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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 $x\geq 20$ (or, equivalently, $Z\geq 2.40$) 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 $x\geq 20$ 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

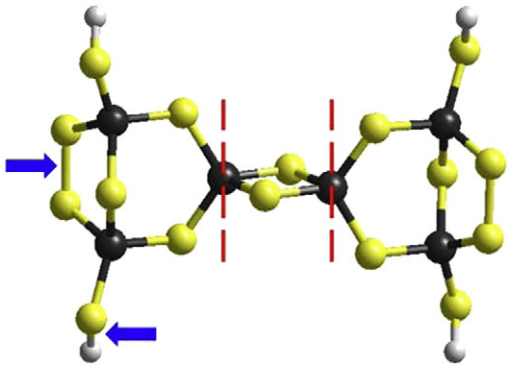

Fig. 1. Fragment of $Ge_{30}Se_{70}$ glass structure (black — four-fold coordinated Ge atoms; yellow — two-fold coordinated Se atoms) forming ORR structural motive of two ES–$GeSe_{4/2}$ and four CS–$GeSe_{4/2}$ tetrahedra terminated by Se—Se dimers. The places, where the extra Se atoms can be incorporated,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

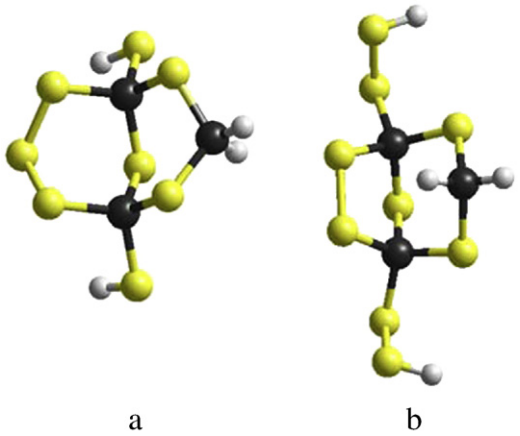

Fig. 2. Possible configurations of structural evolution in side-ORR cluster proper to $Ge_{27.25}Se_{72.75}$ glass: a 6-fold ring with one extra Se atom incorporated into Se—Se dimer and over-constrained ($n_c=3.67$) ≡Ge—Se—Ge≡ inter-cluster bridge; b 5-fold ring and extra Se atom forming optimally-constrained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

Table 1
Compositional evolution of ORR structural fragments in Ge_xSe_{100-x} glasses within $18.75<x<30$ range (the most energetically favourable configurations are bold-distinguished).

Glass	Full-ORR cluster			Side-ORR cluster				
Formula	Formula	Z	n_c	Formula	Z	Topology	n_c^{Inter}	E_f, kcal/mol
$Ge_{30}Se_{70}$	Ge_6Se_{14}	2.60	3.35	$Ge_{2.5}Se_6$	2.59	5-fold ring	3.67	−5.6
$Ge_{27.25}Se_{72.75}$	Ge_6Se_{16}	2.545	**3.21**	$Ge_{2.5}Se_7$	2.53	**5-fold ring**	**3.00**	**−9.7**
			3.32			**6-fold ring**	**3.67**	**−9.7**
$Ge_{25}Se_{75}$	Ge_6Se_{18}	2.50	3.10	$Ge_{2.5}Se_8$	2.48	5-fold ring	2.71	−13.6
			3.19			**6-fold ring**	**3.00**	**−12.8**
			3.19			7-fold ring	3.67	−13.3
$Ge_{23}Se_{77}$	Ge_6Se_{20}	2.46	3.00	$Ge_{2.5}Se_9$	2.43	5-fold ring	2.22	−15.9
			3.09			6-fold ring	2.71	−16.0
			3.09			**7-fold ring**	**3.00**	**−15.6**
			3.09			8-fold ring	3.67	−16.1
$Ge_{21.5}Se_{78.5}$	Ge_6Se_{22}	2.43	2.92	$Ge_{2.5}Se_{10}$	2.40	5-fold ring	2.45	−18.5
			3.00			**6-fold ring**	**2.67**	**−18.0**
			3.00			7-fold ring	2.71	−18.6
			3.00			**8-fold ring**	**3.00**	**−18.0**
			3.00			9-fold ring	3.67	−18.8
$Ge_{20}Se_{80}$	Ge_6Se_{24}	2.40	**2.85**	$Ge_{2.5}Se_{11}$	2.37	**5-fold ring**	**2.38**	**−20.1**
			2.93			**6-fold ring**	**2.45**	**−20.2**
			2.93			**7-fold ring**	**2.67**	**−20.2**
			2.93			8-fold ring	2.71	−20.3
			2.93			9-fold ring	3.00	−20.5
			2.93			10-fold ring	3.67	−20.3
$Ge_{18.75}Se_{81.25}$	Ge_6Se_{26}	2.375	2.33	$Ge_{2.5}Se_{12}$	2.34	5-fold ring	2.79	−22.1
			2.86			**6-fold ring**	**2.38**	**−21.6**
			2.86			7-fold ring	2.45	−22.2
			2.86			**8-fold ring**	**2.67**	**−21.6**
			2.86			9-fold ring	2.71	−22.4
			2.86			10-fold ring	3.00	−22.0
			2.86			11-fold ring	3.67	−21.9

