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# Melt dynamics, nature of glass transition and topological phases of equimolar $Ge_xAs_xS_{100-2x}$ ternary glasses



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#### ABSTRACT

The Topological Phases (TPs) in specially homogenized equimolar Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> ternary glasses are established here by performing detailed Raman scattering, together with Modulated-DSC and Volumetric measurements over a wide range of compositions, 5% < x < 25%. Our results show the presence of an Intermediate Phase (IP) residing in the 9.0% < x < 16.0% range, with compositions x < 9.0% in the flexible phase, and compositions x > 16% in the stressed-rigid phase. The novel use of ex-situ Raman profiling on the entire batch of compositions indicates very slow dynamics that is tracked with time and composition and reveals the impact of homogenization on physico-chemical properties of glasses. Stressed-Rigid glasses exceeding the chemical threshold composition are all found to be nanoscale phase separated. In the presently synthesized specially homogenized melts/glasses, we observe (i) evidence for the elusive 537 cm<sup>-1</sup> Raman active mode of the S = As stretch in quasi-tetrahedral S =  $As(S_{1/2})_3$  local structure, (ii) a square-well like variation of the non-reversing enthalpy of relaxation  $\Delta H_{nr}(x)$  at  $T_g$  displaying the Reversibility window and defining the Intermediate Phase (IP), (ii) a square-well like variation of molar volumes,  $V_m(x)$  coinciding with the IP composition range defining a Volumetric window, (iii) Melt fragility index, m(x), variation showing a global minimum in the IP compositions with m(x) < 20, and with the fragility index, m(x) > 20 for non-IP compositions, defining a Fragility Anomaly, and finally a variation in the specific heat jump near  $T_{e}$ ,  $\Delta C_p(x)$ , that tracks part of the observed anomalies in m(x) and  $\Delta H_{nr}(x)$ . The location of each of these anomalies/windows coinciding with those of the IP highlights the privileged nature of the window edge compositions that represent respectively rigidity- ( $x_r = 9.0\%$ )- and the stress- ( $x_s = 16.0\%$ ) elastic phase transitions determined within the Topological Constraint Theory of glasses.

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# 1. Introduction

Multicomponent Sulfides not only form an interesting class of glasses or starting materials used for optoelectronic applications, they also represent archetypal covalently bonded networks which progressively stiffen as their connectivity increases upon chemical alloying. They can undergo light-induced changes or even spectacular photo contraction effects, so that a large amount of research continues to be undertaken in order to characterize their physicochemical properties.

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Over the past 40 years, Topological Constraint Theory (TCT) has evolved [1–6] into an efficient tool to understanding glass network functionalities in terms of the connectivity of the underlying covalently bonded network. In this approach the glass network is viewed as a network of chemical bonds linking atoms, with the bonds between nearest neighbor (nn) atoms, and bond-angles between 2nd nn atoms serving as mechanical constraints. The network as a whole is then viewed to be either in a Flexible phase (FP) or an isostatically rigid Intermediate Phase (IP) or a Stressed-rigid phase (SRP) if the number of constraints per atom,  $n_c$ , is respectively lower than, equal to or higher than the number of degrees of freedom, i.e., 3 in 3D networks [1,3,4].

The inclusion of T-dependent constraints [7-13] has extended the original theory, a strictly T = 0 K description of glasses to finite T. One could then investigate glassy melts, and model these systems

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using MD simulations [11,12,14]. The existence of IPs with remarkable properties such as nearly reversible glass transitions [4,15–18], reduced aging [17,19] forming compacted networks with reduced molar volumes [20–23], forming networks than can adapt [24], minimum creep [25–27], maximum fracture toughness [28] came to the fore, and these developments have stimulated much excitement in not only theory [29] and experiments [16,17,22,23] but also applications [30] of glasses.

First attempts to observe the Topological Phases of the equimolar  $Ge_xAs_xS_{100-2x}$  ternary glasses [31,32] were made some years ago. In these early measurements one could observe the IP but the phase boundary between the FP and the IP, which defines the rigidity transition, and the one between the IP and the SRP, which defines the stress transition, were found to be smeared [31,32]. The onset of rigidity in the group IV (Ge) chalcogenides is widely acknowledged [1–3] and observed [4,6] near a critical mean coordination number, <r ><sub>c</sub> = 2.40. The situation for the case of a group V (As) chalcogenides was also of interest but less well understood at that time. For a glass network composed of atoms with Coordination Number (CN) = 1, 2, 3, 4 and greater, the general condition for percolation of rigidity is defined by [33,34].

$$\langle r \rangle_{c} = 2.40 - 0.4 (n_{1}/N)$$
 (1)

Here  $\langle r \rangle_c$  represents the critical mean coordination number for rigidity to percolate in a glass network possessing a count of n<sub>1</sub> atoms that are 1-fold coordinated, and with N representing the total number of atoms in the network. For networks with no dangling ends ( $n_1 = 0$ ), as in the case of  $Ge_xSe_{100-x}$ , one recovers the usual Phillips–Thorpe [1–3] condition,  $\langle r \rangle_c = 2.40$  from (1). For a group V (P, As) Chalcogenide, two types of isostatic ( $n_c = 3$ ) local structures can form, a Quasi-tetrahedral  $S = As(S_{1/2})_3$  unit representing the  $5^+$  state of oxidation of As with a < r > = 2.28, and/or a Pyramidal As  $(S_{1/2})_3$  unit representing the 3<sup>+</sup> state of oxidation of As with <r>= 2.40. Such units are rather well documented in P-based chalcogenides where they have a specific Nuclear Magnetic Resonance (NMR) signature [35] but for As-based glasses, their presence continues to be debated [36,37] albeit QT units lead to a well-defined spectroscopic signature in Infrared Absorption, as recently demonstrated from ab initio simulations [38]. For a network composed of QT As-local structure, such as  $S = As(S_{1/2})_3$ , As is 4-fold coordinated with one S as a dangling end and 3S, which are bridging to the rest of the network. Thus, one has  $n_1 = 1$ , and N = 3.5, leading to  $n_1/N = 1/3.5$ . In Eq. (1) that substitution for  $n_1/N$ , yields then a critical mean coordination number,

$$\langle r \rangle_{c} = 2.40 - 0.4/3.5 = 2.28$$
 (2)

for the onset of rigidity. For these reasons, one expects [39] that the onset of rigidity in group V (P, As) chalcogenides would occur near < r > = 2.28, i.e., at a much lower value of < r > than known for the group IV chalcogenides (< r > = 2.40), provided QT based group V local structure forms part of the glass structure.

#### 1.1. The crucial effect of glass homogenization

Of special importance for the purpose of this contribution is the recognition that melts/glasses of the chalcogenides undergo delayed homogenization as recently revealed [15,16,40]. This issue has been largely overlooked in the literature although it appears that such material processing is crucial in determining the location and nature of the underlying elastic phase transition defining the TPs. Even the determination of molar volumes is subjected to large variations and changes depending on the materials processing. Specifically, one found [15,16,40] that even 2 g sized batch compositions of e.g.  $Ge_xSe_{100-x}$  melts, took nearly a week of alloying at 950 °C to achieve a variance <  $\Delta x$  > in Ge atom concentration 'x' across the batch to

reduce to 0.1%. This was made possible by ex-situ Raman profiling of melts encapsulated in evacuated quartz tube, as melts were steadily alloyed till the Raman spectra along the length of the melt column became identical, when the melt/glass was taken to be homogeneous. At that level of homogeneity, one could observe abrupt rigidity- and stress-transitions as documented by the Enthalpy of relaxation at Tg,  $\Delta H_{nr}(x)$  displaying a square-well like reversibility window [15,16,22,23]. The finding is consistent with the percolative nature of the rigidity-, and stress-transitions, which are sharp and predicted to be first order [41]. These contributions led to the recognition that ex-situ Raman is the method of choice to ascertain the quality of glasses in terms of homogeneity.

#### 1.2. Motivation

Our goal to re-investigate the Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> ternary in the present work is based on several considerations. We used Raman scattering as a method to profile melts/glasses during synthesis to obtain especially homogenized glasses. Raman scattering was also used as a benchmark to establish the different As- and Ge-centered local structures formed in glasses as a function of composition 'x'. In an earlier study [31], glasses were typically alloyed for 2–3 days at 900 °C, which we recognize now is insufficient time to homogenize melts/glasses. In the present work, we find using FT-Raman profiling of 1.5 g batches that it typically takes 5 weeks or more of alloying to homogenize melts/glasses of these Sulfides. Once homogenized, we now can directly observe the elusive As = S stretch mode of Quasi-Tetrahedral  $S = As(S_{1/2})_3$  units near 537 cm<sup>-1</sup> in Raman scattering [22]. This mode was not observed [31] earlier, and appears to be specific to homogenized glasses. The width of the IP in the present work resides in the 9.0% < x < 16.0% range of composition, or spanning a range of mean coordination number, 2.27 << r > < 2.48. The IPwidth in these homogeneous glasses is also found to be wider than the one reported earlier for the less homogeneous glasses [31].

The present results confirm that the onset of rigidity transition occurs close to the expected value of  $\langle r \rangle = 2.28$  and is due to the presence of the QT As local structures. We have also investigated melt dynamics by establishing trends in melt fragility index, m(x), with glass composition x, and find evidence that m(x) < 20 for the IP range of melt compositions, and m(x) > 20 for non-IP compositions, displaying an asymmetric triangular-like Fragility Anomaly. As a result, the super-strong character of IP composition melts serves as a barrier for melt diffusive mixing to occur, thus leading in part to the delayed homogenization of the Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> melts. The behavior is found to be generic of IP compositions in a variety of glass systems that were homogenized using FT-Raman profiling [17,21–23,40]. Finally, in the present homogeneous glasses we also observe a Volumetric window illustrating that the molar Volumes  $V_m(x)$  in the IP compositions are lower than the average behavior seen for non-IP compositions [20].

Chalcogenides glasses have proved to be indispensable material for widespread applications. They have been widely used for phasechange memory [42] devices such as in the new 3D-X-point [43,44]. Additionally, researchers have explored their applications in acoustic and acousto-optic devices [45], optical fibers, waveguides and Continuum emission in the IR [46–50]. In these applications, it has been observed that the glass chemical compositions have a bearing on the glass functionality which in a broader sense is related to the underlying nature of such Glass Topological Phases.

