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Topological controversies in the adaptability concept for glassy germanium selenides

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ABSTRACT

Cluster modelling based on *ab-initio* calculations testifies lack of intermediate optimally-constrained phase in binary Ge_xSe_{100-x} system within expected reversibility window ($20 \le x < 26$) in terms of global connectivity. Network of these glasses within $20 \le x < 26$ compositional range can be composed of over-constrained "outrigger raft" structural motives built of two edge- and four corner-shared $GeSe_{4/2}$ tetrahedra interconnected via optimally-constrained ≡Ge—Se—Se—Ge≡ bridges, extra Se atoms forming ring-like configurations instead of Se—Se dimers.

1. Introduction

Self-organization approach developed recently opens a conceptually new insight on the problem of network glass formation [1]. Within Phillips–Thorpe mean-field rigidity theory [2,3], the glass structure is considered to be floppy or under-constrained if average number of constraints per atom n_c is less than the space dimensionality ($n_c < 3$), rigid and stressed or over-constrained if $n_c > 3$ and rigid but not stressed or optimally-constrained if $n_c = 3$. The self-organization (alternatively, self-adaptation) means that glass avoids formation of over-constrained stressed regions, keeping $n_c = 3$ as long as possible unless there is no alternative [1,4–6].

Covalent-bonded network glasses such as chalcogenide glasses (ChG) can be considered as model objects for understanding this phenomenon, since their wide glass-forming regions allow one to obtain under-, optimally- and over-constrained structures by variation in chalcogen content only. Owing to high-coordinated atoms incorporated into the glass backbone (such as As or Ge), ChG reveal compositional domains, where all underlying networks are optimally-constrained called also intermediate phases or reversibility windows [5–7].

In this view, the binary Ge_xSe_{100-x} is an important canonical ChG system widely explored in experimental and theoretical studies of self-adaptability concept [6,7]. Intermediate phase was reported in this system within $20 \le x < 26$ compositional range using temperature-modulated DSC measurements [7]. It was also supported by conventional DSC measurements showing non-ageing ability of the glasses within this compositional domain [8]. However, the recent data on X-ray diffraction (XRD), X-ray absorption fine structure (XAFS) spectroscopy [9] as well as molecular dynamics simulation [10] did not yield any evidence for a direct structural signature of this intermediate phase. Moreover, according to high-resolution X-ray photoelectron spectroscopy (XPS) data [11], the network of Ge_xSe_{100-x} glasses within $20 \le x < 26$ compositional domain is built of structural fragments having almost constant ratio between edge-shared (ES) and corner-shared (CS) $GeSe_{4/2}$ tetrahedra like in high-temperature modification of crystalline $GeSe_2$ [12]. It means that self-organization in terms of global optimally-constrained network with $n_c = 3$ is not character to this binary system, revealing a more complicated topological-structural evolution within glass-forming region.

In this paper, we verify structural evolution tendencies in binary Ge_xSe_{100-x} ChG using quantum mechanics modelling based on experimental results of high-resolution XPS [11].

2. Method

In order to explain glass-forming tendencies in Ge—Se system, the corresponding structural backbones of these ChGs were divided into separate building blocks or so-called network-forming clusters (NFC). In such a way, the glassy network can be adequately reproduced by infinite multiplication of NFC connected in respect to "8-N" rule. This simplification known also as glass-forming structural units was firstly introduced by R.L. Muller about a half century ago to predict properties-composition relation in ChG-forming systems [13].

The NFC diversity within our approach is determined by glass composition. Each structural imperfection, like wrong homopolar covalent bonds in ChG of stoichiometric compositions or multimember chalcogen-based ring structures, is reflected in separate NFC, which weighted superposition would reproduce a whole glassy network of a chosen chemical composition. Thus, a complicated and time-consuming modelling procedure for real glassy networks usually evolved hundreds and even thousands of atoms can be replaced by a more simple simulation route for relatively small NFC using available software (like HyperChem).

