I, Siddhesh V Bhosle, hereby submit this original work as part of the requirements for the degree of Master of Science in Electrical Engineering.

It is entitled:
Direct evidence for abrupt rigidity and stress transitions in dry and homogeneous bulk Ge_{x}Se_{100-x} glasses

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Direct evidence for abrupt rigidity and stress transitions in dry and homogeneous bulk Ge$_{x}$Se$_{100-x}$ glasses

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Abstract

We introduce a Raman profiling method to track heterogeneity of melts over days as starting materials are reacted and batch compositions homogenize. Results on 2 gram sized dry Ge_xSe_{100-x} melts, reacted at 950°C, show that they homogenize on a scale of 10 microns after 168 hours in a process that has two steps. In the first step, elements of local structure evolve, followed by extended range structures forming as the Ge/Se stoichiometry across a batch composition equalizes by a slow diffusive process with a Diffusion constant, D = 2 x 10^{-6} cm^2/sec. Such homogenization is precursive to self-organization. We have synthesized 21 glass compositions spanning the range, 10% < x < 33.33%, and have examined their thermal, optical and mechanical behavior in modulated DSC, Dispersive Raman scattering and Molar volume experiments respectively. These data, on glasses of unprecedented homogeneity, reveal sharply defined rigidity transition near x_c(1) = 19.5(5)% and stress transition near (x_c(2) = 26.0(5)%, with optical elastic power-laws in the Intermediate Phase (IP: 19.5% < x < 26.0%) of p_1 = 1.10(10), and in the Stressed rigid phase (x > 31.5%) of p_2 = 1.50(3). The variation of non-reversing enthalpy, ΔH_{nr}(x), at T_g is found to display three regimes, a global minimum (~0) in the IP, and an increase outside the IP, but with sharply defined walls at x_c(1) and x_c(2), the two elastic thresholds deduced from optical measurements. Variation of Molar volumes, V_m(x), also displays three regimes of behavior with a global minimum in the IP and an increase outside that phase. The ΔH_{nr} term ages over weeks outside the IP glass compositions but not inside the IP. The variation of glass transition temperature, T_g(x) in the 10% < x < 33.33% range is well described by a polynomial. A sharp cusp in ΔH_{nr}(x) term is observed near x = 31.5(5)% , and it coincides with a maximum in the slope of T_g with x, features that we identify with the first appearance of Ge-Ge bonds with increasing x, and demixing from the network backbone. In the
composition range, $31.5\% < x < 33.33\%$, glasses are viewed as being nanoscale phase separated into Se-rich and Ge-rich regions for which substantial evidence comes from Raman and ssbauer spectroscopy experiments. The fraction $R(x)$ of Edge-Sharing to Corner-Sharing tetrahedra, is found to increase in the $0.20 < R(x) < 0.37$ range with $x$ in the $20\% < x < 33.33\%$ range, in harmony with neutron scattering results. Melts containing traces of water synthesized at select compositions homogenize much quicker than their dry counterparts, however their physical properties including $T_g, \Delta H_{nr}, V_m$ are measurably different from their dry counterparts. The intrinsic physical behavior of dry and homogeneous chalcogenides glasses can vary sharply with composition near elastic and chemical phase transitions, showing that the physics of network glasses may be far more interesting than hitherto recognized.
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CHAPTER 1

Introduction

Amorphous thin-films and melt-quenched alloy glasses of the chalcogenides and oxides are nano-structured materials. They form networks made of local structural units such as tetrahedra, pyramids and chain segments bridged across Se, S or O atoms. Their properties systematically and continuously change with chemical stoichiometry. These materials continue to fascinate us both at a fundamental level and in engineering applications. Some of the applications relate to Information Technology, wherein Phase-Change materials\(^1\) have played a central role as both passive information storage devices, and also as active memories in computers. In the communication industry optical fibers made of SiO\(_2\) glass have almost completely replaced Cu wires\(^2,3\).

