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Glass transition, topology, and elastic models of Se-based glasses

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Abstract

Features intrinsic to disorder and network aspects are ubiquitous in structural glasses. Among this important class of materials, chalcogenide glasses are special-they are built of short-range covalent forces, making them simpler than silicate glasses that possess mixed ionic and covalent forces. Selenium-based glasses also display complex elastic phase transitions that have been described from various models, including mean-field approaches to molecular simulations. These point to the presence of two sharply defined elastic phase transitions, a rigidity and stress transition that are non-mean-field in character, and separate the three distinct topological phases of flexible, isostatically rigid, and stressedrigid. This article reviews the physics of these glassy networks. The elastic phases and glass transition temperature are explained on a molecular level in terms of topological constraint theory (TCT), connectivity, and the open degrees of freedom. The broader aspects of TCT in relation to phase change materials, high-k dielectrics, and cements are also commented upon.

KEYWORDS

chalcogenides, differential scanning calorimetry, glass transition, molecular dynamics, Raman spectroscopy

INTRODUCTION 1

Glass science often begins with silica, because it has been forming long before the dawn of human existence in the form of fulgurite¹ created by lightning strikes on

sandy beaches. Once window glass was developed, the inventions of the telescope, microscope, and flat panel displays soon followed impacting human civilization in an unprecedented manner. Beginning in the latter half of the 16th century, planetary motion studies by Galileo Galilei,

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Johannes Kepler, and Tycho Brahe soon led to the creation of classical mechanics with the emergence of Isaac Newton's *Principia*.² Scientific progress in studying bacteria followed directly from the invention of microscopes that quickly opened new research into biology at the molecular level and culminated in an understanding of the structure of proteins and DNA as studied by Watson and Crick.³ The fascination of glass science continues to the present day as the United Nations has declared the current year 2022 to be the Year of Glass.

Beginning in the early parts of the 20th century, the chemical bonding of oxide glasses that involve both covalent (short range) and ionic (long range) interactions became understood, and from this new atomic scale understanding of modified oxide glasses, the notion of self-organization was developed,4-7 which defines the stability of window glass,⁸ including the hard Gorilla glass⁹ that covers the displays of cellphones. Starting in the early 1950s, the field of glass ceramics also appeared, and the systematic incorporation of crystalline materials in glasses opened up a new avenue to control physical properties of these composites to tailor them for select applications.¹⁰ The remarkable progress in glass science over the past 50 years has undoubtedly impacted our understanding of glass ceramics on a basic level and will continue to do so into the foreseeable future.

Like oxide glasses, chalcogenide glasses (Se and Te), often alloyed with group IV and group V elements, have had their own revolution in terms of innovation, understanding, and technology. The chalcogenides are attractive for a variety of reasons. They are much simpler than oxide glasses in which they have no ionic bonding, and they exclusively form covalently bonded networks of shortrange forces only. Elemental selenium is also a remarkable material because it is a unique elemental glass former. and when left to age at room temperature for over 4 months or longer, although the glass transition temperature ($T_g = 40.5^{\circ}$ C) remains unchanged, the full width at half maximum of T_g narrows fivefold¹¹ and is traced to a super-flexible^{11,12} phase of the under-coordinated polymeric chains of Se_n that steadily correlate upon $aging^{11,12}$ (where interchain correlation occurs at room temperature $(23^{\circ}C)$ as the quasi-linear Se_n chains become nearly quasihelical as in trigonal Se due to interchain interactions mediated by van der Waals forces). The base Se glass is thus quite a soft material, but the progressive alloying of Ge hardens the glass, and one finds that the glass transition temperature of the Se base glass, $T_g = 40.5^{\circ}$ C, increases up to a maximum $T_g = 425^{\circ}$ C with Ge concentration until the stoichiometric GeSe₂ glass is reached.^{13–15} These glasses exhibit a rich variety of elastic and structural network phase transitions, which can be explained in detail at the molecular level as illustrated in the present work.

In terms of applications, Se glass is also light sensitive and is widely used as the photoreceptor in electronic copying machines pioneered by Xerox¹⁶ and now made by many others, including Hewlett Packard.¹⁷ Finally, amorphous alloy thin films of Ge and Sb with Te form an important class of optoelectronic materials. They are now widely used as memory storage devices^{18–26} using either phase change materials (PCM) or the ovonic threshold switching (OTS) process.

1.1 | Mean-field topological constraint theory of network glasses

The glass-forming tendency of melts is known to optimize when they acquire an ideal connectivity.²⁷ Treating a covalent glass as a network of trusses made of bars (the bonds) and nodes (the atoms), ideal connectivity occurs when the Maxwell–Phillips stability criteria^{27,28} of $n_c = n_d = 3$ are fulfilled. Here, n_c represents the count of bonding constraints due to the radial and angular forces per atom, and n_d is the number of degrees of freedom/atom in a 3D network. In general, by enumerating these chemical bonding constraints per atom, $\langle n_c \rangle$, due to radial ($n_{\alpha} = r/2$) and angular ($n_{\beta} = 2r - 3$) forces, where *r* represents the coordination number, one obtains the mean count of constraints:

$$\langle n_c \rangle = \langle n_\alpha \rangle + \langle n_\beta \rangle = 5/2 \langle r \rangle - 3$$
 (1)

One finds $\langle n_c \rangle$ to increase linearly with the mean coordination number $\langle r \rangle = (\Sigma n_r r)/N$ of the entire glassy network (where n_r represents the count of atoms possessing a coordination number r, and N is the total number of atoms in the network). The central finding of topological constraint theory (TCT)^{29,30} is that a glass network will display a rigidity transition (RT) when $\langle n_c \rangle = 3$, which occurs when the mean coordination number of a glass network acquires a special value of $\langle r \rangle_{\rm RT} = 2.40$ from Equation (1).

The determination of the elastic origin of the transition has been obtained from the vibrational analysis of bond-depleted random networks constrained by bondbending (BB) and bond-stretching (BS) interactions. It has been found that the number of zero frequency (floppy) modes $f = 3 - \langle n_c \rangle$ (i.e., the eigenmodes of the dynamical matrix, which act as the order parameter of the transition) vanishes when rigidity percolates in the network. The Maxwell–Phillips stability criteria $n_c = n_d = 3$, therefore, define an elastic phase transition, above which redundant constraints produce internally stressed networks, identified with a stressed-rigid phase. Glassy networks possessing a mean count of constraints that is less than three, $\langle n_c \rangle < 3$, form part of a *flexible phase* where local deformations with a low cost in energy are possible,³¹ whereas those with an $\langle n_c \rangle > 3$ form a *stressed-rigid phase*.

The prediction of an RT between the flexible and stressed-rigid phases has continued to stimulate the field of glass science since the early 1980s as both experimental^{5,31,32} and numerical^{33,34} methods were used to examine the nature of this transition.

Beginning in the year 1998, Raman and calorimetric experiments on several families of chalcogenide glasses displayed^{14,35–37} evidence for not only one but two elastic phase transitions, an RT, as predicted, followed by a stress transition (ST) as the mean coordination number $\langle r \rangle$ was increased. Fascinatingly, these findings illustrated the existence of a new phase of disordered condensed matter³⁸ between the flexible and the stressed-rigid phases, an isostatically rigid intermediate phase (IP) between the two elastic phase transitions. Networks in the IP display a set of remarkable properties, such as the absence of network stress as documented directly from pressure Raman scattering experiments.³⁹ This absence of network stress is the result of a network that is self-adapting.⁴⁰ Specifically, IP glass compositions show that the minimal enthalpy of relaxation at T_g induces weak aging effects,^{35,38} a property that improves stability and which is of vital interest in applications of glasses. Topological phases (TPs) and their underlying molecular structures have been probed in a variety of methods. These include diffraction methods,⁴¹ first-principles molecular dynamics (MD) simulations,⁴²⁻⁴⁴ NMR,⁴⁵ Raman scattering,¹⁴ and Mössbauer spectroscopy.⁴⁶ In the past three decades, an AC variant of differential scanning calorimetry (DSC), known as modulated-DSC (MDSC), has proven remarkably useful¹⁴ in tracking the three TPs using the enthalpy of relaxation at the glass transition, ΔH_{nr} . The ΔH_{nr} term in an MDSC experiment provides a direct measure of the open degrees of freedom for a glass network to relax as illustrated in Section 2.3.

1.2 | From mean-field approaches to self-organized networks

In order to account for the experimentally determined double transition, a certain number of scenarios have been proposed to describe the observed behaviors. As a preliminary remark, it is important to emphasize that the Maxwell–Phillips estimate of topological constraints (Equation 1) is of the mean-field type because ensemble-averaged quantities are used and fluctuations are neglected, that is, it is assumed that all atoms of a given type have the same number of constraints and the same coordination number. However, as in ordinary phase transitions, large fluctuations in constraints or in the order parameter (*f*) may be expected close to the critical point $\langle r \rangle_{\text{RT}} = 2.40$.



FIGURE 1 Evidence of a stress-free intermediate phase (IP) from the pebble game analysis. Fraction of sites for isostatically rigid and stressed-rigid percolating clusters in a self-organized network as a function of the network mean coordination number $\langle r \rangle$. The IP that is rigid, but unstressed, exists in these classes of T = 0 models between $\langle r_{c1} \rangle = 2.375 < \langle r \rangle < \langle r_{c2} \rangle = 2.392$ and coalesces in random networks. This generic behavior is also observed from a spring network,⁵⁴ showing regions that are flexible (blue), isostatic (marginally constrained, black), and stressed-rigid (red). *Source*: Pebble game analysis: Adapted from Ref. [4]. Permission from the American Physical Society

Early modifications of TCT have attempted to incorporate fluctuations and non-mean-field effects in the theoretical treatment,^{4,47} which has led to the possibility of the phenomenon responsible for the IP being an isostatic phase (see below) with network adaptation lowering the stress induced by the increasing cross-link density.

There are basically two classes of models that have emerged. Some utilize the role of fluctuations and network self-organization^{4,40,47-49} to predict theoretically a double transition that defines an IP between the flexible and the stressed-rigid phases. These contributions assume that glasses with an increasing cross-linking density will adapt over the select compositional interval during the glass transition in order to avoid stress. Using a graphtheoretical approach, Thorpe et al.,⁴ for instance, used a smart constraint counting algorithm⁵⁰ on simple bar networks at T = 0 to identify the nonlocal characteristics of rigidity. In the case of simulated adaptive networks, the addition of new bonds will be accepted only if this leads to isostatically rigid clusters, so that the emergence of stressed rigidity is delayed upon increasing connectivity. As a result, the network will undergo a series of transitions: percolation of rigidity (an RT at $\langle r_{c1} \rangle$), which first leads to an unstressed isostatic structure (Figure 1), and then percolation of stress at a second transition at r_{c2} . Other approaches have built upon the same idea of network adaptation, using either a spin cavity method⁵¹ or cluster expansions.48,52 Importantly, certain models do not incorporate temperature effects and use infinite energy

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barriers, but these can be included.^{49,53} An important outcome from all of these models is that an increased sensitivity for single bond addition or removal exists close to the IP, and this suggests that the system is maintained in a critical state on the rigid-floppy boundary throughout the IP.

