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Pseudo-self-organized topological phases in glassy selenides for IR photonics

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Network-forming cluster approach is applied to As-Se and Ge-Se glasses to justify their tendency to self-organization. It is shown that reversibility windows determined by temperature-modulated differential scanning calorimetry using short-term aged or as-prepared samples do not necessary coincide with self-organized phase in these materials. The obtained results testify also pseudo-self-organization phenomenon in Ge-Se glasses: over-constrained outrigger raft structural units built of two edge- and four corner-shared tetrahedra are interconnected via optimally-constrained ≡Ge-Se-Se-Ge≡ bridges within the range of compositions identified previously as self-organized phase by temperature modulated differential scanning calorimetry technique.

1 Introduction Chalcogenide glasses (ChG) remain in a sphere of tight interest of many researchers due to variety of useful applications, especially in IR photonics. Laser power delivery, chemical sensing, imaging, scanning near field microscopy/spectroscopy, fiber IR sources/lasers, optical amplifiers/switches are only few examples of such applications [1-3]. Therefore, structure and physical-chemical properties of ChG are intensively studied by numerous research groups.

One of the most promising approaches, proposed recently to explain structural features of ChG and compositional trends in their physical-chemical properties, is topological self-organization or, alternatively, self-adaptivity concept [4-7]. It is based on the original idea of Phillips about rigidity percolation of disordered covalent networks at the point where constraints and degrees of freedom balance [8]. At this point the existence of optima of various quantities, as well as thresholds and singularities in compositional dependences are expected, such as those associated with other kinds of phase transitions. Indeed, extrema and thresholds are observed experimentally for many ChG systems at the point, where number of constraints per atom (n_c) is equal to a space dimensionality (n_c = 3, for three-dimensional space) [9,10]. In this view, the covalent networks having n_c<3 are considered as under-constrained (or floppy), those with n_c=3 as optimally-constrained (or unstressed-rigid) and networks with n_c>3 as over-constrained (or stressed-rigid) [8,11]. The classic Maxwell constraints counting algorithm predicts a solitary transition from floppy to rigid networks at n_c=3 with increasing backbone connectivity (which is related to n_c) by changing the glass composition [8,11]. However, it is shown by theoretical calculations [4,6] that for the networks, which have a possibility to avoid stresses by structural variation, this solitary transition splits into two points: the second-order transition from floppy to unstressed-rigid and first-order transition from unstressed-rigid to stressed-rigid network. In such a way topological self-organization occurs, the range of compositions with self-organized networks forming a so-called self-organized phase. Theoretical width of self-organized phase, however, is shown to be narrow [4,6,12].

To a much surprise, P. Boolchand et al. claimed on the basis of temperature modulated differential scanning calorimetry (TMDSC) data that width of self-organized phase could be ~one order of magnitude greater [13,14]. He used the marginality of non-reversible heat flow component in TMDSC as universal criterion for compositional limits of self-organized phase (the intermediate phase or reversibil-

ity window in his terminology) [7,13,14]. From the other hand, the recent reports on collapse of reversibility windows in ChG after long-term natural storage [15,16] or under the influence of external factors [17], supported by lack of direct experimental evidences for structural signature of self-organized phase [18], have raised a question on the validity of this criterion for correct identification of self-organized phases.

In the present report, we analyze a possibility for topological self-organization in two canonical selenide systems As-Se and Ge-Se. On the basis of experimental results and cluster-modeling data obtained via *ab-initio* calculations we show that reversibility windows observed with TMDSC technique do not necessary coincide with a self-organized phase. The anomalies in compositional trends of various physical-chemical properties including TMDSC data can be alternatively explained by pseudo-self-organization phenomenon, when over-constrained building blocks are interconnected via optimally-constrained bridges.

2 Experimental We have used for our investigations the As_xSe_{100-x} and Ge_xSe_{100-x} glass samples prepared near two decades ago by traditional melt-quenching technique, as described elsewhere [15,19]. After synthesis all samples were sealed in hermetic plastic bags and stored in darkness under room conditions. The vitreous state of the aged samples was checked again after the storage by conventional X-ray diffraction measurements showing typical for glassy substances pattern without any sharp reflexes character to crystalline inclusions. So, no phase separation or crystallization occurred in the considered samples during their prolonged storage. In addition, the compositions and purity of the aged glasses were checked by high-resolution x-ray photoelectron spectroscopy (Scienta ESCA-300).

