Intermediate Phases in Disordered Networks

Our current experimental efforts [1-8] are directed towards identification of Intermediate phases in several network glass systems including chalcogenides, oxides and chalcohalides. The tools have included Raman scattering, Mossbauer spectroscopy, Temperature Modulated Differential Scanning Calorimetry, Dynamic Mechanical Analysis, and Lagrangian Constraint Counting Algorithms. The nature of Intermediate phases, particularly their molecular structures and physical properties are examined.

T-modulated-DSC and Raman scattering studies on binary Ge\textsubscript{x}Se\textsubscript{1-x} glasses[8], binary As\textsubscript{x}Se\textsubscript{1-x} glasses[3], and on ternary As\textsubscript{x}Ge\textsubscript{1-2x}Se\textsubscript{2x} glasses[5,6] reveal the opening of the intermediate phase (hashed green region in adjacent figure) in between the floppy (labeled red) and the rigid (labeled brown) phases in the As-Ge-Se ternary glass system. The pink regions in the rigid phase represent nanoscale phase separated compositions [7].

The Intermediate Phase in the As-Ge-Se ternary here straggles the blue line, corresponding to a mean coordination number, r = 2.40. The blue line serves to define the phase boundary between elastically floppy and stressed rigid glasses within a mean-field theory developed by J.C. Phillips and M.F. Thorpe [11]. It is noteworthy that the intermediate phase occurs at r < 2.40 in the As-Se binary but at r > 2.40 in the Ge-Se binary, details that bear on the nature of possible local and medium range structures in these glasses [3].

Intermediate phases possess rather exotic physical properties. They possess low molar volumes; exhibit excellent glass-forming tendency, and display facile photo-melting [8] effects. The challenge of Intermediate Phases is that one cannot simply predict these from a mean-field description of random networks [9-11]. Intermediate Phases are stress-free structures that are optimally rigid. The requirement imposes severe constraints on possible local and medium range structures, which in turn also hold the key to understand their unusual physical behavior.
The broader interest in these phases stems from the fact that disordered systems far removed from glass science also manifest these phases. Some of these include, electronic glasses, such as impurity-doped semiconductors that display a metal-insulator transition in two steps, which serve to define the bounds of the intermediate phase [10]. Fullerites and high-$T_c$ oxide superconductors display insulating, superconducting and Fermi-liquid phases as a function of carrier concentration, which are thought to represent [10] analogues of the floppy, intermediate and stressed rigid phases of molecular glasses.

We have ongoing communication with theoretical modeling efforts of Intermediate Phases, with groups in Paris [9], Rutgers [10] and Michigan State [11]. We collaborate with a group at Central Michigan University on ab-initio cluster calculations of Raman and IR modes [12] that has permitted to reliably ascertain optical mode assignments in these experiments.

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