Intermediate Phases, structural variance and network demixing in chalcogenides: The unusual case of group V sulfides

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ABSTRACT

We review intermediate phases (IPs) in chalcogenide glasses and provide a structural interpretation of these phases. In binary group IV selenides, IPs reside in the $2.40 < r < 2.54$ range, and in binary group V selenides they shift to a lower r, in the $2.29 < r < 2.40$ range. Here, r represents the mean coordination number of glasses. In ternary alloys containing equal proportions of group IV and V selenides, IPs are wider and encompass ranges of respective binary glasses. These data suggest that the local structural variance contributing to IP widths largely derives from *four isostatic* local structures of varying connectivity r, two include group V based quasi-tetrahedral ($r = 2.29$) and pyramidal ($r = 2.40$) units, and the other two are group IV based corner-sharing ($r = 2.40$) and edge-sharing ($r = 2.67$) tetrahedral units. Remarkably, binary group V (P, As) sulfides exhibit IPs that are shifted to even a lower r than their selenide counterparts; a result that we trace to excess S_n chains either partially (As–S) or completely (P–S) demixing from network backbone, in contrast to excess Se_n chains forming part of the backbone in corresponding selenide glasses. In ternary chalcogenides of Ge with the group V elements (As, P), IPs of the sulfides are similar to their selenide counterparts, suggesting that presence of Ge serves to reign in the excess S_n chain fragments back in the backbone as in their selenide counterparts.

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1. Three types of glass transitions

Glasses are intrinsically non-equilibrium solids and their physical properties generally evolve over long times, i.e., these solids slowly age. The aging of glasses is itself a fascinating subject and has been debated since the early work of Kohlrausch [1–3]. There is now evidence to suggest that the stretched exponential relaxation observed in glasses may well be characterized by specific exponents, which are determined [2] largely by the nature (of long or short range) of forces that control how traps or defects diffuse as networks relax. For a long time it was widely believed that glass transitions are also hysteretic and age [3] as observed in a traditional differential scanning calorimetry. There are new findings showing that under select conditions [4–6] aging of glasses may not occur.

New insights into the nature of the glass transition [4,7] have now emerged using modulated-DSC (m-DSC). A significant advantage of m-DSC over traditional DSC is that the method permits deconvoluting the total heat flow into a reversing heat flow term (which captures the local equilibrium specific heat) and a non-reversing heat flow term (which captures non-equilibrium effects of the changing structure). The thermally reversing heat flow term usually reveals a rounded step-like jump. One defines the glass transition temperature, T_g, from the inflexion point of the step, and the specific heat jump, ΔC_p in going from the glass to the liquid state from the height of the step. On the other hand the non-reversing heat flow term usually shows a Gaussian like peak as a precursor to T_g, and the integrated area under the Gaussian lineshape, provides the non-reversing enthalpy (ΔH_{nr}) of T_g. Experiments on wide variety of glasses reveal [8–10] that the ΔH_{nr} term depends on factors such as sample purity, sample homogeneity and sample aging. Kinetic factors such as scan rate and modulation rate used to record a scan also influence ΔH_{nr} and T_g, although their influence can be corrected by a judicious choice of procedure in these experiments [11].

Experimental data on covalently bonded glasses examined systematically as a function of their network connectivity (or mean coordination number r) show that there are, in general, three types [4,7] of glassy networks formed in freezing as characterized by

their elasticity. The first type is the elastically flexible networks which form at low connectivity ($r \sim 2$), such as a Se glass consisting of a chain in which each atom has two neighbors. Such networks display a non-reversing enthalpy (ΔH_{nr}) of T_g that is usually narrow (~ 15 °C) and symmetric in temperature and, which slowly ages with waiting time as a stretched exponential [2]. The second type of glass network is elastically rigid but stress-free. These networks form at intermediate connectivity ($r \sim 2.4$); the endotherm has a *vanishing* ΔH_{nr} term that shows little or no aging. The third type of glass network is elastically rigid but also stressed. They occur at high connectivity ($r \sim 3$), and show a ΔH_{nr} profile that is broad and asymmetric with a high-T tail, and age with waiting time. In this category are chalcogenide glasses with covalently bonded alloys of group IV (tathogen, $r = 4$) and group V (pnictide, $r = 3$) elements with group VI (chalcogen, $r = 2$) elements. They usually bond in conformity with the 8-N rule, thus making possible an estimate of their connectivity from their chemical stoichiometry alone provided that the resulting components do not segregate [12] or demix on a nano- or microscale [13]. These systems are particularly attractive because they form bulk glasses over wide range in connectivity r, permitting calorimetric [14], dielectric [15–17], optical [18–21] and electrical [22] measurements to be performed to establish the global behavior. Remarkably, physical properties of glasses can sometimes change with composition sharply [23,24] rather than slowly [12,25,26]. Thus it can be risky to infer the global behavior by merely investigating stoichiometric glass compositions alone.