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The *ab-initio* calculations in this paper were based on the restricted Hartree–Fock self-consistent field method with STO-3G basis set [14]. The individual NFC was terminated at the borders by hydrogen H atoms to form molecular-like fragment in full accordance to the "8-N" rule. After geometrical optimization and single point calculation, the NFC-forming energy was corrected on these terminated H atoms according to the procedure developed elsewhere [15–17]. Finally, this energy (E_f) was normalized in respect to single $GeSe_{4/2}$ tetrahedron.

To verify self-organization tendency, the constraints counting algorithm developed within the mean-field theory was applied to each NFC [2,3]. The number of Lagrangian constraints per atom n_c was calculated using corrections on dangling bonds and rings [3]. Then, the constraints additivity rule was used to make a decisive conclusion on global connectivity of tested backbone: the average number of Lagrangian constraints per atom for whole glassy network was determined as a weighted sum of n_c for separate NFC and corresponding inter-cluster bridges (chalcogen-based chains) interconnecting them.

3. Results and discussion

The main principles of network-forming structural organization of binary Ge_xSe_{100-x} ChG were proposed at the basis of recent XPS data [11]. In particular, it is accepted that structure of Ge_xSe_{100-x} glasses with $x<12$ (corresponding to glass compositions with average coordination numbers $Z<2.24$) is determined mainly (within ~5–6% accuracy) by terms of "chains crossing" model [18], while those with $x\geq20$ (or, equivalently, $Z\geq2.40$) are described as a mixture of specific "outrigger raft" (ORR) clusters [19]. Within intermediate $12\leq x<20$ range ($2.24<Z<2.40$), the glasses are composed of superimposed "chains crossing" and ORR models. In other words, the network of Ge_xSe_{100-x} glasses with $x<12$ can be imagined as a homogeneous distribution of $GeSe_{4/2}$ tetrahedra interconnected via Se chains of a comparable length, while the network of those with $x\geq20$ relies on structural fragments proper to high-temperature modification of crystalline $GeSe_2$, consisting of two edge-shared ES–$GeSe_{4/2}$ tetrahedra connected with four corner-shared CS–$GeSe_{4/2}$ ones (Fig. 1) [11]. The XPS results are in good agreement with Raman scattering data showing ES–$GeSe_{4/2}$ tetrahedra in glass compositions with $x>15$ [20,21].

Almost constant ratio of CS and ES tetrahedra in Ge_xSe_{100-x} within a whole range of the expected reversibility window ($20\leq x<26$) as identified by XPS, testifies on a conservation of basic ORR structural motive (two ES–$GeSe_{4/2}$ tetrahedra interconnected with four CS–$GeSe_{4/2}$ ones) throughout these compositions [11]. So, we can assume that within $20\leq x<26$ compositional domain accepted as possible reversibility window in binary Ge_xSe_{100-x} system [7], the structural fragments proper to high-temperature modification of crystalline $GeSe_2$ form main glassy backbone. Extra Se atoms according to glass composition have only two possibilities to be attached to this backbone: instead of side Se—Se dimer within separate ORR clusters or between them as Se-chain inter-cluster bridges (shown by arrows in Fig. 1).

To check the above possibilities, we have built NFC as ORR clusters having symmetric Se-chain legs as inter-cluster bridges between them for some distinguished compositions of binary Ge_xSe_{100-x} system: $Ge_{30}Se_{70}$, $Ge_{27.25}Se_{72.75}$, $Ge_{25}Se_{75}$, $Ge_{23}Se_{77}$, $Ge_{21.5}Se_{78.5}$, $Ge_{20}Se_{80}$, $Ge_{18.75}Se_{81.25}$. To simplify calculation procedure, only side-ORR cluster fragments terminated by two H atoms linked with Ge atom were simulated. In other words, each full-ORR cluster was conditionally divided into three ones: one central-ORR and two side-ORR parts (the cutting is line-dashed in Fig. 1). Then, we have performed quantum mechanics calculations for different side-ORR clusters corresponding to the chosen glass composition and compared the obtained cluster-forming energies calculated in respect to the total energy of single $GeSe_{4/2}$ tetrahedra.