At a fundamental level we continue to seek appropriate theory to understand the molecular origin of this very select property of glass formation of melts encompassing a wide range of material systems. These include melts of oxides and chalcogenide, H-bonded system, and metallic alloys melts. The basic nature of the glass transition,\(^4,5\) an intrinsically non-equilibrium process, continues to elude us. But profound progress has occurred. The emergence of Rigidity Theory in the early 1980s brought\(^6\) to the fore ideas on network topology (connectivity) in controlling the physical behavior of network glasses. Sophisticated experiments\(^7-10\) since 1997, to probe the rigidity onset in these nanostructured materials give clear evidence for three distinct elastic phases- *flexible, rigid but stress free and stressed–rigid* with increasing network connectivity. Producing these phases requires that samples be homogeneous and dry- an issue that is still not generally recognized in the field. In this work we
dwell on this issue in some detail, and show that presence of water and the lack of sample homogeneity drastically alter their local structure. Thus it is possible that a recent report\textsuperscript{11} questioning the existence of the intermediate phase (rigid but stress-free) in binary Ge\textsubscript{x}Se\textsubscript{100-x} glasses could be directly related to the use of batches that were intrinsically heterogeneous.

Although synthesis of glasses is a fairly straightforward process, involving super cooling melts to bypass crystallization, the fact is that there are no set rules or laid out procedures for synthesis of truly homogeneous glasses. Melt quenching as a method to synthesize bulk glasses has been widely used for over 50 years. The parameter space of quenching, annealing, etc. is large, and raises the issue whether samples synthesized using different conditions have the same final structure. Specifically, in what kind of a vacuum should starting materials be sealed to synthesize chalcogenides? At what temperature and for how long should melts be reacted? Does the size of the melt play a role on the duration for which it much be reacted to achieve homogeneity? How can we establish heterogeneity of a melt during synthesis? Does the spatial scale of homogeneity (1mm, 250 microns, 1 micron, 10 nm) matter? There are a few issues that are central to synthesis of high quality samples which give \textit{reproducible} results. In this work I provide answers to the questions posed above.

We have developed a Raman profiling method to determine the structure of frozen melts during synthesis, and can establish the spatial heterogeneity of samples on a scale of 50 microns or less. The Raman profiling method consists of taking spectra all along the length of a sample while it is inside an evacuated reaction quartz tube wetting the inner surface. The spectra taken at different locations must have identical Raman spectra for the batch to be truly homogeneous, and representative of the actual stoichiometry. If the observed line shapes vary along the tube, clearly we must assume that the batch preparation is not homogeneous. Using this method as a
guide we have optimized the growth of the binary Ge-Se and ternary Ge-Se-I samples over a wide range of compositions.

Batch sizes play a role in kinetics of homogenization of melts. This is illustrated in Fig. 1, which showcases Raman scattering from a binary Ge$_x$Se$_{100-x}$ glass at $x = 19\%$ as a function of reaction time of the starting materials from present work. We find that the longer sized sample of 2 grams (fig. 1a, b), takes much longer to homogenize than a $\frac{1}{4}$ gram sample (Fig. 1c). After 6 hours of alloying, the 2 gram batch continues to be quite heterogeneous as evidenced by the large scatter in the 9 line-shapes recorded along length of the sample. But after 168 hours of nanoscale mixing, melts homogenize and all the 9 lineshapes coalesce (Fig. 1b) into a single line shape characteristic of a batch preparation. For the $\frac{1}{4}$ gram batch on the other hand, note after 6 hours of nanoscale mixing of the starting materials (Ge and Se), the batch has already homogenized. These data clearly emphasize that smaller sized samples homogenize much quicker than larger ones. Clearly then, even larger sized batches of 10 grams and 20 grams used recently in NMR experiments by Sen et al.$^{12}$ and in Neutron scattering experiments by P. Salmon et al$^{13}$, might be expected to take even longer than 168 hours to homogenize. The use of small samples ($\frac{1}{4}$ gram) in $^{129}$I and $^{119}$Sn Mossbauer effect studies$^{14}$ on binary Ge-Se glasses in the early 1980-90s, suggests that those samples must have been homogeneous because batch sizes were kept near $\frac{1}{4}$ gm. In this present work we use the term homogeneity to describe spatial variations in glass stoichiometry across a length scale of 50 microns. This is set by the laser spot size in the Raman profiling experiments. There is evidence to suggest that had we set the laser spot size at 250 microns, samples would have appeared to be homogenized in a shorter time, 4 days instead of 7 days.
Fig. 1 Raman spectra taken at 9 spots along the length of a Ge$_{19}$Se$_{81}$ glass sample in a quartz tube used for synthesis, (a) 6 hours (b) and 168 hours of reaction of the starting materials (Ge, Se). The data in (a) and (b) is for a 2 gram batch size. (c) gives the data on a ¼ gram batch size taken 6 hours after reaction, and reveals the sample to be already homogeneous.
Sample dryness plays a role on glass structure. We illustrate that role in Fig. 2 wherein we compare Raman scattering of a wet glass sample with a dry one.