Conversely, mean-field treatments can also lead to an IP. and these are used in the context of jamming transitions. Here, fluctuations in, for example, coordinations or constraints are thought to be limited, but particles are coupled spatially via elasticity. These local rules permit organizations into locally distinct configurations that promote an IP. Using the phenomenology of the elasticity of soft spheres combined with weak noncovalent interactions, it has been found that an IP can result from an interplay between temperature and the relative strength of these weak forces.^{54–56} These mean-field approaches for the IP are also followed by other authors using either a rigidity percolation model on a Bethe lattice,^{57,58} which shows that the IP has a low density of redundant bonds and has, therefore, a low self-stress. The double-transition solution is found to depend on the coordination and the degrees of freedom contrast and might be directly comparable to experiments, although important coordination contrasts do not necessarily correspond to situations encountered in the presently considered chalcogenides.

1.3 | Coupling to molecular dynamics simulations

Heating-cooling cycles as those performed in experiments¹⁴ can be realized from simulations using MD and have substantiated the atomic scale picture of reversibility window (RW) glasses, at least in densified silicates that are known to undergo RTs as well.⁵⁹ MD numerical cycles can, indeed, be performed across the glass transition from a high-temperature liquid leading to a hysteresis curve between the cooling and the heating curves that only overlap at high temperatures and in the glassy state (Figure 2). The hysteresis simply reflects the nonequilibrium nature of glasses that are able to slowly relax at $T < T_g$ and decrease in volume or enthalpy as the glass is heated back to the liquid phase.

As in experiments, for select thermodynamic conditions (here, pressure), the hysteresis becomes minuscule, and the cooling/heating curves nearly overlap, even in the glass transition region.^{44,60} The area ΔH (ΔV) of the enthalpy (volume) vanishes for select pressure intervals (inset of Figure 2A) where the isostatic nature of the network has been independently established from dedicated MD-based constraint counting algorithms (Figure 2B).

These thermal anomalies reveal that the RWs are actually linked with minima in activation energies for diffusion and viscosity,^{61,62} with anomalies in fracture toughness⁶³



FIGURE 2 (A) Volume-temperature dependence during a cooling (blue) and heating (red) cycles for selected pressures in a liquid silicate across the glass transition.⁴⁴ The volumes have been rescaled with respect to their evolution in the glassy state V_{glass} . Curves at 0 and 5 GPa have been shifted by multiples of 0.1. The cycle leads to a hysteresis that is due to structural relaxation but is also controlled by rigidity. The inset shows the hysteresis area of the enthalpic (A_H) and volumetric (A_V , red curve, right axis extracted from the main panel) hysteresis as a function of the applied pressure P, defining a reversibility window (gray zone). (B) Calculated total number of constraints per atom. The horizontal red line represents the isostatic line $n_c = 3$ and separates flexible from stressed rigid networks.

and relaxation time,⁶⁴ and lead to structural signatures in the low wavevector region of the structure factor,⁶⁵ including for the As–Se system (see below⁶⁶).

2 | CALORIMETRY AS A PROBE OF GLASS FUNCTIONALITY

2.1 | The glass transition and enthalpy of relaxation

The glass transition temperature, T_g , and the enthalpy of relaxation at the glass transition, ΔH_{nr} , are two calorimetric observables that have proved invaluable to our understanding of the physical nature of glasses. Both observables are obtained from measurements of the heat flow response of a glass sample when measured in a calorimeter. Using MDSC, the total heat flow response can be separated into a reversing (ergodic) heat flow and non-reversing (non-ergodic) heat flow.⁶⁷ A typical MDSC scan of 10-20 mg sample uses a ramp rate of 3°C/min with a modulation amplitude of $\pm 1^{\circ}$ C every 100 s. For a complete description of the operating parameters used in MDSC, sample preparation, and a procedure for obtaining and analyzing heat flows for the calorimetric results of T_{σ} and ΔH_{nr} , please see the "Supplemental Material I" section. The endotherm that occurs at the glass transition is made up of two observables: (i) a specific heat capacity, C_n , which displays a rounded step in the reversing heat flow, and (ii) the enthalpy of relaxation, ΔH_{nr} , which displays a Gaussian-like peak in the non-reversing heat flow. The inflexion point of the rounded step in $C_n(T)$ is then used to define unambiguously the glass transition temperature T_g . The integrated area under the Gaussian-like peak, ΔH_{nr} , provides a measure of the enthalpy of relaxation and represents the non-ergodic events surrounding the transition. Here we show that ΔH_{nr} also provides a direct measurement of the open degrees of freedom for a glass network to relax. It is also shown that for various chalcogenidebased glasses, select glass compositions have a ΔH_{nr} term that nearly vanishes and allows one to define an RW of structurally isostatic and stress-free compositions.³⁸ Glasses across such compositional windows display a thermal reversibility of the glass transition T_g , which is a unique feature characteristic of self-organized³⁸ networks. These calorimetric results, along with Raman scattering, IR reflectance, NMR, diffraction, and MD simulations, serve to elucidate glass functionality in terms of structural topology and TPs on a molecular scale.

Traditionally, glass transitions have been examined using DSC since the beginning of the early 1960s.^{69,70} More recently though, starting in the late 1990s, a new AC variant of DSC known as MDSC has been introduced by TA Instruments. With MDSC, one is able to impose a sinusoidal temperature modulation onto the traditional linear temperature ramp as used in DSC.⁶⁷ The new information and significant benefits that have been obtained on the nature of glass transition using MDSC can be exemplified by taking the case of the simplest glass, that of pure Se.

2.1.1 | Pure Se glass

Selenium and selenium-based alloys have been significantly studied using DSC^{69,71–77} and also recently with MDSC.^{11,12,14,68,78–80} The observed glass transition event for pure Se glass is illustrated in Figure 3 by both DSC and MDSC methods for both the fresh and aged glasses.¹¹ In both cases, an endotherm is observed to occur at the glass transition temperature, but for the MDSC scan, because of the sinusoidal temperature modulation and phase-sensitive lock-in detection, the endotherm of the



FIGURE 3 Differential scanning calorimetry (DSC) scans of pure Se glass (15 mg) (A) when aged $t_w = 4$ months at 23°C and (B) fresh $t_w = 0$ months using a 10°C/min scan rate. The same Se glass sample was studied with modulated-DSC (MDSC) after being aged (C) $t_w = 4$ months at 23°C using a 1/3°C/min scan rate and (D) in the fresh state $t_w = 0$ months using a 3°C/min scan rate. The modulation amplitude for (C) and (D) was $\pm 1°C$ every 100 s. The total heat flow (THF) in MDSC is similar to the heat flow in DSC, but in MDSC, the THF can be separated into a reversing heat flow (RHF) and a non-reversing heat flow (NHF). One observes a significant narrowing of the width (W) of the glass transition (T_g) event in the RHF from aging by nearly a factor of 5, and a fivefold increase in the enthalpy of relaxation ΔH_{nr} . In MDSC, it is linearly proportional.^{11,68}

total heat flow signal (black) can be deconvoluted into the reversing (red) and non-reversing (blue) heat flow signals (Figure 3C,D) (labeled RHF and NHF, respectively). Examination of the reversing and non-reversing heat flows from MDSC allows one to obtain the glass transition temperature T_g from the location of the inflection point of the step of $C_p(T)$, and the change in enthalpy, ΔH_{nr} , from the integrated area under the Gaussian-peak of the non-reversing heat flow (see Figure 3C,D). The $C_p(T)$ contribution tracks the programed sinusoidal T-variation, whereas the ΔH_{nr} does not.

In DSC, one cannot separate the two signals that make up the glass transition event⁸¹; this creates a significant ambiguity when measuring the glass transition temperatures T_g and ΔH_{nr} . The problem occurs because in DSC, seen in the scans of pure Se (Figure 3A,B), one only observes the total heat flow signal and finds the endothermic heat flow peak shifts from 45.5 to 52.5°C as Se glass ages. In DSC, this shift of the endothermic peak is entirely due to kinetic effects and is caused by the measurement process. The aging of elemental Se and Ge–Se glasses has been previously studied using DSC^{82–84} and the kinetic effects and shift in the endothermic peak of Ge–Se glasses were observed. The shift is created artificially because when one uses a large scan rate of 10°C/min (common Journal

in DSC) to increase signal strength, the glass relaxes at a much lower rate than the impressed scan rate as the enthalpy of relaxation builds up upon aging. As a result, DSC appears to incorrectly imply that the glass transition temperature changes with aging. With MDSC, however, because the total heat flow (black) (Figure 3C,D) can be uniquely deconvoluted into the reversing heat flow (red) and the thermally non-reversing heat flows (blue), the kinetic effects are completely avoided provided one has at least four modulation cycles across the thermal event that permits the phase-sensitive lock-in detection signal to be fast-Fourier analyzed. An MDSC scan can, therefore, be acquired in a quasi-static mode underscoring that the MDSC signals are scan rate independent. The results show that the T_g of 40.5(3)°C of selenium glass remains unchanged upon aging, which is consistent with the theoretical understanding that the T_g is determined largely by the connectivity of the polymeric Se_n chain structure⁸⁵ of the glass. Thus, MDSC solves a previously unresolved conflict between the theoretical and experimental results.

In a pure selenium glass, every Se atom has two nearest neighbors, r = 2, to which it is covalently bonded, and this defines the connectivity of the glass backbone. Thus, two chemical bonding constraints per atom give $n_c = 2$ from Equation (1), leading to one open degree of freedom per atom, $n_f = n_d - n_c = 3 - 2 = 1$, because the chains are part of a 3D network ($n_d = 3$). A fascinating result emerges from the aging experiments; notice that the temperature width of the glass transition, W, decreases nearly fivefold from 7.1°C in the fresh state to 1.5° C upon 4 months of aging the Se glass at 300 K, whereas the ΔH_{nr} saturates¹¹ near 0.90 cal/g. In the MDSC measurements of the fresh Se glass, a scan rate of 3°C/min is used, whereas, for the 4month aged glass as the T_g width narrowed, a lower scan rate of 0.33°C/min was necessary to adequately analyze the heat flow term by Fourier transform (so that four sinusoidal temperature modulations occur within the range of the glass transition). The weakly connected (r = 2) nature of the polymeric Se chains gives rise to a vibrational excitation called the floppy mode excitation,^{30,86} which was recognized in inelastic neutron scattering³¹ and Mössbauer Debye–Waller factor³² measurements. The measured ΔH_{nr} of 0.90 cal/g in the aged Se glass provides a direct measure of that one open degree of freedom in an Se_n chain glass due to a floppy mode, as commented later in Section 2.3.

