Comment on “Structure of Covalently Bonded Glass-Forming Melts: A Full Partial-Structure-Factor Analysis of Liquid GeSe₂”

In this Letter [1], the full power of isotopic substitution and abundant neutron statistics is demonstrated in the context of the structure of glass-forming liquid GeSe₂. While there is little that can be added to this diffraction tour de force, we wish to comment here on the structural consequences of the occurrence of homopolar bonds in GeSe₂ that Penfold and Salmon [1] for the first time directly demonstrate from their diffraction experiments. Although the authors support the “outrigger raft model” which provides for such bonds at the edges of a crystallike fragment [2], they rightly temper this bold conclusion with the reservation that “homopolar bonds will also occur in a defected chemically ordered continuous random network (COCRN) model in which well-defined layers need not be present.”

Fortunately, the underlying reservation regarding homopolar bonds was addressed nearly a decade ago in related Mössbauer effect experiments [3] on Sn-doped Ge₂Se₁₋ₓ glasses, where it was shown that not only is there a finite concentration of Ge-Ge bond signature (site B) at x = ½, but also that the rate γ at which the concentration of such bonds increases with x (near x = ½) is substantially higher than the maximum permissible within bond statistics of a COCRN. Specifically, in Ref. [3] it was shown that the fractional integrated intensities of non-tetrahedral Ge sites [I₉/I = I₉/(I₄ + I₉)] amount to 0.16 at x = ½, and this translates into a Ge-Ge bond concentration of 0.02 for GeSe₂ glass. [The factor of 8 reduction from sites to bonds results since each Ge-Ge bond gives a pair of non-tetrahedral Ge sites (labeled as B site) but four Ge-Se bonds are needed to form a tetrahedral Ge site (labeled A site).] In these Mössbauer-effect experiments, it was further found that the growth rate [3] γ of B sites near x = ½ is γ = 32(2), which is substantially higher than the value of γ = 18, the maximum value within a COCRN. This latter result unambiguously shows that the Ge-Ge bond signatures in GeSe₂ glass may not be identified as defects in a COCRN. Furthermore, recent [4] T-dependent Debye-Waller factors for the A and B sites lead to qualitatively different vibrational temperatures of these species, Θ[B]/Θ[A] = 130(5)/100(5). This fact is hard to reconcile within a COCRN model since both sites (A,B) are then formed in a completely polymerized network and have four nearest neighbors of almost the same mass (Ge = 72.6, Se = 79). On the other hand, if these sites are formed in two different types of clusters, the qualitative reduction in the vibrational temperature of the B sites in relation to A sites may be traced to an intercluster displacement of the smaller cluster as a whole in relation to the larger cluster.

In summary, the original Raman-scattering results [2], the Mössbauer-effect results on both the anion- [5] and cation-site [3] chemical order, and now the new neutron partial structure factors [1] on the GeSe₂ melt all provide a sound basis to visualize the molecular structure of this prototypical chalcogenide glass and melt in terms of phase separation into Ge-rich and Se-rich molecular fragments. Indeed, if the Se-rich clusters are layered, then when the glass is crystallized by laser irradiation with sample temperature far below the glass transition temperature, growth of the β phase (layered) will be favored. Moreover, growth of the α (β) phase can be promoted by annealing just above (below) the glass transition temperature [6]. Note that the (3D) α phase contains only corner-sharing tetrahedra.

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