

# Correlating Melt Dynamics and Configurational Entropy Change with Topological Phases of As<sub>x</sub>S<sub>100-x</sub> Glasses and the Crucial Role of Melt/Glass Homogenization

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by

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### Abstract

Glass topological phases and melt dynamics of especially dry and homogeneous binary As<sub>x</sub>S<sub>100-x</sub> melts/glasses are studied in Raman scattering, Modulated-DSC and volumetric experiments. In the S-rich glasses (12% < x < 23%), unambiguous and direct evidence for the elusive 537 cm<sup>-1</sup> stretch vibrational mode of the Quasi-Tetrahedral (QT),  $S=As(S_{1/2})_3$ , local structure is observed in Fourier Transform -Raman (FT-Raman) scattering once the melts homogenized and the glasses cycled through  $T_g$ +10°C for an extended period. The enthalpy of relaxation at  $T_g$ ,  $\Delta H_{nr}(x)$ , fragility index, m(x), Molar volumes  $V_m(x)$  – each display three distinct regime of variation. Specifically,  $\Delta H_{nr}(x)$  shows an abrupt square-well like variation (Reversibility window), and m(x) shows a Gaussian like global minimum (Fragility window) whereas V<sub>m</sub>(x) shows a Gaussian-like local minimum (Volumetric window) in the isostatically rigid phase (22.5% < x < 28.5%). At low x (< 20%) in the Flexible phase, glasses are segregated with a S<sub>8</sub>-rich nanophase that decouples from the As-S glassy backbone. At medium x (22.5% < x < 28.5%) glassy backbones form an isostatically rigid phase displaying a vanishing  $\Delta H_{nr}(x)$  term, and compacted structures with corresponding melts being super-strong (m  $\leq$  20). At high x (28.5%) < x < 40%) in the Stressed-Rigid phase, glasses possess an increasing  $\Delta H_{nr}(x)$  term, and melts become increasingly fragile, with m(x) > 20 as x increases. Taken together, these results demonstrate that super-strong melts yield isostatically rigid glasses, while fragile glasses form either Flexible or Stressed-Rigid upon cooling. The onset of the rigidity transition near  $\langle r \rangle = 2.22$  instead of the usual value of  $\langle r \rangle$ = 2.40, is identified with the presence of QT local units in addition to pyramidal  $As(S_{1/2})_3$  local units in the glassy backbone, and with a small but finite fraction of polymeric S<sub>n</sub> chains being decoupled from the backbone.

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&

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28.5% range (light-blue panel). (b) The inverse of activation energy  $E_a$ , for enthalpy relaxation times is also plotted. (a) Glass reversibility window is plotted in light blue panel. (b) Compositions having m < 20 defines the fragility window. (c) Local minimum in molar volumes illustrates the volumetric window in glasses. For a better understanding,  $V_m(x)$  results at x > 30% are redrawn on a coarser ordinate scale on the right to illustrate the reduction in  $V_m$  in both glassy and crystalline As<sub>2</sub>S<sub>3</sub> [14.10(2) cm<sup>3</sup>] [16].

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**Figure A1:** Eigenvectors of the Raman and IR active vibrational modes of PYR and QT local structures obtained by NRLMOL calculations. The figure is taken from [12].

**Figure A2: (a)** Compositional trends in the normalized Raman Scattering Strength of the 537 cm<sup>-1</sup> of the QT local structures ( $S=As(S_{1/2})_3$ ) and (b) <sup>31</sup>P NMR signal of QT ( $Se=P(Se_{1/2})_3$ ) local structures in binary P-Se glasses. Both the maxima occurs precursive to respective Intermediate Phases [18].

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**Table 1:** Raman and IR vibrational modes of As-S clusters.

### **Chapter 1**

### Introduction

#### **1.1 Topological Constraint Theory**

In 1979, J.C. Phillips suggested that the glass forming tendency in covalently bonded networks, such as  $Ge_xSe_{100-x}$  or  $As_xSe_{100-x}$ , would be optimized when the mean coordination number,  $\langle r \rangle$ , were neither too high nor too low [1]. The general view was that networks with high- and low  $\langle r \rangle$  usually crystallize. Phillips analyzed the glass forming tendency in binary  $Ge_xSe_{100-x}$  glasses and using the notion that near-neighbor (nn) bond-stretching forces and  $2^{nd}$  nn bond-bending forces in these covalent networks can be viewed as Lagrangian constraints. And when the count of constraints/atom, n<sub>c</sub>, equals the degrees of freedom per atom, glassy networks become isostatic. He then concluded that in binary  $Ge_xSe_{100-x}$  melts the glass forming tendency would be optimized near an optimal or magic mean coordination number of

$$< r >_{c} = 2.40$$
 (1)

M.F. Thorpe [2] examined the vibrational behavior of these covalent networks with increasing mean coordination number, <r>. He found that networks with <r> < 2.40 or  $n_c < 3$ , possessed zero frequency modes – he called them floppy modes [3]. And when networks became isostatic, i.e., when <r> = 2.40 or  $n_c = 3$ , in a mean-field description, the count of floppy modes vanished. Thus, he suggested that the isostatic

condition coincided with flexible networks (with floppy modes) becoming rigid when  $n_c$  increased to 3. Thus, the flexible to rigid transition near  $n_c = 3$ , was then broadly viewed as percolation of rigidity [4], [5] in glassy networks.

The case of the two stoichiometric glasses,  $As_2S_3$  and  $As_2Se_3$ , drew special attention because these glasses not only possessed excellent glass forming tendency, but their networks are isostatic, and possess a mean coordination number,  $\langle r \rangle$  of 2.40. These two stoichiometric glasses are composed of  $As(X_{1/2})_3$  pyramidal units with As and X = S or Se possessing a coordination number of 3 and 2 respectively. In a formula unit of the pyramidal (PYR) local structure, we have one As, and 3/2 S atoms, and thus the mean coordination number of the PYR unit becomes,

$$<\mathbf{r}>=[3+2\mathbf{x}1/2\mathbf{x}3]1/[2.50]=2.40$$
 (2)

Furthermore, if one counts the number of constraints/atoms,  $n_c$ , due to bondstretching forces (r/2) and bond bending forces (2r-3), one obtains for a PYR unit,

$$n_{c} = \left[ (3/2 + 3)_{As} + 3/2(1 + 1)_{S} \right] / 2.50 = 3$$
(3)

And as the field emerged it was not entirely obvious that percolation of network rigidity would occur in both these stoichiometric glasses near x = 40%, largely because these glass compositions are also at the chemical threshold. At the chemical threshold composition only heteropolar bonds, As-X, exist. At x < 40%, homopolar bonds, S-S, Se-Se, proliferate, while at x > 40%, As-As bonds form. The maximum of the glass transition temperature  $T_g(x)$  occurs at x = 40%, and it was clearly in harmony with their chemically ordered structure.

# **1.2 Three Topological Phases and the Reversibility Window in Group V Chalcogenides**

The search for the isostatically rigid compositions i.e.,  $n_c = 3$  in real network glasses eventually revealed their presence in off-stoichiometric compositions, with a finite compositional width but rarely at a solitary glass composition as first suggested by Phillips and Thorpe [1], [4]. Thus, for example, calorimetric measurements over a broad range of compositions on binary Si<sub>x</sub>Se<sub>100-x</sub> [6] and Ge<sub>x</sub>Se<sub>100-x</sub> [7] glasses showed that the non-reversing enthalpy of relaxation at T<sub>g</sub>, revealed a square-well like variation with the enthalpy vanishing in the 20% < x < 26% range. The vanishing of the enthalpy was signature of the isostatic character of the compositions [8], also called thermally reversing windows or Intermediate Phases. In these phases, glass transitions became dynamically reversible, networks could adapt [9] and selforganize [10]. Experiments also showed that elastically flexible glasses occurred with  $n_c < 3$ , or <r> < 2.40, and elastically stressed-rigid ones with  $n_c > 3$ , or <r> >2.40. The observation of the IP in binary  $As_x Se_{100-x}$  glasses [11], in the 29% < x < 37% range, and in binary  $As_xS_{100-x}$  glasses[12], in the 22.5% < x < 29.5% range, showed unquestionably that IPs can be manifested at a mean coordination number <r> < 2.40. The observation added more excitement to an already interesting situation. In 2009, it was suggested [13] that the shift of the IP to compositions at <r> < 2.40 with the group V chalcogenides, most likely, is related to the presence of Quasi-tetrahedral local structure of the type  $S=As(S_{1/2})_3$  (Figure 1.1) that are also isostatic and possess a mean coordination number, <r> = 2.28, which is less than the magic value of 2.40.



**Figure 1.1:** Local structures of Quasi-Tetrahedral,  $S=As(S_{1/2})_3$  on the left and Pyramidal,  $As(S_{1/2})_3$  on the right. Both structures are isostatic, with  $n_c = 3$ . The structure on the left possesses a lower mean coordination number (<r>) of 2.285 than the one on the right, with a <r> = 2.40. Both these structures contribute to the formation of the IP in  $As_xS_{100-x}$  glasses.

# **1.3 Delayed Homogenization of Glass Forming Chalcogenide** melts

In 2011, an important breakthrough occurred in the field of experimental glass science. One discovered that usual chalcogenides and modified oxide glasses, when synthesized by alloying usual precursors in evacuated quartz tubing generally undergo delayed homogenization [14], [15]. Thus, for example, in the case of the binary Ge<sub>x</sub>Se<sub>100-x</sub> glass system, one found that 2 gram batches of Ge and Se when alloyed at 950°C, the variance of Ge across the batch composition,  $<\Delta x>$  is typically 3% after 2 days of alloying, but it then steadily decreases to about 0.1% after almost 7-9 days of alloying. The result emerged when melts were steadily ex-situe FT-

Raman profiled along the 1-inch length of melt column at 8 locations, and one found Raman spectra became identical at these 8 locations after 7 to 9 days of alloying.

#### **1.4 Goals of the Present Thesis project**

We made a deliberate effort to synthesize homogeneous  $As_xS_{100-x}$  glasses over a wide composition range 10% < x < 40% range. In contrast to the earlier study of 2008, when we were unaware of the challenges of delayed homogenization, melts were typically alloyed at 650°C for 2 to 3 days [12]. In the present work we have found melts needed to be alloyed for at least 4 weeks to achieve homogenization, i.e., the variance in As content 'x' across the synthesized batch to be about 0.1%. The challenges in synthesizing homogeneous and dry  $As_xS_{100-x}$  glasses/melts at more than a dozen compositions, "x", over a wide composition range 10% < x < 40%, has paid rich dividends as we comment next.

We observe (**Figure 1.2**) (i) evidence of a sharp <u>reversibility window</u> in the 22.5% < x < 28.5% range, (ii) a <u>volumetric window</u> that is completely localized in the reversibility window, (iii) a <u>fragility window</u> with the fragility index m < 20 in the IP and with m > 20 outside the IP. (iv) Finally, we observe unambiguous <u>evidence</u> for the elusive 537 cm<sup>-1</sup> mode of the As=S stretch vibration of quasi-tetrahedral S=As(S<sub>1/2</sub>)<sub>3</sub> local structures once glasses are homogenized. To observe the 537 cm<sup>-1</sup> multi-step processing was employed to promote growth of the As-S glass backbone in the S-rich concentrations (x < 20%). The presence of an amorphous S<sub>8</sub> ring phase that forms in the S-rich glass compositions, serves as an impediment to homogenization of glasses, and in turn serves to make observation of the 537 cm<sup>-1</sup> mode more challenging.



**Figure 1.2:** Compositional trends of  $As_x S_{100-x}$  glasses in (a) enthalpy of relaxation at  $T_g (\Delta H_{nr})$  (b) melt fragility index and (c) glass molar volumes displaying local minima in the 22.5% < x < 28.5% range, the light blue panel. In (b) we also plot the inverse of the activation energy,  $E_a$ , for enthalpy relaxation times. In (a) the light blue panel gives the glass reversibility window, (b) compositions for which m < 20 defines the fragility window, and in (c) the local minimum in molar Volumes illustrates the volumetric window in glasses. To better illustrate  $V_m(x)$  results at x > 30%, we have redrawn the data on a coarser ordinate scale on the right to illustrate the reduction in  $V_m$  in both g- and c-  $As_2S_3$  [14.10(2)] cm<sup>3</sup> [16].

In Figure 1.3c we show the IP in the  $P_xSe_{100-x}$  binary glass system and find the rigidity- and stress- transitions occur respectively near  $\langle r \rangle = 2.28$  and 2.40. The binary represents a textbook example of a group V selenide in which the edges of the IP are determined by the QT Se=P(Se<sub>1/2</sub>)<sub>3</sub> and the PYR P(Se<sub>1/2</sub>)<sub>3</sub> local structure, possessing respectively the mean coordination number of 2.28 and 2.40. <sup>31</sup>P NMR experiments further reveal that the concentration of the QT local structure shows a maximum near  $\langle r \rangle = 2.35$ . In the group V sulfides as illustrated in Figure 1.3a, again we find that the concentration of the QT local structure shows a maximum at <r>> below the onset of the IP as in case of Figure 1.3c. In the sulfide glass, the 537  $cm^{-1}$  stretch mode is not observed at < r > < 2.18 largely because of the formation of an amorphous S<sub>8</sub> ring phase in the S-rich glasses as illustrated by the hashed marked region. But as we will show in the Thesis, the QT  $S=As(S_{1/2})_3$  local structure does indeed form at <r> < 2.18 as the other two normal modes of that local structure are, indeed, clearly observed in Raman scattering. A parallel situation prevails in the companion equimolar  $Ge_x As_x S_{100-2x}$  ternary glasses as shown in Figure 1.3b. In summary, by synthesizing homogeneous As-S binary melts/glasses, we have for the first time shown in this work, shown a close connection between glass structure, melt dynamics and glass Topological Phases. Previous attempts to the non-observation of the 537 cm<sup>-1</sup> mode in As-S glasses is entirely tied to the synthesis of heterogenous glasses [17].