2.1.2 | Binary $Ge_x Se_{100-x}$ glasses

Alloying group IV (Si, Ge, and Sn) and group V (P, As, and Sb) elements into a base selenium glass increases the overall network connectivity of the glass as the alloyed elements cross-link the long chains of selenium. The

increase in connectivity leads, in general, to profound changes in T_g and ΔH_{nr} . Elastic phase transitions are then observed as the flexible and under-constrained ($n_c < 3$) selenium glass becomes ideally constrained $(n_c = 3)$ and then over-constrained $(n_c > 3)$ as the connectivity or mean coordination number, $\langle r \rangle$, of the glass increases with the amount group IV and group V elements alloyed. The RT from flexible to the ideally constrained network occurs at $\langle r \rangle = 2.28$ and $\langle r \rangle = 2.40$ for group V and group IV modified Se glasses, respectively. For example, upon alloying Ge into a base Se glass, one observes that the polymeric Se_n chains become steadily cross-linked by the fourfold coordinated Ge species. In the $Ge_x Se_{100-x}$ binary, corner-sharing (CS) GeSe4 tetrahedra and edge-sharing (ES) tetrahedra GeSe₂ local structures emerge as observed in Raman scattering.^{13,14} In MDSC measurements, one observes that the ΔH_{nr} steadily decreases with composition, x, over the range 0% < x < 19%, only to abruptly vanish at around x = 20% (see Figures 4 and 5), and then to continue to remain miniscule in the 20.0% < x < 26.0%range, eventually the ΔH_{nr} reappears at x > 27.0%. For Ge_xSe_{1-x} , the increased connectivity of the glass backbone $\langle r \rangle = 4x + 2(1 - x) = 2(1 + x)$ upon Ge alloying, x, leads the glass transition $T_g(x)$ to monotonically increase⁸⁵ from 40°C for pure Se to 425°C near x = 33.3% or GeSe₂, as shown in Figure 5. The square well-like variation of ΔH_{nr} in the 20.0% < x < 26% range represents the RW, as commented further in Section 2.3. It is the signature of the isostatically rigid IP bordered by the RT, x = 20% $(\langle r \rangle = 2.40)$, on the low x end and the ST, x = 26% $(\langle r \rangle = 2.52)$, at the high *x* end.

Experiments show that the square well-like variation of the ΔH_{nr} is only observed in glasses that are dry and homogeneous, that is, glasses in which the variance of Ge, across a 2 g batch composition synthesized, $\langle \Delta x \rangle_{Ge}$, is less than <0.1%. Observing sharp elastic phase transitions and obtaining high-quality samples require special handling of the starting materials in a dry ambient environment and alloying them in evacuated $(2 \times 10^{-7} \text{ Torr})$ quartz tubing at 950°C (for $\text{Ge}_x \text{Se}_{100-x}$) over a period of up to 7-9 days.^{13,14} Glass compositions synthesized by alloying starting material at 950°C for 2 days or less were found to be heterogeneous, ^{15,87} and the Ge variance $\langle \Delta x \rangle_{Ge}$ across such glass samples was found to be larger than $\sim 2\%$, nearly two orders of magnitude greater in heterogeneity, leading the otherwise sharp and percolative variation of the $\Delta H_{nr}(x)$ window to be smeared out and triangular⁸⁷ (Figure 5) with no sharp transitions observed near x = 20% and 26%. Theory predicts the rigidity and ST to be first-order transitions in 3D glasses.⁸⁸ It is understandable that connectivity, which determines the elastic phase transitions, would then be smeared and variable in such heterogeneous glasses. Additionally, trace amounts of water in $\text{Ge}_x \text{Se}_{100-x}$ glasses



FIGURE 4 Modulated-differential scanning calorimetry (MDSC) scans of binary Ge_xSe_{1-x} glass (10–20 mg sample size) at indicated compositions (*x*).¹⁴ (A) x = 10%, (B) x = 19%, (C) x = 20%, (D) x = 33.3%. Each panel shows a total heat flow (green) that has been decomposed into two constituent parts: the reversing (blue) and the non-reversing heat flows (red). All scans include an up cycle (right pointing arrow) where the glass sample is heated 50–75°C above the T_g , and a down cycle (left arrow) where the glass is cooled 50–75°C below the T_g . The T_g is measured from the inflection point of the step in the reversing heat flow. The change in the enthalpy of the non-reversing heat flow, ΔH_{nr} , is obtained from the area under the endotherm ($\Delta H_{nr} = H_{up} - H_{down}$). The modulation parameters used are a ramp rate of 3°C/min and a modulation amplitude of $\pm 1°C$ every 100 s.

are known to lower T_g and increase the ΔH_{nr}^{14} and also to promote homogenization as shown in the Raman work of Bhosle et al.¹⁴. We will comment further in the next section on the FT-Raman profiling method that has been developed to assess homogenization and how it is rou-





FIGURE 5 Modulated-differential scanning calorimetry (MDSC) results for binary $\text{Ge}_x\text{Se}_{100-x}$ glass compositions that show (A) variations in $T_g(x)$ (∇) ¹⁴ and dT_g/dx (∇).⁸⁷ (B) The change in enthalpy of the non-reversing heat flow $\Delta H_{nr}(x)$. Trends in the $\Delta H_{nr}(x)$ of fresh (F) glasses (∇), glasses aged (A₁) for 2 weeks at rigidity transition (RT) (\circ), and glasses aged (A₂) at 240°C for 2 weeks (\Box). Trends in $\Delta H_{nr}(x)$ reported by Feng et al. (\diamond) display a triangular variation with *x* are included for comparison. After homogenizing, the $\Delta H_{nr}(x)$ window appears more square well–like.

tinely used to determine when a glass sample has fully homogenized.

MDSC experiments show that in homogeneous glasses, the melt fragility index, *m*, displays a Gaussian-like minimum of m = 15 near the center of the RW. The superstrong character of IP melts formed in the RW is responsible for the delayed homogenization of all glass compositions. All sulfur-^{36,37,89} and selenium-bearing^{13,14,90–92} chalcogenide glasses, which have been homogenized and studied by FT-Raman profiling over the last decade, have shown the delayed nature of homogenization. In glasses that have been homogenized, the sharply defined RWs are then clearly manifested.

2.2 | Molecular origin of delayed homogenization of chalcogenide glasses

The standard practice of alloying small pellets (3 mm) of group IV and group V elements into a base Se glass is by heating the starting materials in an evacuated quartz tube held near a suitable temperature in the 700–950°C range. However, it has been found that alloying even 2 g sized batches for a period of 1–2 days is insufficient

to generate stoichiometrically homogeneous glasses.^{13,14} For $\text{Ge}_x\text{Se}_{100-x}$, up to 10 days of alloying was needed.^{13,15} We address the molecular origin of this behavior in this section.

Consider, for example, the Ge_xSe_{100-x} glass samples of 2 g batch size, which were encased in evacuated $(2 \times 10^{-7} \text{ Torr})$ 5 mm ID and 7 mm OD quartz tube and alloyed at 950°C for 10 days in a box furnace held vertically.¹³ Starting materials of selenium shot and germanium pieces of 99.999% purity and small 2–3 mm diameter were used and handled in an N₂-flushed glove bag to avoid exposure to laboratory ambient water in the air and exclude any moisture uptake. Once the glasses were synthesized, *all manipulations on the glasses*, such as sealing them in hermetically sealed aluminum pans and lids, were performed in a glove box model, HE-493/MO-5. Hermetically sealed samples were then used for MDSC measurements to establish T_g , ΔH_{nr} , and fragility index, *m*.

For Raman profiling measurements, a Thermo Nicolet NXR FT-Raman module attached to a 900 Research bench was used to establish homogeneity. Raman scattering was excited using 1064 nm radiation from an Nd–YAG laser with a laser spot size of 50 μ m. The instrument has a motor-controlled *x*–*y*–*z* digitized stage that permits the laser light to be focused onto the quartz/glass interface along the quartz tube's diameter. During the alloying process, the samples were periodically removed from the furnace and water quenched. The glass samples, which are 2 cm long glass columns, wet the quartz tube. Raman spectra were taken at several locations along the melt column (Figure 6A), the collected spectra were then overlaid, and this allowed for one to check the stoichiometric variance in Ge concentration (see the inset of Figure 6B).

A typical profiling scan involves taking the spectra acquired at six spot locations or more, and this takes approximately 7 min of accumulation time per spot (200 scans). Once profiling has been performed, the glass sample is heated further in a box furnace to continue the alloying process, and the profiling process is repeated until the Raman lineshapes become identical at various locations, and the glasses can then be declared to be homogeneous. From the observed Raman lineshapes, the glass composition x can be deduced locally by tracking the scattering strength ratio of the CS mode to the Se_n chain mode. Figure 6B provides a result obtained for the x = 23% Ge_xSe_{100-x} sample. The plot provides a quantitative depiction¹⁵ of how the Se moves down and the Ge moves up throughout the melt column of the vertically held quartz tube as the bulk glass homogenizes.

Several features become apparent from the plot of Figure 6B. (i) Between the first and second days of alloying, the variance in Ge concentration across the melt column decreases from 12% to 3%. (ii) In the blue highlighted range



FIGURE 6 Top (A) shows the xyz stage setup on which FT-Raman experiments are performed using the Thermo Nicolet Model iS50. The laser light, 50 μ m spot size, is focused using the z-adjustment onto a sample encapsulated in a guartz tube. The y-adjustment allows for additional spot locations to be examined. Panel (B) shows the variation in stoichiometry (x) for various spots along the melt column,¹⁵ where h represents the height (2.5 mm per spot increment). The different curves show the stoichiometric variance as a function of the reaction time. After 1 day (24 h) of alloying, there is significant stoichiometric variance between the top and bottom of the sample column, and a total of 9 days (216 h) of alloying is needed before the stoichiometry is homogenous throughout the sample. The inset of panel (B) shows the stoichiometric variance of Ge, $\sigma_{\rm x}$ in %, along the melt length column as a function of time. For example, the 23% glass took nearly 200 h to fully homogenize, that is, to obtain a Ge variance of less than 0.1% along the length of the column

of compositions, the alloying process slows down qualitatively, and it further takes another 7 days of alloying for the Ge variance, $\langle \Delta x \rangle_{Ge}$, to decrease from 3% to 0.1% (see inset in Figure 6B). (iii) In the composition range 22% < x < 23%, where the Ge_xSe_{100-x} melt fragility index shows a global minimum of m = 15 (see Section 2.4) (and the viscosity, which is inversely proportional to fragility, is the highest), the melts are seen to take the longest time to homogenize. These results provide direct evidence of the molecular origin of delayed homogenization in chalcogenide melts within the IP range (Figure 5B).