DSC measurements were performed using NETZSCH 404/3/F microcalorimeter pre-calibrated with a set of standard elements, the DSC curves being recorded in the ambient atmosphere with 5 K/min heating rate. Three independent DSC measurements were performed to confirm reproducibility of the obtained results. Proteus® software was used for DSC data treatment. To reach an as-prepared state of the investigated aged samples, the rejuvenation procedure involving heating above T_g and subsequent cooling [20] was performed just in the microcalorimeter chamber.

In order to analyze structural networks of the investigated ChG, their backbones were divided into separate building blocks or so-called network-forming clusters (NFC). In such a way, the whole glassy network of chosen chemical composition can be adequately reproduced via infinite multiplication of NFC, covalently bonded to each other in respect to "8-N" rule via inter-cluster bridges. This simplification, known also as glass-forming structural units, was firstly introduced by R.L. Muller about half a century ago to predict properties-composition relation in ChG-forming systems [21].

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

The *ab-initio* calculations in this paper were based on restricted Hartree–Fock self-consistent field method with STO-3G basis set [22]. The individual NFC was terminated by hydrogen H atoms to form molecular-like fragments in full accordance with "8-N" rule (as it is shown for single pyramid in Fig. 1a). After geometrical optimization and single point calculation, the NFC-forming energy was corrected on these H atoms according to a procedure developed elsewhere [23]. Finally, this energy was normalized to single $AsSe_{3/2}$ pyramid or $GeSe_{4/2}$ tetrahedron.

To check a self-organization tendency, constraints counting algorithm was applied to each NFC, the n_c value being calculated with corrections on dangling bonds and rings [11]. Then, the constraints additivity rule was used to make a decisive conclusion on global connectivity of tested backbone: the average number of constraints for a whole glassy network was determined as a weighted sum of n_c for separate NFC and corresponding inter-cluster bridges (chalcogen-based chains).

3 Results and discussion In general, self-organization can be defined as spontaneous creation of a globally coherent pattern out of local interactions [24]. As a rule, the self-organization phenomenon is proper to disordered systems, which are far from thermodynamic equilibrium and satisfy "variety" and "selectivity" criteria [24]. Covalent network glasses, such as ChG, can be considered as a convenient model objects for understanding this phenomenon, because they are obtained in non-equilibrium state by rapid quenching from the melt and their wide glass-formation regions allow variation of constituent structural units (NFC) by changing chalcogen content only. The latter circumstance satisfies "variety" criterion of self-organization, while possibility of the network to fit the environment by choosing the most energetically favorable units among different NFC convinces "selectivity" criterion. Topological self-organization occurs when the covalent glassy network can locally avoid the creation of stressed over-constrained structural units (expected due to the changes in composition), forming global optimally-constrained network with n_c=3. In other words, the network keeps n_c=3 as long as possible unless there is no alternative. Therefore, NFC with n_c=3 should be the most energetically favorable during network formation.

So, if one could show the energetic preference of NFC with n_c=3 over the rest possible structural units in the range

of ChG compositions, this range can be accepted as the topologically self-organized phase. Then, such NFC should be experimentally verified to make a final decision on the compositional boundaries of self-organized phase.

We have constructed main NFC for As_xSe_{100-x} glasses with x<40 (Fig. 1a,b) to check the existence of self-organized phase within $28 \le x \le 37$ compositional range, as claimed on the basis of TMDSC [13]. The calculations show that corner-shared $AsSe_{3/2}$ blocks (Fig. 1c) having n_c=3 within As-Se network are more energetically favorable, than edge-shared ones (Fig. 1d) or optimally-constrained quasi-tetrahedral Se=$AsSe_3$ units (Fig. 1b).

