8th. World Congress on Computational Mechanics (WCCM8)
5th. European Congress on Computational Methods in Applied Sciences and Engineering (ECCOMAS 2008)
June 30 – July 5, 2008
Venice, Italy

COMPUTATIONAL CLUSTER-MODELING APPROACH TO SELF-ORGANIZATION EFFECTS IN COVALENT-BONDED GLASSY NETWORKS

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Key Words: *Computational Model, Rigidity Transition, Reversibility Window, Glass.*

ABSTRACT

Covalent-bonded glasses such as chalcogenide vitreous semiconductors have been in a sphere of tight interests for scientists because they exhibit a large variety of possible useful device applications. In general, these disordered solids possess many glass-forming compositions in dependence on their connectivity defined in mean coordination number Z taken as average number of covalent chemical bonds per one atom of structural unit.

In respect to Phillips-Thorpe mean-field rigidity theory [1,2], the covalent-bonded networks proper to chalcogenide glasses reveal three distinct phases in dependence on Z – floppy, intermediate and rigid. Network glasses having less than 3 Lagrangian constrains per atom are under-constrained and stressed ones (they form the floppy phase), while those having more than 3 Lagrangian constrains per atom are over-constrained and enthalpically-stressed ones (they form the stressed-rigid phase). Transition from floppy to stressed-rigid glasses predicted to be solitary one in terms of mean-field constraints theory [1,2], but it split into two points with accepting that covalent bonds within glass-forming network are not distributed randomly revealing a tendency to self-organization [3-5]. Thus a second-order transition occurs from floppy to unstressed-rigid (optimally-rigid or isostatically-stressed) phase, and a first order transition occurs from unstressed-rigid to stressed-rigid phase [5]. In such a way, the stressed-free intermediate phase having just 3 Lagrangian constrains per atom appears forming so-called reversibility window in glass compositions in dependence on Z.

In device application, the self-organized intermediate-phase glasses are the most attractive since they reveal unique non-aging ability being subjected to a prolonged storage under natural conditions. In contrast, the under-constrained glasses exhibit a pronounced drift in their physical properties caused by thermodynamically-driven forces to achieve a more favorable energetic state, this effect being known as physical ageing [5]. The over-constrained glasses can be affected by ageing too, but only at higher temperatures.

Compositional boundaries of reversibility windows for different glass-forming systems were determined experimentally by temperature modulated differential scanning

calorimetry (DSC) [4,5]. The main criterion was the absence or marginality of non-reversible heat flow for all glass compositions inside the window [6].

In the present report, we shall try to examine computational cluster-modeling approach in order to justify energetically the validity for previously-reported boundaries of reversibility windows in two basic glass-forming systems As-S and Ge-S.

Quantum mechanical calculations were performed using the *HyperChem Realise 7.5* program. *Ab initio* calculations with RHF/6-311G* basis set were used to determine the total energies of clusters in dependence on their intercluster linkaging (corner-, edge or face-shared structural units). Thus, the typical clusters like as As_mS_n, Ge_mS_n, S_m-rings/chains were examined. All boundary S atoms belonging simultaneously to two clusters were terminated by H atoms to be two-fold coordinated. Only half-part contributions from these atoms in the average formation energy of cluster calculated per one atom were considered after subtraction both energies of H atoms and -S-H bonds from the total cluster energy. This value was taken by us as a measure for cluster formation probability in the studied glass-forming systems.

The performed calculations showed that corner-shared $AsS_{3/2}$ structural blocks (pyramids) with Z=2.4 within As-S network are more energetically favorable than edge-shared ones. Thus, the self-organized phase in the case of As-S glasses should be formed only by corner-shared $AsS_{3/2}$ pyramids having 3 Lagrangian constraints per atom in obvious contrast to previous results [5], where compositionally-dependent reversibility window was predicted to be in this system from Z=2.285 to Z=2.38. The optimally-constrained quasi-tetrahedral $S{=}AsS_3$ structural units (Z=2.285) is energetically impossible in this system.

In the case of Ge-S glasses, this situation looks absolutely different. According to our calculations, besides S-S-linked $GeS_{4/2}$ tetrahedra (Z=2.4) with 3 Lagrangian constraints per atom, two other energetically-favorable states are possible – edge- and corner-shared tetrahedra. The edge-shared tetrahedral which also have 3 Lagrangian per atom are more preferential in view on their formation energy. At the same, the over-constrained corner-shared tetrahedra appear at high Z, giving the observed transition to stressed-rigid phase at Z=2.52 in full accordance to known experimental results [4,5]. These calculations give clear energetic evidence for self-organization in binary Ge-S system in respect to network adaptability to avoid stress due to redundancies [5].

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