Since 2011, when the phenomenon was first noted in the $\text{Ge}_x\text{Se}_{100-x}$ binary,^{13,14} delayed homogenization has been

observed in all families of chalcogenide glasses that have been studied^{36,37,89–92} to date.

Water impurity doping is known to speed up the kinetics of homogenization but lowers the T_g , lowers the molar volumes, and increases the ΔH_{nr} due to the creation of dangling ends (–OH, –H) that alter the glass structure.^{13,14} The observables, T_g , ΔH_{nr} , molar volumes V_m , and the fragility index *m* have proved to be invaluable for characterizing dry and homogeneous glasses compared to their wet and heterogeneous counterparts, which is further discussed in the Supplemental Material I.

A central result to emerge from homogenization studies performed using the FT-Raman profiling method is that the molar volumes of homogenized glasses are significantly greater than their heterogeneous counterparts. The heterogeneous glasses usually result when large batches (2 g or more) are typically alloyed for 2 days or less at a suitable alloying temperature. This is suggestive that the long-range van der Waals interactions are better developed in the homogenized glasses. This is explicitly discussed for the case of binary $\text{Ge}_x \text{Se}_{100-x}$ glasses^{13,93} in Supplemental Material I. Molar volume results on the $As_x S_{100-x}$ binary show a parallel behavior, namely, that $V_m(x)$ results on the homogenized glasses exceed those on their heterogeneous counterparts⁹⁴ measurably.³⁷. Because these glasses are widely used as optoelectronic materials, it would be of interest to establish the role of glass heterogeneity on device performance.

2.3 | Linking the enthalpy of relaxation at T_g with network topological constraints

The effects of aging on the enthalpy of relaxation of pure Se glass have recently been studied using MDSC as summarized in Figure 7.

The results show that the enthalpy of relaxation ΔH_{nr} of Se glass acquires a saturated value of 0.90 cal/g after 4 months of room temperature aging (Figure 7A). As an Seglass ages at room temperature, Raman scattering shows that a portion of the Se_n chains convert to Se_8 rings, and experiments reveal that after 4 months of aging, 36% of the Se atoms⁹² have become Se₈ rings with the remaining 64% being Se_n chain. As the Se_8 rings decouple from the glass backbone, the ΔH_{nr} term due to polymeric Se_n chains takes on a value of 0.90/0.64 = 1.40 cal/g. The ΔH_{nr} of 1.40 cal/g. in pure Selenium glass translates directly into a vibrational mode of 4.84 meV/atom excitation energy, which is remarkably close to the value obtained from inelastic neutron scattering of 5.0 meV/atom.³¹ Recently, independent confirmation has come from calorimetric results on the binary $P_x Se_{100-x}$ glasses⁹¹ where the enthalpy of relaxation of the decoupled quasi 1D ethylene-like chains of P_2Se_{2+x}



FIGURE 7 (A) Enthalpy of relaxation at the glass transition, $\Delta H_{nr}(x)$, of binary $\operatorname{Ge}_{x}\operatorname{Se}_{100-x}$ glasses¹¹ with Ge concentration *x* in fresh ($t_{w} = 0$), 4-month ($t_{w} = 4$ m), and 8-month ($t_{w} = 8$ m) glasses aged at room temperature (23°C). In pure Se, the ΔH_{nr} saturates at 0.90 cal/g upon aging. In alloyed glasses, the $\Delta H_{nr}(x)$ steadily decreases with *x*% illustrating the open degrees of freedom decreasing upon Ge alloying. (B) The $\Delta H_{nr}(x)$ term in binary $\operatorname{P}_{x}\operatorname{Se}_{100-x}$ glasses⁹¹ was studied as a function of room temperature aging in the $0 < t_{w} < 4w$ range. In the fresh glasses, the reversibility window is manifested. But upon aging, the increase of $\Delta H_{nr}(x)$ as $\langle r \rangle < 2.40$ is identified with the quasi-1D flexible ethylene-like $\operatorname{P}_{2}\operatorname{Se}_{3+x}(0 < x < 2)$ chains that decouple from the main 3D Se backbone with aging. After 4*w* of aging, note the $\Delta H_{nr}(x)$ (•) that linearly scales with the open degrees of freedom (•) as the quasi-1D ethylene-like $\operatorname{P}_{2}\operatorname{Se}_{3+x}$ chains become flexible at $\langle r \rangle < 2.40$.

(x = 3, 2, 1) is found for f = 1 open degree of freedom, to have a value of $\Delta H_{nr} = 1.40$ cal/g (Figure 7B).

These results unequivocally demonstrate that the enthalpy of relaxation at T_g of pure Se glass directly gives the floppy mode excitation energy. As discussed below, the ΔH_{nr} provides a quantitative measure of the open degrees of freedom in a glass network, and the observation of a square well–like RW of stress-free and isostatically rigid compositions is the result of there being no open degrees of freedom for the glass to relax.

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FIGURE 8 Homogeneity of Ge–Se glasses prepared in university laboratories improved from 1996 to 2013, with reduction in the fragility index by >50%. Observed variation in the fragility index (•) using modulated-differential scanning calorimetry (MDSC) for especially homogenized $\text{Ge}_x\text{Se}_{100-x}$ binary melts,¹⁵ and in viscosity measurements (•) by Stølen et al.⁹⁹ and (green triangles) by Senapati et al.¹⁰⁰

2.4 | Linking the enthalpy of relaxation with melt fragility

The enthalpy of relaxation, ΔH_{nr} , is a property of the glass, and the melt fragility index, *m*, is a property of the melt. It is attractive to use MDSC in this context to measure both the enthalpy of relaxation of the glass and the fragility index of the melt. Sample ambiguity is, thus, removed as otherwise, if one were to measure the melt fragility using viscosity (which often requires a larger sample) and glass enthalpy of relaxation using MDSC (which requires a separate small sample), one risk variation in the compositional makeup of the sample inaccurately altering the result.

The fragility index, m(x), of glassy melts can be easilv measured^{14,37,90} using MDSC (see the "Supplemental Material I" section for information about operation parameters, setup, and linearity). This is achieved by recording the complex specific heat, C_p , with the same glass specimen used in Tg measurements. One examines the outof-phase C_p in a T-cool down mode, which shows a peak when one scans across the T_g and allows for the enthalpy relaxation time, τ , to be measured. The isostatically rigid local structures (IRLSs) in the glass and melt close to T_g are expected to be the same. The scans are recorded at several modulation frequencies⁹⁵ to deduce the thermally activated variation of $\tau(T)$, thus fixing the melt fragility index m.^{90,92} The results show a Gaussian-like minimum of fragility index nearly centered⁹⁶ in the IP range of compositions of the $\text{Ge}_x\text{Se}_{100-x}$ (Figure 8). From the fragility index m, one then obtains the activation energy for the enthalpy of relaxation E_a using the following relation:

In binary glasses, there are two IRLSs (see Section 3.1) in the IP; these are the CS and ES structures for Ge_rSe_{100-r} and the quasi-tetrahedral (QT) and pyramidal (PYR) structures for $P_x Se_{100-x}$. In binary glasses, the minimum in m(x) is located near the IP center where both IRLSs contribute, and the fragility index steadily increases at the edges of the IP where flexible or stressed-rigid admix with predominantly one IRLS. These IRLSs also form compacted networks as revealed by observed minima in molar volumes in the IP^{14,37} and possess no open degrees of freedom for the network to relax, thus rendering such melts near the IP center to be superstrong according to the strong-fragile classification⁹⁷ of glass-forming melts. From Adam–Gibbs,⁹⁸ one expects the configurational entropy S_c of a melt as it cools to possess a rather high value near the center of the IP because E_a and S_c are inversely related.^{37,90,92} Specifically,

$$S_c = Bk_B / E_a \tag{3}$$

The maximum of S_c in glasses examined coincides with a minimum in the fragility index composition,⁹⁸ and the finding is in harmony with thermodynamic considerations⁵⁶ that highlight the role of entropy in stabilizing the IP.

In Figure 8, the minimum of the fragility of m = 15 near the center of the IP melt compositions is a pattern that has been noted in other systems³⁷ as well as ternary alloys (see Section 3.1). The low value of m shows melts to be superstrong or in other words highly viscous melts, as also verified from MD simulations (see section 4.2 below).

3 | ISOSTATICALLY RIGID LOCAL STRUCTURES STABILIZE TOPOLOGICAL PHASES AND MELT DYNAMICS OF CHALCOGENIDE GLASSES

3.1 | Group IV and group V chalcogenides

For the group IV selenides or sulfides, the two IRLSs consist of the CS and ES tetrahedra as shown in Figure 9A,B. However, for the group V Selenides or Sulfides, the two IRLSs consist of QT and pyramidal (PYR) units as shown in Figure 9C,D. The mean coordination number, $\langle r \rangle$, of each species is shown in each panel. The count of constraints due to BS and BB forces per atom is 3 in each case, justifying the label IRLS. In both calorimetric and Raman scattering (for both ambient pressure and high pressure) measurements on chalcogenide glasses, one observes compositional thresholds at select compositions corresponding to the connectivity of these IRLSs, under-



FIGURE 9 Isostatically rigid local structures (IRLSs) of group IV (Ge) (green atom) based, (A) corner-sharing (CS) and (B) edge-sharing (ES) units. IRLS of group V (P, As) (red atoms) based, (C) quasi-tetrahedral (QT) and (D) -pyramidal (PYR) units are formed with S or Se (yellow atoms).

scoring the special role played by these local structures in determining glass and melt functionality as illustrated in Sections 3.2 and 3.3.

3.2 | Topological phases and melt dynamics of binary glasses

3.2.1 | Flexible phase

We will first consider the case of the Ge_xSe_{100-x} binary glass system. As Ge is progressively alloyed into a base Se glass, *isostatically rigid* CS GeSe₄ tetrahedral units (Figure 9A) form followed by *isostatically rigid* ES tetrahedral units (Figure 9B) in which Ge is fourfold coordinated as confirmed in Raman scattering¹⁴ and in firstprinciples MD simulations.¹⁰¹ The mean coordination number of the alloyed Ge_xSe_{1-x} glass steadily increases as $\langle r \rangle = 4x + 2(1 - x) = 2(1 + x)$, with the count of available open degrees of freedom, $f = 3 - n_c$, steadily decreasing with *x*, and eventually at x = 0.20, the number of open degrees of freedom, $f = 3 - n_c = 6 - 5(1 + x) = 0$, is found to vanish. The sharp kink observed in the ΔH_{nr} defines the calorimetric signature of onset rigidity near x = 0.20 or 20 mol% of Ge (Figure 5B). These results show that in the flexible phase of the $\text{Ge}_x\text{Se}_{100-x}$ binary, the nonzero ΔH_{nr} term results from the degree of freedom available from the floppy modes.

