Glass homogeneity precursive to self-organization

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Raman profiling of chalcogenide melts provides a powerful method to track the structural homogenization of batches in real time. Recent results on 2 gram sized Ge_xSe_{100-x} melts reacted at 950°C in high vacuum show such melts to homogenize in 168 hours on a scale of 10μm. In such dry and homogeneous glasses, sharply defined *rigidity* and *stress* transitions are observed, leading to a *square-well like* reversibility window. The window is signature of the self-organized Intermediate Phase (IP) with remarkable properties. In oxide glasses, reversibility windows are also observed, and are sharply defined even though melts were reacted for less than 6 hours.Modified oxides apparently homogenize quicker than those of chalcogenides. The variations in the non-reversing enthalpy at T_g , stretched exponents β, and molar volumes, each studied as a function of glass composition appear to be strongly influenced by sample heterogeneity and purity. Glass homogeneity appears to be precursive to network self-organization.

1. Background

The growth of crystals in a melt is initiated by formation of crystal nuclei. As atoms diffuse the nuclei grow and acquire macroscopic dimensions with translational symmetry and a unique stoichiometry characteristic of a crystalline solid. Such crystal growth occurs even if melts are not homogeneous and have impurities, largely because long- and short- range atomic interactions influence the placement of substituent atoms appropriately on the growing seed. On the other hand, glasses are a replica of melts when formed by melt-quenching. One is *not* assured of glass homogeneity until the melt itself is homogeneous. In recent years, interest in glass homogeneity has been stimulated [1] because their properties can change quite abruptly with composition [2] particularly near elastic phase transitions [3, 4] leading to self-organization [5-7]. Hence, homogeneity is required to ensure the consistency of glass properties and the ultimate performance of glass products.

Melt quenching has been widely used to synthesize bulk glasses. A perusal of the literature reveals that in typical synthesis melts are reacted for about 24 hours and then water quenched. Less clear at present is how long melts must be held at high temperatures to homogenize. The homogenization process itself is driven by chemical reactions of the batch materials and thermal convection of the resulting melt. In industrial settings, homogenization is also assisted through the use of mechanical stirrers.

Recently, we introduced a Raman profiling method to track homogenization of chalcogenide melts in real time [8, 9] non-invasively, and showed that the process of

homogenization is actually quite slow. Indeed, the lack of agreement between different groups on a wealth of experimental data on the chalcogenides could arise from sample make up. Synthesis of homogeneous bulk glasses of high purity holds the key to the manufacture of consistently high-quality industrial glass, to resolving differences in reported properties of ostensibly identical samples and hence unraveling the underlying *physics of network glasses*.

2. Melt heterogeneity monitored in Raman profiling experiments.

Fig. 1 illustrates an example of slow homogenization of a Ge_xSe_{100-x} melt at x = 19% taken from ref [8]. The starting materials (Ge,Se) were reacted at 950°C for extended reaction time-t_R and FT-Raman scattering recorded along the length of the melt-quenched glass column at 9 locations with the glass sample sealed in evacuated quartz tube. The data show lineshapes to vary considerably with position at t_R < 24 hours (Fig 1a,b) because of the nucleation of α-$GeSe_2$ at the tube bottom. Liquid Ge (ρ= 5.60 gms/cm^3) is heavier [10] than liquid Se (ρ= 3.99 gms/cm^3) and one may expect Ge-rich crystalline phases to nucleate at the tube bottom in the first step of reaction of the elements. This pattern is observed at all other glass compositions studied [9]. Continued reaction (t_R = 96h) of melts, promotes homogeneity (Fig 1c), but a fully homogeneous melt is realized only after t_R>168h (Fig 1d) when all 9 line shapes completely overlap. The slow kinetics of batch homogenization was

noted [9, 11] for all the 20 glass compositions examined in the Ge-Se binary, and is characteristic of *dry* samples.

