[129]I Mössbauer Emission Spectroscopy: A Rewarding Structural Probe of the Disordered State of Matter

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Most materials can be rendered amorphous by vapor deposition onto cold substrates, but very few liquids can be cooled to bypass crystallization to form a glass. Bulk glasses form over as a *very small part* of thermodynamic phase space, and good glasses (those which can form at even slower quench rates) select an even smaller part of that accessible phase space. What is so special about these materials? Recently, new insights have emerged both from theory and experiment that suggest that these sweet spots of glass formation occur in *Intermediate Phases* (IPs) that consist of rigid but stress-free networks [1]. Such phases have now been observed in several families of covalently bonded glassy alloys of the group IV and group V elements with the group VI elements [2,3]. These material systems represent some of the best glass formers known in nature. IPs are thought to represent a new type of *self-organized* structural phases which can exist in otherwise disordered states of matter – and they possess unusual functionalities that are the subject of much current study.

We first discuss the *stoichiometric* chalcogenide glass $GeSe_2$. Unlike its crystalline counterpart, the glass is neither fully chemically ordered nor fully polymerized, in that Ge must occur only in $Ge(Se_{1/2})_4$ tetrahedral form and that these units act only as polymeric crosslinks between Se chains. This realization first emerged when the full power of [129]I Mössbauer spectroscopy was brought to bear on understanding the molecular structure of $GeSe_2$ glass two decades ago [4]. In these experiments, traces of [129m]Te dopant (presumably replacing Se sites) were alloyed in the bulk glass, and the chemical environment of the daughter [129]I established from the Mössbauer hyperfine structure using the 27.8 keV gamma rays. A bimodal (A,B) distribution of [129]I sites was observed, with the integrated intensity ratio of the chemically disordered (B) to the chemically ordered site (A), I_B/I_A, of nearly 1.5! This was a big surprise! Why are chemically disordered sites so strongly populated? It emerged that the glass

network is intrinsically segregated into Se-rich and Ge-rich clusters, with the oversized [129]Te chalcogen displaying a strong preference to replace Se sites at the edges or surfaces of the Se-rich clusters forming the B sites. Such boundary segregation of the oversized dopant permits it to relax in the intercluster van der Waals gap, stressing the network less than by replacing Se ordered sites (A) in the interior. When account is taken of the strong selectivity of Te for Se-surface sites, one obtains the concentration ratio of homopolar Se-Se bonds to heteropolar Ge-Se bonds in the stoichiometric glass of about 0.02. This finding was corroborated by [119]Sn Mössbauer spectroscopy (Sn replacing Ge) that detected the concentration of homopolar Ge-Ge bonds of the network [5], and somewhat later with the use of isotopic substitution in neutron diffraction experiments [6], which showed evidence of Ge-Ge nearest neighbors in the partial pair correlation functions.

We review now the corresponding structural studies of *non-stoichiometric* binary Ge_xSe_{1-x} glasses. The compositional trend of the glass transition temperature $T_g(x)$ is a good indicator of the connectivity of the glass network backbone. The slope dT_g/dx displays a maximum near x = 0.31. The decreasing slope for x > 0.31 suggests that additional Ge alloying leads to segregation of Ge-rich clusters and lowers the connectivity of the network. Beyond x = 0.31, Ge-Ge bonds are seen in Raman scattering and [119]Sn Mössbauer spectroscopy [5,7]. This is consistent with the findings discussed earlier in the stoichiometric (x = 1/3) glass. (Similar findings have also been reported in GeS_2, As_2S_3, and As_2Se_3 glasses, and are in sharp contrast to those on the archetypical SiO_2 glass, where bond ionicity insures a chemically ordered network of $(SiO_{1/2})_4$ tetrahedra composed only of Si-O homopolar bonds.)