A recent collection of papers on "Topology of Disordered Networks and their Applications" [51] has revealed that Topological Phases in glasses are not only manifested in binary- and Ternary-Chalcogenides [22,23,52] and modified oxides [21,53], but also in Amorphous Hydrogenated Boron Carbide [54] and Calcium Silicate Hydrates [55]. For the case of the Chalcogenides and modified oxides, one has further noted that variations of fragility index show a global minimum in the Intermediate Phase formed in between the onset of rigidity- and stress-elastic phase transitions in glasses. The correlation between melt dynamics and Topological Phases appears to be generic. Recent MD Simulations on Sodium silicate glasses have shown [56] that the Dynamic and Stress signatures of the rigid Intermediate phase are also observed in glass forming liquids. These simulations have thus rather elegantly confirmed that the reversibility windows observed in calorimetric experiments constitute signature of the Maxwell [57] stability criterion for isostatically rigid structures ( $n_c = 3$ ) and are closely tied to the properties of corresponding liquids. Finally, the existence of these Topological Phases in glasses will serve as precursive to decoding the atomic genome of glasses [58].

In the next section we present Methods and materials, followed by the Experimental results. A Discussion of salient issues brought forth by the new findings in this work is given in section following Experimental results. The Conclusions are summarized at the end.

#### 2. Methods and materials

#### 2.1. Synthesis of melts/glasses

Ternary Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> bulk glasses were synthesized in the range of compositions  $2\% \le x \le 25\%$  by weighing the starting materials, which are elemental pieces about 3 mm in diameter of 99.999% pure S flakes, 99.999% pure  $As_2S_3$  lumps from Strem Chemicals and 99.999% pure Ge lumps from Alfa Aesar to give a total of 1.5 g sized batches in the desired weight ratio. These were purged with N<sub>2</sub> gas in Glove bag with relative humidity of < 4%, and then placed in (5 mm ID, 1 mm wall thickness) guartz tubes, which were dried in a vacuum oven at 90 °C for 24 h. Sulfur elemental pieces were placed in a high vacuum pumping system and evacuated to 10<sup>-6</sup> Torr for 24 hr prior to use. The guartz tubes were sealed under vacuum  $(2 \times 10^{-7} \text{ Torr})$  using a liquid Nitrogen trapped diffusion pumping system. The sealed tubes were held vertically in a T-programmable box furnace and heated by increasing the temperature gradually at 1 °C/min from 25 °C to 650 °C and alloyed for four weeks until the batch homogenized. Finally, we decreased the furnace temperature to 500 °C and equilibrated at that temperature for 2 h before coldwater quenching.

FT-Raman spectra of water quenched melts were taken at six locations along the length (14 mm) of the melt column, and this process was continued until the spectra at all the 6 locations became identical. The FT-Raman profiling measurements [15,16] showed that to homogenize 1.5 g size batch composition, it took between 30 and 60 days with the exact time dependent on the glass stoichiometry x as we describe in the section on Experimental results.

## 2.2. FT-Raman profiling

A Thermo-Nicolet Model Nexus 870 FTIR with a Raman module, using InGaAs detector or a Ge detector, and 126 mW of 1064 nm radiation from a Nd-YAG laser with 50 µm spot size, was used to examine the molecular structure of ternary glasses. Glasses enclosed in evacuated quartz tubes were mounted on a digitally controlled xyz stage. The x-axis adjustment is made to ensure the laser beam is directed along the quartz tube diameter. This ensures that the glass sample area looked at is flat. The z-axis adjustment is made to focus on the glass surface wetting the quartz tube. The y-axis adjustment allows probing the glass column at multiple locations.

Ex-situ FT-Raman profiling of glass forming melts during synthesis was first introduced [59] in the year 2011, and it has shown to provide a remarkably powerful means to quantitatively characterize batch heterogeneity as constituents are alloyed in evacuated quartz tubes. The case of binary Ge–Se glass forming melts [59] was examined as the starting materials (Ge, Se) were progressively alloyed in evacuated quartz tubes held vertical with no shaking over several days. And one found that the variance in Ge content along a 1-inch long melt column could be steadily reduced from about 3% after  $t_R = 2$  days of alloying to less than 0.04% after  $t_R = 7$  day of alloying, i.e., by nearly 2 orders of magnitude [40]. The delayed homogenization of these Ge-Se melts is an emerging story in the field [22,23].

FT-Raman spectra were taken at six locations along the melt column. At each location, 100 scans were recorded with a 2 cm<sup>-1</sup> resolution. It took 42 min to profile the entire batch. All the spectra were normalized to the Corner Sharing (CS) mode of GeS<sub>4</sub> tetrahedra [60] near 342 cm<sup>-1</sup> to observe the change in scattering strength of the Sulfur modes upon alloying. FT-Raman spectra of a Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> glass sample at x = 9% at six locations along the glass column (Fig. 1a, b) shows, how the variance in Ge or As stoichiometry,  $<\Delta x >$ , decreases from 5.06% after 35 d of alloying to 0.03% after 65 d of alloying. In spectrum (b), one can observe the 537 cm<sup>-1</sup> mode of  $S = As(S_{1/2})_3$  QT local structures [22] after the glass been homogenized by prolonged (65 d) alloying of the melt at 650 °C. Fig. 1c gives a pictorial of the starting materials sealed in evacuated quartz tube (A). The actual sample at x = 6.7% is shown as B in Fig. 1c.

#### 2.3. Dispersive Raman scattering

A T64000 Dispersive Raman scattering from Horiba Jobin Yvon Inc using an Olympus Model BX41 microscope with an 80× objective was used to examine the molecular structure of the homogenized  $Ge_xAs_xS_{100-2x}$  ternary glasses. Raman scattering was excited using the 514 nm radiation from Ar-ion laser, which leads typically to band-band excitation.

#### 2.4. Modulated differential scanning calorimetry

A model Q2000 TA Instruments MDSC was used to establish the calorimetric properties [16,61] of glasses including the glass transition temperature T<sub>g</sub> and the enthalpy of relaxation  $\Delta H_{nr}$  of a glass at T<sub>g</sub>. Our glass samples were hermetically sealed in T<sub>zero</sub> Al pans. The pans and lids were dried in vacuum oven for two days prior to their use to avoid wetting the glass samples during use. The Q2000 TA system was calibrated before its use for temperature and heat flow using an Indium melting scan, and for the specific heat C<sub>p</sub> using a standard of sapphire disk. The sealed samples were heated up at ramp rate of 3 °C/min, modulation time of 100 s and modulation amplitude at ± 1 °C and cooled down at the same condition. Moreover, the fragility index "m" of melts has examined by using MDSC. We elucidate the principles of both methods next by illustrating select results on Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> ternary glasses at x = 15%.

2.4.1. Glass transition temperature,  $T_{g}$ , and enthalpy of relaxation,  $\Delta H_{nn}$  of glasses

Glass transition temperature,  $T_{g}$ , and the Enthalpy of Relaxation,  $\Delta H_{nr}$ , of a glass serve as two crucial calorimetric characterization of glass softening transition. In a traditional DSC it is difficult to uniquely deduce these quantities. The advantage of using MDSC [61] rather than the traditional DSC is that it provides  $T_g$  and  $\Delta H_{nr}$  uniquely, nearly independent of scan rate. This is the case because in MDSC one can uniquely deconvolute the total heat flow into a thermally reversing (ergodic) and a thermally non-reversing heat flow (non-ergodic) component to establish the two terms independently. The scan rates used in MDSC are typically 3 °C/min, significantly lower than the ones used (10–20 °C/min) in DSC, suppressing kinetic effects. Furthermore, by taking the mean value of  $T_g$ in a heating scan followed by a cooling scan, we obtain a  $T_g$  that is also nearly scan rate independent.

We illustrate the deconvolution of the total heat flow signal (shown in brown), into the reversing heat flow signal (shown in



**Fig. 1.** Left panel shows FT-Raman spectra of a  $Ge_xAs_xS_{100-2x}$  glass composition at x = 9%, profiled after being alloyed at 650 °C for (a)  $t_R$  = 35 days and (b) after 65 days. The scattering strength ratio of the  $S_8$  ring mode at 217 cm<sup>-1</sup> normalized to the backbone mode near 342 cm<sup>-1</sup> decreases from (a) 1.45 to (b) 0.83 as the glass homogenizes. The variance in Ge or As content x, i.e., <  $\Delta x$  > deduced from the spread in scattering strength ratio yields a value of (a) 5.06% and (b) 0.03% using the calibration curve of Fig. 7a. When the glass is homogenized the As=S stretch vibration of a QT local structure, S =  $As(S_{1/2})_3$  near 537 cm<sup>-1</sup> is observed. In the right panel (c), We show a pictorial of the starting materials (Ge, As<sub>2</sub>S<sub>3</sub> and S) encapsulated in quartz tube, A, before alloying. The synthesized glass at x = 6.7% after alloying at 650 °C appears as B. The glass column examined at 6 locations was 1.4 cm along. The melt column of 1.8 cm long contained the meniscus.



**Fig. 2.** MDSC scan of a glass at x = 15% taken at 3 °C/min scan rate, modulation time of 100 s, and modulation amplitude at ± 1 °C, showing the three signals, viz, total (brown), reversing (green) and non-reversing heat flow (blue) in heating up and then cooling down cycles as shown by arrows. The frequency corrected enthalpy of relaxation  $\Delta H_{nr}$  at T<sub>g</sub> is determined by subtracting the exotherm in cooling down shaded in red from the endotherm in heating up cycle. The T<sub>g</sub> is obtained from the average value of the inflection point in heating and cooling of the references to color in this figure legend, the reader is referred to the web version of this article.)

green) and the non-reversing heat flow signal (shown in blue) in Fig. 2 for a glass sample at x = 15%. The reversing heat flow signal shows a rounded step, permitting one to establish the  $T_g$  from the inflection point of the step, and from the step height obtain the change in the specific heat between the liquid and glass,  $\Delta C_p$  across the glass transition event. From the  $T_g$  = 229.4 °C (5) in the heating cycle, and T = 227.7 °C (5) in the cooling cycle, we deduced the mean

value of  $T_g = 228.5 \,^{\circ}C$  (5) as the scan rate independent  $T_g$ . The nonreversing heat flow signal shows a Gaussian-like peak and the red hashed area gives the enthalpy of relaxation in the heating cycle [62]. By taking the difference in the enthalpy of relaxation in the heating cycle from the cooling cycle, we obtained the modulation frequency independent [61,63] enthalpy of relaxation of  $\Delta H_{nr} = 0.00(5)$  cal/g at x = 15%. As discussed below, the non-reversing heat flow provides a measure of the configurational entropy change between the glass and the melt, while the reversing heat flow gives a measure of the vibrational entropy difference between the glass and the melt.