![Raman scattering graphs](image)

**Fig. 2** Dispersive Raman scattering in Ge$_x$Se$_{100-x}$ glasses in the dry (—) and wet (—) state at (a) $x = 19\%$ and (b) at $x = 33.33\%$. Note residual scattering in wet samples is larger than in dry ones.

These data unambiguously reveal that residual scattering in the wet sample exceeds that in the dry sample. In particular we note that for the sample at $x = 19\%$ (Fig. 2a) even the scattering strength of the Se$_n$ chain mode near 250 cm$^{-1}$ in the wet sample is lower than in the dry sample. A dry sample refers to one in which the starting materials, Ge and Se, were small (3 mm diameter lumps. These lumps were sealed in an evacuated quartz tubings at high vacuum, $< 10^{-7}$ Torr to avoid water doping.
Fig. 3 Modulated DSC scans of Ge$_{19}$Se$_{81}$ glass samples in (a) dry state and (b) wet state. Note that $T_g$ decreases and the non-reversing enthalpy at $T_g$, $\Delta H_{nr}$ increases in the wet sample compared to the dry sample. Also see Table 1 See text for details.

A wet sample refers to the use of finely ground Ge and Se powders, used as starting materials, and these were stored at laboratory ambient environment for 24 hours prior to vacuum encapsulation at $10^{-6}$ Torr. In the latter samples water is adsorbed on the surface of the Ge and Se particles and it is difficult to remove all water by pumping in a high vacuum line. These data suggest that some of the bridging Se atoms comprising Se$_n$ chain segments have been replaced by H and OH terminal bonds. The slicing of the chain segments is reflected in the lowering of the glass transition temperature ($T_g$) of the wet sample ($T_g = 158^\circ$C) compared to the dry one ($T_g = 171.6^\circ$C) as revealed by the modulated DSC scans of these samples shown in Fig. 3. The
blue curves show the reversing heat flow, and \( T_g \) is fixed by the inflexion point of the rounded step observed near the glass transition. The lowering of \( T_g \) by 13\(^o\)C is consistent with the notion that the connectivity of the network has been lowered by the presence of water traces in the wet sample, and will be discussed in more details later. Furthermore, the enthalpy of relaxation at \( T_g \) (\( \Delta H_{nr} \)) available from the non-reversing heat flow (red curve) of Fig. 3 also show the term to increase significantly in the wet sample compared to the dry one (Table 1 below). A small change in sample synthesis procedure shows astonishingly large differences in Optical, Thermal and even molar volumes of the glass samples. A perusal of Table 1 shows the molar volume of the wet sample of 18.03(4) cm\(^3\) is measurably lower than that of the dry sample (18.14(4) cm\(^3\)). We shall discuss these results in Chapter 2.

<table>
<thead>
<tr>
<th></th>
<th>( T_g )(^(\circ)C)</th>
<th>( \Delta H_{nr} ) (cal/g)</th>
<th>( V_{mol} ) (cm(^3)mol(^{-1}))</th>
<th>Reaction time ( (t_R) )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>19% Dry</strong></td>
<td>171.6</td>
<td>0.36</td>
<td>18.34</td>
<td>( t_R = 168 ) h</td>
</tr>
<tr>
<td><strong>19% Wet</strong></td>
<td>158.0</td>
<td>0.55</td>
<td>18.03</td>
<td>( t_R = 42 ) h</td>
</tr>
<tr>
<td><strong>33.33% Dry</strong></td>
<td>425.7</td>
<td>0.52</td>
<td>18.87</td>
<td>( t_R = 192 ) h</td>
</tr>
<tr>
<td><strong>k33.33% Wet</strong></td>
<td>420.6</td>
<td>0.74</td>
<td>18.14</td>
<td>( t_R = 72 ) h</td>
</tr>
</tbody>
</table>

In the dry and homogeneous Ge\(_x\)Se\(_{100-x}\) glasses we find the rigidity and stress transitions near \( x = x_c(1) = 19.5\% \) and \( x = x_c(2) = 26.0\% \) to be respectively abrupt! They are < 0.5\% wide in \( x \). We describe these findings in the present Thesis.