A parallel circumstance occurs at the onset of rigidity in As_xS_{100-x} binary glasses but with an important difference. Here, the two *isostatically rigid local structures* include the As-centered QT and pyramidal (PYR) units (Figure 9C,D). The As-centered QT has a terminal S neighbor (a dangling end) (Figure 9C), and so one must use the more general¹⁰² form to enumerate constraints for the onset of rigidity,

$$\langle r \rangle = 2.40 - 0.4 \, (n_1/N)$$
 (4)

where n_1/N represents the fraction of onefold coordinated atoms in the network. For As QT units, one selenium is dangling $n_1 = 1$, and the total number of connected atoms is N = 3.5, leading the rigidity to onset at $\langle r \rangle = 2.40 - 0.4(1/3.5) = 2.285$, corresponding to the RT observed at $\langle r \rangle = 2.28$. Observation of the As QT was first detected in Raman scattering³⁷ recently when a dedicated effort to homogenize the binary $As_x S_{100-x}$ melts was made. The presence of these structural units is acknowledged in corresponding P-based chalcogenides¹⁰³ and has recently received support from ab initio simulations with specific signatures in the infrared spectra at large wavenumber.¹⁰⁴

3.2.2 | Intermediate phase

As predicted from the phenomenological models (Figure 1), networks possessing a constraint number $n_c > 3$, in general, can be expected to be stressed-rigid as the network accumulates more stress and the mean coordination number $\langle r \rangle$ exceeds $\langle r \rangle_{rigid}$. Further, if there are two or more IRLSs present in the glass network, there are several channels for network self-organization or adaptation^{35,40} forming the IP, causing network stress to disappear,^{4,105} as demonstrated independently from pressure Raman measurements,³⁹ and proposed from the various non-mean-field models. Thus, in addition to a rigidity transition $(\langle r \rangle_r)$, one also observes, as predicted, a second transition, a stress transition ($\langle r \rangle_s$), as illustrated for the two binary glass systems $As_x S_{100-x}$ and $Ge_x Se_{100-x}$ (Figure 10C). In these calorimetric measurements, the vanishing ΔH_{nr} term in the IP of $\text{Ge}_x\text{Se}_{100-x}$ glasses in the 2.40 $<\langle r \rangle <$ 2.54 range directly confirms that the two IRLSs, that is, CS and ES tetrahedra (Figure 9A,B), are formed in the IP.47 These IRLSs possess no open degree of freedom, thus leading ΔH_{nr} term to vanish. Further, because these networks are stress-free,³⁹ the ΔH_{nr} term remains minuscule upon aging as observed in experiments.37,90,92



FIGURE 10 Compositional trends in (A) the residual configurational entropy, S_c , (B) melt fragility index, *m*, and (C) the enthalpy of relaxation at T_g , ΔH_{nr} , in freshly synthesized binary $\text{Ge}_x \text{Se}_{100-x}$, ¹⁴ and $\text{As}_x \text{S}_{100-x}$, ³⁷ glasses. The data is from samples that have not been aged. The intermediate phase (IP) is localized in the 2.23 < $\langle r \rangle$ < 2.29 range for the $\text{As}_x \text{S}_{100-x}$ binary and in the 2.40 < $\langle r \rangle$ < 2.52 range for $\text{Ge}_x \text{Se}_{100-x}$ glasses. Symbols A, B, and C represent the three phase transitions in $\text{Ge}_x \text{Se}_{100-x}$ glasses. Also see Figure 11.

3.2.3 | Stressed-rigid phase

In binary $\text{Ge}_x \text{Se}_{100-x}$ glasses, as $\langle r \rangle$ exceeds the ST $\langle r \rangle_{\text{stress}} = 2.52$ (at x = 26%), pressure Raman experiments³⁹ confirm that network stress accumulates a result that is compatible with the abrupt increase of n_c for highly connected networks obtained from molecular simulations (Figure 2B) or from toy models (Figure 1). In addition, one also observes experimentally a power-law variation in the

blueshift of the Raman vibrational modes of the Ge CS and ES local structures¹⁴ in ambient pressure Raman scattering. The increase of ΔH_{nr} in the stressed-rigid phase (Figure 10C) is explained as follows: Ge-centered CS tetrahedra with coordination number r = 4 possess two BS (r/2 = 2) constraints and five BB or angular constraints (2r - 3 = 5), with the bond-angle ϑ near 109° for a tetrahedron. The BS constraints are about three times stronger than the BB ones. At x > 26%, when $n_c > 3$ and as network stress grows,³⁹ some of the weaker BB constraints soften, whereas the stronger BS constraints sustain the structure, and this leads to an increased bending motion that induces increased second moments (bond-angle variance) for the corresponding bond angle distributions. This assumption has been confirmed from molecular simulations,^{106,107} as discussed below. An increased bond-angle variance, $\sigma(\vartheta)$, leads the linewidth, Γ , of the symmetric stretch CS mode in Raman scattering¹⁴ to show an increased width. In Figure 11, the observed variation of the linewidth of the CS mode $\Gamma_{CS}(x)$ leads to the evidence of three distinct transitions. They are (i) the RT (A) near x = 20%, (ii) the ST (B) near x = 26%, and (iii) nanoscale phase separation (NSPS) transition (C) near x = 31.5%. We, therefore, view the broken BB constraints as the opening of a new degree of freedom for the glass to relax, which leads the ΔH_{nr} term to steadily increase as $\langle r \rangle$ exceeds the ST $\langle r \rangle_{\text{stress}} = 2.54$ (Figure 10C). Then, at x = 31.5%, the $\Delta H_{nr}(x)$ shows a spike, which is evidence that the fully polymerized network prevailing below x < 31.5% has NSPS into two partially polymerized clusters, one Ge-rich and the other Se-rich.^{14,46} One, thus, understands the global variation of the $\Delta H_{nr}(x)$ (Figure 10C) and the square well-like RWs. The first-order nature of the two elastic phase transitions near $\langle r \rangle_{rigid}$, and $\langle r \rangle_{stress}$, which are percolative in nature, leads to abrupt changes (kinks) in the ΔH_{nr} values near the rigidity and stress transitions in glasses, provided the glasses are dry and homogeneous, which can be seen for both the $As_x S_{100-x}^{37}$ and the $Ge_x Se_{100-x}$ binaries¹⁴ (Figure 10C). In the RW's center, one has two IRLSs consisting of As-centered QT and PYR (Figure 9C,D), for the $As_x S_{100-x}$ binary, and the Ge-centered CS and ES tetrahedra (Figure 9A,B), for $Ge_x Se_{100-x}$, leading the nature of the glass transition to become thermally reversing because the endotherm of the non-reversing part of the heat flow at T_g (from which the ΔH_{nr} is derived) vanishes.

3.2.4 | Fragility of strong melts (m = 15)

It is useful to mention that the minimum fragility index of m = 15 observed at the IP center composition (Figure 10B) in both the As–S and Ge–Se melts is fully consistent with



FIGURE 11 (A) Observed compositional variation of the linewidth $\Gamma_{CS}(x)$ of the Raman Ge-corner-sharing (CS) mode in $\text{Ge}_x\text{Se}_{100-x}$ glasses¹⁴ reveals three thresholds: (A) rigidity transition at x = 20.0%, (B) stress transition at x = 26.0%, and (C) nanoscale phase separation (NSPS) transition at x = 31.5%. (B) Variance of the six Se–Ge–Se bond angles in CS GeSe₄ tetrahedra deduced from molecular dynamic (MD) simulation.¹⁰⁷ GeSe₄ tetrahedra have six bond angles centered around the Ge atom (0) with four Se neighbors 1, 2, 3, 4. MD simulations show the angular deviation for three of the bond angles 104, 204, 304 increase and that the constraints soften, whereas the angular spread of the other three bond angles 102, 103, 203 remain intact. The broken angular constraints in the stressed-rigid phase account for the observed broadening of the CS mode.

the lowest fragility index observed in glasses as guided by the recent viscosity results on more than 200 modified oxide glass compositions examined at Corning,¹⁰⁸ which reveal that the viscosity η varies from a maximum value of 10^{12} Pa s at T_g to $\eta_{\infty} = 10^{-3}$ Pa s at high-*T*. The minimum slope $m = \left[\frac{d(\log \eta)}{d(\frac{T_g}{T})}\right]_{T \to T_g}$ then yields a fragility index of m = 15.

A parallel circumstance occurs in oxide glasses as discussed for the case of the $(Na_2O)_x(P_2O_5)_{1-x}$ ultraphosphates elsewhere.¹⁰⁹ After a dozen of attempts to synthesize one of the most hygroscopic P_2O_5 base glass materials to obtain the driest form, it was found that the

variation of T_g with ΔH_{nr} had a remarkable correlation. As the base P₂O₅ glass synthesis yielded a steady dryer glass, one found that the ΔH_{nr} steadily decreased as the T_g steadily increased. For the driest glass, it was found that the ΔH_{nr} vanished, and the T_g acquired a maximum value of 435(2)°C. The structure of the base P₂O₅ glass is viewed to consist of QT P atoms bonded to three bridging and one terminal O atom. The structure is isostatic, $n_c = 3$, and one expects the enthalpy of relaxation to, therefore, vanish, thus confirming that the nature of the driest sample synthesized had to be the sample with a vanishing term. Remarkably, the fragility index of the driest glass was then measured,¹⁰⁹ and a value close to m = 15 was observed.

Further perusal of the calorimetric results on the ultraphosphates $(Na_2O)_x(P_2O_5)_{1-x}$ revealed the existence of three TPs, with the IP occurring in the 37.6% < x < 46.0% range.¹⁰⁹ Measurements of melt fragility index revealed a minimum value of 15 in the IP. These results are reassuring that the minimum fragility index in network glasses is near 15. These glassy melts represent the strongest melts largely because of the isostatic character of the local structures that comprise the IP.

3.3 | Topological phases and melt dynamics of ternary glasses

The TPs and melt dynamics of the two binary chalcogenide glasses (As_xS_{100-x} and Ge_xSe_{100-x}) (Figure 10B,C) suggest that if one were to examine an equimolar ternary glass alloy made from a group V (As or P) with a group IV (Ge) chalcogenide (S or Se), one would expect to observe a much wider IP because the group V (As, P) selenide forms two IRLSs (QT, PYR) in the 2.28 $\langle r \rangle < 2.40$ range (Figure 10C), whereas the group IV (Ge) selenide forms two more IRLSs (CS and ES) at higher network connectivity in the $2.40 < \langle r \rangle < 2.54$ range (Figure 10C). The increased range in which IRLSs form results in a much wider IP spanning the 2.28 $\langle r \rangle <$ 2.54 range (Figure 12C), and this result has been directly confirmed in the equimolar ternary glass sys*tems* of the $\text{Ge}_x \text{As}_x \text{Se}_{100-2x}^{90}$ and $\text{Ge}_x P_x \text{Se}_{100-2x}^{92}$ where the IP-width span the 2.28 $\langle r \rangle <$ 2.54, nearly twice as wide as seen in corresponding binary glasses as illustrated in Figure 12C.

