polymerization transformations are possible in ChSG, provided two neighboring bonds are re-switched simultaneously, so changing only type of covalent bonding [7]. At the end of the 1970-s, Kastner [8] improved the VAP concept, considering Coulomb interaction between opposite charged defects, thus distinguishing the intimate VAP (IVAP) and spatially separated random pairs (RP) of coordination defects. Soon later, this concept was employed by Street [9,10] to reversible photostructural changes in ChSG, connecting their origin with exciton self-trapping. The possibility to transfer optically induced IVAP into more stable RP resulting from different defect-conserved bond switching reactions in amorphous As_2S/Se_3 was considered by Shimakawa et al. [11,12].

At the beginning of the 2000-s, the comprehensive and convincing verification for defect-related origin of induced metastability in ChSG was presented by Uchino and Elliott [13–15], who performed *quantum-chemical simulation* of different disturbed atomic configurations for glassy networks built of neighboring $AsS_{3/2}$ pyramids using GAUSSIAN 98 program. They proved that four-fold

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coordinated As atoms conjugated with one-fold coordinated S atom (but not directly linked) or, alternatively, (As_4^+; S_1^-) defect pair (the superscript is for charge, and subscript is for local atomic environment) contributed to photoinduced mid-gap absorption below 2 eV in amorphous As_2S_3. This was most realistic justification for defect nature of induced metastability in this glass, while an alternative explanation was ascribed to some hypervalent defect configurations characterized by essentially smaller formation energies in respect to energies of regular covalent bonds [16–18]. Though there were no direct evidences for essential role of hypervalent configurations, nevertheless, such defects have been appeared in quantum-chemical models of many ChSG like As_2S_3 [15–20].

At the end of the 1990-s, different equilibrium quasi-molecular hypervalent configurations in amorphous S and As_2S_3 were analyzed by Dembovski et al. [20]. The quantum-chemical modeling employing semiempirical MNDO and PM3 methods testified in a favor of VAP stabilization in the form of directly linked negative C_1^- and positive C_3^+ atoms. Such (C_3^+; C_1^-) defects named as dipole VAP (VAP-*d*) were assumed to be possible only in labile chain- and ring-like S structures forming *cis*- and *trans*-configurations, where their stabilization need relatively small gains of configuration entropy due to reduced interatomic displacements [20]. Nevertheless, recently such VAP-*d* were speculatively ascribed by Kavetskyy [21] to other ChSG, including those which possess more constrained structural networks even composed by topologically rigid $GeS_{4/2}$ tetrahedrons and $AsS_{3/2}$ trigonal pyramids. Thus, the VAP-*d* of (S_3^+; Ge_3^-) type were assumed to be formed under high-energy γ-irradiation in As_2S_3–GeS_2 glasses instead of thermodynamically stable edge-shared (ES) GeS_4 configurations (where two $GeS_{4/2}$ tetrahedrons are linked through common two S atoms) [21]. Even without strong quantitative simulation, the origin of such VAP-*d* in As- and Ge-based ChSG seems to be questionable from simple steric consideration assuming extraordinary deviations in some interatomic bond lengths and angles to accommodate such defective atomic configurations.

In the present work, we quantitatively examine the probability of VAP-*d* formation in three types of glass-forming structural networks built of edge-shared $GeS_{4/2}$ tetrahedrons, $AsS_{3/2}$ pyramids and regular S_n chains using *quantum-chemical* cluster modeling algorithm from *first principles* known as CINCA (cation-interlinking network cluster approach) [22].

2. Models and calculation procedure

The *ab-initio* quantum chemical modeling was performed using HyperChem 7.5 PC-aided program package based on *the restricted Hartree–Fock (RHF) self-consistent field method* using split-valence double-zeta basis set with single polarization function 6-311G* [23,24]. The final geometrical optimization and single-point energy calculations for selected clusters were performed employing *the Fletcher–Reeves conjugate gradient method* until the root-mean-square gradient of 0.1 kcal/(Å mol) was reached.