The slow melt homogenization broadly consists of a 2-step process. In step-1, α-GeSe$_2$ [12] nucleates at the tube bottom, and the evidence consists of the narrow modes (arrows) observed in Fig 1a and b. Melts become steadily Ge-deficient (Ge$_8$Se$_{92}$) towards the top of the glass column (Fig.1a) as estimated from the increased scattering strength ratio of the chain-mode (CM, near 250 cm^{-1}) to corner-sharing mode (CS, near 200 cm^{-1}) [12, 13]. With increasing t_R > 24h, the crystalline phase dissolves in the glassy matrix. At t_R = 96h, the crystalline phase completely vanishes, but a heterogeneous melt persists (Fig 1c) with Ge content 'x' varying almost linearly from 21% at tube bottom to 17% at the top of the glass column. At this point appropriate local structures characteristic of melts /glasses have evolved but the glass continues to be heterogeneous. In step-2, as further reaction of the melt proceeds note that the Ge/Se fraction across *the whole batch equalizes* when t_R ~ 168 h , as the Ge(Se) concentration gradients vanish determined by diffusion of Ge and Se atoms in melts at 950°C. The 2-step behavior of homogenization of melts observed at x = 19% is representative of that   observed at other compositions in the present Ge$_x$Se$_{100-x}$ binary [9].

3. Water impurities, kinetics of melt   homogenization and glass structure.

An equally interesting finding is that water traces in melts speeds up the kinetics of homogenization in step-1 as discussed in ref. [8]. Water impurities in chalcogenide glasses leads to bridging S or Se atoms being replaced by dangling (SeH, OH) ends, thereby reducing network connectivity. The result of a change in network topology is to (i) a *lower T_g* , (ii) *lower molar volumes,* and (iii) *promote alloying* of Ge with Se by cutting the length of Se-chain segments. T_g provides a measure of network connectivity [14] and one expects it to decrease as water is doped in a network. A wet glass sample at x = 19%, possesses a T_g of 156.6 (2.9)°C, lower than that of a dry glass sample (170.8 (2.0)°C), a pattern noted at other compositions as well. Furthermore, molar volume of a wet glass sample at x = 19% of 18.03(5) cm^3 is smaller than that of a dry sample (18.34(5) cm^3), a pattern also seen at other compositions (Fig.2). In Fig 2 we compare molar volumes of the present homogeneous glasses (●), with two earlier reports [15, 16]. Broadly speaking, trends in molar volumes display three distinct regimes of variation with glass composition- molar volumes barely change in the Intermediate Phase (IP) regime (19.5% < x < 26.0%), and then increase rapidly as one goes away from the IP both at x < 19.5%, the *flexible phase*, and at   x > 26% in the *stressed rigid phase*.
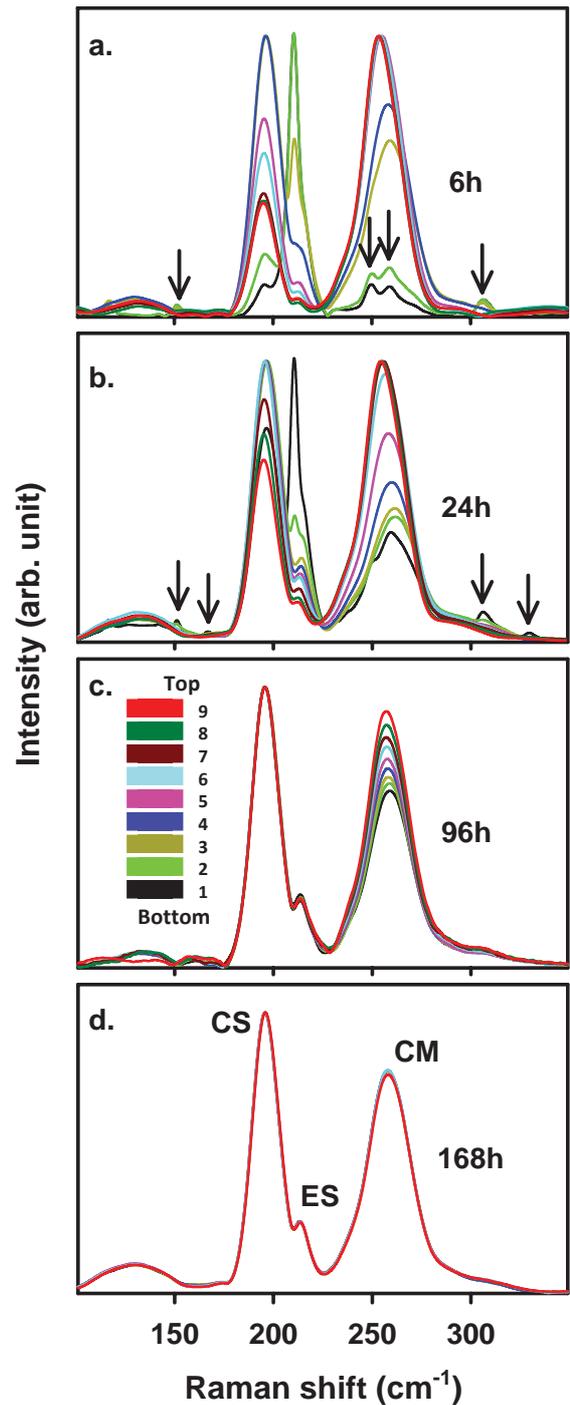
Fig. 1. FT-Raman spectra taken along the length of a quartz tube containing a Ge$_{19}$Se$_{81}$ melt(glass) held vertically and reacted at 950C for indicated times. Spectra were taken at 9 location spaced 2.5 mm apart along a glass column about 25 mm long. The spread in lineshape in (a) after 6h of reaction of the starting materials (Ge,Se) indicates quite a heterogeneous melt(glass). The sharp modes at the arrow locations come from α-GeSe$_2$. (b) after 24 hours of reaction, the fraction of α-GeSe$_2$ decreases substantially.(c) after 96 hours of reaction, although the crystalline phase dissolves in the glass matrix, the glass continues to be heterogeneous.(d) After 168 hours of reaction the melt(glass) homogenizes. This figure was taken from ref. [8].
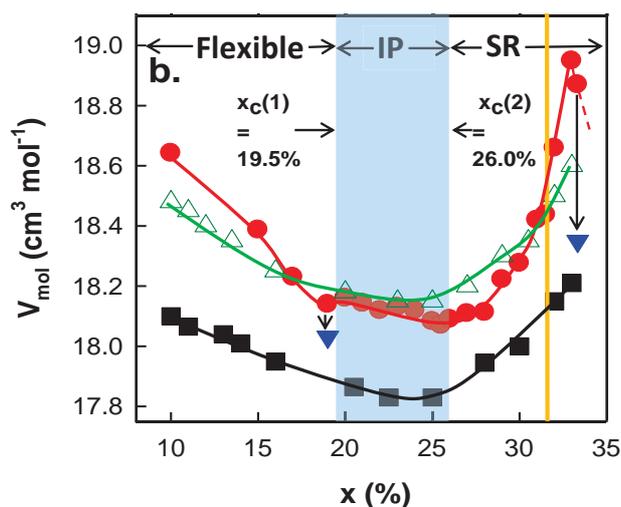
Fig. 2. Molar volumes of the present glasses (●) are compared to two previous reports, one by Feltz et al. (■)[15], and the other by S.Mahadevan et al.(△)[16].