In these alloys, the comprehensively examined Raman scattering^{90,92} results directly reveal the existence of the four expected IRLSs (Figure 9A–D) by their normal modes. Here one cannot overemphasize the role played by the four IRLSs, two at the center near $\langle r \rangle = 2.40$ and one at each of the edges near $\langle r \rangle = 2.28$ and near $\langle r \rangle = 2.54$, which lead not only to the formation of a self-organized and self-adapted³⁵ IP glass phase but also to a fragility index minima localized



FIGURE 12 Observed variation of (A) the residual melt configurational entropy, S_c , (B) the melt fragility index, *m*, and (C) the enthalpy of relaxation at T_g , $\Delta H_{nr}(x)$, in freshly synthesized equimolar $\text{Ge}_x \text{As}_x \text{Se}_{100-2x}^{90}$ and $\text{Ge}_x P_x \text{Se}_{100-2x}^{92}$ ternary glasses deduced from modulated-differential scanning calorimetry (MDSC) experiments. The data is from samples that have not been aged. The square well–like reversibility windows in (C) define the intermediate phases (IPs) (blue panels). In (B), the *m* reaches a minimum of 7.7 in the $P_x \text{Se}_{100-x}$ binary glasses.⁹¹

near the IP center (Figure 12B). Because the melt fragility index, m, is measured only a few degrees above T_g , one expects the IRLSs in the melt and glass to be similar. In the melt, the IRLSs track fragility through diffusion and

functionally serve as "*strong entities*" because the "structures" have *no open degrees of freedom to relax*, fill space compactly,¹⁴ and are most populated near the IP center. Toward the edges of the IP, the flexible and stressed-rigid local structures admix with the IRLSs to drive the melts fragile as supported here in both binary (Figure 10B) and ternary (Figure 12B) melts.

There are several new features of glass structure recently observed in the $\text{Ge}_x P_x \text{Se}_{100-2x}$ ternary⁹² and $P_x \text{Se}_{100-x}$ binary⁹¹ that have shed new light onto melt dynamics and deserve special mention. The strong Pauling single-bond-strength of the P–P bonds (51.3 kcal/mol) serves to nucleate quasi-1D ethylene-like $P_2 \text{Se}_{2+x}$ (x = 0, 1, 2, 3) chains in P-bearing glasses. The chains decouple from the main 3D glass backbone formed in both the $\text{Ge}_x P_x \text{Se}_{100-2x}$ ternary⁹² and $P_x \text{Se}_{100-x}$ binary.⁹¹ Further, near $\langle r \rangle = 2.40$, the IP center of the $\text{Ge}_x P_x \text{Se}_{100-2x}$ ternary, chains of IRLSs⁹¹ of P_2Se_3 form serving as superstrong local structures in the melts. It is for this reason that the observed m = 17.0 near the IP center found in the $\text{Ge}_x \text{As}_x \text{Se}_{100-2x}$ ternary⁹⁰ decreases to a value of m = 14.0 in the IP center of the $\text{Ge}_x P_x \text{Se}_{100-2x}$ ternary.⁹²

Furthermore, in the case of the $P_x Se_{100-x}$ binary,⁹¹ an entirely new structural feature manifests in that the 3D backbone comprises not only PYR and QT local structures but also their three-membered ring counterparts.⁹¹ Our experiments show that the presence of *superstructures formed from three-membered rings of isostatic QT and PYR units* in $P_x Se_{100-x}$ glasses significantly lower melt diffusion near the IP center as evidenced by the fragility index *m* plummeting to 7.7 (Figure 12B).

Glassy networks, in general, exist under a finite residual pressure (P_r) that varies with network connectivity $\langle r \rangle$, as revealed in pressure Raman experiments.^{39,110} Here, P_r represents the residual pressure in a glass network that exceeds ambient pressure and provides a quantitative measure of the network stress in a glass.³⁹ When glasses are subjected to an external $P > P_r$, vibrational modes typically blueshift as they do in crystalline solids^{110,111} at P = 0. Interestingly, P_r vanishes³⁹ in the IP but then abruptly reappears in both the stressed-rigid and flexible phases and increases by an order of magnitude as one leaves the IP.39 Remarkably, these trends in P_r track those in the enthalpy ΔH_{nr} term,³⁹ underscoring that both features originate from the presence of the open degrees of freedom prevailing in the two non-IP phases. One can, thus, reconcile the aging of the enthalpy ΔH_{nr} in the flexible and stressedrigid phases but its near absence in the IP.^{14,37,90-92} The vanishing of P_r in the IP leads to a substantial reduction of aging due to the absence of network stress, which is a feature that one broadly associates with crystalline networks.111

4 | INSIGHTS FROM MOLECULAR DYNAMICS SIMULATIONS

4.1 | Model structures of chalcogenides

A convenient means to determine the constraint density n_c under various thermodynamic conditions (x, T, and P) builds on MD simulations. Although classical MD that uses the solution of Newton's equation of motion can be safely used in oxides glasses, there has been a general failure in using the same approaches for chalcogenides and, specifically, for selenides. Therefore, one has to rely on First Principles (FPMD) using, for example, the Car–Parrinello scheme¹¹² in combination with densityfunctional theory (DFT), in order to treat appropriately the covalent bonding and charge transfer between atoms. As a result, most classical MD simulations do not correctly reproduce the local structure of Se-based glasses¹¹³ (see Figure 14).

The correct electronic DFT scheme uses generalized gradient approximations¹¹⁴ that permit one to obtain the first sharp diffraction peak in the structure factor, and also an exchange–correlation function that does not overestimate the metallic character of the bonding¹¹⁵ is used. In most simulations performed on Se-based glasses, exchange energy obtained by Becke and the correlation energy according to Lee, Yang, and Parr^{116,117} were used. Together, these permit an explicit treatment of the valence electrons and norm-conserving pseudopotentials of the Troullier– Martins type to account for core-valence interactions and lead successfully to reproduce structure functions accessed from neutron or X-ray scattering (Figures 13 and 14). These considerations work for both the glassy and in the liquid state, and for different system sizes.^{96,106,118}

Specifically, these DFT modeling schemes permit one to fully reproduce the different structural features detected in, for example, Ge-Se glasses at short distance, that is, one obtains three typical distances in GeSe₂ (Figure 14A) at 2.44, 3.03, and 3.68 A that correspond to the homopolar Ge-Ge bond part of an ethylene-like unit, to the ES (Figure 9B) and CS (Figure 9A) tetrahedral connections, respectively. These are detected thanks to isotopic substituted neutron diffraction in GeSe₂¹¹⁹ and GeSe₃.¹²⁰ The presence of homopolar Ge-Ge in the latter composition continues to be debated as simulations predict a nonzero fraction of them,¹⁰⁶ whereas neutron diffraction does not acknowledge such structural defects. The presence of homopolar As-As is also detected in As-Se glasses¹²¹ for which the DFT model accurately reproduced the measured total (Figure 14C) and partial pair correlation function (Figure 14B). Interestingly, such homopolar defects do appear at compositions belonging to the IP.⁶⁶



FIGURE 13 Interference function I(k) of $Ge_x Se_{1-x}$ glasses (A) and liquids (B) are calculated for different compositions (red¹²²), and experimental results from neutron scattering (blue) for glassy^{123–125} and liquid Ge–Se are compared.^{119,126}

4.2 | Dynamic anomalies

The structural models for binary $Ge_x Se_{100-x}$ glasses^{96,106} validated by neutron scattering (Figures 13 and 14) have been used to obtain diffusivities in the liquid at different temperatures using the long-time limit of calculated mean-square displacement accessed from first-principles MD simulations (Figure 15A).^{96,122} At a global level, one expects diffusivities to decrease with cross-link density in a regular liquid, but here one finds that the Ge diffusivities $(D_{Ge} \text{ red data points}, D_{Se} \text{ blue data points})$ show a striking global minimum near x = 22%, about a factor 2–3 less with respect to what would be expected from a smooth decrease of D_{Se} (broken line), which is consistent with the stiffening of the network structure. This minimum is correlated with a minimum for the corresponding jump probability for the atoms (inset of Figure 15A) revealing that the atomic motion will be substantially reduced for this particular interval in composition.¹²² The anomalous decrease



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FIGURE 14 (A) Calculated partial pair correlation functions $g_{ii}(r)$ (blue) of amorphous GeSe₂, compared to experiments (red¹¹⁹); (B) calculated partial differential pair distribution functions $\Delta_{Asg}(r)$ and $\Delta_{\text{Seg}}(r)$ (solid lines) in amorphous As₂Se₃, compared to experimental data (circles¹²⁷) obtained from anomalous X-ray scattering; (C) calculated total pair correlation function g(r) for amorphous GeSe₂ and As₂Se₃, and compared to experimental data (circles^{128,129}). The red curve is the result from a classical force field.113

of diffusivities is also consistent with the large increase in the relaxation time (Figure 15B) that is accessed from the long-time decay of density-density correlations and parallels the one obtained from a calculated viscosity using the Eyring equation $\eta = k_B T/6\pi RD$, where D is the calculated diffusivity and R is related to the liquid density ρ via $R = 0.5 \rho^{-1/3}$.

The question of dynamic anomalies that are linked with the presence of the IP is not restricted to Ge-Se liquids as such behaviors have been also calculated for As-Se liquids,^{66,130} which exhibit a maximum for diffusivity at compositions belonging to the IP, in conjunction with minima in activation barriers for atomic motion. Once ternary liquids are being considered (As-Ge-Se and As-Ge-S), these extrema detected in the related binaries vanish, and instead, a simple threshold behavior is obtained at the flexible-to-rigid boundary of the IP^{89,90} that also leads to a dramatic increase of D for chalcogen-rich systems.

These different numerical studies clearly indicate that the IP contains obvious dynamic features that manifest in extrema in a certain number of calculated properties and echo experimental results on fragility at the glass transition (Figures 10B and 12B). It is, therefore, tempting to conjecture that the topology of the underlying phases existing at low temperatures leads to remarkable kinetic effects once the phase space of the system can be explored starting from the glass transition region and up to the liquid state.