The present results represent a paradigm shift in the field. Physical properties of glasses do not always change smoothly and slowly with composition as widely believed. It is now
evident that they can change abruptly with chemical composition or connectivity, particularly near the \textit{elastic phase transitions} and \textit{chemical phase transitions}. To observe the intrinsic physical behavior of these glasses, use of homogeneous samples is a prerequisite.

The Thesis is organized as follows. In Chapter 2 we review the equilibrium phase diagram of Ge$_x$Se$_{100-x}$ binary and present experimental results on the binary glass, and discuss these results in chapter 3. Conclusions from this work are presented in Chapter 4.
CHAPTER 2

Binary chalcogenide Ge$_x$Se$_{100-x}$ Glasses

2.1 Equilibrium Phase diagram of Ge-Se binary

![Phase Diagram of Ge$_x$Se$_{100-x}$ binary](image)

Fig. 4 Phase Diagram of Ge$_x$Se$_{100-x}$ binary taken from Isper et al.$^{15}$

The equilibrium phase diagram of the Ge$_x$Se$_{100-x}$ binary taken from Isper et al.$^{15}$ appears in Fig. 4. In the Se-rich domain, there is a eutectic near $x = 5.5(5)$ % of Ge with a eutectic temperature $T_e = 212^\circ$C. At the eutectic temperature, liquid Ge$_{5.5}$Se$_{94.5}$, c-Se and c-GeSe$_2$ coexist as suggested by the solidus (horizontal line) at $212^\circ$C. The phase diagram shows that the liquidus ($T_1$) steadily increases (broken line) from $212^\circ$C at $x = 5.5\%$ to $742^\circ$C at $x = 33.3\%$, and serves as a guide in synthesizing glasses as we discuss in Chapter 3. Congruently melting stoichiometric crystalline compounds exist at $x = 0$ (c-Se) and at $x = 33.3\%$ (c-GeSe$_2$). In
addition, there is a metastable crystalline composition c-Ge$_4$Se$_9$ formed at $x = 30.7\%$. The structure of this metastable crystalline phase has a close bearing to the 2D form of GeSe$_2$ ($\alpha$-GeSe$_2$). The metastable form present in the phase diagram plays a role in the aging experiments performed on the bulk glasses performed in the present binary, and we discuss the issue in section chapter 3.

The phase diagram shows that when a melt of Ge$_{15}$Se$_{85}$ composition is cooled past the liquidus to $T = 300^\circ$C, it will decompose into a liquid of Ge$_{10}$Se$_{90}$ composition and c-GeSe$_2$. Cooling it further to the Eutectic temperature of $212^\circ$C, will result in segregation of the sample into two phases, which can be described by the following stoichiometric relation,

$$\text{Ge}_{15}\text{Se}_{85} = 55 (\text{Se}) + 15 \text{GeSe}_2$$ (1)

Thus, it is quite reasonable to expect if Ge$_x$Se$_{100-x}$ melts in the $0 < x < 33.33\%$ range are cooled across $T_1$ they may either (i) completely segregate to form c-Se and c-GeSe$_2$ upon slow cooling, or (ii) upon a fast quench form a completely homogeneous glass of the melt stoichiometry and avoid decomposition. Alternatively, an intermediate circumstance could occur; the bulk glass formed may possess Se-rich and GeSe$_2$-rich regions that would result in microscopic heterogeneities (MH) determined by the considerations above (Fig. 4). We find that using Ge and Se as melts composed of the starting materials, at short reaction times ($< 6$ hours), melts are indeed, quite heterogeneous, and do indeed possess Se-rich and Ge-rich glassy regions, and even crystalline GeSe$_2$–rich regions. But as they are reacted for extended time, melts homogenize rather slowly if they are dry, and rather quickly if they are wet, a process that we have monitored in real time by Raman profiling the quenched melts.
2.2 Synthesis and homogenization of Ge$_x$Se$_{100-x}$ melts