# 2.4.2. Fragility index (m(x))

The melt viscosity  $(\eta)$  increases extremely to  $10^{12}$  Pa. s as the melt cools down to the glass transition temperature  $T_g$ , and is described by plotting the log  $(\eta)$  as function of  $T_g/T$ . The fragility index (m) of the melt is defined by the following equation.

$$m(x) = \left[\frac{d\log(\eta)}{d(T_g/T)}\right]_{T \to T_g}$$
(3)

which relates to the slope of the log  $\eta$  versus  $T_g/T$  curve taken near  $T_g$ . The classification of melts as strong or fragile [64,65] depends on the fragility index defined by Eq. (3). If the melt viscosity displays an Arrhenius variation the melt is called a strong melt. SiO<sub>2</sub> melt possess a fragility index, m(x) = 20, and it is viewed as strong. On the other hand, if the melt viscosity displays a non-Arrhenius variation, it is viewed as Fragile. Super-strong melts [66] possess a fragility index, m(x) < 20, while fragile ones possess an m(x) > 20.

To establish the melt fragility index, the in-phase  $C''_p$  and out of phase  $C'_p$  were examined as a function of modulation frequency ( $\omega$ ) [61,67]. The peak in  $C'_p$  shifts to a higher temperature as the modulation frequency is increased because the melt must relax faster to track the increasing modulation frequency ( $\omega$ .  $\tau = 1$ ). From the slope of (log  $\tau$ ) as a function of T<sub>g</sub>/T, the fragility index was established



**Fig. 3.** The left panel (a) shows the observed variation of the in-phase  $C'_p$  and out of phase  $C''_p$  components of the specific heat of a melt at x = 15% examined as a function T at different modulation frequency,  $\omega = 2\pi/t_m$ . As  $\omega$  increases, the peak in  $C'_p$  shifts to higher T ( $\omega$ .  $\tau = 1$ ). In the right panel (b), the semi-log plot of log( $\tau$ ) as a function of T<sub>g</sub>/T yields the fragility index (m) of 15 from the slope m =  $\begin{bmatrix} \frac{d(\log(\tau))}{d(\frac{T_g}{T})} \\ \frac{1}{d(\frac{T_g}{T})} \end{bmatrix}_{T \to T_g}$ .

(see Supplementary Information (SI)). And by using Eq. (4) we obtained the activation energy  $(E_a)$  for enthalpic relaxation.

$$E_a = m(x). T_g. \ln(10)$$
 (4)

In Fig. 3a, we show an example of the results of complex specific heat C<sub>p</sub> for a Ge<sub>15</sub>As<sub>15</sub>S<sub>70</sub> melt as a function of the modulation time period in the range (80 s < t<sub>m</sub> < 120 s). When the modulation frequency is increased =  $\frac{2\pi}{t_m}$ , the step in  $C_p''$  and the peak in  $C_p'$ , both steadily shift to higher T. By determining the endothermic peak location, one obtains the T at which the melt has obtained an enthalpic relaxation time  $\tau$ . The fragility index(m) is obtained by plotting log ( $\tau$ ) against T<sub>g</sub>/T (Fig. 3b), and the value of a fragility index of m (x) = 15(1) is obtained for a glass composition, x = 15%.

### 2.5. Volumetric measurements

Molar volume measurements on glasses provide information on network packing. The densities of Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> ternary glasses were measured using Archimedes' principle. We used a hooked quartz fiber suspended from a Mettler Toledo B154 model digital microbalance. We determined the density of alcohol using a Si single crystal wafer of known density ( $\rho_{Si} = 2.33 \text{ g/cm}^3$ ) and weighted Si crystal in the air and in 200 proof alcohol.

Next, we measured the density of a Ge single crystal five times to ascertain the accuracy of our measurements and found a value of Ge density of  $5.326(5) \text{ g/cm}^3$  in harmony with the standard value ( $\rho_{Ge} = 5.323 \text{ g/cm}^3$ ). Glass samples of 150 mg of weight or more were used to attain an accuracy of 0.25% or less. We provide an example of Molar Volume measurement on Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> ternary glasses at x = 12%.

We calculated the density of alcohol by weighting a Si single crystal ( $\rho_{Si} = 2.33 \text{ g/cm}^3$ ) in air ( $W_{Si}^{air}$ ) = 110.60 mg and in alcohol ( $W_{Si}^{alcohol}$ ) = 73.2 mg.

$$\rho_{alcohol} = \frac{W_{si}^{air} - W_{si}^{alcohol}}{W_{si}^{Air}} \rho_{si} = 0.788g/cm^3$$

The density of  $Ge_xAs_xS_{100-2x}$  ternary glasses at x = 12% as the following:

Weight of the sample in the air  $(W_{glass}^{air}) = 207.2 \text{ mg}$ ; Weight of the sample in alcohol  $(W_{glass}^{alcohol}) = 144.8 \text{ mg}$ ;  $(\rho_{alcohol} = 0.788 \text{ g/cm}^3)$ .

The molar volume of the  $Ge_xAs_xS_{100-2x}$  ternary glasses were then obtained from molar mass divided by the density.

$$\rho_{glass} = \frac{W_{glass}^{air}}{W_{glass}^{air} - W_{glass}^{alcohol}} \rho_{alcohol} = 2.62 \frac{g}{cm^3}$$

#### 3. Experimental results

#### 3.1. Synthesis and kinetics of melt/glass homogenization

## 3.1.1. Homogenization of a S-rich $Ge_xAs_xS_{100-2x}$ ternary melt at x = 7%

In the present work we have used FT-Raman profiling to characterize the growth of ternary  $Ge_xAs_xS_{100-2x}$  melts/glasses as the starting material lumps of  $As_2S_3$ , Ge, and S were steadily statically reacted at 650 °C in evacuated quartz tube over a period ranging from 5 d <  $t_R$  < 60 d in working with batches 1.5 g in size. Intermediate chemical reaction steps between the starting materials could also be identified as homogenized melts of the ternary were eventually realized after  $t_R$  = 64 days of alloying (Fig. 4).

A glance at the 6 spectra of Fig. 4 shows the formation of monomeric and crystalline phases [68–70] to occur in the early alloying process (Fig. 4a and b) at  $t_R < 33$  d, as narrow vibrational features are observed. We discuss the issue later. And as the alloying time  $t_R > 33$  days, one observed (Fig. 4c–f) the ternary glass backbone (the broad mode centered near 342 cm<sup>-1</sup>) to be manifested and to steadily grow with significant amount of S<sub>8</sub> crowns that decoupled from the glass backbone to steadily reduce in scattering strength.

The results of spectra of Fig. 4a-d show the variance in Ge or As content of the glasses, i.e.,  $\langle \Delta(x) \rangle_{Ge/As}$  to steadily decrease from 14% at  $t_R = 10 d$  to nearly 0.01% at  $t_R = 60 d$  as glasses finally homogenized. Furthermore, we noticed that as the glass homogenizes the mode at 537 cm<sup>-1</sup> is then manifested. Next, we heated the glass at 80 °C for 2 d, to assist fragmented backbone segments to melt and coalesce (Fig. 4e). We recognize that the temperature T = 80 °C chosen here, slightly exceeds  $T_g$  of the glass but is less than the S- polymerization transition temperature,  $T_{\lambda} = 160$  °C. The final step then consisted of heating the glass to 650 °C for 2 more days followed by a water quench (Fig. 4f) leading to a substantial growth in the fraction of Sulfur that alloyed in the glass backbone as S<sub>n</sub>-chains, which led the segregated amorphous S<sub>8</sub> ring content in the glass samples to measurably decrease, and the scattering strength of the 537 cm<sup>-1</sup> mode to increase. The later mode is ascribed to the quasi-tetrahedral  $S = As(S_{1/2})_3$  local structure formed in the glass as expected from ab initio vibrational mode calculations [71] (see SI).

In Fig. 5, we reproduce the Raman spectra recorded at the two lowest positions S1 and S2 of Fig. 4a. In Fig. 1c we provide a pictorial of the starting materials encased in an evacuated quartz tube. Upon heating to 650 °C, in the early stages S vapor from the elemental S will be available, and thereafter some of the  $As_2S_3$  will then



**Fig. 4.** FT-Raman spectra of a  $Ge_xAs_xS_{100-2x}$  glass composition at x = 7%, after alloying at 650 °C recorded at 6 spots along the melt column. Spectra in (a) and (b) show how the initial chemical reaction is taking place. In (c) the bulk glass is formed but is heterogeneous. In (d), (e) and (f) the bulk glass steadily homogenizes, and the elusive 537 cm<sup>-1</sup> mode is manifested.



**Fig. 5.** Panel (a) shows reference Raman spectra of select crystalline phases, and panel (b) the formation of crystalline phases at spot (S1) and spot (S2). This figure is companion of the Fig. 4.

decompose to release S by the following two reactions:

$$2As_2S_3 = As_4S_4 + 2S$$
 (5)

$$2As_2S_3 = As_4S_3 + 3S$$
 (6)

The released S converts the Ge platelet surface to sulfide, and the products consist of c-GeS (238 cm<sup>-1</sup>, 267 cm<sup>-1</sup>) and  $\alpha$ -GeS<sub>2</sub> (345 cm<sup>-1</sup> and 360 cm<sup>-1</sup>) for which the Raman evidence can be seen in the relevant vibrational modes observed Fig. 5. One expects more of the c-GeS will form compared to the  $\alpha$ -GeS<sub>2</sub> as the Ge platelet surface is converted first in a mono-sulfide, which then converts into the disulfide. It also stands to reason that it is the high temperature ( $\alpha$ -GeS<sub>2</sub>) that will form as the quartz tube is heated to react the starting materials.