FIGURE 15 Dynamic anomalies in the intermediate phase (IP) for $Ge_x Se_{1-x}$ glasses obtained from molecular dynamics simulations: (A) calculated Ge and Se diffusivities as a function of Ge content in a 1050 K liquid.⁹⁶ The inset shows the jump probability that an atom has hopped by a distance of about 3 A within 25 ps¹²²; (B) calculated Eyring viscosity (blue) and relaxation time (red, right axis) as a function of Ge content in 1050 K liquids. The gray zones indicate the location of the IP (see Figure 10).

4.3 **Constraint count**

The link with the rigidity status of the simulated glasses is provided by MD-based constraint counting algorithms^{107,131} that enumerate radial and angular constraints from the atomic-scale time-dependent motion during the MD trajectory. To determine the number of radial interactions, one focuses on neighbor distribution functions⁴² around a given atom *i*, the global sum of all such functions yielding an i-centered pair correlation function $g_i(r)$ (Figure 14), the integration of which up to the first minimum gives the coordination numbers r_i and, hence, the corresponding number of BS constraints $n_c^{BS} = r_i/2$. An analysis on As₂Se₃¹²¹ or Ge-S glasses¹³² shows that three (1.5 BS constraints) and four neighbors (two constraints) contribute to the rigidity of As and Ge atoms, respectively.

To determine BB constraints, partial bond angle distributions are used, and these split the usual bond angle distribution into partial contributions defined by a central



FIGURE 16 Calculated constraint density in different chalcogenide glasses as a function of network mean coordination number $\langle r \rangle$: glassy (blue boxes) and liquid (blue triangles⁹⁶) Ge–Se, glassy Ge–S (red¹³²), and amorphous Ge–Sb–Te (black boxes¹³⁴). The broken line represents the mean-field constraint count $n_c = 2+5 \langle r \rangle/2$.²⁹ The red horizontal line corresponds to the isostatic criterion and serves to identify intermediate phase (IP) compositions.

atom 0 and the *N* first neighbors that define individual N(N - 1)/2 possible triplets or angles, and these are followed with time over the MD trajectory. The standard deviation of each distribution individual gives a quantitative estimate of the angular excursion around a mean angular value and provides an indication of the BB interaction strength. Small angular excursions (standard deviations) correspond to an intact BB constraint that maintains a rigid angle at a fixed value, whereas large values correspond to a BB weakness giving rise to an ineffective or *broken* constraint.¹⁰⁷

Figure 16 represents the calculated total constraint density for different network chalcogenides as a function of the network mean coordination number $\langle r \rangle$. In group IV chalcogenide glasses, one acknowledges a numerical estimate of the constraint density n_c that closely follows the mean-field estimate of Phillips and Thorpe²⁹ (broken line) except for chalcogen-poor compositions (e.g., Ge₄₀S₆₀) for which a reduction of n_c results from a softening of bending interactions (Figure 11B) under the stress induced by cross-linking Ge,^{107,132} as is also observed in pressurized chalcogenides.¹³³

It is important to emphasize that systems with a more loose connectedness or a partial breakdown of the octet (8-N) rule (e.g., Ge–Sb–Te in Figure 16) can be also investigated using such MD-based constraint counting algorithms^{134,135} so that the identified isostatic criterion provides a hint for optimal glass-forming range. Interestingly, the IP region ($\langle r \rangle \approx 2.4$) covering isostatic compositions in Ge–Se manifests by a weak dependence of n_c with temperature⁹⁶ that also serves to relate the weak dependence of topological degrees of freedom $3 - n_c$ with the weak dependence of liquid viscosity,¹⁰⁸ that is, a minimum in fragility. This picture of isostatic glass-forming liquids being strong glass formers⁹⁶ is globally consistent with the systematic experimental observation of a fragility minimum in the IP (Figure 12B).

5 | SOLITARY, NANOSCALE, AND MACROSCOPICALLY PHASE SEPARATED CHALCOGENIDE GLASSES

As mentioned previously (Figure 9), chalcogenide glasses display a rich structural variety of morphology that leads to a remarkable and diverse set of functionalities. Many of these traits have been decoded by calorimetry, Raman scattering, and Mössbauer spectroscopy and are theoretically supported through MD simulations. Three examples of phase separation are now illustrated. The first case involves little to no phase separation as in the case of the 3D-glass backbone of the $Ge_x P_x Se_{100-2x}$ and $Ge_x As_x Se_{100-2x}$ ternary glasses near the chemical threshold. The second case will be of the binary $Ge_x Se_{100-x}$ glass system wherein two quite distinct structural transitions occur,¹³⁸ the first below and the other at the chemical threshold of x = 1/3 (which is x = 33% when $\langle r \rangle = 2.67$). Finally, the third example will be of glass systems such as the $P_x Se_{100-x}$ wherein two distinct backbones appear, first a 3D backbone and then a 1D backbone completely decoupled from each other and the remarkable set of structural anomalies that manifest as a result.

5.1 | 3D solitary glass network structure of equimolar ternary glasses

The first case is that of glasses where there is no significant evidence of phase separation at the chemical threshold, such as in the Si_xSe_{100-x}, binary³⁵ or the Ge_xP_xSe_{100-x} and Ge_xAs_xSe_{100-x} ternaries.^{90,92} The signature of there being no phase separation is that the glass transition temperature, T_g , increases monotonically with the composition and does not display a threshold (i.e., a maximum) behavior. This is in sharp contrast to the appearance of NSPS observed in the stoichiometric binary Ge_xSe_{100-x} and As_xSe_{100-x} glasses where a T_g maximum occurs¹³⁸ at the chemical threshold. In the equimolar Ge_xP_xSe_{100-2x} and Ge_xAs_xSe_{100-2x} ternary glasses, the phase separation near the chemical threshold (x = 18.18%) is qualitatively suppressed, and the glasses form a single 3D solitary glass network backbone over a large range of compositions 0 < x < 22%. Only at higher stressed-rigid compositions, x > 22%, does one observe a region of NSPS in the ΔH_{nr} of the Ge_xP_xSe_{100-2x} where the molecular cages of P₄Se₃ separate and isolate from base selenium glass backbone. The NSPS then leads to a deviation of T_g from linearity. For these reasons, the equimolar ternary systems are ideal glass systems for exploring connectivityrelated elastic phase transitions due to the absence of NSPS effects.^{89,90,92,139}

5.2 | Nanoscale phase separation of binary $\text{Ge}_x\text{Se}_{100-x}$ glasses near x = 31.5%

The $Ge_x Se_{100-x}$ binary glass system has been extensively investigated over the past five decades. In 2011, the three distinct TPs of flexible, intermediate, and stressed-rigid were observed for carefully homogenized glasses.^{13,14} In the stressed-rigid phase, and particularly, in the 26% < x < 31.5% range, the network backbone is viewed as composed of CS and ES tetrahedra that crosslink Se-chain fragments that steadily increase with Ge content, until near x = 31.5%, when a new feature appears. Raman scattering shows evidence of vibrational modes of $Ge_2(Se_{1/2})_6$ ethane-like local structure manifests that isolate and break away from the base glass network of Ge cross-linked selenium chains. As a result, the slope of the glass transition as a function of composition, dT_{g}/dx , no longer increases, shows a maximum, and then begins to decrease.

If one recalls the theoretical interpretation of the glass transition T_g being a measure of the network connectivity,85 then these features are consistent with the understanding that the Ge-Ge homopolar bonds are forming in a separate nanophase that is decoupled from the main backbone, thus lowering the overall network connectivity, and the T_g is observed to saturate as $\langle r \rangle$ approaches the chemical threshold near $\langle r_t \rangle = 2.67$. In Figure 17, the deviation of the T_g of the $\text{Ge}_x \text{Se}_{100-x}$ from the theoretically predicted T_g of SAT model for $\text{Ge}_x\text{Se}_{100-x}$ is due because the SAT model does not take into consideration the existence of homopolar Ge–Ge bonds. Thus, as x increases to 33.3%, one expects and indeed observes the stoichiometric GeSe₂ glass to possess a finite broken chemical order documented from diffraction experiments^{128,140} and both ¹¹⁹Sn absorption and ¹²⁹I Emission Mössbauer spectroscopy⁴⁶ experiments. The presence of the NSPS leads to (i) lightinduced photo-structural reconstruction of the pristine GeSe₂ glass in Raman scattering experiments,¹⁴¹ and, as stated, to (ii) the $T_g(x)$ to show a local maximum at the



FIGURE 17 Glass transition temperature T_g plotted as a function of mean coordination number $\langle r \rangle$ for (A) the $P_x Se_{100-x}$ binary^{91,136} and equimolar $Ge_x P_x Se_{100-x}$, ternary⁹², and (B) the $As_x Se_{100-x}$ binary¹⁰³ and $Ge_x As_x Se_{100-x}$, ternary,⁹⁰ with both panels compared to the $Ge_x Se_{100-x}$ binary^{14,137} and SAT model⁸⁵ for $Ge_x Se_{100-x}$. The T_g is observed to increase with connectivity,⁸⁵ and the deviation from the SAT model in the $Ge_x Se_{100-x}$ results due to phase separation caused by homopolar Ge–Ge bonds. For the $Ge_x Se_{100-x}$ and $As_x Se_{100-x}$ binaries, the T_g maximizes as one expects at the chemical threshold.

chemical threshold, and also (iii) to the optical bandgap to show a maximum at the chemical threshold. These NSPS effects are absent in the Si_xSe_{100-x} binary glasses in which T_g continues to increase with x near the chemical composition SiSe₂, and none of the three effects (i)–(iii) are manifested.

5.3 | Observation of three-membered pyramidal and quasi-tetrahedral local structures and evidence of macroscopic phase separation of $P_x Se_{100-x}$ glasses

Phosphorus forms select local structures with selenium that include $P(Se_{1/2})_3$ pyramids (Figure 9C), Se- $P(Se_{1/2})_3$

QT units (Figure 9D), and ethylene-like $P_2(Se_{1/2})_4$ units. In a recent study of binary P_xSe_{100-x} , where a deliberate attempt to synthesize homogeneous glasses and melts⁹¹ was made, Raman scattering revealed two rather welldefined vibrational features in the 200–225 cm⁻¹ range that could be identified with the presence of three-membered rings of pyramidal $[P(Se_{1/2})_3]_3$ and separately QT [Se- $P(Se_{1/2})_3]_3$ superstructures. Remarkably, the concentration of both these two superstructural rings showed a local maximum near x = 15%, which far exceeded the concentration of single PYR and QT units cross-linking the polymeric Se_n chains. These local structural species define the main 3D backbone of the P_xSe_{100-x} binary formed in the 0 < x < 40%range of P.