Ge$_x$Se$_{100-x}$ melts of 2 grams in size were synthesized using 99.999% Ge and 99.999% Se pieces (3-4 mm diam.) from Cerac Inc. The starting materials were mixed in the desired ratio by weight, sealed in evacuated ($10^{-7}$ Torr) quartz tubing (5mm ID) using a hydrogen/oxygen torch. The vacuum line consisted of a liquid nitrogen trapped High Vacuum pumping system. Prior to sealing, quartz tubes were held in a vacuum oven at 80°C for 24 hours. A total of 21 sample compositions spread in the 10% < x < 33.33% range of Ge were prepared. The quartz ampoules were held vertically in a T-programmable box furnace for varying time periods, $t_R$, ranging from 6 hours to 168 hours at 950°C. Upon heating melts to 950°C, liquid column was noted to reflux vigorously. Periodically melts were quenched from 50°C above $T_l$ (liquidus, Fig. 4) and examined in Raman profiling experiments (see below). Once homogenized, the as-quenched melts in quartz tubes were taken to $T_g + 20°C$ in the box furnace, held there for 10 minutes, and then slow cooled to room temperature at 3°C/min to realize homogeneous bulk glasses. We describe the homogenization of melts in 2.2.1 and 2.2.2, and will discuss the physical properties of the homogeneous glasses in 2.3.1.

2.2.1 Raman profiling of melts

All Raman profiling measurements on melts made use of a Thermo Nicolet FT-Raman 960 bench, using a 1.064 micron radiation from an Nd-YAG laser with a laser spot size of 50 microns. Spectra were acquired at 9 locations, spaced about 2.5 mm apart covering 25 mm length of the melt column. At each location, an acquisition took 7 minutes, and used 100 mW of laser power, with 200 scans yielding 2 cm$^{-1}$ resolution. A typical profiling scan, involving spectra taken at 9 locations, took about an hour of accumulation time.
Fig. 5 Thermo Nicolet FT-Raman view stage is shown. A sample is shown placed on the stage which is driven by a motor along the horizontal and vertical axis. The laser spot size can be adjusted at 50 µm using the micro setting and at 250 µm using the macro setting.

Profiling experiments were performed at all the 21 compositions after reacting them for about 168 h, and in each case melts were found to be homogeneous on a scale of 10µm (see below). At three compositions, x = 15%, 19% and 33.33%, data were recorded as a function of t_R over 192h to monitor growth of melt homogeneity. We describe these data below.
Ge$_{19}$Se$_{81}$ melt: Such melts in the initial stages ($t_R = 6$ hours, Fig. 6), were found to be quite heterogeneous. We observe narrow modes at the tube bottom (location 1), which are identified$^{17}$ with $\alpha$-GeSe$_2$. The scattering strength of the narrow modes decreased as one moves up from (location) 1 to 3, and vanish at 4. The scattering strength of the Se-chain mode (near 250 cm$^{-1}$) increases from 4 to 9, while that of the symmetric stretch of GeSe$_4$ tetrahedra (200 cm$^{-1}$) decreases in the same position range, showing that melts become steadily Ge deficient in going from 1 to 9.

Fig. 6  Raman scattering of a quenched Ge$_{19}$Se$_{81}$ melt taken along the length of a quartz tube used for reacting the melt at 950°C for 6 hours, and then lowering its temperature to $T_1 + 50$C, and water quenching. Note that spectra along the length of the tube, at indicated 9 points, show the lineshapes to systematically change. The narrow modes at arrow locations are those of $\alpha$-GeSe$_2$.$^{17}$
The Raman line-shapes of Fig. 6 are superimposed in Fig. 7a, and provide a pictorial view of melt heterogeneity. Continued reaction ($t_R = 24$ h) of melts (Fig. 7a), leads the $\alpha$-GeSe$_2$ (Fig. 7.b) phase to dissolve into the melt, but it is only after $t_R = 96$ h (Fig. 7c) that the phase has completely dissolved. At that point melt stoichiometry narrows to vary from 17% at 1 to 21% at 9.