#### **1.5 Structure of the Thesis presentation**

In Section 2 we provide the *Methods and Materials* used in the current project, followed by Section 3 where we provide the *Experimental results*. In Section 4 on Discussion we discuss select issues of general interest in understanding the

Topological phases in the present  $As_xS_{100-x}$  binary glasses and the correlation of these phases with the corresponding melt dynamics. The conclusions from the present work are summarized in **Section 5**.



**Figure 1.3:** Compositional trends in the normalized Raman Scattering strength of the 537 cm<sup>-1</sup> of the Quasi-Tetrahedral (S=As(S<sub>1/2</sub>)<sub>3</sub>) local structures observed in (a) As<sub>x</sub>S<sub>100-x</sub> glasses (b) in Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> glasses. In (c) we plot the observed <sup>31</sup>P NMR signal of Quasi-Tetrahedral (Se=P(Se<sub>1/2</sub>)<sub>3</sub>) local structures (•) in binary P-Se glasses

and the observed IP (•) that extends in the 2.28 < <r> < 2.40 range from Georgiev et al. [18]. Note that the maxima in scattering strength of the QT mode in each panel indicated by arrows are compositions that are precursive to the onset of rigidity. The hashed line curve line in (a) and (b) represents the expected variation of in the scattering strength of the 537 cm<sup>-1</sup> mode observed in the S-rich glasses (<r> < 2.18), had there been no S<sub>8</sub>-ring based amorphous phase (light blue hashed marked region). In each case studied (a)-(c), the QT local structure is observed across the IPs. The other local structures contributing to the IP include As(S<sub>1/2</sub>)<sub>3</sub> in (a), both As(S<sub>1/2</sub>)<sub>3</sub> and Ge(S<sub>1/2</sub>)<sub>4</sub> and ES GeS<sub>2</sub> and in (c) P(Se<sub>1/2</sub>)<sub>3</sub> that are not shown.

### Chapter 2

### **Materials and Methods**

#### 2.1 Sample Synthesis

 $As_x S_{100-x}$  bulk glasses were synthesized in the range 12 mol % < x < 40 mol % using 99.9999% As<sub>2</sub>S<sub>3</sub> lumps having diameter typically 3 mm and 99.9999% elemental S platelets from Cerac Inc. The precursor materials were weighed accurately and placed inside dry quartz tubes of 5 mm internal diameter and 1 mm wall thickness, which were stored inside a vacuum oven at 80°C for at least 24 hours prior to use. This was done to make sure that no trace of moisture encounters the precursor materials during the synthesis process. Both the starting materials of As<sub>2</sub>S<sub>3</sub> lumps and S platelets were stored inside  $N_2$  purged glove box with a relative humidity of less than 0.1%. In addition, the elemental S platelets were vacuum dried by pumping to 10<sup>-6</sup> Torr for 48 hours to remove every bit of moisture content. Sample preparation procedure was undertaken inside a glove bag with relative humidity less than 5%. The quartz tubes containing the starting materials were then placed on a Veeco LN<sub>2</sub> trapped diffusion pump system and evacuated to  $3 \times 10^{-7}$  Torr. As soon as the desired pressure reached, the quartz tubes were sealed using a hydrogen – oxygen torch under vacuum. The sealed quartz tubes were then placed vertically inside a box furnace. The starting materials were then alloyed by slowly increasing the temperature of the furnace to 650°C and held there for varying alloying times, t<sub>r</sub>, to ensure the melts completely homogenized. Post alloying, the reaction temperature is decreased to 50°C above the liquidus temperature and held there for a few hours to

allow the alloyed melt to settle at the bottom of the quartz tube. In the final step of the synthesis, the quartz tubes containing the alloyed materials are quenched in a bucket of cold water.



**16% 18% 20% 24% 26%** 

**Figure 2.1:** Picture of synthesized glasses showing a change of color from a dull yellow at low x (16.0%) transitioning to darker yellow at x = 18%, and to darker orange as x increased to 26.0%. Each glass sample displays a clean looking meniscus. At x = 20%, we used the 1.8 cm long glass column below the meniscus to acquire ex-situ Raman scattering at 5 locations as melts were alloyed. Batch compositions were considered homogeneous when these spectra became identical.

### 2.2 Raman Spectroscopy

### 2.2.1 Brief introduction

Raman scattering takes place when light interacts with molecules. There are two types of light scattering phenomena observed, the predominant one is elastic light scattering also known as the Rayleigh light scattering and a very small amount of light scattered is inelastic, known as Raman scattering. In Raman spectroscopy, when a light is incident on a sample, it gets excited onto a virtual state for a short period of time. When molecules return to their ground state, photon is emitted. The photon energy can either be higher or lower than the incident light. This is known as inelastic scattering (**Figure 2.2**). Inelastic scattering can be either Stokes or Antistokes. If it is a stokes scattering, then the incident energy of the light will be higher than that of the emitted photon energy. If it is anti-stokes, the molecule is in excited vibrational state after incident light excitation. The photon emitted will have higher energy compared to excitation energy.



**Figure 2.2:** Schematic of an energy level diagram showing the states involved in Raman spectra. In stokes scattering, scattered photon is of lesser energy compared to incident beam and in anti-stokes scattering, scattered photon is of greater energy compared to incident beam.

# 2.2.2 FT – Raman Scattering

To examine the molecular structure of glasses, a Thermo-Nicolet model Nexus 870 FTIR with InGaAs/Ge detector module was used. Inside evacuated quartz tubes, glasses were encapsulated, mounted on an xyz stage of the Raman module. The glasses were examined by focusing 125 mW of the 1064 nm radiation with a 50-

micron spot size (micro-configuration) from a Nd:YAG laser. Under ideal conditions, one should use the smallest spot size to determine a realistic estimate of the glass heterogeneity [19]. Typically for a Raman scattering experiment, 200 scans were recorded yielding a 2 cm<sup>-1</sup> resolution. It took about 15 minutes for a scan to be acquired. For a glass specimen examined at 5 locations typically, it took 75 minutes to record the Raman spectra along the length of the melt column. The bandgap of Arsenic-Sulfide glasses varies in the range 2.3 eV  $\leq E_g \leq 2.8$  eV [20] across the composition range 40% > x > 12% studied in this work. 1064 nm (1.67 eV) radiation is transparent to all As<sub>x</sub>S<sub>100-x</sub> glasses examined and yielded high signal/noise ratio spectra. To check for batch homogeneity, all the Raman spectra was normalized to the vibrational mode with the highest scattering strength, which in the context of the present work was either the  $S_8$  – ring and  $S_n$  chain mode for S – rich glasses (x < 17%), or the broad band centered around 340 cm<sup>-1</sup> which is made up of glass backbone modes for high As composition glasses (x > 17%). After recording and normalizing the Raman spectra at 5 locations, the spread in scattering strength of other vibrational modes with sample location, directly permitted to establish the variance in As content.  $\langle \Delta x \rangle_{As}$  across 1.5-gram batch size composition. It served as a quantitative measure of batch heterogeneity in these Raman profiling experiments.



**Figure 2.3:** FT-Raman scattering of  $As_{19}S_{81}$  glass alloyed (a) for  $t_r = 6d$ , show Asvariance  $\langle \Delta x \rangle_{As} = 4.20\%$ , (b) for  $t_r = 18d$ , the variance reduced to 1.88%, (c) for  $t_r = 25d$ , it reduced further to 0.74%, (d) and for  $t_r = 33d$  saturates to 0.28%. The reduced As variance across the 1.5 gm batch composition is taken as evidence of glass homogenization upon continued alloying. In (d), the homogenized melt/glass upon thermal quench from 650°C displays a segregated backbone immersed in sea of S<sub>8</sub>-ring fragments. In (e) heating the glass at  $T_g + 10°C = 105°C$  for 2d, results in fragments of the backbone coalescing, and the observation of the 537 cm<sup>-1</sup> mode of QT units. In (f) by taking the glass of (e) to 650°C for 2d and water quenching it, leads to further growth of the elusive 537 cm<sup>-1</sup> mode, and substantial amount of

additional Sulfur alloying in the backbone inferred from the qualitative reduction of the  $S_8$ -ring fraction between spectrum (e & f).

### 2.3 Calorimetry

# 2.3.1 Brief overview

Differential Scanning Calorimetry (DSC) has been used primarily for thermal characterization. There are certain shortcomings in the technique of DSC; hence, a new sophisticated technique known as Modulated Differential Scanning Calorimetry (MDSC) has been introduced. I am going to discuss both the techniques and then state why in our research we use MDSC as opposed to DSC.

DSC uses a linear heating rate with a single total heat flow signal occurring at any point in the experiment. [Len Thomas papers] [figure of DSC scan]. These experiments run at a heating rate of 10°C/min. But there remain some challenges in interpreting the data. It is not possible to extract various thermal events that occur during phase transitions in sample.


**Figure 2.4:** DSC experiment with a linear heating rate of 10°C/min (blue signal) and the output heat flow (green signal) which is the sum of all heat flows occurring at any point in temperature or time of the experiment.

In the case of Modulated DSC experiments, the linear heating rate typically used is 3°C/min along with a sinusoidal heat flow superimposed on top of it (see Figure 8). The equation written below represents the modulated heal flow mathematically.

$$\frac{dH}{dt} = Cp\frac{dT}{dt} + f(T,t)$$



Figure 2.5: Sinusoidal heat flow superimposed on linear heating rate.

 $\frac{dH}{dt} = \text{Total heat flow caused by linear heating rate}$  $C_{p} \ge \frac{dT}{dt} = \text{Reversing Heat Flow from modulated heating rate}$ 

f(T, t) = Non-reversing Heat Flow calculated by subtracting the difference between Total and Reversing Heat Flow.

An advantage and appealing feature of MDSC is that both glass and melt properties can be studied using the same glass sample sealed in hermetically sealed aluminum pans. In our lab we use a model Q2000 MDSC from TA Instruments Inc. to study the nature of glass transitions [15] [21].

#### 2.3.2 Tg and Enthalpy of Relaxation of glasses

Before using the Q2000 calorimeter, system was calibrated thoroughly for Temperature using Indium metal as reference and the specific heat  $C_p$  using a standard sapphire calibration. The cell constant was established and uploaded in the software before running any experiment. The basic calibration procedure is as follows:

(i) Baseline calibration – In this step, an empty cell is heated through the temperature range required for all our subsequent experiments. The software then automatically applies the required constants to make the baseline flat and zero the heat flow signal.

(ii) Cell constant calibration – In this step, an Indium standard is heated across its melting transition. The software then automatically calculates the heat of fusion by comparing the calculated value to the theoretical value. The ratio between the two values is calculated and then inserted in the software as cell constant.

(iii) Cell temperature calibration – Indium standard is heated again across its melting transition. The software automatically extrapolates onset of recorded melting point of the indium metal and compares it to the known melting point. Difference between these two values is used by the instrument as temperature calibration constant.

(iv) Heat capacity signal calibration – This step requires a sapphire standard. The sapphire standard is run under the exact same conditions as the experimental conditions. The calibration constant is then calculated with the following equation:

Calibration constant = Theoretical value / Measured value

The calculated calibration constant is then put into the software before running the experiments.

The figure below illustrates a measurement of  $T_g$  along with enthalpy of relaxation at  $T_g$ ,  $\Delta H_{nr}$  for a sample of As<sub>26</sub>S<sub>74</sub> glass (**Figure 2.6**). Approximately 15 mg of glass sample in platelet form was hermetically sealed in  $T_{zero}$  aluminum pans [21]. The sample sealing was conducted inside an inert dry ambient atmosphere. The MDSC experiment was carried out in a heating cycle scan rate of 3°C/min, and a modulation time period of 100 sec. A modulation temperature amplitude of 1°C was used. The heating cycle across the  $T_g$  was followed by a cooling cycle as illustrated in figure below.



**Figure 2.6:** Modulated Differential Scanning Calorimetry scan of an  $As_{26}S_{74}$  glass sample. The top three curves show the heating cycle and the bottom three curves show the cooling cycle across  $T_g$ . The total heat flow (green) is deconvoluted into reversing heat flow (blue) and non-reversing heat flow (brown) signal with the hashed mark area depicting the integrated area yielding the enthalpy of relaxation in

the heating and cooling cycles. The  $T_g$  of the glass sample is established by taking the average of the inflection point of the reversing heat flow signal in the heating and cooling cycles. Here it reveals a  $T_g$  value to be 134.8(3) °C. The frequency corrected enthalpy of relaxation,  $\Delta H_{nr}$  [21], is the difference between the endotherm obtained in heating and exotherm in cooling cycles, and yields a value of 0.07 (3) cal/gm.