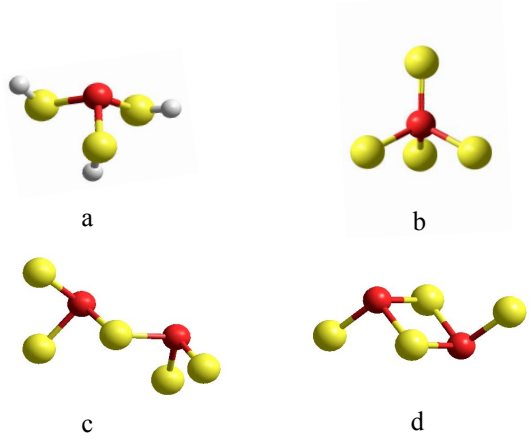

Figure 1 NFC in As_xSe_{100-x} glasses with $x \le 40$ (a,b) and possible interconnection of the most energetically favorable pyramids in As_2Se_3 glass (c,d). Red three-fold coordinated spheres denote As atoms, two-fold coordinated yellow – Se atoms, one-fold coordinated grey – H atoms.

Owing to the latter result, it is doubtful that As_xSe_{100-x} ChG network is formed by the interconnected Se=$AsSe_3$ units, as it is required for the whole network to be optimally-constrained within $28 \le x \le 37$ compositional range. So, the first composition of possible self-organized phase should be stoichiometric As_2Se_3 (x=40) formed by corner-shared $AsSe_{3/2}$ pyramids with n_c=3. This theoretical consideration is supported by experimental results testifying absence of Se=$AsSe_3$ quasi-tetrahedral units in the network of conventionally obtained As_xSe_{100-x} glasses [15].

Analysis of possible NFC in binary Ge_xSe_{100-x} ChG is performed on the basis of XPS data [25]. It is shown that network of these glasses with $x \ge 20$ (note, that reversibility window is claimed on the basis of TMDSC data within $20 \le x \le 25$ compositional range [14]) contains structural fragments proper to high-temperature modification of crystalline $GeSe_2$, consisting of two edge-shared $GeSe_{4/2}$ tetrahedra connected with four corner-shared $GeSe_{4/2}$ ones (Fig. 2a) [25]. This so-called outrigger raft structural motive was used as a basic NFC for our quantum mechanical modelling [26]. With increase in Se content, additional Se atoms can be attached to these NFC instead of Se-Se dimers (place I in Fig. 2a) or in the legs between neighbouring outrigger raft NFC (place II in Fig. 2a). The performed quantum mechanics calculations show that all glass compositions of binary Ge_xSe_{100-x} system within $20<x<28$ range are more energetically preferable in the atomic configurations, which involve two Se atoms incorporated between separate outrigger raft NFC as optimally-constrained ≡Ge-Se-Se-Ge≡ inter-cluster bridges (Fig. 2b) [26]. Other Se atoms, which do not participate in the backbone connectivity, form Se-rich fragments attached to a place I in Fig. 2a as arbitrary shown in Fig. 2b.

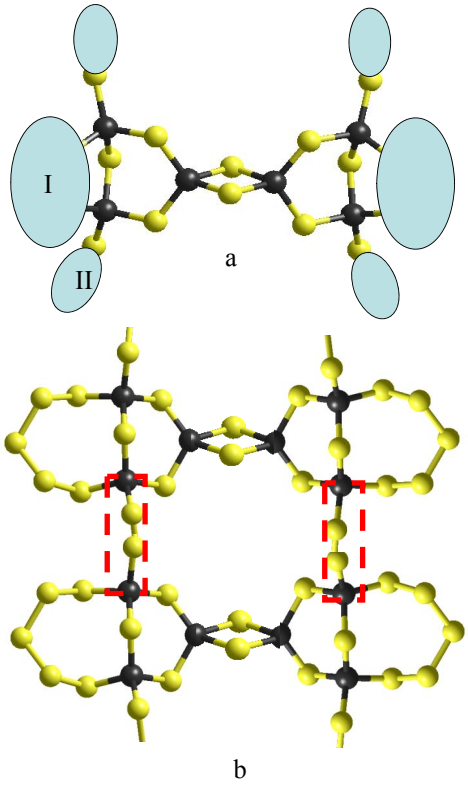

Figure 2 Outrigger raft structural motive in Ge_xSe_{100-x} glasses within $20 < x < 28$ compositional range (a) and most energetically favourable connection for optimally-constrained $Ge_{21.5}Se_{78.5}$ composition (b). Area I denotes the place of initial Se-Se dimers, area II shows a place of inter-cluster bridges (denoted also by red dashed rectangle). Black four-fold coordinated spheres denote Ge atoms, two-fold coordinated yellow – Se atoms.