Because the average stoichiometry of a pair of threemembered PYR and QT rings together is close to PSe₂, the concentration in the base Se glass at x = 15%, which shows a local maximum, represents strong evidence of P-rich regions immersed in an Se_n chain glass. These structural features⁹¹ display a rather striking eutectic at x = 15% accompanied by a fragility anomaly at x = 15%. Fragility index measurements show a local minimum near the same composition of x = 15%, underscoring⁹¹ that melt viscosities take a pronounced jump due to these superstructural rings are manifested in an Se_n-rich glass hindering the melt diffusive flow. Three-membered ring configurations have similarly been observed and were first noted in a planar ring of B_2O_3 glass.¹⁴² The present finding on $P_x Se_{100-x}$ glass, to the best of our knowledge, represents the first example of three-membered rings formed in a chalcogenide glass.

Both the $P_x Se_{100-x}$ and $As_x Se_{100-x}$ binaries possess the same chemical threshold of $\langle r \rangle = 2.40$. The glass transition temperature T_g of the As_xSe_{100-x} binary maximizes at the chemical threshold (Figure 17B). A key structural feature of the $P_x Se_{100-x}$ glass that distinguishes it from any other chalcogenide binary is the presence of two backbones, a 3D backbone composed of P-centered Pyramids and QT in the 0 < x < 40% range, and a second backbone composed of ethylene-like chains. The nature of phase separation is quite unique. Such chain fragments already begin to nucleate near x = 20% and then grow precipitously as x > 40%, in large part because the P–P bonds are by far the strongest covalent bond (51.3 kcal/mol) to form in the present glasses. Thus, at x > 40%, the Quasi 1D ethylene chains define the second backbone formed. The T_g maximum observed near x = 50% comes from the chemical threshold of the Quasi 1D chains of P_2Se_2 stoichiometry. In the 50% < x < 57% composition range, molecular cages of P₄Se₃ stoichiometry rapidly emerge at the expense of the 1D chains and melts at x = 57% when cooled leading to a complete loss of glass formation.

6 | **BROADER ASPECTS**

Having identified the key structural features of RTs and the IP in relationship to the underlying structural properties of the networks, it is interesting at this point to ask whether such frameworks are able to describe in an improved fashion some more challenging networks, such as those of phase change materials, optimization of high-*k* and low-*k* dielectrics, and cements.

6.1 | Phase change materials

A first field of application of such methods is that of chalcogenide thin films that represent an attractive class of optoelectronic materials for applications in nonvolatile memory devices. There are two primary types of chalcogenide-based memory devices that have been demonstrated effective. The first are phase change memory (PCM) devices that work based on a change in phase from the amorphous state to a crystalline state promoted by light irradiation. PCMs are fast and reversible memory devices that have been well developed. The second memory device utilizes an amorphous film that is subjected to a characteristic threshold voltage and then undergoes a significant change (five orders of magnitude or more) in electrical resistance¹⁴³ and is known as an OTS selector. In an OTS memory device, select local defect structures form in the amorphous film and create mid-gap (MG) states. At the threshold voltage bias or threshold electric field, charge carriers from the MG states are promoted to the conduction band, which then lowers the electrical resistance of the amorphous film by four to six orders of magnitude, which provides the two states needed for a memory device. The chalcogenide material used in OTS memory devices remains amorphous between the two states, which is in contrast to the PCM memory device where a complete change in molecular structure from a high-resistance amorphous state into a low-resistance crystalline state occurs. A PCM memory involves a complete structural phase change, and such memory devices perform remarkably well. Theoretically, however, it is believed the OTS memory device, a largely electronic device, may one day switch faster than PCM memory devices, but this has not yet been successfully demonstrated. Recently, a 3D stacking technology, described as the 3D Xpoint,^{20,144} has been commercialized to increase storage density by integrating the volatile OTS selector with a nonvolatile PCM cell to facilitate the opening and shutting off of each memory unit with no Si-based transistors.

To understand the chalcogenide materials used in modern memory devices,¹⁴⁵ it is useful to plot their compositions on a phase diagram. One finds that along the



FIGURE 18 A phase diagram of Ge–Sb–Te ternary¹⁴⁷ that shows new synthetized glasses along the Ge_xSb_xTe_{1-2x} join (filled and open red squares) and close to the location of the isostatic condition at $x_c = 8.5\%$ (yellow point¹³⁴) investigated by ab initio simulations. The cyan region corresponds to previously Sb-poor glass compositions around the GeTe6 eutectic. The GeTe₆ composition has led to an ovonic threshold switching (OTS) device, whereas the GST 124, GST 225, and GeTe to PCM Devices. Two other chalcogenides, the GeS and GeSe, have also led to OTS devices. See text.

Sb₂Te₃ to GeTe black tie-line in the Ge–Sb–Te ternary (Figure 18), reside the presently used PCM devices that have compositions of GeSb₂Te₄ and Ge₂Sb₂Te₅²¹ and GeTe composition.²² These materials reside in the stressed-rigid phase of the Ge-Sb-Te ternary that is expected given that in the stressed-rigid phase, the glass forming tendency is poor and materials have a strong tendency to crystallize. This result has been established from a combination of ab initio MD simulations and MD-based constraint counting algorithms (Figure 16) along the $Ge_xSb_xTe_{1-2x}$ join, thus permitting one to identify an isostatic condition (flexible to rigid transition) for $x_c = 8.5\%$.¹³⁴ Close to this composition and as already anticipated from what is known in Ge-Se on optimal glass-forming tendency,¹⁴⁶ glasses can be produced in this highly crystallizing Ge–Sb–Te ternary alloy,¹⁴⁷ and now extend the glass-forming domain that was previously limited to Sb poor compositions close to the GeTe₆ eutectic (cyan-colored region in Figure 18) and has also been used to develop a successful OTS device.²³

Since the first OTS material composition $As_{30}Ge_{10}Te_{48}Si_{12}$ announced by Ovshinsky et al.,¹⁸ who launched the field of commercializing chalcogenidebased memory devices, many other materials have now emerged, including those of GeTe₆,²³ amorphous GeSe²⁴ and GeS²⁵ thin films. Except for the GeTe₆ OTS that resides in the flexible phase, almost all OTS memory devices belong to the stressed-rigid TP. Recent reports on the GeS OTS memory device show that one can achieve 10^8 cycles with stable on-off switching and selectivity in a current change of 10^6 . With the GeSe OTS memory device, one can achieve 10^6 cycles with stable on-off and a selectivity of 10^5 in current. On the other hand, with the GeTe₆ OTS memory device, one can only get 600 cycles with a selectivity of 10^4 in current.

The scientific interest to better understand OTS memory devices is currently directed in understanding the nature of the localized defect structures that contribute to the formation of the MG states. With the Ge–S- and Ge–Se-based OTS memory devices, there is evidence to suggest that the Ge–Ge bonds form chain-like structures,¹⁴⁸ and these could provide a conductive path. The nature of the defect configurations that populate the high-resistance amorphous phase and lead to the MG states needs to be reliably ascertained to permit one to better understand how devices can withstand the repeated cycling of 10⁸ or greater in the OTS memory devices. Currently, there is also a need to have a better performing OTS selector material to work with the existing PCM to realize higher quality 3D memory chips.

6.2 | Rigidity and materials functionalities in general: a few examples

The role of molecular rigidity and the presence of anomalous features for IP compositions or conditions (i.e., extrema in physicochemical properties) have led to a series of applications that extend outside of the field of glasses.¹⁴⁹ We briefly mention those as a final outlook that might serve for further inspiration for the analysis of complex disordered networks.

Optimization of low- and high-dielectric-constant (low-/high-*k*) materials can, for instance, be viewed purely from the perspective of TCT.^{150,151} Here, topological constraints on, for example, a-SiC:H networks play underlying roles in determining the electrical and mechanical properties of the materials as well as interfaces that are important for modern micro- and nanoelectronic devices.^{152,153}

More recent developments in the extension of rigidity theory have led to the identification of an IP in concrete,¹⁵⁴ which is by far the most heavily manufactured material in the world. By capturing the important atomic topology from MD-based models of a calcium–silicate–hydrate network (i.e., the binding phase of concrete), MD-based constraint counting has led to the prediction of the compositional dependence of mechanical properties,^{63,155,156} revealing an anomalous behavior in fracture toughness, fracture energy, mechanical reversibility, and creep compliance within a compositional window at the vicinity of the isostatic threshold.¹⁵⁷ These features are argued to constitute a mechanical signature of an IP that is accompanied by a clear structural signature of the IP in the structural medium-range order of this system, indicative of an optimal space-filling tendency.

These few examples indicate that rigidity concepts represent a promising tool to accelerate the discovery of new materials with tailored properties.

7 | SUMMARY

Presence of IRLSs ($n_c = 3$) in network glasses fundamentally plays a pivotal role in the formation of IPs and their superstrong melt counterparts due to the compacted and stress-free nature of these networks,¹⁵⁸ which do not have open degrees of freedom for the glass/melt structures to relax. Flexible $(n_c < 3)$ and stressed-rigid $(n_c > 3)$ glass networks, on the other hand, possess open degrees of freedom that are traced, respectively, to the floppy modes in the flexible phase and the partially broken BB constraints in the stressed-rigid phase. Further, the open degrees of freedom in these non-IP networks leave them intrinsically stressed $(P_r \neq 0)$. These considerations permit an understanding of the origin of the square well-like variation of the enthalpy of relaxation, ΔH_{nr} ,⁴⁴ and a Gaussian-like fragility index (*m*) minimum for compositions in the IP center. Calorimetric probes of ΔH_{nr} and *m* in conjunction with Raman scattering have proved remarkably insightful in exploring the physics of glasses and their melt dynamics.^{13-15,36,37,89-92,109,159} The dynamics is, indeed, anomalous, and mean-field theories of the double transition show an increased sensitivity for single bond addition or removal close to the IP and strongly suggest that the glass is maintained in a "self-organized critical state" on the rigid-floppy boundary throughout the IP.³³ Further, MD simulations coupled to constraint counting algorithms show that the experimental RWs for the IPs are linked to minima in activation energies for diffusion and viscosity,^{61,62} with anomalies in fracture toughness⁶³ and relaxation time,⁶⁴ which lead to structural signatures in the low wavevector region of the structure factor.65

The construction of global TP diagrams of several chalcogenides^{14,37,90–92} will serve to link glass structure with function and facilitate the construction of the glass genome.¹⁶⁰ In the present review, we have focused on chalcogenide glasses. There is an ongoing parallel effort in isolating TPs of modified oxide glasses and enhancing our fundamental understanding of oxide glasses as well as their applications.

In addition, more generally, the identification of new "smart" glasses with multiple functionalities and superior performances that can be obtained through similar topological predictions and engineering of physical properties enabling the intelligent design of new materials as exemplified with the recent discoveries in high-dielectric materials and concrete.

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SUPPORTING INFORMATION

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