3.1.2. Homogenization of a S-deficient  $Ge_xAs_xS_{100-2x}$  ternary melt at x = 12%

We next consider the case of homogenization of a S-deficient ternary  $Ge_xAs_xS_{100-2x}$  melt at x = 12%, possessing a significantly higher concentration of As and Ge crosslinkers than the one we considered earlier. The FT-Raman spectra in Fig. 6a–f provide a global view of how such a S-deficient melt forms, homogenizes and eventually displays the vibrational feature of the As-QT local structure at 537 cm<sup>-1</sup> mode. This composition is of interest for another reason, it resides in the Intermediate Phase (IP), and we find the kinetics of melt homogenization to slow down qualitatively in relation to the one encountered at x = 7%. The details of FT-Raman line-shape analysis at x = 12% parallel those at x = 7% and are described in detail in SI.

All glass compositions synthesized in this work were, indeed, subjected to FT-Raman profiling to ascertain their homogeneity. In Fig. 7a we display the empirical calibration curve used to deduce the variance in As or Ge content,  $<\Delta x > _{As/Ge}$ , of the glasses at a select location along the melt/glass column by measuring the scattering strength ratio of the S<sub>8</sub> and S<sub>n</sub> mode to the backbone band at



**Fig. 6.** FT-Raman profiled spectra of a Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> glass composition at x = 12%, obtained after melt alloying at 650 °C for (a)  $t_R = 10 d$  shows the variance in Ge or As <  $\Delta x$  >  $_{Ge/As} = 12.78\%$ . Progressive alloying led the variance in x to steadily decrease in spectra shown in (b), (c), (d), (e) and (f). The variance reduced to 0.08% in panel (f). Panel (a) and (b) shows how chemical reaction has occurred and what intermediate species have formed during the alloying process. In (f) the glass is fully homogenized, and the elusive 537 cm<sup>-1</sup> mode has manifested.



**Fig. 7.** Panel (a) shows the variation in the scattering strength ratio of S band near 473 cm<sup>-1</sup> to the backbone band near  $342 \text{ cm}^{-1}$  in fully homogenized glasses in the composition range 1% < x < 19% (•), serving to define an empirical curve used to extract the variance in x for a composition at x = 7%. The variance in Ge or As-concentration x decreased from 14% to 0.01% when the alloying time increased to 60 days. Panel (b) shows a plot of the variance < x > with alloying time  $t_{R}$ , and reveals a graphic view of delayed homogenization of weighted glass at x = 7%. In panel (c) we plot the observed variation of  $< \Delta x >$  with alloying time and find that IP melt compositions take the longest alloying time to homogenize. Subsequently when we measured the fragility index of IP melts, we found them to be the lowest, m(x) < 20.

 $342 \text{ cm}^{-1}$ . To illustrate the utility of the calibration curve we show in Fig. 7b the measured scattering strength ratios of the S-modes to the glass backbone mode, and the deduced glass composition spread as a function of the alloying time t<sub>R</sub>. In Fig. 7c, we project the variation in the Ge or As-variance with t<sub>R</sub> for ternary glasses at various x. There is a clear pattern; as x increases from 7% to 16%, the kinetics of homogenization of melts/glasses slow down qualitatively, and this generic feature is intimately tied to aspects of relaxation/diffusion of melts encoded in their fragility index, as discussed below.



**Fig. 8.** Observed FT-Raman spectra of fully homogenized  $Ge_xAs_xS_{100-2x}$  ternary glasses at (a) high Ge or As content "x" in the 16% < x < 26% range, (b) at 8% < x < 17% range, and (c) at low "x" content in the range 1% < x < 9% and c-Sulfur. In (b, c) the 537 cm<sup>-1</sup> QT<sub>3</sub> mode is observed over the range 6.7% < x < 15%, and the scattering strength of the sulfur modes, viz. monomeric  $S_8$  species, and polymeric  $S_n$  chains steadily decreases as "x" increases, while the scattering strength of the backbone modes increases. In (a, b and c) the observed vibrational modes are Corner Sharing mode labeled CS, Edge sharing mode labeled ES, Ethane-like mode at x > 18% labeled Eth, QT S"As( $S_{1/2}$ )<sub>3</sub> local structures labeled QT<sub>1</sub>, QT<sub>2</sub> and QT<sub>3</sub> and Pyramidal As( $S_{1/2}$ )<sub>3</sub> local structure labeled PVR. The frequency of these modes is near to normal modes that is predicted by theory in Table S1.1 (see SI). The S-S dimer modes at  $x > x_c$  = 18.18% which are identified with monomeric  $\beta$ -As<sub>4</sub>S<sub>4</sub> and  $\beta$ -As<sub>4</sub>S<sub>3</sub> species.

# 3.2. Evolution of local structures from Raman scattering with glass composition

Once the homogenization is established and verified, the observed Raman scattering results on the present Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> glasses (Fig. 8) were systematically analyzed to decode aspects of local structure and the variation in the mode frequencies of these local structures with glass composition. In the observed line shapes one can observe the growth of modes of the Ge-centered and Ascentered local structure at the expense of S<sub>8</sub> and S<sub>n</sub> chain modes as x is increased. The observed line shapes were least-squares fit in terms of a superposition of the requisite number of Voight line-shapes (Lorentzian: Gaussian) which was kept fixed. We were guided in this process by the following considerations. (i) Three normal modes of the Ge-centered Corner-Sharing (CS) and Edge-Sharing (ES) tetrahedra local structures, and four normal modes of the As-centered local structures (OT, OT2, OT3, PYR) were expected. The vibrational mode frequencies and Raman cross-sections were available from the Naval Research Laboratory Molecular Orbital Library (NRLMOL) calculations [60,71] (see SI). The mode frequency and widths of the S<sub>8</sub> rings and polymeric S<sub>n</sub> chains were known from the previous work on pure S [72–74] and binary As–S glasses [22]. Furthermore, the reliability of these mode calculations were tested in analyzing Raman spectra of binary Ge-S [17] and As-S [22] glasses. (ii) The nature of the vibrational mode near 490 cm<sup>-1</sup> has been identified [22] as due to S-S dimer between a pair of either As or Ge atoms



**Fig. 9.** Deconvoluted FT-Raman scattering results on  $Ge_xAs_xS_{100-2x}$  glasses at x = 7%, 9% and 12%. The modes are assigned using reference modes established from NRLMOL calculations, (see Supplementary Information).



**Fig. 10.** Variations in the scattering strength ratios of Raman modes normalized to the total scattering strengths as a function of composition for (a) Corner Sharing (CS), Edgesharing (ES) tetrahedra, and the fraction of  $I_{CS}/I_{ES}$  (b) Quasi-Tetrahedra (QT1), quasi-tetrahedra (QT2), quasi-tetrahedral (QT3), (c) Pyramidal (PYR) units and S-S Dimer (D) units. The right panel displays compositional trends in Raman mode frequency (d) of Corner sharing (CS), Edge sharing (ES), (e) Quasi-Tetrahedral (QT1), Quasi-Tetrahedral (QT2), (f) Pyramidal (PYR) and S-S Dimer (D) modes. Note that each mode examines blue shift as x > 9%, the rigidity transition, as glass networks stiffen with increasing x.

as elucidated recently [22]. (iii) Mode frequency variation of the CS – and ES –  $GeS_4$  tetrahedra clearly revealed a threshold behavior near x = 9% corresponding to the rigidity transition. We also established an elastic power law for the CS-mode frequency in the IP [59] and found a value of 1.02.

In Fig. 9 we provide examples of the line-shape analysis for glass compositions at x = 7%, 9% and 12%. Note that the highest frequency mode near 537 cm<sup>-1</sup> is clearly observed at x = 7%, but its scattering strength steadily decreases as x decreases to 12%. In Fig. 10a, the scattering strength of Ge-centered CS and ES tetrahedra are plotted as a function of x. The scattering strength ratios,  $I_{ES}/I_{CS}$ , display a trend that is quite similar to the one encountered earlier in binary Ge-S glasses [17], except the fraction in the present ternary glasses varies in the  $0.70 < I_{ES}/I_{CS} < 0.78$  range, while in the Ge–S binary the variation resided in a lower range  $0.20 < I_{ES}/I_{CS} < 0.46$  range. In Fig. 10b, we show the observed scattering strength ratio for the three modes associated with the As centered QT local structure. The sharp reduction in QT<sub>3</sub> mode scattering strength is due to the presence of the S<sub>8</sub>-ring amorphous phase, which grows precipitously in the S-rich glasses (x < 8%) and inhibits the As = S mode to be manifested as melts are cooled to a T < 200 °C upon a water quench. The As=S bond is viewed to be formed on the surface of the fragmented glass backbone phase, and the terminal S atom decouples to attach with S<sub>8</sub> rings formed once T <  $T_{\lambda}$  = 150 °C.

The 3 bridging S near neighbors of the As centered QT local structure remain intact in the glass backbone as suggested by frequency of the QT<sub>1</sub> and QT<sub>2</sub> modes (Fig. 10e) that are distinctly different from the PYR mode frequency (Fig. 10f). In Fig. 10c, we note that the PYR mode scattering strength shows a monatomic increase over the measured range of x. This is broadly consistent with the fact that the stoichiometry of the PYR unit of As<sub>2</sub>S<sub>3</sub>, which corresponds to a < r > = 2.40 or an x = 13.3%. The scattering strength of the D-mode shows a maximum near x = 11%, corresponding to an < r > = 2.33, which represents the mean value of the connectivity of AsS<sub>3</sub> of < r > = 2.25 and of GeS<sub>4</sub> of < r > = 2.40 in respective binary glasses as discussed elsewhere [22]. We observe the broad maximum in the scattering strength of the D-mode close to 10% instead of 11%.