The tested network-forming clusters were examined in terms of the CINCA [22,25–27]. For calculation purposes, the dangling bonds of outer S atoms in the examined clusters were terminated by hydrogen H atoms to form self-consistent molecular configuration (this procedure is most suitable and often used [28], since H atoms possess negligible bonding energy in similar covalent linked structures).

The ES cluster structures as closest defect-free atomic configurations were chosen as prototypes of VAP-*d* configurations. Such choice guarantees that defect formation process under consideration involves minimal atoms and covalent bonds being changed in the cluster. Thus, the non-defective Ge-based $Ge_2S_6H_4$ and As-based $As_2S_4H_2$ clusters as precursors of defect-related VAP-*d* configurations were built of two ES $GeS_{4/2}$ tetrahedrons or $AsS_{3/2}$ pyramids, respectively. In the case of pure S, where there are no cation-type atoms, the non-defective S_6H_2 cluster was constructed in the form of regular S_5 chain. For defective clusters of the same chemical compositions, the homopolar S–S bonds were introduced instead of the destroyed Ge–S, As–S or S–S ones (as it was shown in [21]). In such a way, the second group of clusters contains VAP-*d* pairs, based on positively charged over-coordinated sulfur S_3^+ and negatively charged under-coordinated germanium Ge_3^-, arsenic As_2^- or sulfur S_1^- atoms.

The calculated energy of geometrically-optimized clusters were corrected on H atoms according to the procedure developed elsewhere [29–31], e.g. the half of the energy of S atoms bonded to H, the energy of all H atoms themselves and corresponding S–H bond energies were subtracted from the total energy E_t to obtain the energy of “pure” network-forming cluster E_{NFC}. Then, the cluster formation energy E_f was calculated as difference between energy of the cluster E_{NFC} and overall energy of constituting atoms E_{at}, divided on the number of atoms in the cluster. Finally, the energetic gain E_g taken as E_f value subtracted from the energy of single $GeS_{4/2}$ tetrahedron (−96.378 kcal/mol [22]), $AsS_{3/2}$ pyramid (−79.404 kcal/mol [32]) or S_8 ring (−73.171 kcal/mol [33]) was accepted as main *energetic criterion* describing relative stability of the tested clusters.

In fact, in our research we does not consider any specifics of the initiating defect-formation process, but just estimate its probability from point of energetic preference for different stationary boundary configurations [22]. Notably, a similar approach named as size increasing cluster approximation (SICA) was applied by Micoulaut [34–36] to describe self-organization structural–topological trends in ChSG using the Boltzmann factor as main energetic criterion to estimate the probability of different structural fragments being stabilized within glass-forming network.

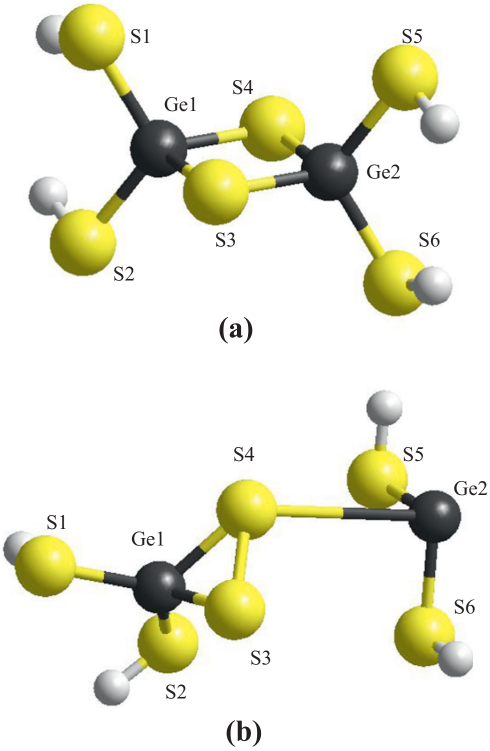

Fig. 1. Ball-stick presentation of geometrically-optimized $Ge_2S_6H_4$ clustering structures: (a) non-defective ES-$GeS_{4/2}$ configuration and (b) defective VAP-*d* configuration.