7-fold ring topologies (Table 1). The calculations testify that the most energetically favourable is 6-fold ring topology with three Se atoms incorporated instead of Se—Se dimers and two Se atoms within optimally-constrained ≡Ge—Se—Se—Ge≡ inter-cluster bridges. In case of $Ge_{23}Se_{77}$ glass ($Z=2.46$), the most energetically favourable atomic configuration of $Ge_{2.5}Se_9$ side-ORR cluster consists of 5 selenium atoms in ring-like fragments (7-fold ring) and optimally-constrained ≡Ge—Se—Se—Ge≡ inter-cluster bridges. Further increase in Se content leads to $Ge_{21.5}Se_{78.5}$ composition ($Z=2.43$), which has already five possible NFC configurations. The most energetically favourable among them correspond to 6-fold ring topology and under-constrained ≡Ge—Se—Se—Se—Ge≡ inter-cluster bridges ($n_c^{Inter}=2.67$), as well as 8-fold ring topology and optimally-constrained ≡Ge—Se—Se—Ge≡ inter-cluster bridges ($n_c^{Inter}=3$). Thus, both of them should be formed in the glassy network of $Ge_{21.5}Se_{78.5}$ with nearly same probability. The calculation procedure for $Ge_{20}Se_{80}$ ($Z=2.40$) glass testifies existence of three possible $Ge_{2.5}Se_{11}$ side-ORR clusters with comparable gains in total energy, having 5-, 6- and 7-fold ring topologies with under-constrained inter-cluster bridges. Continuing insertion of Se atoms, we get seven possible $Ge_{2.5}Se_{12}$ side-ORR configurations for $Ge_{18.75}Se_{81.25}$ glass ($Z=2.375$), but, again, the most energetically favourable variants (with 6- and 7-fold rings) do not include optimally-constrained ≡Ge—Se—Se—Ge≡ bridges.

So, the performed quantum mechanics calculations (Table 1) show that all glass compositions of binary Ge_xSe_{100-x} system within $20<x<27$ range are more energetically preferable in such atomic configurations, which involve two Se atoms incorporated between separate ORR clusters as optimally-constrained ≡Ge—Se—Se—Ge≡ inter-cluster bridges.

The maximum possible number of Se atoms within ring-like fragments at the place of initial Se—Se dimers depends on character value of local free volume proper to high-temperature crystalline modification of $GeSe_2$ [12] and steric parameters of Se chains/rings. The latter were analyzed in details in [22]. It was shown that first and seventh Se atoms in ring-like configuration tend to overlap with each other, and hence such configuration tends to be excluded from the structure due to large steric repulsive energy. So, we argue that the largest NFC can include no more than six Se atoms in 8-fold ring-like topology. This requirement is satisfied for $Ge_{20}Se_{80}$ composition, which is also evident from our quantum mechanics calculations. Thus, it is not a surprise, that all glasses with $x<20$ possess structural networks with long …—Se—Se—Se—… fragments between NFC.

Therefore, with increase in Se content, the structural evolution of binary Ge_xSe_{100-x} system occurs in such a way to keep optimally-constrained inter-cluster bridges (≡Ge—Se—Se—Ge≡) with increased number of Se atoms in ring-like fragments incorporated at the place of Se—Se—dimers. Therefore, the whole glassy network is only quasi-adaptive in the range of expected reversibility window ($20\le x<26$) [7], being built of locally over-constrained ($n_c>3$) ORR clusters interconnected via optimally-constrained ($n_c^{Inter}=3$) inter-cluster bridges. This evolution trend is restricted by $Ge_{27.25}Se_{72.75}$ and $Ge_{20}Se_{80}$ glass compositions giving a reason for marginality of irreversible heat flow in temperature-modulated DSC measurements [7].

According to constraints counting algorithm [3], only one glass composition $Ge_{21.5}Se_{78.5}$ with 8-fold ring topology and optimally-constrained ≡Ge—Se—Se—Ge≡ inter-cluster bridges possesses $n_c=3$ in a global sense, e.g. for both full-ORR cluster and inter-cluster bridges (see Table 1). But effect of global optimally-constrained connectivity in this glass is hidden because of other competitive variant with 6-fold ring topology and under-constrained inter-cluster bridges ($n_c^{Inter}=2.67$). Thus, there is no structural signature for intermediate phase in this glassy system in terms of global optimally-constrained network in good agreement with [9].

We believe the low limit of reversibility window as observed by temperature-modulated DSC in Ge_xSe_{100-x} system [7] is determined by disappearing of Se—Se—Se chain-like sequences in glassy backbone, which occurs near $x\approx 20$–21. Then, we have conserved ORR clusters interconnected through optimally-constrained ≡Ge—Se—Se—Ge≡

bridges, the extra Se atoms forming ring-like configurations at the place of Se—Se dimers. This is happening up to glass composition where number of Se atoms is not enough to keep ≡Ge—Se—Se—Ge≡ bridges. The border glass composition where all connections between separate ORR clusters are possible through the optimally-constrained ≡Ge—Se—Se—Ge≡ inter-cluster bridges is $Ge_{27.25}Se_{72.75}$ ($Z=2.545$).

4. Conclusions

Topological–structural network evolution in binary Ge_xSe_{100-x} glasses is probed via cluster-forming energy using quantum mechanics calculations. It is shown that $20 \le x < 26$ compositional domain within this system forms a specific quasi-adaptive phase: locally over-constrained ($n_c > 3$) atomic clusters within "outrigger raft" structural motive are interconnected via optimally-constrained ≡Ge—Se—Se—Ge≡ inter-cluster bridges ($n_c^{Inter} = 3$). The extra Se atoms, which do not participate in the formation of glass backbone, the most probably, form the ring-like configurations at the place of Se—Se dimers of "outrigger raft" clusters.

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