Recently, we have examined ionically bonded [24,27] (alkaligermanates and -silicates) and fast-ion conducting [28] (solid electrolyte) glasses in m-DSC experiments and have confirmed the three elastic phases mentioned above. These new findings underscore the generic nature of the three types of glass phases. Indeed, a simple measurement of the glass transition endotherm in an m-DSC experiment makes it now feasible to identify whether a glass sample possesses a flexible network, or a rigid but stress-free one, or a rigid but stressed one.

2. Self-organization and reversibility windows in chalcogenide glasses

As mentioned earlier, in a wide variety of systems the three types of glass transitions mentioned above occur sequentially with composition as connectivity of their networks is systematically increased. The most unexpected finding [25,29–31] is the existence of the second type of glass structure, which spans a small range of compositions with rather sharply defined edges in some cases. These compositional windows are known as reversibility windows (RWs) since T_gs become almost completely thermally reversing ($\Delta H_{nr} \sim 0$). These windows represent calorimetric signatures of different vibrational regimes in networks as we discuss next.

The inspiration to look for these elastically special network glasses came in the early 1980s from the pioneering work of Phillips [32] and Thorpe [33]. They predicted [32–34] the existence of a *solitary* elastic phase transition in a covalent amorphous network from an elastically flexible phase to a stressed-rigid phase when its connectivity increases to $r = 2.40$. Lamb–Mossbauer factors in [119]Sn Mössbauer spectroscopy of binary Ge_xSe_{1-x} glasses confirmed [31,35,36] the existence of a vibrational threshold behavior in them. Starting in 1996, detailed Raman scattering experiments on two group IV selenide glasses (Si–Se and Ge–Se) revealed the existence of *two* [31,37] elastic phase transitions and not the isolated one predicted. Numerical simulations on self-organized networks subsequently showed [38] that the first transition at low r (=r_1) was between *floppy* (or *flexible*) and *rigid* phases, while the second transition at higher r (=r_2) was to a *stressed* network. The

intervening region, ($r_1 < r < r_2$), also called the intermediate phase (IP), separates the *flexible* phase from the *stressed-rigid* one. Subsequently, experiments on several other glass systems [5,26,39–43] including ternary chalcogenides, confirmed that IPs observed in vibrational spectroscopy coincide with RWs observed in calorimetric measurements [31,37]. These optical and thermal measurements are but two fingerprints of the IP as being a remarkable new kind of disordered solid [6]. Glassy networks in this phase are rigid but stress-free. Their quasi-equilibrium state is much like a crystalline solid, with nearly absent aging of structure.

There have been several attempts in recent years to simulate IPs in amorphous networks numerically. For example, the vibrational behavior of 3D amorphous Si networks [38,44] provided suggestive evidence of an IP existing in a narrow range of connectivity, $2.376 < r < 2.392$. IPs have also been observed in 2D triangular networks and their nature exhaustively explored by equilibrating networks using activation relaxation techniques [44]. Although chemically not realistic, these models serve to confirm the existence of IPs in numerical simulations, bringing theory and experiments closer together. The rigidity and stress phase boundaries of more realistic analytic models consisting of small networks formed by agglomerating corner-sharing (CS) and edge-sharing (ES) tetrahedra have also displayed an IP whose width appears to be controlled by the fraction of ES to CS tetrahedra. These analytical calculations [45,46] on binary Si–Se and Ge–Se glasses predict IP widths that are much closer to experiments. Mauro and Varshneya [47,48] modeled binary Ge_xSe_{1-x} glasses using empirical potentials, and were able to provide evidence of a rigidity transition near $r \sim 2.4$. Numerical simulations of the IP in real glasses pose formidable challenges not the least of which is constructing large and space filling structural models with appropriate local structures. This is an area of active interest in the field [49,50].

The aim of the present review is to focus on IPs of the group V sulfides and selenides. The IP in As–Se [26] and P–Se [41] binaries were reported a few years ago. Now, IPs in binary As–S [9], and P–S [51] glasses have become available. These new results on group V chalcogenides along with earlier ones on group IV ones provide a platform to discuss trends in IPs in general, and we will address here such questions as what aspects of local and intermediate range structure of glasses control the width and centroid of the IP in these covalently bonded solids?

In Section 3, we discuss trends in T_g and molar volumes, which provide important clues on glass structure. In Section 4, we give an overview of observed RWs in group V sulfides, and in Section 5, Raman scattering results on these systems. These data then permit a discussion of the IPs and their connection to glass structure in chalcogenides in Section 6. A summary of our findings appears in the conclusions.

3. Compositional trends of T_g

3.1. Variation of glass transition temperatures-role of network connectivity

In the past 8 years reliable data on the variation of T_g as a function of glass composition in binary and ternary chalcogenide glasses has evolved using m-DSC. What underlying physics resides in these findings? Can we connect these trends to aspect of glass structure? Here we will show that the connectivity of the underlying networks controls in a crucial fashion the observed variations of T_g. Many of these ideas have been made possible by Stochastic Agglomeration Theory [52] and Lindeman melting criteria [36] .