Therefore, with increase in Se content, the structural evolution of binary Ge_xSe_{100-x} system occurs keeping optimally-constrained inter-cluster bridges (≡Ge-Se-Se-Ge≡) and Se atoms in ring-like fragments at the place of Se-Se dimers. The x=21.5 composition is the last one in our set of NFC used for modelling where this tendency is still fully preserved [26]. According to the above scheme of structural evolution, only one glass composition $Ge_{21.5}Se_{78.5}$ shown in Fig. 2b possesses n_c=3 in a global sense. All the rest glasses in the range of expected reversibility window ($20 \le x \le 25$) [14] possess networks built of locally over-constrained (n_c>3) outrigger raft NFC interconnected via

optimally-constrained inter-cluster bridges. This evolution trend is restricted by $Ge_{27.25}Se_{72.75}$ and $Ge_{21.5}Se_{79.5}$ glass compositions (determined with the accuracy of x-step used in our modelling [26]), which form a so-called pseudo-self-organized phase. Thus, our modelling shows that there is no structural signature for intermediate phase in this binary glass system in terms of global optimally-constrained network in good agreement with [18].

So, why there is a huge discrepancy between TMDSC reversibility windows and width of self-organized phases determined according to Phillips-Thorpe theory?

By definition, self-organized glassy network should be characterized by a negative feedback to small external perturbations. It means, that small disturbances (including thermal fluctuations at below T_g temperatures) once appeared in self-organized network should not lead to any structural effects, because surrounding network performs negative feedback influence on the disturbed subsystem and returns it to the initial state. In this view, the self-organized phase should be characterized by a high stability and non-ageing ability, which has been put forward as main advantage for device application of self-organized ChG [7]. It means that physical ageing can serve as a good indicator of topological self-organization phenomenon.

The effect of physical ageing is revealed in DSC or TMDSC curves as strong endothermic peak measured in the region of glass-to-supercooled liquid transition [15,19,20]. Besides structural relaxation of glass network while going through the glass transition region, this peak also includes component connected with regaining of entropy lost during ageing. The under-peak area A is directly proportional to the enthalpy losses ΔH and can be used as reliable control parameter to quantify physical ageing. In fact, the A values can be roughly compared to the value of non-reversible heat flow component ΔH_{nr} in TMDSC experiments (Fig. 3). This result testifies that physical ageing can be adequately probed either by conventional DSC or TMDSC techniques with the same reliability in good agreement with [27]. In general, the enthalpy losses ΔH follow a sigmoidal time dependence, which depends on the choice of ageing temperature T_a in respect to T_g [20,28]. Thus, for some glass compositions with fast component of natural physical ageing (for example, with lower T_g) a significant non-reversible component of heat flow can be detected within short experimental timescale, while for glass compositions with more extended kinetics (higher T_g) the marginal value of this component just after synthesis (or short-term periods of physical ageing) can lead to misleading conclusions. The longer periods of storage depending on specific kinetics for chosen glass composition are needed to conclude on the existence of ageing process [20,28]. Obvious collapse of the reversibility window in As_xSe_{100-x} glasses after prolong physical ageing (Fig. 3) [15,16] fully supports the above consideration. The observed onset of self-organized phase around stoichiometric $As_{40}Se_{60}$ composition is in good agreement with the previous conclusion made out of quantum mechanics calculations. So, instead of the ΔH_{nr} marginality criterion, the calorimetric experiments in real time-scale chronology from earliest stages of as-prepared to long-term aged state can be proposed as more reliable criterion to determine the compositional boundaries of self-organized phases in covalent-bonded network glasses.

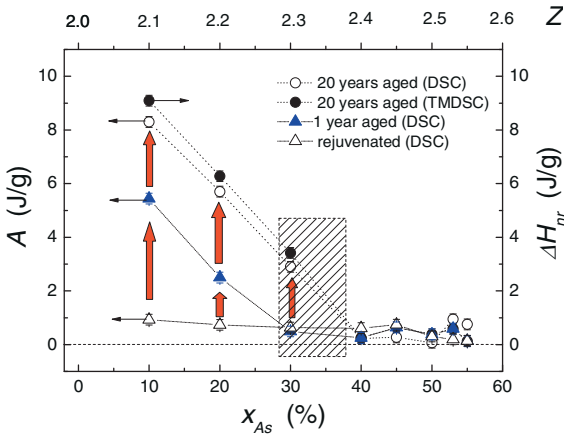

Figure 3 Areas A under the endothermic peaks of DSC curves recorded with 5 K/min heating rate for aged and rejuvenated As_xSe_{100-x} glasses. TMDSC ΔH_{nr} values are taken from [15] for comparison. Cross-hatched area shows the reversibility window determined in [13].