The reversing heat flow signal in **Figure 2.6** shows a rounded step, which permits one to fix the T<sub>g</sub> by recording the inflection point. In the heating cycle, a T<sub>g</sub> of 136.2(2) °C was obtained in the heating cycle, and a T<sub>g</sub> of 133.5(2) °C was obtained in the cooling cycle, which yields a mean value of 134.8(3) °C as the scan rate independent T<sub>g</sub> of the As<sub>26</sub>S<sub>78</sub> glass. The non-reversing heat flow term shows a Gaussian like peak in the heating cycle and hashed mark region gives the enthalpy of relaxation  $\Delta H_{nr}$  of 0.99(3) cal/gm and in the cooldown cycle, an exotherm is observed with a  $\Delta H_{nr}$  term of 0.92(3) cal/gm. The frequency corrected  $\Delta H_{nr}$  term which is the difference between the two terms yielded a value of 0.07(3) cal/gm. There are set procedures to draw the baselines which I am going to discuss next.

#### **2.3.3 Baseline Integration**

It is indeed very important to pay special attention in analyzing the MDSC scans of the samples we run. It is because different scans have different types of baseline for the non-reversing heat flow signal. If a proper mathematical expression is not used to assign a baseline while calculating the integrated area, then the results of the integrated non-reversing heat flow area will vary a lot. There are four different baselines which TA Instruments provides with their analysis software:

- (i) Linear Baseline
- (ii) Sigmoidal Horizontal baseline
- (iii) Sigmoidal Tangential baseline
- (iv) Extrapolated baseline

For our experiments, mostly the first three baselines are used to analyze the scans.

Below, I will discuss the baselines which we more commonly use in our research.

#### **Linear Baseline**

This is used if there is a linear variation of non-reversing heat flow with time. This means, a straight line needs to be drawn from before the starting of the peak to after the completion of the peak as shown below in **Figure 2.7**.



**Figure 2.7:** Example of heat flow signal having a linear baseline analyzed using the linear integration.

#### Sigmoidal Horizontal Baseline

This type of baseline is used if the non-reversing heat flow signal baseline remain flat before the start of the peak and after the peak, but is DC shifted from each other as shown in **Figure 2.8** below.



**Figure 2.8:** Example of heat flow signal having a flat baseline before and after the peak but shifted from each other. Sigmoidal horizontal baseline is used to analyze this type of baseline.

#### Sigmoidal Tangential Baseline

If the baseline of the scan shows a bowing before and after the peak, then this type of baseline integration is used to analyze the scan as shown below in **Figure 2.9**.



**Figure 2.9:** Example of heat flow signal showing a bowing baseline and hence is analyzed using a sigmoidal tangential baseline.

## 2.3.4 Fragility Index

According to Angell plot (**Figure 2.10**), very few melts show Arrhenius behavior of viscosity as a function of temperature. But, there are large number of melts which display Super Arrhenius behavior of viscosity w.r.t temperature and are termed as fragile melts [22], [23]. Fragility index can vary from about 17 to 145 for fragile melts [19], [24], [25]. Fragility index is defined as a dimensionless parameter that describes the rate of the viscous slowdown undergone by melt at vicinity of  $T_g$  as shown by equation below.



**Figure 2.10:** Variation of log of viscosity as a function of reaction temperature, normalized to  $T_g$ . The Arrhenius variation of viscosity with temperature is termed as having strong melts while the super Arrhenius variation of viscosity with temperature is termed as having fragile melts.

According to Carpentier [26], MDSC experiments helps to analyze the generated heat flows in terms of complex  $C_p$ ,  $C_p^*$  formalism. The complex  $C_p$  (in-phase  $C_p$ ), shows a rounded step like variation like the reversing heat flow signal and the  $C_p^*$  (out-of-phase  $C_p^*$ ) shows a gaussian like peak like the non-reversing heat flow as shown in **Figure 2.11a**.

The fragility index is measured using the MDSC technique in the cool down mode from the melt to the glass to extract the melt properties. In doing so, the modulation frequency is varied for different scans and the out-of-phase  $C_p^*$  peak shift with temperature is observed. At the peak location, the product of enthalpic relaxation of time and angular frequency is equal to 1 ( $\omega \tau = 1$ ). It means when the frequency increases, melt tends to relax faster and hence the peak shifts to higher temperature location.

Maxwell equation establishes a relationship between viscosity  $\eta$  and shear modulus at infinite frequency  $G_{\infty}$  with  $\tau$  which is the shear relaxation time.

$$\eta = G_{\infty} \tau$$

The fragility equation can be rewritten as:

$$m = \left[\frac{\partial(\log_{10}(\tau))}{\partial(Tg/T)}\right]_{T \to Tg}$$



**Figure 2.11:** (a) Complex  $C_p$  in terms of its constituents – the in-phase  $C_p$  and outof-phase  $C_p^*$ . (b) Show the variation of relaxation time as a function of temperature.

The above equation is used to make a plot of the variation of the relaxation time as a function of temperature (**Figure 2.11(b**)). The fragility index is extracted by

calculating the slope of the plot. Typically for my research, the experimental parameters used to calculate fragility index in MDSC are:

Ramp rate =  $0.5^{\circ}$ C/min Amplitude = +/- 1°C Modulation period = 120s to 80s

## 2.4 Molar Volumes

The mass density " $\rho$ " was obtained for our glasses by using the Archimedes' Principle. The weight of the sample was measured in air and then in liquid – 200 Proof alcohol in this case. A Model 185 Mettler Toledo digital microbalance with a quartz fiber suspended from the pan with a hook at the bottom to support a sample was used to measure the weight in air, followed by weight in a liquid. The glass sample size typically exceeded 125 mg in order to achieve 0.25% of accuracy in density measurements. Molar volumes "V<sub>m</sub>" were obtained from the known molecular weights and measured glass densities. Density of ethyl alcohol was obtained using Si single crystal wafer of known density ( $\rho_{Si}$ ) of 2.33 g/cm<sup>3</sup>. A Ge single crystal of known density ( $\rho_{Ge}$ ) of 5.323 g/cm<sup>3</sup> was used separately to confirm the accuracy independently for density measurements.

To obtain weight of a glass sample in alcohol, the quartz fiber was submerged in alcohol while being in suspension mode from the digital balance. The balance was then tried to nullify the effect of the buoyant force of alcohol on the fiber (taring) before positioning the glass sample on the quartz fiber hook.



**Figure 2.12:** Illustration of Archimedes' Principle in practice. Sample is shown hanging from quartz fiber, attached to the balance, and submerged in a liquid.

#### <u>Sample calculation of As<sub>x</sub>S100-x = 26 mol% density:</u>

Weight of sample in air ( $w_{air}$ ): 142.4 mg Weight of sample in alcohol ( $w_{alc}$ ): 103.3 mg Density of alcohol ( $\rho_{alc}$ ) = 0.7905 g/cm<sup>3</sup>  $\rho_{sample} = w_{air}/(w_{air} - w_{alc}) * \rho_{alc} = 2.739(4)$  g/cm<sup>3</sup>

Finally, by knowing the molar mass of the sample for which the density was found, we can calculate the Molar Volume.

The molar mass of the x = 26 mol% sample is 43.204 g/mol and the density of the x = 26 mol% sample as mentioned above is 2.739(4) g/cm<sup>3</sup>.  $V_m = 43.204/2,739 = 15.776(25)$  cm<sup>3</sup>/mol

## **Chapter 3**

## **Experimental Results**

#### 3.1 Kinetics of Melt/Glass Homogenization

The kinetics of As<sub>x</sub>S<sub>100-x</sub> melt/glass homogenization was established across a broad range of compositions, 12% < x < 40%. FT-Raman profiling technique was used to study the homogenization behavior of these glasses [27]. Two broad aspects of behavior emerged after analyzing the FT-Raman spectra. In the S-rich compositions, 12% < x < 20%, the kinetics of homogenization are found to be quite slow and therefore it required alloying the 1.5 grams batches at 650°C for approximately 6 weeks to fully homogenize. In the S-deficient compositions, that is in the range of 20% < x < 33%, the kinetics of melt homogenization are relatively faster. It was observed that the melts/glasses homogenized in approximately 4 weeks. In general, there are several obstructions which needs to be overcome in order to homogenize S-rich melts. The melting point of elemental S is 115.2°C, and acquires a vapor pressure of 1 atmosphere at 445°C, which increases to 10 atmospheres at 640°C [28]. Moreover, S has a unique property of undergoing a polymerization transition which is also called  $T_{\lambda}$  transition [29]. This temperature occurs around 150°C, with S<sub>8</sub> monomers prevailing at T <  $T_{\lambda}$ . The rings slowly open up ad transform into polymeric  $S_n$  chains at T>T<sub> $\lambda$ </sub> [30], which leads to a pronounced increase in viscosity [29]. The S<sub>8</sub> rich nano-phase acts as an impedance to the growth of As-S glassy backbone. This feature is believed to qualitatively suppress the growth of the As-S backbone as shown below using FT-Raman profiling experiments.

## 3.1.1 S<sub>8</sub>-rich As<sub>x</sub>S<sub>100-x</sub> melts in the 10% < x < 12% range

Figure 3.1 shown below reproduces the FT-Raman profiling results of As<sub>18</sub>S<sub>82</sub> melt. The melt was heated gradually at the rate of 1°C/min up to 650°C inside a quartz tube held vertically in a box furnace. After alloying the glass for 5 days, Raman profiling experiments revealed the variance in As content  $<\Delta x_{As}>$  to be nearly 5% across the batch (Figure 3.1a). These experiments establish the glass heterogeneity by taking the scattering strength ratio of the S-rich modes  $(S_8 + S_n)$  near 470 cm<sup>-1</sup> to the broad band centered 350 cm<sup>-1</sup> providing a measure of As in the As-S glass backbone. The measure of S to As content of the melt locally where the laser beam scatters off the vertical glass column in an evacuated quartz tube is obtained by calculating the scattering strength ratio of the S-rich modes to As modes. The variance in the As content  $<\Delta x_{As}>$  decreases steadily to less than 0.4% after alloying the melt for 40 days. During the alloying process, As diffuses up the melt column and S diffuses down the melt column. But even after 40 days of alloying, substantial amounts of S remain segregated in the form of S<sub>8</sub> rings (the features are labelled in the spectra). The glass was then heated to 95°C and held at that temperature for 2 days (Figure 3.1e) post which Raman profiling revealed an unmistakable evidence of a vibrational mode near 537 cm<sup>-1</sup>, which is believed to represent the As=S stretch mode of  $S=As(S_{1/2})_3$  quasi-tetrahedra (Table 1). The point to be noted here is that the temperature 95°C is higher than the glass transition temperature of this glass composition ( $T_g = 85^{\circ}C$ ) but is lesser than the Sulfur polymerization temperature ( $T_{\lambda}$  $= 159^{\circ}$ C). In this important heating step, the backbone of the As-S glass softens and flows through the S<sub>8</sub>-rich nanophase permitting backbone fragments to coalesce and grow. At 95°C, the S<sub>8</sub>-rich nanophase remains almost intact. In the last step, the glass

is reacted again at 650°C and held at that temperature for 2 more days followed by water quench. Raman scattering results now display (Figure 3.1f) a clear evidence for a substantial growth of the 537 cm<sup>-1</sup> mode. If noted closely in the spectra of Figure 3.1f, the scattering strength of the S<sub>8</sub> ring modes has drastically reduced with respect to the spectra of Figure 3.1e. By heating the glass to 650°C in the final step, a significant fraction of Sulfur apparently alloys into the backbone thereby facilitating the growth of the backbone, but it also appears that some of the S<sub>n</sub> chains decouple from the backbone. The chain fragments must be small (n < 8) for them to not be a part of the S<sub>8</sub>-rich nanophase. Very similar results are observed at other compositions in the 12% < x < 22% range with striking evidence of growth of the 537 cm<sup>-1</sup> mode. The slow kinetics of homogenization especially in the S-rich glasses, x < 18% is apparently controlled by the segregated S<sub>8</sub>-rich nanophase, which hinders the growth of the glass backbone. Calorimetry measurements easily detect the S<sub>8</sub>-rich nanophase by the T<sub>λ</sub> transition [12] as we comment in the upcoming section calorimetry results.



**Figure 3.1:** FT-Raman scattering of an  $As_{18}S_{82}$  glass alloyed (a) for  $t_r = 5d$ , display an Arsenic variance  $\langle \Delta x \rangle_{As} = 5.08\%$ , (b) for  $t_r = 20d$ , the variance decreases to 2.04(5)%, (c) for  $t_r = 35d$ , it reduces to 0.97(5)%, and (d) for  $t_r = 40d$  nearly saturates to 0.40(5)%. Reduced Sulfur variance across the 1.5-gram batch composition is taken as evidence of glass homogenizing upon continued alloying. In (d), the homogenized melt/glass upon a thermal quench from 650°C displays a segregated backbone immersed in a sea of S<sub>8</sub>-rich fragments. In (e) heating the glass to T<sub>g</sub> + 10°C = 95°C for 2 days, results in fragments of the backbone coalescing thereby leading to the observation of the 537 cm<sup>-1</sup> mode of QT units. In (f) by heating the glass of (e) back at 650°C for 2 days followed by water quenching leads to large

growth of the 537 cm<sup>-1</sup> mode, and substantial amount of extra Sulfur alloying in the backbone inferred from the qualitative reduction of the  $S_8$ -ring fraction between spectrum (e) and (f). A schematic illustration of the structural changes that takes place in going from (d) to (f) is shown in Figure 3.2.