The total fraction of Sulfur either segregated as  $S_8$  rings or forming part of the  $S_n$  chains in the glass backbone steadily declines to vanish as x increases to 18% the chemical threshold as expected (Fig. 7a). These results provide internal consistency to the data deconvolution performed. Fig. 10b provides the scattering strength variation of the three normal modes of the QT local structure (Table SI.1),  $S = As(S_{1/2})_3$  as a function of glass composition. At x < 7%, the QT<sub>3</sub> mode associated with As = S stretch becomes impossible to observe because of the majority amorphous  $S_8$  ring phase overwhelms the glass backbone phase (Fig. 7a) in which most likely the As = S mode formed on the surface reconstructs with the a-S<sub>8</sub> phase.



**Fig. 11.** FT-Raman spectra in (a) compared with Dispersive-Raman one in (b) on fully homogenized glass of the composition  $Ge_9As_9S_{82}$ . Note that the 537 cm<sup>-1</sup> mode is observed in FT-Raman scattering excited by 1046 nm near mid gap radiation, but it is not observed in Dispersive Raman excited by 514 nm of near band gap energy as shown in (c). The Compositional variation of the band gap ( $E_g$ ) and  $E_g/2$  for present glasses in (c) is taken from [76].

The variations in mode frequency of the Ge-centered CS- and ES- tetrahedra as a function of x (Fig. 10d) display a broad trend; one observes a steady blue-shift across the three TPs with a change in slope near the rigidity transition x = 9.0% that is clearly less obvious than in corresponding binaries [17]. In the present ternary we recognize that the stressed-rigid phase is Nano Scale Phase Separation (NSPS) at x > 18%. These observations are taken as signatures of a stiffening of the glass backbone as one goes from the flexible to the IP, and then from the IP to the stressed-rigid phase. The observation of a parallel behavior in the present ternary provides for internal consistency of the line-shape deconvolution procedure and is in harmony with the glasses being fully homogeneous. In some earlier reports, the mode frequency showed an oscillatory behavior [75] with x, underscoring the heterogeneity of glasses synthesized.

We conclude this section with a final remark. All Raman scattering results presented here (Figs. 1, 4–6, 8, and 9) were acquired with 1064 nm radiation using a Nd-YAG laser. For the equimolar  $Ge_xAs_xS_{100\mathchar`2x}$  glasses the band-gap (Fig. 11c) varies [76] in the  $2.75 \text{ eV} > E_g > 2.0 \text{ eV}$  range as x increases in the 10% < x < 20% range. Thus, in the FT Raman measurements one excites the scattering in the mid-gap region, as illustrated for a glass sample at x = 9.0%(Fig. 11a). Notice the  $537 \text{ cm}^{-1}$  mode (QT<sub>3</sub>) is clearly observed under such excitation conditions. When the same glass sample was examined in visible Raman scattering using 514.5 nm excitation however, (Fig. 11b) we observed all the other modes except the 537 cm<sup>-1</sup> mode. The result suggests that the electronic states corresponding to the As centered QT local structure reside in the mid-gap region, typical of defect coordination [77]. In previous work [78,79] Raman scattering was excited using 785 nm, or 1.58 eV radiation, but no evidence for the 537 cm<sup>-1</sup> mode was observed.

#### 3.3. Onset of nanoscale phase separation in S-rich glasses

Modulated-DSC experiments performed on the present ternary Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> glasses as a function of glass composition 'x', have permitted to establish trends in glass transition temperature, T<sub>g</sub>(x), (Fig. 12a), the heat capacity jump across T<sub>g</sub>,  $\Delta C_p(x)$  (Fig. 12b), and the enthalpy of relaxation at T<sub>g</sub>,  $\Delta H_{nr}(x)$  (Fig. 12c). And in sharp contrast to DSC, Modulated-DSC permits establishing these calorimetric parameters independent of the scan rate. Finally, trends in  $\Delta H_{nr}(x)$  for glasses synthesized the usual way [31] showed the Reversibility window (RW) to be nearly halved in width, and the edges of the window to be smeared (Fig. 12d) reflecting the larger variance in Ge-and As-content across such glasses.

These trends in Calorimetric observables yield crucial insights in glass structure evolution with the As and Ge content in these ternary Sulfides. The steadily increasing value of  $T_g(x)$  underscores that the connectivity of the glass backbone increases linearly with x. Since one expects Ge, As and S atoms to chemically bond in harmony with the 8-N bonding rule, one expects their coordination-numbers to be 4, 3, and 2 respectively. One can thus write the connectivity of the glassy backbone as.

$$= 4x + 3x + (1-2x)2 = 2 + 3x$$
 (7)

The monotonic increase of  $T_g(x)$ , observed at least at values of x < 18.18%, is in harmony with Eq. (7), suggesting that  $T_g$  provides a good measure of network connectivity [80].

The Sulfur polymerization transition temperature,  $T_{\lambda}$ , was also observed [81] near 150 °C in the S-rich glasses at x < 9.0%. (Fig. 12a). The transition represents [81] an endotherm, which is identified with the opening of S<sub>8</sub> rings leading steadily, at higher temperatures, to an increase in the viscosity of melts as polymeric S<sub>n</sub> chains are formed at elevated temperatures,  $T > T_{\lambda}$  of T = 300 °C and higher [81]. Observation of the  $T_{\lambda}$  and a  $T_{g}$  transition constitutes evidence of



**Fig. 12.** Variation in (a) glass transition temperature  $T_g(x)$  (•) which is quasi-linear and  $T_\lambda$  transition (•) of  $Ge_xAs_xS_{100-2x}$  glasses. In (b) the trends in the specific heat  $\Delta C_p$ , and in (c) the variation in enthalpy of relaxation  $\Delta H_{nr}$  in the fresh (•) and 6 m aged (•), with composition. In the  $9\% \le x \le 16\%$  range  $\Delta H_{nr}$  vanishes because of the isostatic nature of glasses ( $n_c = 3$ ), while  $\Delta H_{nr}$  increases outside IP in Flexible and Stressed-Rigid phases. There is no aging accrued on  $\Delta H_{nr}$  in the IP. The variation in the enthalpy of relaxation  $\Delta H_{nr}$  at  $T_g$  of  $Ge_xAs_xS_{100-2x}$  ternary glasses aged for 1-month (•) and 6 months (•) from [31] in (d), and in homogenized glasses of present work for fresh (•) and 6 months (•) samples in (c). The Reversibility window in the present work in (c) is wider and the edges sharper near the rigidity and stress transitions even in fresh samples when compared with work of Qu et al. in (d). The pink shaded area represents the Nanoscale Phase separation (NSPS). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Nanoscale Phase separation of S-rich glasses. Our obtained values of  $T_g$  and  $T_\lambda$  are compatible with measurements performed earlier using Raman spectroscopy [82,83], and are also close to the value  $T_\lambda$  = 159 °C determined for elemental Sulfur.

As x increases to 18.18%, one approaches the chemical threshold  $(x_{chem})$ . At this composition one has just enough S for the valence of Ge of 4, As of 3 and S of 2 to be fully met bonding locally with S atoms. At  $x > x_{chem}$  there is not enough S present in the backbone, and one expects As–As and Ge–Ge bonds to be manifested, as noted earlier from Raman scattering results (Fig. 8a). In general, one can write the glass stoichiometry,

$$Ge_{x}As_{s}S_{1-2x} = \left[x\left(Ge_{1}S_{\frac{4}{2}}\right)\right]\left[x\left(As_{1}S_{\frac{3}{2}}\right)\right]\left[S_{1-2x-\frac{4x}{2}-\frac{3x}{2}}\right]$$
(8)

And one defines the chemical threshold, as the composition  $x = x_{chem}$ , wherein the excess S-content vanishes., i.e.,

 $x_{chem}(\%) = 18.18\%$ 

#### 3.4. Thermally reversing window

Perhaps the most striking result to emerge from the trends in  $\Delta H_{nr}(x)$  (Fig. 12c) is the square-well nature of its compositional dependence, leading one to define the 3 Topological phases. Specifically, the vanishing of the  $\Delta H_{nr}(x)$  term in the square-well range, 9.0% < x < 16.0%, constitutes signature that the glass transitions become thermally reversing, leading to the reversibility window [16,22,23]. The feature is identified with the Intermediate Phase (IP) when the T<sub>g</sub> become dynamically reversible [80,84]. Our results also show that the walls of the reversibility window are abrupt, a finding that is fully consistent with the homogeneous nature of the bulk glasses synthesized in the present work. The sharp threshold in  $\Delta H_{nr}$ (x), near x = 9.0%, represents the rigidity transition in the present glasses corresponding to < r > = 2 + 3x = 2.27, and separately the sharp threshold in  $\Delta H_{nr}(x)$  near x = 16.0% or < r > = 2.48, corresponds to the stress transition. These percolative elastic phase transitions [3] theory shows to be first order in nature. In glasses that are homogeneous, such as those characterized in the present contribution, i.e., glasses in which the variance in Ge and As across the glass batch compositions synthesized is typically less than 0.05% (Fig. 7c), one can, indeed, expect to observe these transitions to be abrupt [16,22,23]. On the other hand, if the glasses are heterogenous, i.e., for example if the variance in Ge and As across the batch compositions exceeds 3%, these elastic phase transitions will appear smeared [16] and the shape of the reversibility window could then become triangular [85,86], or even Gaussian [39] as noted in earlier studies on binary Ge-Se glasses.

We have also recorded the variation in the enthalpy of relaxation  $\Delta H_{nr}(x)$ , as a function of RT (23 °C) aging the glasses for 6 months (blue data set, Fig. 12c) and find the heat flow term to increase for non-IP glass compositions appreciably but to remain virtually unchanged for the IP glass compositions. The qualitatively reduced aging in the  $\Delta H_{nr}$  (x) term in the IP is due to such glass structures weakly evolving as a function of waiting time, a result that arises from reduced relaxation phenomena [7,87]. That feature of these glassy networks is intimately tied to their stress-free nature [88], and it is akin to a property we routinely associate with crystalline networks.