Long-term physical ageing in Ge_xSe_{100-x} glass system also confirms the above suggestion. The compositional dependences of A values measured with DSC technique for aged and rejuvenated Ge_xSe_{100-x} samples are shown in Fig. 4. All ChG with $x<20$ are affected by long-term physical ageing at natural conditions and those with $x\geq20$ do not exhibit any essential changes under prolonged natural storage. So, in view of the above consideration the onset of self-organized phase in this system should occur near $Ge_{20}Se_{80}$ glass. According to our quantum mechanics calculations with outrigger raft structural unit as a basic motive of Ge_xSe_{100-x} glass backbone within $20<x<28$ compositional range [26], only $Ge_{21.5}Se_{78.5}$ glass (Fig. 2b) possesses $n_c=3$ in a global sense. Thus, a narrow self-organized phase is expected to exist in these glasses around $x \approx$ 20-22 compositions in good agreement with [4,6,12]. Therefore, broad features of various physical-chemical quantities (including DSC or TMDSC data) within $20\leq x\leq25$ compositional range could be rather explained by the existence of pseudo-self-organized phase formed by locally over-constrained ($n_c>3$) outrigger raft NFC interconnected via optimally-constrained inter-cluster bridges.

So, despite progress in ChG characterization with TMDSC [7,13,14,16,17], the marginality of ΔH_{nr} cannot be accepted as quite reliable criterion to identify the optimally-constrained phases. Indeed, ΔH_{nr} depends on a lot of factors: conditions of TMDSC experiment (heating ramp, modulation parameters), glass composition and prehistory, completeness of physical ageing, etc. [15,20,27,28].

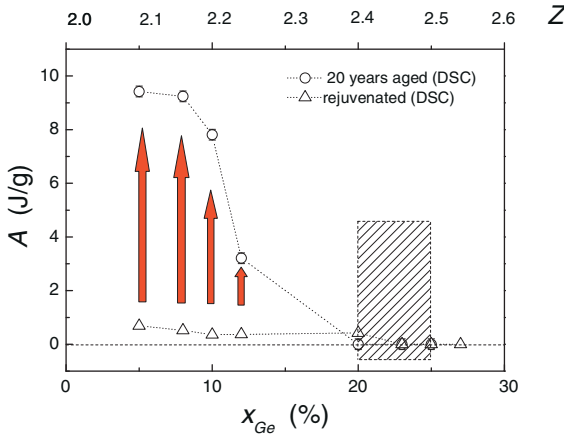

Figure 4 Areas A under the endothermic peaks of DSC curves recorded with 5 K/min heating rate for aged and rejuvenated Ge_xSe_{100-x} glasses. Cross-hatched area shows the reversibility window determined in [14].

It also depicts the average cooperative rearranging region size distribution during transition from glassy to supercooled liquid state [29]. Thus, the relevance of ΔH_{nr} to connectivity of glass backbone and self-organization phenomenon is not simple. The observed compositional features in ΔH_{nr} (shoulders, plateaus, valleys, flattening regions etc.) can be rather explained by changes in the structure of glass-forming units corresponding to different heat-flow-absorption networks.

4 Conclusions Self-organized optimally-constrained intermediate phases are possible in glasses, which network allows formation of the variety of optimally-constrained NFC (n_c=3) at low energy cost. Pseudo-self-organization occurs when rigid structural units (either optimally-, n_c=3, or over-constrained, n_c>3) are linked via optimally-constrained inter-cluster bridges. Marginality of non-reversible component of complex heat flow in TMDSC experiments does not necessary reflect self-organized intermediate phase, since it has time-dependent kinetics. More accurately, the boundaries of self-organized phase can be determined by non-ageing ability of ChG using either DSC or TMDSC techniques. However, even in this case, various structural imperfections can significantly hinder data interpretation.

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