Cluster	$\omega (\mathrm{cm}^{-1})$	IR	I <sup>Ram</sup>			
			Iso.	Total	ρ	Description
AsS <sub>3</sub> H <sub>3</sub>	165	0.18	5.0	7.28	0.23	Umbrella
	352	0.18	31.3	34.0	0.06	Symmetric stretch
	355	0.78	0.00	6.63	0.75	Asymmetric stretch
AsS <sub>4</sub> H <sub>3</sub>	146	0.20	1.10	4.48	0.57	Umbrella
	335	0.21	59.5	60.7	0.01	Symmetric stretch
	365	1.17	0.00	14.3	0.75	Asymmetric stretch
	537	1.58	12.1	21.9	0.34	S = As

TABLE I. Raman and IR vibrational modes of As–S clusters. The frequencies and Raman/IR cross sections and depolarization ratios for each cluster are given, along with a description of the eigenvectors.

Table 1: Raman and IR vibrational modes of As-S clusters.



**Figure 3.2:** Schematic representation of structural changes underlying the coalescing of the backbone fragments (from small brown circles to larger rectangles) and leading to the observation of the 537 cm<sup>-1</sup> mode in  $As_{18}S_{82}$  glass as shown by the Raman scattering results of **Figures 3.1d-f**. (i) After 40 days of alloying at 650°C the melt is viewed to be composed of  $As_{18}S_{82}$  rich circular domains immersed in a sea of polymeric  $S_n$  chains (thin yellow lines). (ii) After water quenching, the  $S_n$  chain regions transform into the more stable  $S_8$  rings, largely decoupled from glassy backbone. (iii) Quenched glass is heated back to 95°C for 2 days, resulted in softening and diffusion of the backbone fragments to coalesce and form the larger rectangular domains. (iv) Heating glass to 650°C leads more  $S_n$  chains to alloy in the backbone. (v) Water quench leads to the growth of chains which is confirmed by Raman scattering that shows  $S_8$ -ring fraction qualitatively reduces in going from **Figure 3.1e to f**.

To illustrate the molecular structure consequences of the Raman results of Figure **3.1d** through Figure 3.1f in a schematic fashion, Figure 3.2 is made. In step (i) of Figure 3.2, the melt is viewed to be composed of the As-S backbone fragments shown as brown small circles that are connected by the yellow threads that represent polymeric  $S_n$  chains when the melt is alloyed at 650°C for 40 days, as the weighed glass at x = 18% homogenizes (Figure 3.1d). Water quenching of the homogenized melts results in the long S<sub>n</sub> polymeric chains to break up into more stable S<sub>8</sub> rings that come together to form an amorphous shown as yellow circles in step (ii) of Figure 3.2. After annealing the glass at 95°C for 2 days, (step (iii) of Figure 3.2) the small brown backbone fragments coalesce to form the larger sized brown rectangular boxes. In step (iv) of Figure 3.2, the melt is alloyed at 650°C for 2 days, the S<sub>8</sub> rings polymerize and assist in growth of the glass backbone (brown rectangular boxes). In the final step (v) of Figure 3.2 the melt is water quenched with larger sized backbone fragments forming and being intermixed with the S<sub>8</sub> ring amorphous phase (shown in yellow circles) when in Raman scattering (Figure 3.1f), unambiguous evidence of the 537 cm<sup>-1</sup> mode is found which is tied to the growth of the QT local structures in the backbone.

In **Figure 3.3**, a summary of homogenization process is shown in a plot of the scattering strength ratio of the Sulfur-band (S<sub>8</sub> rings + S<sub>n</sub> chains) near 470 cm<sup>-1</sup> to the As-centered broad band near 350 cm<sup>-1</sup> as a function of weighed As mole% x. The broad band comprises [30] of vibrational modes of the glass containing As – Pyramids and As – Quasi-tetrahedra. In **Figure 3.3**, the red data points define an empirical curve which is derived after fully homogenizing the glasses. In this empirical curve the observed extremum in scattering strength ratios from Raman profiling experiments is projected to deduce the As-content variance,  $<\Delta x>_{As}$  of a batch composition. This helped in establishing the variance  $<\Delta x>_{As}$  of a batch

composition in real time,  $t_r$ , in days, as homogenization of the alloyed melt proceeds. The measured variance is across the whole batch composition and not a local point in the melt/glass column as one would measure once the glass is extracted from the quartz tube and used in a traditional Raman scattering experiment. In a batch composition, changes in glass stoichiometry at one location will influence the global stoichiometry at one location will influence the global stoichiometry at one location will influence the global stoichiometry of the batch. These Raman profiling experiments measure the global homogeneity of a batch composition and not merely homogeneity at a local point in a glass specimen.

The FT-Raman profiling experiments also show that in S-rich glasses (x < 20%), where a substantial amount of S segregates as  $S_8$  rings, the typical alloying time to achieve homogeneity of the melts is nearly 6 weeks. The variance in S content of a S-rich glass starts out usually near 5% after 5 days of alloying, and it decreases by an order of magnitude to < 0.5% after 40 days, when the melt/glass is rendered homogeneous.



**Figure 3.3: (a)** Observed variation in the ratio of the scattering strength of S-related band near 472 cm<sup>-1</sup> to the backbone band near 340 cm<sup>-1</sup> plotted against the As content of glasses. The red data points are results obtained on fully homogeneous glasses from x = 16% to x = 22%, with the smooth red curve serving as an empirical curve. Superposed on the calibration plot are the results obtained for a glass sample weighed at x = 18% as it was alloyed from 5 days to 40 days, and the variance in S-concentration to narrow from 5.08% to about 0.4%. (b) The narrowing data of the S-variance taken to be the same as the As-variance is plotted as a function of alloying time,  $t_r$ , in days for As<sub>18</sub>S<sub>82</sub> glass. It provides a pictorial view of the process of delayed homogenization at x = 18% composition. (c) A global view of how the S-

variance of the batches reduces with alloying time  $t_r$  in days at different As content x. Note, at x = 18%, the kinetics are slowest, and these decrease both at low x (< 18%) and high x (> 18%). The x = 18% composition also is the one where the QT faction is the highest.

## 3.1.2 S<sub>8</sub>-deficient As<sub>x</sub>S<sub>100-x</sub> melts in the 20% < x < 40% range

The other domain of interest in these glasses is at higher As concentration (Figure 3.4) when the amount of  $S_8$ -ring concentration minimizes. These glasses homogenize relatively quicker, i.e. after alloying for 24 days at 650°C as shown in **Figure 3.4** for x = 26% glass composition. In this composition, the 537 cm<sup>-1</sup> mode of QT units is observed once the glass is homogenized. After alloying for 4 days, the S-variance across the batch is around 5% (Figure 3.4a), it then decreases to 1% after 12 days of alloying (Figure 3.4b) and it reduces to 0.1% after 24 days of reaction (Figure 3.4d) when the batch has homogenized. Homogenization kinetics documented at x = 26% has been observed at various other compositions in the 20% < x < 40% range, i.e. the compositions encompassing the Intermediate Phase and the Stressed-Rigid Phase. In the present case, likewise the case in x = 26% composition, upon heating the glass to  $T_g + 10^{\circ}C = 144^{\circ}C$  for 2 days, one observes clear evidence of the 537 cm<sup>-1</sup> mode (Figure 3.4e) for the first time. Upon annealing the glass further at 650°C for 2 more days followed by water quench the scattering strength of the 537 cm<sup>-1</sup> mode increased substantially (Figure 3.4f) and that of the  $S_8$ -ring mode near 217 cm<sup>-1</sup> reduces.



**Figure 3.4:** FT-Raman profiling results of an As-S binary glass at x = 26% composition revealing the As variance  $\langle \Delta x \rangle_{As}$  (a) to be 5% after alloying for  $t_r = 4$  days (b) the variance  $\sim 1\%$  after  $t_r = 12$  days, (c) variance reducing to 0.53% after 12 days (d) variance = 0.1% after  $t_r = 24$  days. (e) When glass is annealed to  $144^{\circ}C = T_g + 10^{\circ}C$  for 2 days, evidence of the 537 cm<sup>-1</sup> mode first appears. (f) When glass was heated next to 650°C for 2 more days followed by water quench, the scattering strength of the 537 cm<sup>-1</sup> mode substantially grew. These changes in Raman lineshapes in going from (e) to (f), closely mimic those seen at x = 18% in Figure 3.1. Particularly note that the 217 cm<sup>-1</sup> mode of S<sub>8</sub>-rings reduces in scattering

strength in going from (e) to (f). These changes in Raman scattering at x = 18% and at x = 26%, particularly the growth of the 537 cm<sup>-1</sup> mode upon T<sub>g</sub> cycling the glass followed by a heating step to 650°C followed by a water quench, which reinforces the schematic structural changes suggested in the model of Figure 3.2.

The S-content variance in 1.5-gram sized batches in the initial stages of alloying derives from the heavier As atoms moving to the upper part of the glass column. The compositional gradient is extremely useful in tracking the growth of homogeneity by merely probing < 1% of the glass column. If someone rocks the melts, it would have been very difficult to track the super-strong melt inclusions in a sea of fragile ones without probing more than 50% of the batch composition, which would have been a difficult task to implement. In previous studies [12] of As-S glasses, melts were typically alloyed at 600 to  $650^{\circ}$ C for 2 to 3 days. It was only in the year 2011 that we became aware that chalcogenide melts undergo delayed homogenization [19], [24], [27]. In this thesis, we present results from present work on As-S binary glasses where we shall discuss the findings in relation to the previous studies bringing out the crucial role of melt homogenization in elucidating the physics and chemistry of these glasses. Once the physics of the homogenization of larger batches over several days rather than several weeks.

#### 3.2 Raman Scattering on As<sub>x</sub>S<sub>100-x</sub> Glasses

FT-Raman scattering on the especially homogenized bulk  $As_xS_{100-x}$  glasses were acquired using a Thermo-Nicolet Nexus 870 FTIR with Raman module with a 1064 nm wavelength of light. The observed lineshapes as function of glass compositions

are summarized in **Figure 3.5**. In the top panel (**Figure 3.5a**) the Raman scattering of the two reference crystalline phases of interest [31] are shown; c-As<sub>2</sub>S<sub>3</sub> and c-As<sub>4</sub>S<sub>4</sub>. In the middle panel we present Raman spectra of As<sub>x</sub>S<sub>100-x</sub> glasses in the high As content range, 40% > x > 24% (**Figure 3.5b**), while in the bottom panel spectra of Raman spectra of glasses is the S-rich region, 20% < x < 12% (**Figure 3.5c**).

# 3.2.1 Raman Scattering in $As_xS_{100-x}$ Glasses in the High As Range of 24% < x < 40%

In the field of glass science, it has been a trend to draw analogies between the Raman spectrum of the stoichiometric glass with its crystalline part. The case of stoichiometric glass at x = 40% and c-As<sub>2</sub>S<sub>3</sub> (orpiment) is not an exception as well [32], because both are viewed as composed majorly of a polymeric network of PYR units. But there are obvious differences too. The stoichiometric glass is Nano Scale Phase Separated (NSPS) into As-rich and As<sub>4</sub>S<sub>4</sub> Realgar units that decouple from the S-rich polymeric network composed of PYR units in which a finite concentration of S-S bonds persists [33], [34]. Moreover, the segregation of As<sub>2</sub>S<sub>3</sub> glass is intimately tied to melt quench temperature  $(T_a)$ , with the segregation [31] increasing as  $T_q > T_{liquidus}$ . The evidence of segregation is unmistakable in Raman spectrum of Figure 3.5b as the triad of modes near 188 cm<sup>-1</sup>, 220 cm<sup>-1</sup> and 352 cm<sup>-1</sup> labeled R in the stoichiometric glass (Figure 3.5b), and it appears at pretty much the same frequency (within 2 cm<sup>-1</sup>) as their counterparts in c-As<sub>4</sub>S<sub>4</sub> (Realgar) (Figure 3.5a). The Realgar is composed of molecular cages made of 8-atom clusters [35] with strong intermolecular interactions mediated by covalent bonds, but weaker intercluster ones deriving from non-bonding Van der Walls interactions.

A close examination of the Raman lineshapes of the stoichiometric glass shows a quartet of modes [31] labeled O (Figure 3.5b) which are also found in c-As<sub>2</sub>S<sub>3</sub> but with a unmistakable difference. The modes in the glasses are blue shifted by about 14 cm<sup>-1</sup> to 21 cm<sup>-1</sup> in relation to those of c-As<sub>2</sub>S<sub>3</sub> (Figure 3.5a). This is demarcated by the vertical broken lines passing through the glass modes, which are found to be systematically shifted to higher frequency in relation to the quartet of modes in the glass is viewed to be the result [31] of the greater molar volume,  $V_m$  (14.10 cm<sup>3</sup>) [16]. The more open structure of the glasses promotes intra-molecular interactions because of the presence of  $\sigma$ -bonds in PYR and QT local structures at the expense of the intermolecular ones mediated by  $\pi$ -bonds between these local structures.

