Physico-chemical nanomaterials science

Network-forming nanoclusters in binary As-S/Se glasses: from *ab-initio* quantum-chemical modeling to experimental evidences

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Network-forming nanoclusters $As_2(S/Se)_m$ with m=3÷9 are employed in order to compare glass forming tendencies in two canonical systems of As-based binary sulfides and selenides. Recently, results of nanoclusters modeling with use the cation-interlinking network cluster approach (CINCA) algorithm and supported by *ab-initio* quantum-chemical calculations, have shown *a instability onset*, where binary As-S/Se glasses demonstrate tendency towards as local chemical decomposition as global phase separation. *The instability onset* is expected near *average atomic coordination number of* Z=2.25 in As-Se [1] and near Z=2.20 in the case of As-S glasses [2].

Theoretical predictions give *Reversibility Window* (RW) at Z=2.38÷2.40 for these glasses. However the announced boundaries of RW occur to essentially shifted towards chalcogen-rich compositions, giving it at Z=2.29÷2.37 for As-Se or even Z=2.225÷2.29 for As-S system [3]. Despite serious doubts in the correctness of such RW determination, resulting surely from artifacts in the experimental measuring procedure, this interrelation is governed, to a great extent, by corresponding shifts in *the instability onsets* observed in these systems. Structural-phase instability of As-S glasses is more sharply defined and strongly revealed under lower Z values, thus limiting the range of glass formation for melt-quenched chalcogen-rich compositions with 2.20<Z<2.45.

1. *Shpotyuk O., Hyla M., Boyko V.,* Compositionally-dependent structural variations in glassy chalcogenides: The case of binary As-Se system // Comp Mat Sci.-2015.-**110.**-P. 144-151.
2. *Shpotyuk O., Hyla M.,* Compositionally-dependent network-forming deviations in S-rich glassy arsenic sulfides // submitted for publication.
3. *Boolchand P., Chen P., Vempati U.,* Intermediate Phases, structural varience and network demixing in chalcogenides: The unusual case of group V sulphides // J Non-Cryst Solids.-2009.-**355**.-P. 1773-1785.