Note that the sequence of position colors in the inset of Fig. 7c is replicated in the scattering strength increase of the Se-chain mode indicating that the Se content of glasses increases as one goes from position 1 to 9. It is useful to mention that the FT-Raman software normalizes spectra to the highest peak (Fig. 7c), and for that reason no scattering is noted on the Ge mode at 200 cm$^{-1}$. Our data show that a fully homogenized melt is realized only after $t_R = 168$ hours (Fig. 7d) when all the 9 spectra coalesce into a single lineshape. Noteworthy is the fact that scatter in the lineshape present (Fig. 7c) at the low frequency range (100-180 cm$^{-1}$), near the Se-chain mode, and near the 300 cm$^{-1}$ (ES mode) is absent in Fig. 7d as melts homogenize. These data show that the small spread in Ge-stoichiometry of 4% prevailing across the melt at $t_R = 96$ h (Fig. 7c) took an additional 72 hours of reaction (Fig. 7.d) to completely disappear, and
the melt to homogenize. The feature of slow homogenization of melts appears also at $x = 15\%$ and $33.33\%$.

**Ge_{15}\text{Se}_{85}** : The homogenization behavior of such melts was similar to the one discussed above for Ge_{19}\text{Se}_{81}. At a lower Ge content, less $\alpha$-GeSe$_2$ formed at the tube bottom, and after 24 h of reaction nearly most of it dissolved in the melt (Fig. 8b). Continued reaction ($t_R = 96$ hours) of melts, lead to increased homogeneity (Fig. 8c) with the variation in Ge stoichiometry across the melt narrowing to about 2% (14% at 1 and 16% at 9), as suggested by the scattering strength variation of the 200 cm$^{-1}$ relative to the 250 cm$^{-1}$ mode. But a fully homogenized melt was realized only after $t_R = 168$ hours (Fig. 8d) when all the 9 line-shapes coalesced into a single one, and with the scattering strength variation in the low frequency (100-180 cm$^{-1}$) and high frequency (320 cm$^{-1}$) domain vanishing. These data along with the those at $x = 19\%$, illustrate that the process of homogenization has broadly two steps, as illustrated on going from Fig. 8a - 8c leading to the appropriate local structures being formed, and the second step from Fig. 8c to 8d,

**Fig. 8** Raman profiling of Ge$_{15}$Se$_{85}$ melt reacted for increasing reaction times appears in (a) $t_R = 6$h, (b) $t_R = 24$h, (c) $t_R = 96$h, (d) $t_R = 168$h, demonstrating that melts homogenize after reacting for 168h.
resulting in a global homogenization of the melt.

\textbf{Ge}_{33.3}\text{Se}_{66.6} : At high Ge concentration new features appear in melts not seen earlier, as illustrated in Fig. 9-11 that reproduce the profiling scans after 6h, 24h and 96 h. Now we observe modes near 170 cm$^{-1}$ and 230 cm$^{-1}$ not seen earlier at lower x. Their origin comes from Ge-rich amorphous phases such as ethanelike Ge$_2$Se$_6$ and distorted rocksalt GeSe phase (section IV). A few sharp modes are observed at 5 (Fig. 9) towards the center of the melt column, and these are readily identified with α-GeSe$_2$.

\textbf{Fig. 9} Raman profiling of GeSe$_2$ melt reacted at 950°C for $t_R = 6$ h, and taken along 9 points along the length of the quartz tube containing the melt. The narrow modes at arrow locations are those of α-GeSe$_2$.$^{17}$
After 24 hours of melt reaction (Fig. 10), modes of the Ge-rich amorphous phases decrease, and now those of $\alpha$-GeSe$_2$ appear already at tube bottom (1, Fig. 10) and persist till the middle of the melt column (6, Fig. 10). The upper half of the melt column shows modes of CS and ES units, but with the Ge-content of melts steadily decreasing from 5 to 9.