The range of intermediate range glass compositions in the 24% < x < 40% posts challenges in uniquely deconvoluting Raman lineshapes as commented in the next section.



**Figure 3.5:** FT-Raman results on (a) c-As<sub>2</sub>S<sub>3</sub> (Orpiment) and c-As<sub>4</sub>S<sub>4</sub> (Realgar), (b) As<sub>x</sub>S<sub>100-x</sub> bulk glasses at high As content in the 40% < x < 24% range, and in (c) at low As content in the range 20% < x < 12% and of crystalline Sulfur. In (c) the three expected modes of QT S=As(S<sub>1/2</sub>)<sub>3</sub> local structures labelled QT<sub>1</sub>, QT<sub>2</sub> and QT<sub>3</sub> are

observed along with the PYR As( $S_{1/2}$ )<sub>3</sub> local structure labeled PYR. These modes occur at frequencies close to those predicted y NRLMOL calculations (**Table 1**). In (**b**) at x = 40%, the four observed modes labelled O with mode frequencies indicated in cm<sup>-1</sup> are because of Orpiment like features and are systematically blue shifted w.r.t the O-modes in c-As<sub>2</sub>S<sub>3</sub> in (**a**) by about 14 cm<sup>-1</sup> to 21 cm<sup>-1</sup>. The stoichiometric glass composition (x = 40%) also displays 3 modes labeled R that occur at frequencies reasonably close to those observed in c-As<sub>4</sub>S<sub>4</sub> in (**a**). The feature D near 490 cm<sup>-1</sup> is observed over a wide range of compositions, 12% < x < 33%. The observation of R modes in the x = 40% glass shows the stoichiometric glass is mildly NSPS as reported earlier by Georgiev et al. [31]. In (**b**) modes of QT species steadily go over into those of O-species as x increases from 24% to 40%. Modes of polymeric S<sub>n</sub> chains (461 cm<sup>-1</sup>) and of monomeric S<sub>8</sub> species (217 cm<sup>-1</sup>, 472 cm<sup>-1</sup>) are observed as per expectations.

# 3.2.2 Raman Scattering in $As_xS_{100-x}$ Glasses in the Low As Range of 12% < x < 20%

The Raman spectrum of S-rich glasses in the 12% < x < 20% range show lineshapes (Figure 3.5b) that reveal the triad of QT modes;  $QT_1 = 335$  cm<sup>-1</sup>,  $QT_2 = 390$  cm<sup>-1</sup> and  $QT_3 = 537$  cm<sup>-1</sup> along with a pair of closely spaced modes of PYR units (352 cm<sup>-1</sup> and 355 cm<sup>-1</sup>) in the broad band centered around 340 cm<sup>-1</sup> as shown in Figure 3.6 for compositions at x = 12\%, 17\% and 18\%.



**Figure 3.6:** FT-Raman spectra observed in low x (< 18%) range deconvoluted in terms of superposition of Voight profiles as shown above (Refer **Table 1** for modes). The observed lineshapes as seen above (**Figure 3.6**) at x = 12% or more, were fitted to a superposition of Voight profiles and the observed mode frequencies of the two local structures are found to be quite close to those revealed by NRLMOL simulations (**Table 1**). The observed integrated intensities of the various modes also

resemble quite closely to the estimated Raman cross-sections of the various modes by the NRLMOL simulations.

The broad band around 350 cm<sup>-1</sup> is composed of the symmetric stretch (ss) and asymmetric stretch (as) of PYR and QT units. The peak near 472 cm<sup>-1</sup> has contributions from S<sub>8</sub> rings and S<sub>n</sub> chains and the highest frequency mode is the S = As stretch mode of QT units. The lineshapes were fit using the Peak Fit software from SPSS Inc. and using Voight profiles. Along with the modes fitted using **Table 1** as reference, there is one more additional mode at 490 cm<sup>-1</sup> labeled 'D' in the spectra (**Figures 3.5, 3.6**) observed all the way from 12% < x < 37% of As content. This mode relates to a stretch vibration of S-S dimer between two As-centered PYR units. This was suggested by the mode scattering strength variation in the Raman spectra which display a local maximum near x = 25% (**see Discussion**). The other modes are composed of S<sub>8</sub> ring modes (217 cm<sup>-1</sup>, 472 cm<sup>-1</sup>) and S<sub>n</sub> chain mode (461 cm<sup>-1</sup>) over a broad range of x. The elusive mode near 537 cm<sup>-1</sup> from the QT, S = As(S<sub>1/2</sub>)<sub>3</sub> local structure labeled as QT<sub>3</sub>. This mode is observed only after homogenizing the glasses in the range 12% < x < 26%.

At higher S content (x < 15%), the concentration of the S<sub>8</sub> nanophase grows and it hinders with the formation of the polymeric As-S backbone. With a low-T annealing of the homogenized glasses at  $T_g + 10^{\circ}$ C, the high frequency mode of QT unit was observed even at x = 12% (**Figures 3.5, 3.6**).

In the transition range, 22% < x < 35% which spans the Intermediate phase and the Stressed Rigid phases of the present As-S binary, evolution of the Raman spectra posts challenges related to uniquely deconvoluting the lineshapes. This is because as the QT local structures starts reducing in concentration and the PYR units starts

growing in concentration, the orpiment-like structures evolve thereby giving rise to the quartet of O-modes whose frequency overlaps with those of the QT local structures formed at S-rich compositions (low x). In **Figure 3.5b** this issue is demonstrated by drawing a continuous red line coming from PYR mode observed at low x (< 20%), to the quartet of O-modes expected at higher As concentration. There are as many as 7 vibrational modes of the O-species and  $QT_n$ -species occur and have overlapping mode frequencies. One can fit the spectra by posing several constraints on mode centroids and widths, but it raises doubts over the uniqueness of the fits.

# **3.2.3 Dispersive and FT-Raman Scattering in As<sub>x</sub>S<sub>100-x</sub> Glasses Comparison**

The As<sub>x</sub>S<sub>100-x</sub> glasses were also examined in Dispersive Raman scattering using 514 nm excitation using a T64000 Micro-Raman system from Horiba Inc. In the figure below (**Figure 3.7**), a spectrum of As<sub>18</sub>S<sub>82</sub> glass composition in FT-Raman scattering excited using 1064 nm laser excitation (**Figure 3.7a**) and separately in Dispersive Raman (**Figure 3.7b**). Several features are common to both spectra which includes the S<sub>8</sub>-ring modes around 151 cm<sup>-1</sup>, 217 cm<sup>-1</sup> and 472 cm<sup>-1</sup>, the As-S centered backbone near 340 cm<sup>-1</sup> and the polymeric S<sub>n</sub> chain mode near 461 cm<sup>-1</sup>. But there is one big difference; the 537 cm<sup>-1</sup> mode is observed in the FT-Raman spectrum (**Figure 3.7a**) but not in the Dispersive Raman spectrum (**Figure 3.7b**).

These findings lead us to believe that the electronic states contributing to the QT local structure are most likely resonantly excited in the mid-gap region by the 1064 nm excitation. The QT are suppressed qualitatively in Dispersive Raman spectroscopy because it uses near band gap excitation as illustrated in **Figure 3.7c** on a plot of the optical band gap of As-S glasses as reported by Yamaguchi [20].

The pattern is not just observed at x = 18% glass but is observed at other compositions (x < 24%). There are also other reports on Dispersive Raman scattering on As-S glasses by [36], [37].



**Figure 3.7: (a)** FT-Raman spectra of  $As_{18}S_{82}$  glass as shown previously in **Figure 3.1f**, (b) Dispersive Raman spectra of the same glass composition, (c) Variation of the optical band gap in  $As_xS_{100-x}$  glasses as reported by Yamaguchi [20]. In (a) the scattering is excited in the mid-gap region using the 1064 nm as illustrated in (c) while in (b) the scattering is excited using 514 nm radiation that excited the scattering in the conduction band region.

# 3.3 Glass Transition Temperature $(T_g(x))$ , Non-reversing Enthalpy of Relaxation $(\Delta H_{nr}(x))$ , and Specific Heat Jump $(\Delta C_p(x))$ at $T_g$

Compositional trends calorimetric observables such as glass transition temperature,  $T_g(x)$ , enthalpy of relaxation  $\Delta H_{nr}(x)$  at  $T_g$  and the specific heat jump at  $T_g \Delta C_p(x)$ , in As<sub>x</sub>S<sub>100-x</sub> glasses deduced from Modulated DSC experiments on present glasses as shown in Figure 3.8 below. The observed variation of Molar Volumes is also illustrated in Figure 3.8. Both calorimetric and volumetric results provide a global view of three distinct regimes of variation. At low x ( $\leq 22\%$ ), two endotherms are observed, one near  $T = 150^{\circ}C$  that shifts minimally in T with increasing x, but with enthalpy of relaxation decreases steadily with increasing x to vanish near x > 22%(not shown in Figure 3.8). On the other hand, second endotherm is found to steadily upshift in T almost quasi-linearly with increasing x in the 15% < x < 40% range. These  $T_g(x)$  trends (Figure 3.8) are like those reported by Wagner et al. [38], who was one of the first to use the technique of MDSC to examine As-S glasses. In their work, Wagner et al. identified the endotherm near 150°C as a second glass transition and viewed the bimodal  $T_g\sp{s}$  observed at x < 25% as proof of phase separation of these S-rich glasses. In a subsequent study by Chen et al. [12], examined many more compositions and recognized that the 150°C endotherm is actually the  $T_{\lambda}$  transition, i.e. presence of S-rich domains composed of S<sub>8</sub>-rings that polymerize into S<sub>n</sub> chains as T exceeds  $T_{\lambda}$ , in these S-rich binary As-S glasses. They noted that the  $T_{\lambda}$  transition established in pure S is seen near the same temperature of around 150°C.

The nature of the second endotherm became clearer when more detailed compositional trends became available [12] and displayed a quasi-linear increase of

 $T_g(x)$  with x (Figure 3.8a) over wide composition range of 12% < x < 40% to represent the glass transition characterizing the As-S network backbone. The enthalpy of relaxation of the endotherm show a sharply defined square-well like variation in the composition range 22.5% < x < 28.5% [12]. In this thesis, we have confirmed the findings of Chen et al. and show that in homogenized glasses, the square-well like variation of  $\Delta H_{nf}(x)$ , which is the reversibility window is observed even in fresh glasses as well as 6-month aged ones (Figure 3.8b). The reversibility windows are now seen in many other glass systems including chalcogenides and oxides [39], [40]. These windows represent signature of the isostatically rigid phases also known as the Intermediate Phase [7]. The sharp and abrupt nature of the onset of the window near  $x = x_r = 22.5\%$  represents the rigidity transition, and the end of the window near  $x = x_s = 28.5\%$  as the onset of the stress-transition [12]. These two elastic phase transitions in the present As-S binary glasses are found to be particularly abrupt in composition 'x' in the present glasses, due to the especially homogenized nature of glasses synthesized as will be discussed later.


**Figure 3.8:** Compositional trends of (a)  $T_{\lambda}$  transition (•) and the glass transition temperature (•)  $T_g(x)$  from present work and  $T_{\lambda}$  transition ( $\Delta$ ) and the glass transition temperature (•) from Wagner et al. [38] (b) enthalpy of relaxation at  $T_g$ ,  $\Delta H_{nr}(x)$  in the fresh (•) and 6 month aged (•) condition in the present work and the enthalpy of relaxation (•) from Wagner et al. [38] (c) the specific heat jump at  $T_g$ ,  $\Delta C_p(x)$ and (d) molar volumes,  $V_m(x)$  in the present  $As_xS_{100-x}$  glasses. The  $T_g(x)$  increases almost quasi-linearly with x while  $\Delta H_{nr}(x)$  shows a square-well like behavior, the reversibility window,  $V_m(x)$  displays a local minimum in the IP, the volumetric window coincides with the IP boundary (light blue panel). Trends in  $V_m(x)$  reported by Chen et al. [12] on glasses (•) that were not as well-homogenized show a smearing of the volumetric window near the edges of the IP where the rigidity and stress transitions occur. The brown data set is from Sundaram et al. [41] on glasses that were reacted for 12-24 hours inside a rocking furnace.

#### **3.4 Variation of Melt Fragility Index with Glass Composition**

The tremendous resource MDSC provides in measuring  $T_g$  and  $\Delta H_{nr}(x)$  of a glass, and establish the fragility index, m(x) from the activation energy  $E_a$  of the enthalpy of relaxation time of melts using the same glass specimen cannot be overemphasized. Generally, fragility index is established through viscosity, flexure, measurements which require much larger glass samples than those used for measuring  $T_g$  and enthalpy of relaxation using DSC or MDSC. Therefore, it also raises concerns about sample homogeneity that is more easily achieved in smaller batch sizes (2 grams or less) than in larger (20 grams or more) ones.