These data suggest that glass samples of ref [15] are most likely not as dry as the ones of ref [16], while those of ref [16] not as homogeneous as the present ones. Molar volumes of the wet samples (▼) are in general lower than those of dry (●) samples. These data are persuasive in suggesting that accurately measured $V_m(x)$ provide a measure of the relative wetness/dryness and homogeneity of samples.

For the high-tech glass industry, the issue of water removal is especially important for optical waveguides, since the presence of even small concentrations of water leads to large optical absorption around the near-infrared wavelengths used in optical communication systems. The successful development of low-loss glass fibers for optical communications was the direct result of the invention of the outside vapor deposition process, in which a glass preform is deposited from reactions of $SiCl_4$ and $GeCl_4$ with oxygen. These preforms are then drawn into water-free high-purity SiO_2 fibers with elevated-index GeO_2-doped cores.

4. Glass homogeneity and Self-organization

The trimodal behavior of *molar volumes* in Fig 2, and particularly the minimum in the Intermediate Phase is *signature of network self-organization*. Numerous other physical properties of these glasses display the tri-modal behavior. For example, the nature of glass transition in the Intermediate Phase (blue region in Fig.2 and 3) differs qualitatively from that seen in the other two elastic phases; the *non-reversing enthalpy of relaxation at T_g (ΔH_{nr})* vanishes in the IP but increases *abruptly* by an order of magnitude both in the flexible phase and the stressed-rigid phase. One observes a square well-like variation (Fig 3) of