# 3.5. Onset of nanoscale phase separation (NSPS) at $x > x_{chem}$

The decoupling of the As-As bonds from the glass backbone at  $x > x_{chem}$  in the form of  $As_4S_4$  and  $As_4S_3$  monomers [70,89] was shown by the Raman scattering (Fig. 8a) where one observed the appearance in the spectra of reasonably sharp modes due to intra-monomer modes. The present calorimetric measurements independently confirm the existence of these NSPS effects at x > 18%which is represented by the pink shaded area (Fig. 12a-c). Specifically, the increase in  $T_g(x)$  at  $x > x_{chem}$ , shows a reduced slope suggesting a reduction in the backbone fraction. This feature is much more pronounced in corresponding selenides [90] with a maximum in  $T_g(x)$  occurring at x = 40%, and has been identified as NSPS. In the Sulfides, this effect is much weaker but the loss of some part of the backbone due to these monomers is also manifested in the variation of  $\Delta C_p(x)$  and  $\Delta H_{nr}(x)$  at  $x > x_{chem}$ . Specifically, we observe  $\Delta C_p(x)$ term and the  $\Delta H_{nr}(x)$  term to show a decrease near x = 21%. The reduction in  $\Delta C_p(x)$  term derives from the vibration entropy loss of the backbone since it comes from the thermally reversing heat flow. On the other hand, the reduction in  $\Delta H_{nr}(x)$  term comes from the loss of configurational entropy due to the decoupling of the As-rich fragments. The presence of a significant part of the backbone due to Ge and the As in the form of QT and PYR units continues to contribute to the  $\Delta H_{nr}(x)$  term.

## 3.6. Fragility anomaly

Modulated-DSC experiments also permit probing melt dynamics using exactly the same glass sample used to measure  $T_g$  and the enthalpy of relaxation at  $T_g$ ,  $\Delta H_{nr}(x)$ . This select advantage cannot be overemphasized, given that the alternative of using a traditional method of measuring viscosity requires much larger bulk glasses (much greater than 25 mg used in MDSC), which brings in its own set of challenges of sample make-up including homogeneity. Melt fragility determined from the temperature dependence of viscosity and from the enthalpic relaxation are usually found to slightly differ [91]. However, when tracked as a function of composition the trend for a given set of data/samples/measurements with x keeps its own consistency and provides some insight into the glass relaxation at play.

The fragility index m(x) of the present ternary sulfide melts displays an asymmetric minimum in the IP as displayed in Fig. 13a, with the minimum in m is located near x = 15%. The observed trends in m(x) show that m < 20 for IP compositions, and takes on a value m > 20 for non-IP compositions. The fragile nature of melts for non-IP compositions and the super strong nature of melts at select IP compositions is a feature we have noted elsewhere in the chalcogenides [16,17,22,23]. Trends in the activation energy  $E_a(x)$  for enthalpy relaxation are plotted in Fig. 13b and show a behavior that mimics the variation of m(x) multiplied by  $T_g$ . The inverse of  $E_a$  (x) is of interest because it scales with the melt configuration entropy as visualized in the Adam-Gibbs picture. We have plotted in Fig. 13c the variation of  $1/E_a$  and find the quantity to display a global maximum near x = 15%. Finally, for the purpose of the discussion we have calculated the anticipated viscosity of melts using the measured  $T_{\rm g}$  and assuming that the enthalpic m(x) is valid for determining the viscosity  $\eta(x)$ , using the MYEGA formalism [92].

$$log_{10}\eta(T) = log_{10}\eta_{\infty} + (12 - log_{10}\eta_{\infty})\frac{T_{g}}{T}exp\left[\left(\frac{m(x)}{12 - log_{\infty}\eta_{\infty}} - 1\right)\left(\frac{T_{g}}{T} - 1\right)\right]$$
(9)

In this equation m(x) designates the experimentally determined fragility index,  $T_g$  the glass transition temperature,  $\eta$  the viscosity, and  $\eta_{\infty}$  the high-T viscosity that is set to at 10<sup>-4</sup> Pa.s. The resulting



**Fig. 13.** Variation in (a) fragility index m ( $\bullet$ ) and deduced melt viscosity ( $\bullet$ ) in Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> glasses. In (b) the activation energy of enthalpy relaxation time E<sub>a</sub> ( $\bullet$ ), and in (c) the excess entropy (1/E<sub>a</sub>) ( $\bullet$ ) are plotted. The viscosity of melts in the blue region (IP compositions) increases by nearly 3 orders of magnitude across the IP. This is the case because the fragility index m in the blue region is < 20. In (a) m < 20 for IP composition melts (shaded light blue color) to reveal a triangular minimum of m = 15(1) at x = 15% (shaded dark blue). These melts are super strong. When m > 20 outside the IP range, and melts are viewed as fragile. The super strong nature of IP melts, m(x) < 20, leads such melts to possess the highest projected viscosity, and thus leads to delayed homogenization of chalcogenide melts observed in several recent reports [22,23,52]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

variation of  $\eta(x)$  at a fixed temperature of 650 °C displays a maximum near x = 15%, controlled by the determined minimum in m(x) (Fig. 13a). There are nearly three orders of magnitude *increase in estimated viscosity* in going from x = 9% to x = 15%. The finding has a direct bearing on the slow kinetics of melt homogenization of such melts. We are unaware of results on viscosity for the Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> that could assist in decoding the effect of mass transport on the kinetics of homogenization. One has therefore to rely on an estimate using Eq. (9).

### 3.7. Volumetric window

The molar volume of glasses has served as a powerful means to establish network packing in glasses [93]. Both strong covalent and weaker Van der Waals interactions are implicated. We established the density of the present ternary sulfide glasses using the Archimedes principle, making certain that we worked with large bulk glass specimen of at last 125 mg in size to achieve an accuracy of 0.25% in V<sub>m</sub>.



**Fig. 14.** The compositional trends in (a) enthalpy of relaxation  $\Delta H_{nr}$  at  $T_{\sigma}$  in the range  $5\% \le x \le 25\%$  (b) Molar volumes of homogenized Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> ternary glasses, and (c) using Raman experiments, we deduced the scattering strength ratio of S<sub>8</sub> rings to the backbone modes, and have plotted them as a function of glass composition x. In (a) the glass reversibility window (blue panel) corresponds to melts that are strong, m < 20. In (b) Molar volume measurements show a minimum in the IP composition range defining a volumetric window;  $V_m$  at x = 0, i.e., for Ortho-Rhombic Sulfur is shown in (b). Glass compositions in the 0 < x < 5% range were found to be partially crystalline as shown in panel (b). Variations in the molar volume  $V_m(x)$  of equimolar  $Ge_xAs_xS_{100-2x}$  ternary glasses reported in (b) by Kincl et al. [94] ( $\bullet$ )and by Yang et al. [76] (•) and Aitken et al. [95] (•) are also displayed for comparison with present work (**•**). The Molar volumes in the current work are greater than earlier reports and the molar volume window localized in the IP showing present glasses to be homogeneous. The inset of (c) shows a plot comparing the variation in fragility index of melts with the Raman scattering strength ratio of S8 rings to the backbone modes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Trends in molar volumes of these glasses are displayed in Fig. 14b. To set these results in context we display the reversibility window of the glasses in Fig. 14a and the fragility anomaly in melts in Fig. 13a. These findings clearly show that  $V_m$  of IP glasses display an additional compaction than glasses outside the IP by about  $0.4 \text{ cm}^3/\text{mol}$ . The average  $V_m$  of glasses of non-IP are displayed by the broken red line in Fig. 14b. We plot Raman scattering strength ratio of S<sub>8</sub> rings to the backbone modes with glass composition in Fig. 14c and discuss it in context of self-adaptation of IP glass compositions later.

#### 4. Discussion

# 4.1. Challenges and rewards in homogenizing equimolar $Ge_x As_x S_{100-2x}$ ternary glasses

The homogeneity of glasses and melts is paramount to observing the rigidity- and stress- elastic phase transitions that border Intermediate Phases in glasses, in general. These elastic phase transitions, theory [41] shows are *percolative* and *first order* in nature in which the network connectivity or mean coordination number <r>is the control parameter as the temperature in an ordinary ferromagnetic phase transition. In the present ternary glasses, glass composition, 'x', controls the mean coordination number < r > = 2 + 3x of the glassy networks. Given the observed "width" of the "rigidity-" and "stress-" elastic phase transitions in many homogenized glasses [16] is less than 0.25% in composition, the variance in x, i.e.,  $<\Delta x >$  across a batch composition synthesized has to be better defined than 0.25% to have observed these phase transitions. It is in this context the results of Fig. 7c unambiguously demonstrate that one needs to statically alloy the starting materials for several weeks to achieve a variance in x, i.e.,  $<\Delta x >$  to be less than 0.1%, to observe the intrinsic Topological phases in these glasses.

There are three other crucial parameters that slow down the alloying rates of the starting materials in synthesis of Sulfide glasses in general. First, the Vapor pressure of Sulfur [96] is nearly 10 Atmospheres at T = 640 °C. Syntheses of these Sulfide glasses in evacuated quartz tubes of the S-rich compositions, x < 10%, at T exceeding 650 °C always runs into the risk of quartz tube exploding. Second, the fragility index, m(x), of IP composition melts, are quite low, <20 (Fig. 13a). The expected compositional variation of viscosity at the alloying temperature of 650 °C involves a change of nearly 3 orders of magnitude across the IP (9.0% < x < 16.0%) (Fig. 13a). A melt at x = 15% with m = 15, has the highest viscosity or the lowest diffusivity of any composition in the ternary, and it serves to control the kinetics of melt homogenization of all glass compositions [16]. This is amply supported by our results (Fig. 7c) wherein the kinetics of homogenization slow down qualitatively as x increases to 16%. Third, in S-rich glasses, especially x < 6.7%, or < r > < 2.19, melts of the ternary glasses once quenched from 650 °C, phase separate into a S<sub>8</sub>-ring based amorphous (a-) phase and fragmented segments of the glass backbone. S<sub>8</sub> rings as part of the decoupled a-phase begin to polymerize at T >  $T_{\lambda}$  = 150 °C, displaying an endotherm. The glass backbone softens at  $T_{\mbox{\scriptsize g}}$  and it steadily increases with x. Both endotherms are readily observed in the MDSC scans (Fig. 12a). and are labeled as  $T_g$  and  $T_{\lambda}$ . To promote growth of the glass backbone, we thus incorporated a long-term thermal anneal of the quenched glasses at a T in the range  $T_g < T < T_{\lambda} = 150 \text{ °C}$ , followed by a high-T water quench.