The observed variation in the fragility index, m(x) of the As<sub>x</sub>S<sub>100-x</sub> melts reveal a Gaussian-like minimum centered around the intermediate phase (blue panel) with m < 20 in the window and acquiring values of m > 20 outside the phase. In Figure 3.9a the fragility index "m" is included for As<sub>2</sub>S<sub>3</sub> glass measured using Dilatometric studies reported by Malek [42]. In the same figure, a broken line is drawn to denote the fragility index of  $SiO_2$  glass near m = 20. The super-strong character of melts, i.e. m < 20 inside the blue panel defines the fragility index window, which coincides with the intermediate phase also known as the reversibility window in glass composition "x", and the results will be discussed in Discussion. Given the measured fragility index m(x), the expected melt viscosity variation with x were projected using the MYEGA formalism [25] and the results (Figure 3.9a) show that near x =2%, the melt viscosity exceeds those at x = 15% or at x = 25% by nearly 2 orders of magnitudes. The activation energy for enthalpy of relaxation  $E_a(x)$  deduced from fragility index results and the inverse of  $E_a(x)$  are plotted in Figure 3.9b and Figure **3.9c** respectively. The Raman profiling results (Figures 3.3, 3.4) show enough proof that the 1.50-gram batch size of  $As_xS_{100-x}$  melts in the present work take several

weeks rather than several days to homogenize. That feature of glass forming melts has been observed earlier [19], [43], [44] in other glass systems as well and is responsible for the delayed homogenization of glass forming melts that encompass a fragility window in general.



**Figure 3.9: (a)** Observed variation in fragility index m(x) (b) Activation energy of enthalpy relaxation time,  $E_a(x)$  (c) Variation of  $1/E_a$  with x in  $As_xS_{100-x}$  melts obtained using mDSC. Also included in (a) is the projected variation ( $\bullet$ ) of melt viscosity ( $\eta$ ) based on the presently measured m(x) and the MYEGA formalism [25].

In (a) the observed Gaussian – like minimum in m(x) centered around the reversibility window (light blue panel) with m < 20 in the window and acquiring values of m > 20 outside the window, serves to define the fragility window. The super-strong character of melts near x = 26% with an m value of 15.0 is illustrated with a darker shade of blue color. The green color data for m(x) of 31 at x = 40% is from Dilatometric measurements of Malek [42].

#### **3.5 Variation of Molar Volumes with Glass Composition**

The Archimedes Principle was used to measure the density of glasses which permitted to extract the behavior of variation of molar volumes,  $V_m(x)$  with x. The compositional trends in  $V_m(x)$  for the specially homogenized bulk glasses (**Figure 3.8d**) are compared to that of published by Chen et al. [12] in an earlier study of the As-S binary system. Also, the  $V_m(x)$  results from previous report of Sundaram et al. [41] are summarized in **Figure 3.8d**. These results when taken together reveal a broad pattern; the reported  $V_m(x)$  results at x > 30% vary significantly between different groups highlighting the challenge in synthesizing reproducible glasses.

Chen et al. [12] used 2 gram batches and alloyed them at 650°C for typically 2 days or 3 days. In the year 2003, the glasses were assumed to be homogeneous after alloying for 2 to 3 days. The present  $V_m(x)$  results show in a rather unambiguous fashion the intimate role played by glass homogeneity on network packing. The local minimum of  $V_m(x)$  in the IP region of the present glasses is localized entirely in the IP presumably because of the homogeneity of the glasses. The smearing of  $V_m(x)$  at the rigidity ( $x_r = 22.5\%$ ) and stress-elastic phase transitions ( $x_s = 28.5\%$ ) observed in previous study by Chen et al. [12] is fully consistent with the expected As-variance in the stoichiometry,  $\langle \Delta x \rangle_{As}$  in those set of glass samples. Glasses synthesized in 2008, the estimated variance in the As stoichiometry,  $\langle \Delta x \rangle_{As}$  across the batch synthesized is about 5% (See **Figures 3.1, 3.2**). Such considerations also have consequences on the measured values of  $V_m(x)$ , outside IP, both in flexible phase (x  $\langle x_r \rangle$ ) and stressed-rigid phase (x  $\rangle x_r$ ) where the present  $V_m(x)$  values measurably exceed (**Figure 3.8d**) earlier reports [41]. These factors underscore directly the crucial role of the variation of  $V_m(x)$  on glass/melt homogeneity of batch compositions. This issue will be discussed further in the Discussion section.

## **Chapter 4**

## Discussion

### 4.1 Glass Topological Phases

### 4.1.1 Topological Phases of As<sub>x</sub>S<sub>100-x</sub> Glasses

Three distinct regimes are observed in the Calorimetric, Volumetric and Raman Scattering results of the specially homogenized As<sub>x</sub>S<sub>100-x</sub> glasses and melts reported in this work as a function of their composition 'x'. The enthalpy of relaxation at T<sub>g</sub> in the glasses,  $\Delta H_{nr}(x)$ , shows a square-well like behavior (Figure 4.1) with the heat flow term becoming minimum in the 22.5% < x < 28.5% range. The link between the calorimetric observation of a miniscule enthalpy of relaxation at  $T_g$  ( $\Delta H_{nr}$  term) with flexibility and rigidity of glassy networks was made by Micoulaut [8]. He showed the vanishing of the enthalpy of relaxation at  $T_g$  is the signature of the isostatic rigid glass, which means a glass in which  $n_c = n_d$ . Here  $n_c$  represents the count of mechanical constraints/atom due to bond-stretching and bond-bending covalent forces, while  $n_d$  represents the number of degrees of freedom/atom = 3 in 3D networks. Such type of networks conform to the Maxwell-Phillips rigidity condition [1], [45] and are viewed as rigid but unstressed, and form part of the Intermediate Phase (IP) [7], [46]. The Intermediate Phase is bounded on the low connectivity side, i.e.  $x = x_r = 22.5\%$  by the rigidity-transition and on the high connectivity side, i.e.  $x = x_s = 28.5\%$  by the stress-transition. In As-S glasses, the As

atoms are 3-fold and S atoms are 2 fold coordinated, hence the mean coordination number is calculated as follows:

$$< r > = 3x + 2(1 - x) = 2 + x$$

The mean coordination number varies linearly with x. Furthermore, since  $\langle r \rangle$  provides a measure of network connectivity, and since  $T_g$  is determined by the connectivity of a glass network [47], it is expected that the  $T_g(x)$  will increase linearly with x (**Figure 3.8a**).



**Figure 4.1:** Compositional trends in (a) Enthalpy of relaxation at  $T_g (\Delta H_{nr})$  (b) Melt fragility index (c) Glass molar volumes displaying local minima in 22.5% < x < 28.5% range (light-blue panel). (b) The inverse of activation energy  $E_a$ , for enthalpy

relaxation times is also plotted. (a) Glass reversibility window is plotted in light blue panel. (b) Compositions having m < 20 defines the fragility window. (c) Local minimum in molar volumes illustrates the volumetric window in glasses. For a better understanding,  $V_m(x)$  results at x > 30% are redrawn on a coarser ordinate scale on the right to illustrate the reduction in  $V_m$  in both glassy and crystalline  $As_2S_3$ [14.10(2) cm<sup>3</sup>] [16].

The increase of  $T_g(x)$  with x (Figure 3.8a) and the observation of the Intermediate Phase (Figure 3.8b) uniquely fixes the three Topological phases of  $As_x S_{100-x}$  glasses. Glass compositions at  $x < x_r$  with low  $T_g$  values and therefore <r> are viewed to be in the Flexible Phase, whereas those at  $x > x_s$  possessing a higher T<sub>g</sub> and thus < r >belong to the Stressed-rigid phase, while those in between,  $x_r < x < x_s$  having an optimal connectivity <r> belong to the Intermediate Phase (Figures 3.8a, 4.1a). The sharp and abrupt nature of the rigidity and stress transitions is fundamentally tied to the percolative nature of these elastic phase transitions [48]. To observe the intrinsic behavior in a laboratory environment requires the glasses synthesized be homogeneous, ideally on atomic scale. Through experiments it is shown that even if the homogeneity of a glass is established on a much larger scale of 50 µm, it is a sufficiently reasonable condition for the elastic phase transitions to be abrupt and sharp [27]. Experimentally, it requires the variance in As content,  $\langle \Delta x \rangle_{As}$  to be less than less than 0.5% (Figures 3.1, 3.3 and 3.4). If the variance  $\langle \Delta x \rangle_{As}$  grows by more than 3%, the two elastic phase transitions are expected to be smeared [14], [15] leading to a Gaussian-like or even triangular shaped reversibility window as reported in previous reports [14], [15]. The Sulfur-rich glasses which contains more than 80% of S pose another challenge. A peculiar feature of Sulfur is that the S8 ring conformation is more stable than a polymeric S<sub>n</sub> chain. Hence, when melts are cooled, the S-rich domains condense into a  $S_8$  rich nanophase once the T < 150°C,

the  $T_{\lambda}$  transition. The segregated  $S_8$  rich nanophase cuts the As-S polymeric backbone and hinders the growth of the backbone. In this thesis, it has been shown that once glass/melts are homogenized, an additional step of low-temperature heating above  $T_g$  for 24 hours or more is crucial to augment fragmented segments of the backbone between the  $S_8$  rich nanophase domains, to observe the elusive mode of the As=S stretch mode near 537 cm<sup>-1</sup> of the As-centered S=As(S<sub>1/2</sub>)<sub>3</sub> quasitetrahedral units.

The assignment of the 537 cm<sup>-1</sup> mode with S=As(S<sub>1/2</sub>)<sub>3</sub> QT units is in complete agreement with the calculated frequency of that As=S stretch mode using NRLMOL code [12]. More significantly, compositional variation of the mode scattering strength unambiguously shows a maximum, near x = 18%, precursive to the onset of rigidity. The QT and PYR units are isostatically rigid (n<sub>c</sub> = 3) and their presence in comparable amounts in the backbone helps in stabilizing the IP by increased configurational entropy (S<sub>c</sub>) of the backbone [49]. The FT-Raman scattering results on the present As-S glasses also show that the scattering strength of the 490 cm<sup>-1</sup> mode shows a maximum around x = 25% in harmony with the assignment as a stretch mode of S-S dimmer linking AsS<sub>3</sub> pyramids. Therefore the earlier assignment [12] of the 490 cm<sup>-1</sup> mode with QT units is clearly not supported by the new results obtained on these especially homogenized glasses.

# 4.1.2 Ageing Behavior of $\Delta H_{nr}(x)$ and Network Configurational Entropy $S_c$

The aging experiments performed on As-S glasses at room temperature for 6 months show that the enthalpy of relaxation,  $\Delta H_{nr}(x)$  increases nearly 4-folds in the flexible

phase (x < 22.5%) and by around 2-folds in the stressed-rigid phase (x > 28.5%) and remains unchanged and near vanishing in the Intermediate phase. These results unambiguously display the stability of the Intermediate phase compared to other phases in these glasses. Particularly, the abrupt nature of the rigidity and stress-elastic phase transition do not change on aging.

In the aging experiments of the present work, the glasses were held at room temperature ( $T_a = 25^{\circ}C$ ). Since the kinetics of aging are determined by  $T_a/T_g$  ratio, the aging of  $\Delta H_{nr}(x)$  is expected to be pronounced in the flexible phase ( $T_a/T_g = 0.80$ ) in comparison to that of the stressed-rigid phase ( $T_a/T_g = 0.69$ ). Also, the  $T_g$  of glasses in the flexible phase (~100°C) are lower than that of the stressed-rigid phase glasses (~140°C). The aging results in the present work are clearly in harmony with that expectation.

The vanishing of the enthalpy of relaxation term in the Intermediate phase implies that network glasses possess melt-like configurational entropy. The aging related increase of the  $\Delta H_{nr}(x)$  term outside the IP suggests that there are entropy sinks contributing to the lowering of the configurational entropy in those areas. The formation of S<sub>8</sub> rings is viewed as entropy sinks in the flexible phase, which lead to the increase of  $\Delta H_{nr}(x)$  term. A scrutiny of the Raman spectra of the glasses (**Figure 3.5**) shows a rather pronounced growth in scattering strength of the S<sub>8</sub> related vibrational features near 217 cm<sup>-1</sup> and 472 cm<sup>-1</sup> as the As content of glasses, x is less than 24%. In the stressed-rigid glasses formed at x > 28.5% the entropy of the glass backbones is expected to steadily reduce since both QT- and PYR- local structures are formed in the IP, but only PYR- local structures remain as x increases to 40%. The steadily reducing chemical disorder as x increases to 40% can be viewed as aspects of local and intermediate range structure that contribute to the lowering of configurational entropy. Since  $V_m$  of c-As<sub>2</sub>S<sub>3</sub> is quite low, the  $V_m(x)$  in the glasses is also expected to decrease as x increases to the stoichiometric composition, x = 40%. This view is independently confirmed by the configurational entropy, S<sub>c</sub> variation within the Adams Gibbs approach, which is determined by the inverse of the activation energy E<sub>a</sub> (**Figure 4.1b**) of the enthalpy relaxation times deduced from fragility index measurements. It is to be noted in **Figure 4.1b** that the variation of  $1/E_a$  versus x shows a maximum in the IP and  $1/E_a$  steadily reduces in the stressedrigid phase.

Although the stoichiometric g-As<sub>2</sub>S<sub>3</sub> possesses a  $\langle r \rangle = 2.40$ , it is quite evident that no IP forms around that composition [50] a suggested by the finite enthalpy of relaxation observed for the stoichiometric glass. The stoichiometric glass is segregated into As-rich nano phase and S-rich As<sub>2</sub>S<sub>3</sub>+ $\delta$ . The NSPS structure does not sustain the Intermediate phase and this result is not unique to As<sub>2</sub>S<sub>3</sub>.