the ΔH_{nr} term in homogeneous glasses. That variation changes over to trapezoidal and then triangular (Fig.3) as glass samples become less homogeneous [8]. Most importantly, the *ΔH_{nr} term ages* for glass compositions outside the IP but not in it. Characteristic Raman *optical elastic power-laws* are observed in the IP and in the stressed-rigid phases underscoring that networks in these two phases possess different topology, the former stress-free the latter stressed with redundant bonds. The lack of aging of IP networks is, most likely, due to their rigid yet stress-free character.
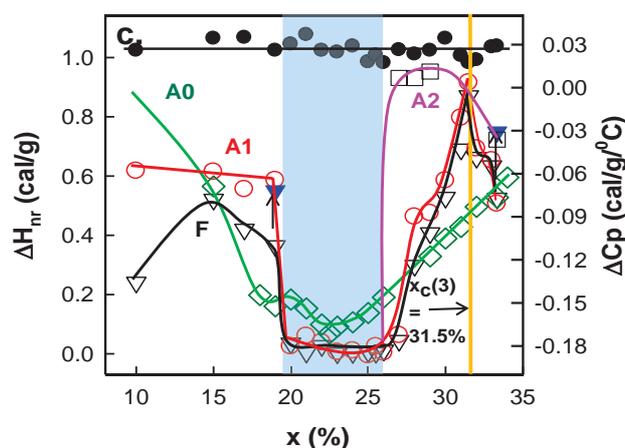
Fig. 3. Variations in the non-reversing enthalpy at T_g, $\Delta H_{nr}(x)$, in present samples in fresh state (inverted triangle) after 2 weeks of aging at 25°C (○) curve A1, after 2 weeks of aging at 240°C (□) curve A2, and results from ref 12 (◊) curve A0 after 2 weeks of aging at 25°C. The shaded panel gives the Intermediate phase. The jump in the specific heat across T_g, $\Delta C_p (x)$ (●) is found independent of x. See Ref. 9 for details.

It is useful to note that while $\Delta H_{nr}(x)$ shows a square-well like variation, the jump in specific heat across $T_g(x)$, $\Delta C_p (x)$, is found to be independent of x in the range investigated (Fig.3).These results on homogeneous glasses support [9] classification of melt fragilities based on $\Delta H_{nr}(x)$ but not on $\Delta C_p (x)$.

IPs have been observed in more than 40 families of glass systems [17-23] including modified oxides, solid electrolytes, chalcogenides, and chalcohalides. Dangling ends such as halogens in the chalcohalides lead to a rather striking collapse of these IPs because they lower the network connectivity[24, 25]. The rigidity and stress transitions are found to be abrupt in glass samples that are dry and homogeneous. And they can be expected to be smeared and even lost in impure and heterogeneous glasses IP network can reconnect easily at T's near T_g and adapt to expel stress, reminiscent of proteins [26] in the transition state, features that are identified universally with network self-organization.

5. Modified Oxides, glass homogeneity and self-organization

Intermediate Phases have also been observed in oxides such as sodium germanates [2] sodium borates [27], and heavy metal oxides [28]. In all these systems, reasonably sharp rigidity and stress transitions are observed in contrast to the case of the chalcogenides even though melts were reacted at several hundred degrees above the liquidus for typically less than 6 hours. The reversibility window in Sodium Germanate glasses [2] is reproduced in Fig 4. It displays a nearly square-well like variation with reasonably sharp rigidity and stress transitions. In these experiments batch sizes were kept at 2 grams and the starting materials (Na_2CO_3 and GeO_2) were reacted at 1350°C for 4 hours after thoroughly mixing the fine powders in a dry ambient. No Raman profiling experiments have been performed on these oxides to date. And even though melts were reacted for only a few hours, we suspect that they must have homogenized since the reversibility window appears to be quite sharp.
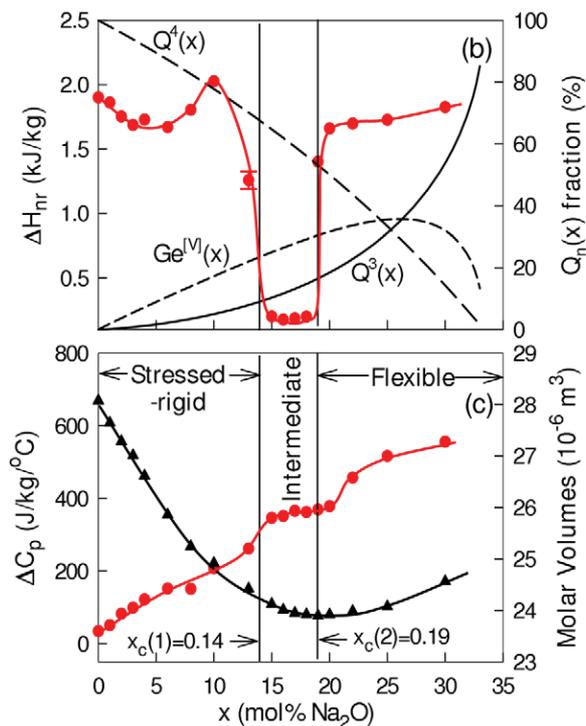
Fig. 4. Compositional trends in (a) ΔHnr(x) (b) ΔCp(x) and molar volumes in $(Na_2O)_x(GeO_2)_{1-x}$ glasses taken from [2]. In these modified oxides we observe a sharply defined reversibility window for glass compositions that possess a minimum of molar volumes, features that are identified with self-organization.