The discovery of the IP introduces new considerations about network structures. In covalent networks, where coordination number of atoms are rather well defined, one can establish if a network is mechanically flexible or rigid by merely counting the number of chemical bonding constraints/atom (n_c) using a well-defined protocol [8]. Thus, one can see that Se glass composed of a polymeric chain of Se_n atoms, in which each atom has two nearest neighbors, is mechanically soft because there are only two constraints/atom ($n_c = 2$). On the other hand, a network of Se-bridging $Ge(Se_{1/2})_4$ tetrahedral units, as in a $GeSe_2$ glass, would be stressed-rigid because $n_c = 3.66$. And it is a straightforward matter of counting to show that for the binary glass $GeSe_4$, (x = 0.20), $n_c = 3$, the number of displacement degrees of freedom of an atom. The latter count leads to a network that is said to be isostatically rigid, because the mean number of chemical bonding constraints is just that necessary to insure the network

is rigid. One thus has a very powerful algorithm that serves to define the IPs as the sweet spots for glass formation – as first recognized by Phillips [9] in 1979. A corollary is that the backbones of IPs in Ge_xSe_{1-x} glasses contain $GeSe_4$-like structural units.

The existence of the IP in these glasses helps explain some 20-year-old puzzling results in Mössbauer studies of them. In these experiments, aspects of glass structure evolution as Ge is alloyed in a base Se glass was captured in the site intensity ratio $I_B/I_A(x)$, mentioned earlier. The observed variation differed from the simplistic mean-field behavior for a chemically ordered continuous random variation in two important respects: (i) the ratio saturated to a value of about 1.5 once $x > 0.31$ instead of going to 0, and (ii) the ratio displayed a local maximum in the $0.20 < x < 0.25$ range. The broad maximum can now be understood [7] as due to the opening the IP in which the ^{129}Te dopant is displaced from the percolating rigid backbone to the flexible Se_n chain fragments, leading to growth of B sites at the expense of A sites. This particular interpretation of the Mössbauer data only became clear with the recognition of the IP window in the lower composition range, which emerged from later Raman scattering and modulated DSC experiments. In the latter experiments, the non-reversing enthalpy ($\Delta H_{nr}(x)$) at the glass transition was found to *nearly vanish* in the $0.20 < x < 0.25$ range, and the glass transition becomes thermally reversible (thermally reversing composition window).

Such thermally reversing windows have now been observed in a variety of chalcogenide glasses, and the bar chart of Figure 1 displays the range of mean coordination number *r* spanned by the reversing window. For example, in binary Ge_xSe_{1-x} glasses, the mean coordination number, $r = (CN\ of\ Ge = 4)x + (CN\ of\ Se = 2)(1-x) = 2(1+x)$, and so the reversing window spans the $2.40 < x < 2.50$ range.

References

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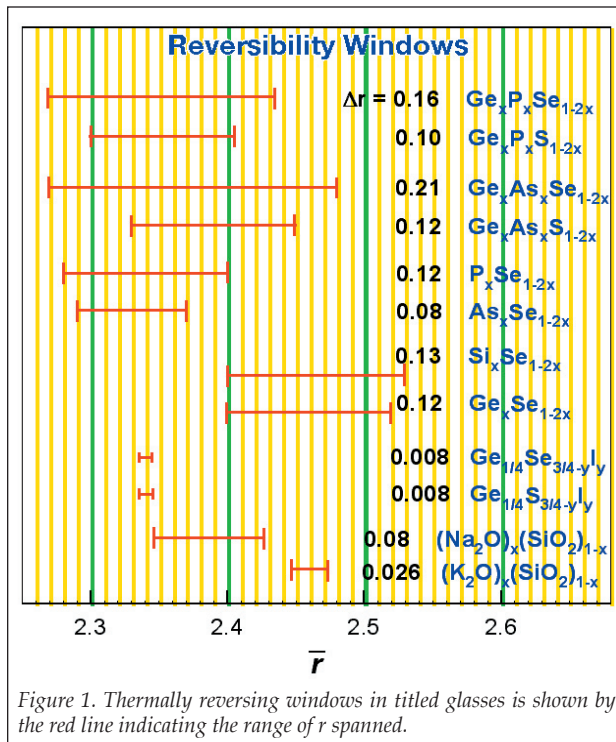Figure 1. Thermally reversing windows in titled glasses is shown by the red line indicating the range of r spanned.