In our synthesis we chose to keep quartz tubes vertical, and not to rock the melt, to facilitate easy detection of melt heterogeneity by probing a merely 2% of the melt column using a 50 µm laser spot size beam. The gravitationally induced segregation of the melt column with the bottom (top) of a melt column being Ge/As-rich(S-rich) respectively, aids in establishing the homogeneity of the glass/melt or lack thereof by probing a minuscule part of it during synthesis. The homogenization kinetics are controlled by the diffusion of the heavier (lighter) atoms moving up (down) the melt column. And we have confirmed if the melt column length were reduced by a factor of 8 the alloying time to homogenize the melt would reduce proportionately [15]. In this work, we were interested to get the most homogeneous melts/glasses to elucidate the physics and chemistry of these Topological phases. We would like to emphasize that FT-Raman profiling yields directly the variance in the glass composition 'x' of the batch composition, and the kinetics are intimately tied to the slow diffusive mixing of IP melt compositions.

Our efforts to synthesize homogeneous melts/glasses led to several rewards. (i) We were able to observe the elusive  $537 \text{ cm}^{-1}$ 

Raman active stretch-mode of the QT S =  $As(S_{1/2})_3$  local structure. Further, we were able to observe four compositional windows of select observables in the IP range. These include (ii) A square-well like Reversibility window in the enthalpy of relaxation (Fig. 12c), (iii) a square-well like Heat capacity change ( $\Delta C_p(x)$ ) window (Fig. 12b), (iv) a square-well like Volumetric window (Fig. 14b), and (v) a melt fragility anomaly (Fig. 13a), across the IP composition range. The observed non-linear variation of these 4 observables yields several new insights on their inter-relations as we comment next.

#### 4.2. Glass homogeneity and molar volumes

The molar volumes of our  $Ge_x As_x S_{100-2x}$  glasses in the IP are the highest of all reports to date (Fig. 14b). It is useful to recall here that in melt rocking synthesis [76,78] 10 g batches were alloyed at 850 °C for 12 h in a rocking furnace. In the study of Kincl et al. [94], 7 g batches were alloyed at 1000 °C for 12 h. In the study of Aitken et al. [95], 36 g batches were alloyed at 925 °C for 24 h. In many of these investigations S-rich compositions (x < 7%) were not synthesized. In sharp contrast, in the present work we used 1.5 g batch sizes and found FT-Raman profiling experiments required typically 40-60 days of alloying time at 650 °C for a one-inch long melt column to homogenize in both S-rich and S-deficient glasses. In our approach we observe homogenization of melts by a diffusion-controlled process as revealed by the ex-situ Raman scattering along the length of a melt column. In our investigations, Raman scattering revealed the 537 cm<sup>-1</sup> mode of QT As-centered local structure to be manifested only once the glasses had homogenized, i.e, when the variance in x (As or Ge content) was reduced to less than 0.1% (Fig. 7c). Neither Yang [76], nor Kincl et al. [94], who examined their glasses in Raman scattering could observe the 537 cm<sup>-1</sup> mode in large part because their batches were much bigger (7 g [94], 10 g [76,78]), which were alloyed for much shorter alloying times (12 h [94], 12 h [76]), but at a higher T (1000 °C [94], 850 °C [76]) than the conditions we presently used. A consequence of using a much higher alloving temperature than we did, is that these groups could not synthesize S-rich glasses with x < 9.0%, (Fig. 7b) because of the high vapor pressure of S. These glasses undergo delayed homogenization because of the superstrong nature, m < 20, of the melts formed in the IP range. Our experiments also show that such homogeneous glasses display the largest V<sub>m</sub> in the IP of the 4 studies documented (Fig. 14b). This is most likely due to the fact that both aspects of local structure mediated by covalent interactions, and extended range structure mediated by the non-bonding van der Waals interactions and Coulomb interactions are well developed in the present glasses. It is the presence of the latter structural organization that molar volumes of the present glasses exceed those in the previous three reports [76,94,95].

# 4.3. Role of glass heterogeneity on aging behavior of the reversibility window

In one of the earliest studies [31] of the Topological Phases of the present equimolar  $Ge_xAs_xS_{100-2x}$  ternary, the reversibility window (RW) was examined as a function of room temperature aging over a period up to 6 months (Fig. 12d). In that study, 2 g batches of the starting materials were alloyed at 900 °C for 48 h. And those bulk glass samples, as we recognize now were heterogeneous. We would estimate the variance in x in those samples to be about 3%. It is thus, useful to directly compare the RW observed [31] in 2005 with the one we have obtained now in present work in 2020 (Fig. 12c). And to assist in understanding the behavior of these RWs, we have included in Fig. 14b the volumetric window obtained on the present homogeneous glasses. Unfortunately, the molar volumes of glasses synthesized in 2005 were not measured. Included in Fig. 12b is the

variation in  $\Delta C_p(x)$  that also reveals a square-well like variation with the walls of the well near those of the RW.

After 1 m of RT aging, the RW in the  $Ge_xAs_xS_{100-2x}$  glasses of 2005 extended from  $x_r = 9\%$  to  $x_s = 16\%$ , with a width,  $x_s - x_r = 7\%$ , (Fig. 12d) close to the one we have observed in the present homogeneous glasses (Fig. 12c) in the fresh state. But after 6 m of RT aging (green data set in Fig. 12d) the RW extended from 11% to 15% and decreased in width to nearly 4%. The behavior is due to the larger variance in the As and Ge content 'x' of the glasses (Fig. 12d) leading to a smearing of the RW edges. Near the outer edges of the RW, non-IP glass compositions occur and these aged as expected, while the IP glass composition towards the inner edges of the RW did not, thus lowering the overall width of the RW after 6 months of RT aging. In sharp contrast the edges of the RW in the present homogeneous glasses are found (Fig. 12c) to be abrupt both in the fresh and 6 maged glasses with the RW width remaining intact even after 6 months of aging. The abruptness of the RW edges, we believe is tied to the Volumetric window which displays a square well-like variation with glass composition (Fig. 14b). There is convincing independent evidence [97] from experiments performed on the Ge<sub>x</sub>Se<sub>100-x</sub> binary that a variance in Molar volumes is invariably linked to a variance in x. The nearly step-like increase in V<sub>m</sub> near x = 9% and x = 16%, thermodynamically must result in the Enthalpy H of the glass to increase abruptly according to Eq. (10).

$$H = U + PV \tag{10}$$

In Eq. (10) the Enthalpy H of the glass is related to its internal Energy U determined by the strong nearest neighbor covalent interactions, and the molar volume V of the glass when the system exists at a pressure P, which in our case would be 1 Atmosphere. The enthalpy of the glass has two components, the reversing heat flow component (related to  $\Delta C_p$ ), and the non-reversing heat flow component ( $\Delta H_{nr}(x)$ ) of the glass backbone. Note that the jump in V<sub>m</sub> (Fig. 14b) closely correlates with the one in the non-reversing heat flow (Fig. 14a), as well as the jump in  $\Delta C_p$  (Fig. 12b), correlates with the rigidity transition near  $x_r = 9.0\%$  and the stress transition,  $x_s = 16.0\%$ . So that one must associate the jump in  $\Delta H_{nr}(x)$  and  $\Delta C_p(x)$  near  $x = x_r$  and  $x = x_s$  as the consequences of the jump in  $V_m(x)$  at the elastic phase transitions.

Equally striking is the reduction in the non-reversing heat flow,  $\Delta H_{nr}$ , and the specific heat jump,  $\Delta C_p$ , in the stressed-rigid glasses in the 19.0% < x < 23.0% composition range (Fig. 12c and d) examined in the previous work [31] and the present work. We believe both these reductions come as a result of NSPS of the monomeric As<sub>4</sub>S<sub>4</sub> and As<sub>4</sub>S<sub>3</sub> molecular units from the glass backbone as observed in Raman scattering results (Fig. 8a). The decoupling of these monomeric species from the backbone, leads naturally to a loss of the two heat-flow terms since they reflect a glass backbone property.

Our final comment relates to the variation of  $\Delta H_{nr}(x)$  heat flow term (Fig. 12c) and reversing heat flow term or  $\Delta C_p(x)$  (Fig. 12b) in the flexible phase, i.e., x < 9.0%. Both these observables in the present homogeneous glasses show a remarkable reduction after a sudden step-like increase at the phase boundary  $x = x_r$ . The reduction is tied to the loss of glass backbone due to the decoupling of S<sub>8</sub> rings from it at x < 9% (Figs. 8c and 14c). This peculiarity is intrinsic to sulfide glasses as the amorphous S<sub>8</sub>-ring phase rapidly grows leading to a loss of backbone. On the other hand, in the heterogeneous ternary glasses of 2005 (Fig. 12d) the observed variation to be a rather smeared version of what transpired in the homogeneous glasses of the present work (Fig. 12c) in the flexible phase. Here we need to recall that both the heat flow terms, reversing and non-reversing, are glass network properties. In sharp contrast to the behavior observed here in the present sulfides, the Selenide glass counterparts display just the reverse behavior in that both these heat flow terms actually increase as glassy networks become more flexible [23]. In the case of the Selenides, polymeric Se<sub>n</sub> chains steadily grow in length, and their intrinsic flexibility leads to the chains to get correlated thereby lowering the configurational entropy of the glass and resulting in the  $\Delta H_{nr}$  term to increase as noted in the Ge<sub>x</sub>As<sub>x</sub>Se<sub>100-2x</sub> ternary [23] and the Ge<sub>x</sub>Se<sub>100-x</sub> binary [16] glass systems. Remarkably as x < 6% in the binary and x < 4% in the ternary, the Se-rich glasses enter a new super-flexible phase[98] in which long polymeric chains of Se<sub>n</sub> reconstruct with each other as van der Waals mediated inter-chains correlations grow at the expense of the covalently bonded intrachain ones. A spectacular manifestation of the underlying structural change is the reduction in the width of the glass transition. The width of T<sub>g</sub> in pure Se is found to decrease from 7.5 °C in the fresh state to 1.5 °C upon room temperature relaxation (aging) for 8 months [98].