The behavior is in sharp contrast to that of the chalcogenides and can be reconciled as follows. In oxide glasses heteropolar bonds are chemically preferred over homopolar ones because of charge transfer effects. These heteropolar bonds already exist in the starting materials used for synthesis of the melts (glasses) in contrast to the chalcogenides where the pure elements are usually used as the starting materials. Finally, the alkali modifier (Na) is a fast diffuser in oxide melts and undoubtedly aids batch homogenization.

The importance of dryness of oxide glasses to ascertain their intrinsic behavior is well documented for the case of B_2O_3 [29, 30], and $AgPO_3$[31]. Modification of $AgPO_3$ glass upon alloying AgI to form a solid electrolyte glass has attracted widespread interest [32] because of the high ionic conductivity realized. Indeed, attempts to synthesize bulk $(AgPO_3)_x(AgI)_{1-x}$ solid electrolyte glasses by an aqueous solution route followed by heating to drive off all traces of water has given rise to samples that do not reveal an Intermediate Phase, probably because of presence of bonded water. It is difficult to remove bonded water by heating largely because of the strong affinity of OH to bond to P and cut polymeric PO_4 chains that comprise the elements of medium range structure of these solid electrolyte glasses. On the other hand, a thorough mixing of the starting materials as fine powders in a dry ambient environment followed by their reaction at elevated temperatures leads to bulk glasses that display a wide and reasonably sharp thermally reversing window [32]. Recently Micoulaut and Malki [33, 34] have identified a characteristic hopping length of the Ag+ carriers that is maximized in the IP of these glasses. These observations underscore the need to pay special attention to synthesis of homogeneous and dry solid electrolyte glasses before a basic understanding of ion-transport [35] in these fascinating materials can emerge.

6. Stretched exponential relaxation.

The observation of stretched exponential relaxation (SER), $A(t) = A_o exp[-(t/\tau)^\beta]$ over many orders of magnitude of time (t) is a characteristic feature of good glasses, and provides yet another means to monitor their homogeneity. In *homogeneous* glasses two magic values of the dimensionless stretched exponent $\beta = 3/5$ and $3/7$ have been observed widely [36] in experiments and understood in terms of theory: the higher value ($\beta = 3/5$) is ascribed to relaxation mediated by short range forces (covalent) while the lower one ($\beta = 3/7$) to long range ones (Coulomb). On the other hand, in heterogeneous glasses β deviates considerably from these magic values [36]. The occurrence of these two particular β values and a crossover between them has been pointed out recently for several disparate systems [37] namely, molecular glasses, research citation statistics in the Web of Science, and in decay of luminescence in $ZnSe_{1-x}Te_x$ semiconducting single crystals. A bifurcation of stretching exponents was also noted in the recent experiments at Corning [38]

comparing the stress relaxation vs. structural relaxation behavior of a homogeneous silicate glass manufactured using the fusion drawn process. The Corning experiments reveal that stress relaxation of the fully equilibrated homogeneous glass samples exhibit $\beta = 3/5$ (relaxation dominated by short-range forces), whereas structural relaxation of the as-drawn glass sheets result in $\beta = 3/7$ (relaxation governed by long-range forces). The topology of compacted glassy systems formed in ideal network glasses appears to be generic to a wide variety of disordered networks encountered in nature.

Acknowledgements

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