## 4.1.3 The Rigidity Phase Transition in As<sub>x</sub>S<sub>100-x</sub> Glasses near x = 22.5%

The Phillips-Thorpe prediction for onset of rigidity in disordered molecular networks [48], [51, p. 204] near  $\langle r \rangle = 2.40$  has been remarkably successful in understanding the Group IV-selenides and sulfides [6], [14], [15], [24], [27] [Ge(or Si)]x(Se)]100-x. The elastic phase transition stems from isostatically rigid (n<sub>c</sub> = 3) local structures such as GeSe<sub>4</sub> or SiSe<sub>4</sub> or GeS<sub>4</sub> tetrahedral units that percolate near a mean  $\langle r \rangle = 2.40$ . On the other hand, the case of group V-chalcogenides like As-Se, P-Se came into attention several years ago, when it was observed that the onset of rigidity is observed at a measurably lower mean coordination number near  $\langle r \rangle =$ 

2.28 [13], [52]. The transition was identified with presence of isostatically rigid ( $n_c = 3$ ) local structures based on QT (Ch =  $P_n(Ch_{1/2})_3$ ) units formed in Pnictide ( $P_n = P$  or As) based chalcogenides (Ch = S or Se). The case of binary P-Se [46] and ternary (P or As)<sub>x</sub>Ge<sub>y</sub>Se<sub>100-x-y</sub> [44], [53], [54] have convincingly shown in Raman scattering and Calorimetric evidence that the onset of rigidity occurs near < r > = 2.28, suggesting that  $P_n$ - centered QT local structures are implicated in the percolation of rigidity at the lower connectivity. It is to be noted that < r > of the QT unit is 2.285.

In this thesis work on As-S binary, where the rigidity transition occurs near  $\langle r \rangle = 2.225$ , which is lower than the usual circumstance near  $\langle r \rangle = 2.285$ . This poses an obvious question; how do we understand the shift to an  $\langle r \rangle$  to an even lower value of  $\langle r \rangle$  than 2.285? We believe these observations have a structural connection.



**Figure 4.2:** The observed reversibility windows in  $P_xS_{100-x}$  [55],  $As_xS_{100-x}$  [56] and  $P_xSe_{100-x}$  [53] glasses. It is to be noted that the rigidity transition,  $x_r = 16\%$  in  $P_xS_{100-x}$ , shifts upwards to  $x_r = 22.5\%$  in  $As_xS_{100-x}$  and then to  $x_r = 28\%$  in the  $P_xSe_{100-x}$  binary.

MDSC experiments on  $P_xS_{100-x}$  glasses display [55] the reversibility window to occur in the 16% < x < 19% range (**Figure 4.2**). Raman scattering measurements unequivocally show three well-resolved vibrational modes near 377 cm<sup>-1</sup>, 416 cm<sup>-1</sup> and 472 cm<sup>-1</sup>. These modes are identified respectively [55] with the stretch modes of S=P(S<sub>1/2</sub>)<sub>3</sub> QT units labeled as P4, P(S<sub>1/2</sub>)<sub>3</sub> PYR units labeled as P3 and polymeric S<sub>n</sub> chains [13]. From the observed scattering strength ratio of the QT and PYR units, the approximate concentration ratio  $N_{P4}/N_{P3}$  ratio is extracted and is found to be 0.60(5). The stoichiometry of the backbone suggested for onset of rigidity transition near x = 16% is then found to be around  $P_{28}S_{82}$ . These results clearly show that the polymeric  $S_n$  chains are largely decoupled from the backbone in these binary  $P_x S_{100}$ . x glasses. The stoichiometry of the P-Se backbone at the onset of the rigidity transitions in  $P_x Se_{100-x}$  glasses also occurs near x = 28%, except in these binary glasses, the polymeric Se<sub>n</sub> chains comprise part of the isostatically rigid backbone. Thus, the structural picture that evolves in that while in the P-Se binary glasses the polymeric Sen form part of the backbone, on the contrary, in binary P-S glasses, the polymeric S<sub>n</sub> chains are nearly completely decoupled from the backbone thereby causing the onset of rigidity to shift down in x. It is not easy to guess from the Raman scattering results alone if the polymeric S<sub>n</sub> chains are part or decoupled from the glassy backbone, but when these optical measurements are correlated with the calorimetric ones, a clear interpretation of the shift in the elastic phase transition to lower x in the P-S binary emerges.

In the present binary As-S glasses, we note the onset of rigidity to occur at  $x_r = 22.5\%$ , which is shifted down from the case of the P-Se binary at  $x_r = 28\%$  by nearly 6% in x. This is almost half-way in between the shift in x observed between the onset of rigidity in the P-Se binary near  $x_r = 28\%$  and the onset of rigidity transition near  $x_r = 16\%$  in the P-S binary glasses. The As-S binary glasses face challenges in uniquely fitting the observed Raman lineshapes to extract the fraction of QT/PYR near x = 22.5%. Nevertheless, from the location of the rigidity transition  $x_r = 22.5\%$  in As-S glasses, it is speculated that in these sulfides, nearly half of the polymeric  $S_n$  chains are decoupled from the backbone. That observation has a correlation with the finding of the Raman profiling experiments that demonstrated in the final step of

melt quenching after  $T_g$  cycling S-rich glasses (x < 22%), the S<sub>8</sub> ring fraction is observed to sharply decrease, underscoring the polymeric S<sub>n</sub> chains has increased. It appears that not all these S<sub>n</sub> chain fragments become part of the backbone. This behavior needs to be explored in future work.

## 4.1.4 Compaction of IP Glassy Networks in Homogeneous As<sub>x</sub>S<sub>100-x</sub> Glasses

Molar volume  $V_m(x)$  variation in the present glasses show three distinct regimes; in the flexible phase, a pronounced growth is observed in  $V_m(x)$  at x < 20%. In the IP, a Gaussian-like local minimum is seen and in the Stressed-rigid phase, a sharp reduction of  $V_m(x)$  occurs at x > 29%. Equally striking is the fact that  $V_m(x)$  in the IP range systematically exceed those published earlier in the glasses synthesized by Chen et al. [12]. Moreover, trends in  $V_m(x)$  in the three phases in the especially homogenized glasses of the present work are totally distinct. At x < 21%,  $V_m(x)$ increases precipitously and at high x, at x > 30%,  $V_m(x)$  decreases remarkably, while in the IP, a Gaussian like minimum is observed. Trends in  $V_m(x)$  in the earlier investigations [12] showed a smearing of the variation near the two elastic phase boundaries (rigidity and stress) separating these three regions. These differences in trends of  $V_m(x)$  are tied to the homogeneity of glasses synthesized in this work.

The pronounced growth of  $V_m$  at x < 20% (Figure 3.8d) appears to be closely correlated with the rather sharp increase in the concentration of S<sub>8</sub> rings observed in Raman scattering (Figure 3.5). It is important to note that the inter-ring forces that stabilize the S<sub>8</sub> ring nanophase is derived from lone pair interactions. At x > 30%, the sharp reduction in V<sub>m</sub>(x) is tied to the pronounced growth of the pyramidal As(S<sub>1/2</sub>)<sub>3</sub> local units with  $\langle r \rangle$  of 2.40 that promotes cross-linking of the glasses as the stoichiometric glass composition of x = 40% is reached. The crystalline phase (orpiment) is fully polymerized and has the lowest Molar Volume of 14.10 cm<sup>3</sup> [16]. The local minimum in V<sub>m</sub>(x) inside the IP which is clearly observed in the present homogeneous glasses confirms the role of the weaker long range forces (Van der Walls forces and Coulombic forces) that come into play when the strong covalent forces (bond-bending and bond-stretching) are balanced exactly by the degrees of freedom of 3 per atom. Network compaction in IP is the fulfillment of the Maxwell-Phillips rigidity criteria, n<sub>c</sub> = n<sub>d</sub>, being fulfilled in that special phase. The absence of the smearing of that local minimum near the edges is a direct reflection of the low variance in  $\langle \Delta x \rangle_{As}$  in these present homogenized bulk glasses.

# 4.2 Correlating Melt Fragility Index with Glass Enthalpy of Relaxation

Th central key finding of this thesis work is that the melt fragility index m(x) in the  $As_xS_{100-x}$  binary is found to be closely tied to the glass enthalpy of relaxation. Glassy melts are specifically examined in the 22.5% < x < 28.5% range (Figure 3.9a) which display a Gaussian-like minimum of the fragility index m(x). A scrutiny of the observed variation in m(x) shows that m < 20 in the above-mentioned range, and m > 20 outside. The melt composition range in which m < 20 is defined as the "fragility window". The fragility index measurements are made using the same homogenized bulk glass samples that were used to establish the square well like reversibility window (Figure 3.8b). The observed trends in the compositional variation of the fragility index, m(x) which is characteristic of melts and enthalpy of relaxation at  $T_g$ ,  $\Delta H_{nr}(x)$  which characterizes the glasses show that there is a presence of an

intimate relationship between melts and glasses. These trends demonstrate that super-strong melts upon cooling to  $T_g$  gives rise to isostatically rigid glasses in the Intermediate phase (**Figure 4.1**), whereas fragile melts formed at non-IP compositions upon cooling gives rise to either Flexible or Stressed-rigid glasses. The fragility index decreases with increasing  $T_g$  in flexible glasses. In Stressed-rigid glasses, the opposite behavior is seen, i.e. fragility index increases with  $T_g$ .

The intimate correlation between the fragility window and the reversibility window as observed in this present work has also been seen in other chalcogenide glassy systems, like Ge-Se binary [19] and Ge-S binary [24]. The melt-glass correlation has also been noted in modified oxides [43] – the case of sodium phosphate glasses. These new findings suggest the intimate correlation between melt dynamics and glass topological phases which may well be a generic feature of the glassy state of matter.

## 4.3 Equilibrium Phase Diagram, Eutectics, and Aging of the Reversibility Window

The equilibrium phase diagram of As-S binary was reported in 1981 by Borisova [57]. In that report, the author showed the existence of a eutectic near an As composition of x = 15% with a eutectic temperature (T<sub>E</sub>) of about 150°C. The phase diagram was later re-investigated in 1990 by Okamoto in Binary Alloy Phase Diagram 2<sup>nd</sup> edition [58]. In this report, there was no evidence of eutectic was shown.

The results on the aging of the reversibility window in the present As-S binary glass system shows in **Figures 3.8b** and **4.1a** is totally compatible with the absence of a eutectic near x = 15%. If at all there was a eutectic near x = 15%, it would have been expected that the rigidity transition will smear with aging time and now show any sharp abrupt change in the enthalpy of relaxation as shows in **Figures 3.8b** and **4.1a**.



**Figure 4.3:** The phase diagram of the  $As_xS_{100-x}$  binary glass system taken from the work of Okamoto [58]. A eutectic is seen near  $x = \sim 1\%$  but nothing is seen in the 1% < x < 40% range of As.

In both  $As_xSe_{100-x}$  and  $P_xSe_{100-x}$  binary systems, the equilibrium phase diagrams show evidence [59], [60] of a eutectic near x = 20%. The existence of a eutectic has attracted interest in the field of glass science. It constitutes signature of phase separation that causes the liquidus to locally decrease. These circumstances aids in rapid cooling of melts and has been used to promote [61] glass formation in metallic systems. The existence of the As-Se and P-Se binary systems has another exciting consequence. Both these binary systems have reported the existence of the reversibility windows. The As-Se binary is reported to have an Intermediate phase in the range of 28% < x < 37% and for the P-Se binary in the 28% < x < 40% [18], [62]. However, in both these systems, aging of glasses inevitably leads to the smearing of the rigidity transition and even narrowing of the reversibility window since the Tg's of the glasses near the rigidity transition are very close to the Eutectic Temperature (T<sub>E</sub>). This is the reason why the reversibility window does to retain its square well like shape on aging of the glasses when heated to T<sub>g</sub>. That circumstance is distinguished from the case when no eutectic occurs in the vicinity of the reversibility window, as is the case of present As-S binary and rigidity- and stress-transition continue to be abrupt both in the fresh and aged glasses [24], [27], [44].

### 4.4 Ideal Glasses, IP, and Configurational Entropy

Adam-Gibbs [63] suggested that the exponential increase in viscosity of a melt as it is cooled to a temperature T can be tied to its loss of excess configurational entropy ( $S_c$ ) with the help of the following equation:

$$\eta = \eta_0 \exp\left(\frac{B}{TS_C}\right)$$

Since the viscosity of a melt is viewed to be a thermally activated process:

$$\eta = \eta_0 \exp\left(\frac{E_a}{k_B T}\right)$$

The above two equations determine that the excess configurational entropy  $S_c$  must vary as the inverse of the activation energy of enthalpy  $1/E_a$ . The MDSC experiments

on the present glasses established  $E_a$  which is the activation energy for enthalpy relaxation (Figure 2.11). The compositional variance of 1/E<sub>a</sub> (Figure 3.9c) shows a pronounced peak centered at the IP. The result suggests that IP melts should possess a high configurational entropy even when melts are cooled to near  $T_g$  [49]. The excess entropy S<sub>c</sub> is defined as the entropy difference between super cooled liquid at T and the state of the glass at which the entropy can no longer be lost [64]. The high configurational entropy of IP glass compositions is precisely what is also implied in the vanishing of the enthalpy of relaxation  $\Delta H_{nr}(x)$  of these special glass compositions. In contrast the sharp and abrupt sizeable increase in the  $\Delta H_{nr}(x)$  term in non-IP compositions is due to such networks possessing entropy sinks. In the flexible phase, the entropy sinks include S<sub>8</sub> monomers for which direct evidence emerges from not only the Raman vibrational mode (Figure 3.5) but also the pronounced increase of molar volumes at x < 22.5% (Figure 4.1c) evolving in the flexible phase. In the stressed-rigid phase the entropy sinks include pyramidal  $(AsS_{1/2})_3$  units that steadily compact the backbone network into structural configurations like those found in orpiment as revealed by Raman scattering (Figure **3.5**) as well as the Molar volume variation (Figure 4.1c). IP glasses represent ideal glasses. They not only possess a high glass forming tendency, they also display minimum aging and form isostatically rigid structures that are adaptive in nature. These ideal glasses also exist only in high configurational entropy structures as found in corresponding melts. These observations on IP glasses as ideal glasses are clearly different with the idea advanced many years ago that ideal network glasses possess low configurational entropy and form at T close to the Kauzmann temperature [22].