Rigidity theory shows [41] that the rigidity- and stress-elastic phase transitions that define the IP (Fig. 12c) are percolative and first order in nature. The controlling parameter is the mean coordination number, < r >, which is given by 2+3x for the present ternary glasses. Ultimately, sharpness of the edges of the RW probed in experiments is tied directly to the variance in < r >, or the variance in x, across the glass specimen synthesized. For these reasons synthesis of homogeneous bulk glasses is a pre-requisite to observe the three Topological phases in network glasses. In homogenized glasses of the present work (Figs. 12 and 14) one unequivocally observes many observables to apparently display a square-well like variation with the IP glass composition limits.

# 4.4. Correlating melt dynamics and configurational entropy with glass topological phases in equimolar $Ge_xAs_xS_{100-2x}$ ternary glasses

The observation of a square-well like variation in the Enthalpy of relaxation at T<sub>g</sub>, the Reversibility Window (Fig. 14a) fixes the three Topological Phases in the present equimolar ternary glasses as we noted earlier. Glass compositions in the RW are isostatically rigid  $(n_c = 3)$ , i.e., in the IP, with the onset near x = 9.0%, defines the rigidity transition, while the end near x = 16.0%, defines the stress transition. Glass compositions at x < 9.0% are in the Flexible phase, while those at x > 16.0% in the Stressed-rigid Phase. Compositional trends in the fragility index, m(x), show IP glass compositions possess m < 20, (Fragility Anomaly) i.e., are super-strong, while non-IP glass compositions possess m > 20, and become increasingly fragile as one goes away from the IP range (Fig. 13a). These results unequivocally show that super-strong melts upon viscous slowdown will give rise to IP glasses, while fragile melts will give rise to either Flexible- or Stressed-rigid glasses. One can also distinguish Stressed-Rigid from Flexible melts as follows. In Stressed-rigid melts the fragility index increases as  $T_g$  increases (compare Fig. 12a with 13a). The reverse circumstance prevails for Flexible Phase melts in which m increases as Tg decreases.

The pattern noted above linking melt dynamics with the glass TPs in the equimolar  $Ge_xAs_xS_{100-2x}$  ternary has been noted in several other chalcogenide glasses [99] and even modified oxides. These select examples, each involved the use of specially homogenized melts/glasses. The case of the  $Ge_xS_{100-x}$  binary [17],  $Ge_xSe_{100-x}$  binary [40], and the  $Ge_xAs_xSe_{100-2x}$  ternary [23] are representative examples wherein melt dynamics are closely correlated to the TPs. Amongst the modified oxides, we have the case of (Na2O)<sub>x</sub> (P2O5)<sub>100-x</sub>, where again the same pattern [21] is noted. It thus appears the said correlation could well be a general behavior [99] in glasses.

 $SiO_2$  melt is widely acknowledged [66] to possess a fragility index of m = 20.  $SiO_2$  glass possesses zero frequency modes associated with Rigid Unit Modes [100] as documented from neutron scattering measurements. For this reason  $SiO_2$  glass cannot be regarded as being fully self-organized but it is closed to being self-organized [101] since the count of constraints per atom,  $n_c = 3$ . The observation of melt fragility index, m < 20, for melts of IP glass compositions suggests that the super-strong character is tied to the absence of floppy modes at T > T<sub>g</sub> in melts, as in the glasses T < T<sub>g</sub>.

We conclude this section with a final remark. Melt configurational entropy,  $S_c$ , can be directly obtained from the measured activation energy for enthalpy relaxation ( $S_c \sim 1/E_a(x)$ ), (Fig. 13c) deduced from the MDSC experiments. A global minimum in  $E_a$  in the IP compositions (Fig. 13b) leads, as expected, to a global maximum of  $S_c$  for the same melt compositions. Such a result was also noted earlier in investigations of chalcogenide glasses [17,22,23,40] wherein a deliberate effort to synthesize homogeneous melts was made by FT Raman profiling. The high  $S_c$  of IP glassy melts is suggestive that networks composed of isostatically rigid local structures such as  $As(S_{1/2})_3$ ,  $S = As(S_{1/2})_3$ ,  $GeS_4$  CS can be reconfigured in a multitude of configurations thereby increasing  $S_c$ . The high  $S_c$  clearly suggests that such melts and the resulting glasses will display minimal aging.

# 4.5. Evidence for adaptability of $S_8$ rings in the intermediate phase of the equimolar $Ge_xAs_xS_{100-2x}$ ternary glasses, and origin of the fragility anomaly

The variation in Fragility index in the Se based chalcogenides have broadly shown a Gaussian-like minimum centered around the IP composition range with m < 20, the fragility anomaly (FA). At the centroid of the FA, the fragility index m is in the 15–17 range. Illustrative examples include the equimolar  $Ge_xAs_xSe_{100-2x}$ , and the binary  $Ge_xSe_{100-x}$ . Specifically, in the  $Ge_xSe_{100-x}$  binary, one finds m (x = 23%) = 15 near the IP centroid composition [40]. In the equimolar  $Ge_xAs_xSe_{100-2x}$  ternary, m = 17 at x = 14%, near the mid-point of the Fragility [23] anomaly.

In the present equimolar Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> ternary sulfides the fragility anomaly is rather asymmetric, in sharp contrast to the case of the Selenide glasses discussed above. Specifically, the fragility anomaly appears to be almost triangular rather than Gaussian, and the minimum fragility of m = 15 is observed close to the melt composition x = 15%, in other words close to the stress transition near x = 16% (Fig. 13a). This super strong melt composition coincidently is manifested when in the glass structure the S<sub>8</sub> -ring fraction vanishes as illustrated in Fig. 14c. Particularly noteworthy is the fact that as the S<sub>8</sub> ring fraction increases as x decreases in the 9% < x < 15% range (Fig. 14c), and we find the fragility index of the melts, m(x) steadily increases in the 15 < m < 20 range. The S<sub>8</sub> rings are monomeric species that enter in van der Waals non-bonding interaction with the glass network backbone. As a glass is heated to  $T > T_g$ , the backbone softens and the S<sub>8</sub> ring species must become mobile, a fact that is translated in an increase of the fragility as depicted in the inset of Fig. 14c. Note as the S<sub>8</sub> fraction increases so does the fragility index. The increase of fragility at x > 15% even though the S<sub>8</sub> ring fraction is vanishing, we believe is tied to the V<sub>m</sub> of melts increasing. And as one enters the Stressed-rigid or the Flexible phase, melts become increasing fragile. Building upon our understanding of the asymmetric variation of the fragility index in the IP of the present ternary; the binary As<sub>x</sub>S<sub>100-x</sub>, although displaying traces of S<sub>8</sub> in Raman scattering, exhibits a symmetric Gaussian like minimum variation across the IP. In the  $As_xS_{100\text{-}x}\!,$  the glass transition is roughly 20  $^\circ\text{C}$ lower than the  $T_{\lambda}$  transition thus suppressing the transformation of the S<sub>8</sub> rings into sulfur chains.

Perhaps the most remarkable result to emerge from Figs. 13a and 14a, is that although the enthalpy of relaxation at  $T_g$ ,  $\Delta H_{nr}(x)$ , remains minuscule across the IP compositions in the glasses, corresponding melt composition become increasingly fragile as the  $S_8$  ring fraction increases in the 9% < x < 15% (inset of Fig. 14c). It is clear that the presence of the  $S_8$  monomeric species in the glass backbone does not influence the isostatic nature of the glass backbone. The IP

glass compositions adapt to the presence of these foreign impurities and retain their isostatic nature. The adaptability of IP compositions was recognized [24] since the discovery of the stress-free nature [102] of the new phase [6]. For example, as Ge is steadily alloyed in binary  $Ge_xSe_{100-x}$  glasses at x > 20%, it selectively bonds in flexible regions driving them isostatically rigid, a process at the heart of selforganization of the IP. The process eventually terminates at x > 26%, when redundant bonds cannot be avoided thus driving the glass as a whole stressed rigid in a first order transition [41].

#### 5. Conclusions

We have synthesized bulk glasses of the equimolar  $Ge_xAs_xS_{100-2x}$ ternary glasses over a wide range of compositions, 5.0% < x < 25.0%, and performed detailed Raman scattering, Modulated-DSC and Volumetric measurements. All batch compositions were homogenized by FT Raman profiling. (i) Our results show that the Intermediate Phase (IP) resides in the 9.0% < x < 16.0% range, with compositions x < 9.0% in the flexible phase, and compositions x > 16.0% in the stressed-rigid phase. (ii) Homogenization of glasses is a prerequisite to observe the 537 cm<sup>-1</sup> Raman active mode of the S = As stretch of quasi-tetrahedral S =  $As(S_{1/2})_3$  local structure. (iii) In addition to establishing the square-well like variation of the nonreversing enthalpy of relaxation  $\Delta H_{nr}(x)$  at T<sub>g</sub> fixing the Reversibility window, we also observed a square-well like lowering of the molar volumes,  $V_m(x)$ , in the IP composition range fixing the Volumetric window. (iv) Melt fragility index measurements showed a global minimum for IP compositions (9.0% < x < 16.0%) with m < 20, and with the fragility index, m > 20 for non-IP compositions, defining a Fragility Anomaly. (v). In the present ternary, the Fragility anomaly is asymmetric showing a global minimum near x = 15% close to the edge of the Stress-transition composition of x = 16.0%. The Fragility anomaly is due to the presence of a small but finite concentration of S<sub>8</sub> rings that steadily decreases to vanish as x increases to 15%. The S<sub>8</sub> concentration leads the composition x = 15% to be super-strong, with m = 15.0. The manifestation of the isostatic nature of the IP with a finite concentration of S<sub>8</sub> rings provides evidence for adaptability of the IP.

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#### **CRediT authorship contribution statement**

All authors contributed equally towards the research undertaken in this project.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.159101.

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