We have started from $Ge_{30}Se_{70}$ glass ($Z=2.60$), which structure is fully built of separate Ge_6Se_{14} full-ORR clusters interconnected via short over-constrained ($n_c^{Inter}=3.67$) inter-cluster bridges ≡Ge—Se—Ge≡ (Fig. 1). In this case, Se—Se dimers in each NFC evolving two ES–$GeSe_{4/2}$ and four CS–$GeSe_{4/2}$ tetrahedra do not form inter-cluster linking within a whole glassy backbone.

With increase in Se content, additional Se atoms can be attached instead of Se—Se dimers or in legs between neighbouring ORR clusters. For $Ge_{27.25}Se_{72.75}$ glass ($Z=2.545$) these two possibilities are shown in Fig. 2a and b as those forming $Ge_{2.5}Se_7$ side-ORR clusters having 6-fold ring or conserving initial 5-fold ring topology, respectively. In the first case, the ≡Ge—Se—Ge≡ inter-cluster bridge contains one Se atom, which corresponds to over-constrained configuration with $n_c^{Inter}=3.67$. In the second case, ≡Ge—Se—Se—Ge≡ inter-cluster bridge with two Se atoms incorporated between two Ge atoms of neighbouring ORR clusters is optimally-constrained with $n_c^{Inter}=3$. Nevertheless, the quantum mechanics calculations show that cluster-forming energies (E_f) are near the same for both configurations (Table 1), testifying almost equal probability of their formation in real glassy network.

The $Ge_{2.5}Se_8$ side-ORR cluster configurations for next $Ge_{25}Se_{75}$ glass ($Z=2.50$) involve already three possibilities with 5-, 6- and

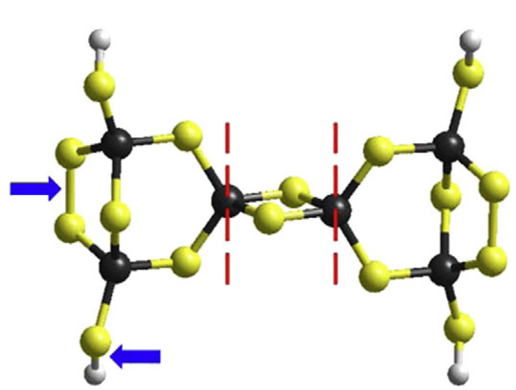

Fig. 1. Fragment of $Ge_{30}Se_{70}$ glass structure (black — four-fold coordinated Ge atoms; yellow — two-fold coordinated Se atoms) forming ORR structural motive of two ES–$GeSe_{4/2}$ and four CS–$GeSe_{4/2}$ tetrahedra terminated by Se—Se dimers. The places, where the extra Se atoms can be incorporated, are shown by arrows; two side-ORR and one central-ORR parts are distinguished by dashed lines.

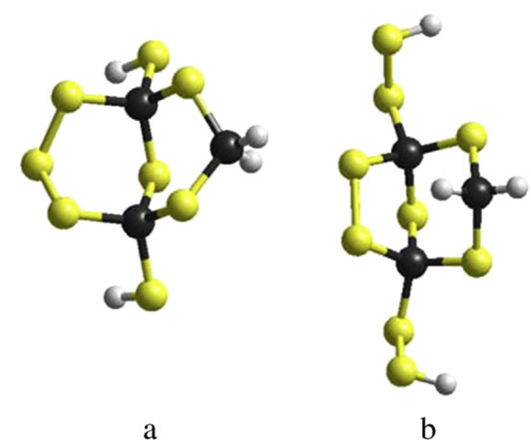

Fig. 2. Possible configurations of structural evolution in side-ORR cluster proper to $Ge_{27.25}Se_{72.75}$ glass: a 6-fold ring with one extra Se atom incorporated into Se—Se dimer and over-constrained ($n_c=3.67$) ≡Ge—Se—Ge≡ inter-cluster bridge; b 5-fold ring and extra Se atom forming optimally-constrained ($n_c=3.00$) ≡Ge—Se—Se—Ge≡ inter-cluster bridge.