## **Chapter 5**

## Conclusions

The especially homogenized As<sub>x</sub>S<sub>100-x</sub> glasses have been examined using Modulated-DSC, Raman scattering and Molar volume experiments over a wide range, 12% < x < 40% and elemental S as starting materials in evacuated quartz tubes, and quenched melts Raman profiled as a function alloying time till the observed lineshapes along the melt of the length column became identical. Sulfurrich (x < 20%) melts needed about 6 weeks while Sulfur-deficient ones (x > 20%) about 4 weeks of alloying time at 650°C to homogenize. In such homogenized glasses the variance in As content,  $\langle \Delta x \rangle_{As}$  across 1.5 gram sized batches decreased by an order of magnitude to become less than <0.5%. A second step of heating glasses at T<sub>g</sub> + 10°C for 2 days, once glasses were homogenized was found to be sufficient to be able to observe the elusive 537 cm<sup>-1</sup> mode of the S=As stretch mode of S=As(S<sub>1/2</sub>)<sub>3</sub> local structures at x < 26% in FT-Raman scattering experiments. In such glasses, the enthalpy of relaxation at  $T_g$ ,  $\Delta H_{nr}(x)$  show a deep square-well like variation in the 22.5% < x < 28.5% composition range even in the fresh state which defines the Reversibility window. The fragility index, m(x), of the corresponding melts show a Gaussian-like local minimum with m < 20 in the same composition range, thus defining a Fragility window. Molar volumes, V<sub>m</sub>(x) of glasses show a local Gaussian like local minimum entirely in the Reversibility window region underscoring the compacted nature of glasses formed in that composition range defining a Volumetric window. On As<sub>x</sub>S<sub>100-x</sub> glasses which were alloyed for 3 days at 650°C [12], the Molar volume window, V<sub>m</sub>(x) was smeared at the edges by

comparison (Figure 3.5d) because of the larger variance in As-stoichiometry  $<\Delta x>_{As}$  across the same size batches synthesized. In S-rich glasses (x < 20%), in the Flexible phase, the glasses segregated into S<sub>8</sub>-rich nanophase and an As-S bearing glassy backbone. For the Intermediate phase (22.5% < x < 28.5%), the glassy backbones are composed of QT and PYR local structures which are the isostatic building blocks of this phase and displays a vanishing  $\Delta H_{nr}(x)$  term, and with corresponding melts showing a super-strong behavior (m < 20) contributes to the delayed homogenization of melts. In the Stressed-rigid phase (x > 28.5%), glasses possess increasing  $\Delta H_{nr}(x)$  values and the corresponding melts are increasingly fragile, m(x) > 20 with increasing x. These results unequivocally demonstrate that superstrong melts yield isostatically rigid glasses, while fragile glasses form either Flexible or Stressed-rigid glasses upon cooling past T<sub>g</sub>. The exceptional nature of As<sub>x</sub>S<sub>100-x</sub> glasses formed in the 22.5% < x < 28.5% range displays a Reversibility window, a Volumetric window, and their melt counterparts shows a Fragility window, are a realization of the self-organized IP formed in these network glasses.

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## **Appendix A**

## **1. NRLMOL** results for vibrational modes of Pyramidal and Quasi-tetrahedral local structures in binary As<sub>x</sub>S<sub>100-x</sub> glasses



**Figure A1:** Eigenvectors of the Raman and IR active vibrational modes of PYR and QT local structures obtained by NRLMOL calculations. The figure is taken from [12].

## 2. Compositional trends in population of S=As(S<sub>1/2</sub>)<sub>3</sub> QT local structures in As<sub>x</sub>S<sub>100-x</sub> glasses

The scattering strength variation of the 537 cm<sup>-1</sup> Raman mode QT S=As(S<sub>1/2</sub>)<sub>3</sub> local structures in As-S binary glasses has been tracked as a function of composition in these present especially homogenized followed by T<sub>g</sub> cycled binary glasses. FT-Raman spectra were normalized to the highest scattering strength mode near 335 cm<sup>-1</sup>. The trends obtained are plotted below in **Figure A2a** and the data is compared with the corresponding trends in the signal of the QT Se=P(Se<sub>1/2</sub>)<sub>3</sub> local structure from <sup>31</sup>P NMR signal from the work of Lathrop et al. [65]. In **Figure A2a** and **Figure A2b**, the Intermediate Phase composition range for the respective binary glasses are also projected. The QT local structures in both Group V chalcogenides are formed precursive to the IP. The IP is stabilized due to the high configurational entropy (S<sub>c</sub>) which is a consequence of the presence of both Pyramidal (P(Se<sub>1/2</sub>)<sub>3</sub>) and Quasitetrahedral (Se=P(Se<sub>1/2</sub>)<sub>3</sub>) local units in the network backbone as shown in **Figure 4.1b**.

There are challenges in uniquely analyzing the Raman lineshapes at higher As content (x > 24%) in the present glasses because of the overlap of the Orpiment-like modes formed at higher x (>24%) from the modes of the QT ones formed at x < 24%.



**Figure A2: (a)** Compositional trends in the normalized Raman Scattering Strength of the 537 cm<sup>-1</sup> of the QT local structures ( $S=As(S_{1/2})_3$ ) and (b) <sup>31</sup>P NMR signal of QT ( $Se=P(Se_{1/2})_3$ ) local structures in binary P-Se glasses. Both the maxima occurs precursive to respective Intermediate Phases [18].

# 3. Molecular origin of the 490 cm<sup>-1</sup> vibrational excitation in As<sub>x</sub>S<sub>100-x</sub> glasses

The molecular origin of the 490 cm<sup>-1</sup> mode in Raman Scattering of As<sub>x</sub>S<sub>100-x</sub> glasses remained unclear. Many researchers [17], [36], [37] suggested that the mode can be identified with S-S dimer in As<sub>x</sub>S<sub>100-x</sub> glasses and have references the work of Ward [32]. Dr. Ward made a comment on his paper about this mode which is, "*The broad, near* – *featureless band centered at 340 cm*<sup>-1</sup> *in the spectra of the arsenic-sulfur glasses is clearly attributable to a polymeric species probably related to the layer lattice existing in As*<sub>2</sub>S<sub>3</sub> *crystal. The weaker peaks at 140, 189, 230, and 490 cm*<sup>-1</sup> *are probably also associated with this polymeric lattice*". There is no clear identification of the 490 cm<sup>-1</sup> to S-S dimer.

In this thesis, the Raman scattering results of As-S glasses is analyzed to establish the scattering strength ratio R(x) of the 490 cm<sup>-1</sup> mode to the S<sub>n</sub> chain mode near 461 cm<sup>-1</sup> as a function of As-content x in **Figure A3**. The results are plotted with the help of the red data points below. It is expected that as x increases to 40%, the S<sub>n</sub> chain mode would vanish. In other words, the red data set sat on a baseline which is not flat. To establish the baseline, a plot of the inverse of scattering strength of the S<sub>n</sub> chain mode is made normalized to its value at x = 33% which generated the blue curve. Upon subtracting the blue curve from the red curve, the D-mode scattering strength variation on a flat baseline was established and it displayed a maximum near x = 25% as anticipated.

On purely statistical considerations, the S-S pair is expected to display a maximum near x = 25% corresponding to a glass composed largely of AsS<sub>3</sub> pyramids linked

by S-S contact. Hence, the observation of the peak in the black curve near x = 25% is suggestive that the 490 cm<sup>-1</sup> mode originated from the S-S mode between the AsS<sub>3</sub> pyramids.



**Figure A3: (a)** Observed scattering strength ratio  $R = I(D)/I(S_n)$  of modes centered 490 cm<sup>-1</sup> and near 461 cm<sup>-1</sup> shown by the (•) data points and the smooth red line in FT–Raman scattering of  $As_xS_{100-x}$  glasses as a function of As content of glasses. Raman lineshape deconvolution of spectra of these glasses are available in **Figure 3.6**. The ratio R increases with x as x increases to 33%. The blue curve plots the chain fraction  $I(S_n)$  normalized to the value at x = 33% concentration, and its rapid increase reflects the loss of  $S_n$  chains as x increases to the near stoichiometric composition (x = 33%). The black line is the difference between the red- and blue-line and gives the contribution of the D-mode scattering strength. The latter displays a local maximum near x = 25%. We obtain the blackline which shows a maximum near 25%. **Figure A3b** illustrates S-S contacts evolving between AsS<sub>3</sub> pyramidal units in the glass backbone. See text.

# 4. Molecular origin of the 490 cm<sup>-1</sup> vibrational excitation in Ge<sub>x</sub>S<sub>100-x</sub> glasses

In the  $Ge_xS_{100-x}$  binary, something similar was expected to happen, this time though the S-S linkages between a pair of  $GeS_4$  tetrahedra could also give rise to the D mode.

On statistical considerations one expects the S–S contacts in the  $Ge_xS_{100-x}$  binary to show a maximum near x = 20%, since such a glass may be viewed as made up of  $GeS_4$  tetrahedra linked by S–S contacts. The observed results of a maximum in the contribution of the I(D) near x = 20% is in harmony with that expectation and serves to confirm that the 490 cm<sup>-1</sup> mode is, indeed, a mode related to the S–S dimer mode in binary Ge–S glasses. These Raman scattering results on both Ge–S and As–S binary glasses are persuasive in suggesting the molecular origin of the 490 cm<sup>-1</sup> mode does come from S–S contacts in both binary glasses


**Figure A4:** The observed scattering strength ratio  $R = I(D)/I(S_n)$  of modes centered near 490cm<sup>-1</sup> and near 461 cm<sup>-1</sup> shown by the (•) data points and the smooth red line in FT–Raman scattering of  $Ge_xS_{100-x}$  glasses as a function of Ge content of glasses. The ratio R increases with x as x increases to 25%. The blue curve plots the chain fraction  $I(S_n)$  normalized to the x = 25% concentration, and its rapid increase reflects the loss of  $S_n$  chains as x increases to the composition x = 25%. The black line is the difference between the red- and blue-line and gives the contribution of the D-mode scattering strength. The latter displays a local maximum near x = 20%. (b) illustrates

S-S contacts emerging between  $GeS_4$  tetrahedra while (c) illustrates the Raman spectrum of a  $Ge_{15}S_{85}$  bulk glass taken from Chakraborty and Boolchand [24].

## **Appendix B**

## **Journal Publications**

- S. Chakravarty, R. Chbeir, P. Chen, M. Micoulaut, and P. Boolchand, "Correlating Melt Dynamics and Configurational Entropy Change with Topological Phases of As<sub>x</sub>S<sub>100-x</sub> Glasses and the Crucial Role of Melt/Glass Homogenization" Frontiers in Materials (2019) https://doi.org/10.3389/fmats.2019.00166
- S. Chakravarty, B.S. Almutairi, R. Chbeir, S. Chakraborty, M. Bauchy, M. Micoulaut and P. Boolchand, "Progress, Challenges and Rewards in Probing Melt Dynamics, Configurational Entropy change and Topological Phases of Group V and Group IV based Multicomponent Sulfide glasses" PSSB (2020) https://doi.org/10.1002/pssb.202000116
- A. Welton, R. Chbeir, M. McDonald, M. Burger, B.S. Almutairi, S. Chakravarty and P. Boolchand, "Unusual Role of P–P Bonds on Melt Dynamics and Topological Phases of the Equimolar Ge<sub>x</sub>P<sub>x</sub>Se<sub>100-2x</sub> Glass System" J. Phys. Chem. C (2020) <u>https://doi.org/10.1021/acs.jpcc.0c07491</u>
- B.S. Almutairi, S. Chakravarty, R. Chbeir, P. Boolchand and M. Micoulaut *"Melt dynamics, nature of glass transition and topological phases of equimolar Ge<sub>x</sub>As<sub>x</sub>S<sub>100-2x</sub> ternary glasses" J. Alloys and Compounds (2021) <u>https://doi.org/10.1016/j.jallcom.2021.159101</u>*

5. M. Burger, A. Welton, M. McDonald, R. Chbeir, S. Chakravarty, S. Mamedov and P. Boolchand, "Isostatically rigid local structures and 3membered rings lead to super-strong melts and stability of Intermediate Phase Glass Compositions in binary  $P_xSe_{100-x}$  system" Manuscript in preparation