**Fig. 10** Raman profiling of GeSe$_2$ melt reacted at 950°C for $t_R = 24$ h taken along 9 points along the length of the quartz tube containing the melt. The narrow modes at arrow locations are those of $\alpha$-GeSe$_2$

Continued reaction ($t_R = 96$ h) of melts, promotes homogeneity (Fig. 11) as $\alpha$-GeSe$_2$ phase, and the two Ge-rich amorphous phases dissolve into melts, but with a surprising result. We observe large scattering at low frequency near 120 cm$^{-1}$. The scattering strength increases as we move
towards the melt column center (Fig. 11). The increased scattering near 120 cm$^{-1}$ (1-6 in Fig. 11) is not a specific mode but really the quasi-elastic scattering increasing at low frequency and being cut off by the spectral response of the FT system near 100 cm$^{-1}$. The buildup of quasi-elastic scattering after 96h of reaction is the signature of long scale heterogeneity of melts particularly towards the melt center, features that are strikingly observed in Fig. 12.c

**Fig. 11** Raman profiling of GeSe$_2$ melt reacted at 950°C for $t_R = 96$h taken along 9 points along the length of the quart tube containing the melt. The peaks at the arrow locations indicate growth in quasi elastic scattering (see text).
The data of Fig. 12d, unambiguously show that GeSe₂ melt homogenizes globally only after reaction time $t_R = 192$ h. These data at $x = 33.33\%$ (Fig 12) along with those at $x = 19\%$ (Fig. 7) and 15\% (Fig. 8), reinforce the view that once melts acquire the characteristic local structures of underlying glasses in the first step of homogenization, it takes an additional 80-100 hours of reaction at 950°C for a batch composition in the second step to globally homogenize. An interesting observation was made during homogenization of GeSe₂ melts. After reacting melts for $t_R = 180$ hours, Raman profiling data showed that the batch had homogenized (Fig. 13), except for just one position, 7, where $\alpha$-GeSe₂ had formed. Further inspection of the sample showed location 7 to coincide with the meniscus cavity tip, a singularity that apparently nucleated crystallization. By rocking the melt for an additional few hours we could completely homogenize the sample. We discuss the observation in chapter 3.
Fig. 13  Raman scattering taken along the length of a quartz tube showing observed lineshapes at various locations of a GeSe$_2$ melt reacted for 180 h. For reference purposes, we have inserted the Raman lineshape of $\alpha$-GeSe$_2$ between 6 and 7. The narrow modes at arrow locations are also observed at position 7 in the melt suggesting nucleation of $\alpha$-GeSe$_2$ at the meniscus well.

2.2.2  Raman profiling, laser spot size and spatial homogeneity of melts

The FT-Raman system optics in its micro-setting has provisions for two laser spot sizes, 250 µm and 50 µm. In an earlier study$^{18,19}$ we had homogenized Ge$_x$Se$_{100-x}$ melts using a laser spot size of 250 µm. In those experiments, we found melts to homogenize in $t_R = 96$ h (Fig. 14), i.e., quicker than in the present work. However, measurements of the reversibility window in the
earlier study\textsuperscript{1,20} were found not to be as sharp as the one observed in the present work (Fig. 29). Clearly, laser spot size in these Raman profiling experiments intrinsically sets the spatial resolution at which melts are homogenized. And it appears dry chalcogenide melts homogenize slowly, and must be homogenized on at least a 50\textmu m scale to observe their intrinsic physical behavior in compositional studies.

\textbf{Fig. 14} FT Raman profiling data on a Ge\textsubscript{30}Se\textsubscript{70} melt taken with a 250 \textmu m spot size (a) 2 days and (b) 4 days after reacting at 950°C. Note that after 4 days of reaction the melt has homogenized. Melts homogenized on a coarser spatial scale (250 \textmu m), homogenize quicker than those homogenized on a finer scale (50 \textmu m as seen in Fig. 6), but display a reversibility window that is not as sharp as in the finely homogenized melts. See text.
Once homogenized, melts were separately examined using a Dispersive Raman system model T64000 from Horiba Inc. with 647 nm radiation (Kr- laser), a confocal microscope attachment using a 10X objective resulted in a 10 µm laser spot size. In Figure 15, we compare the Dispersive Raman profiled data on a GeSe$_2$ glass sample taken at 10 µm resolution with FT-Raman profiled data taken at 50 µm resolution. A perusal of these data unequivocally shows that reaction of melts at 950$^\circ$C at 168 h leaves them homogenized on a scale of 10 µm.

![Raman profiling](image)

**Fig. 15** Raman profiling of a GeSe$_2$ melt taken (left) at 10 µm laser spot size in a Dispersive measurement and (right) at a 50 µm laser spot size in an FT Raman measurement. The data suggest that melts homogenized on a 50 µm scale in an FT measurement are actually homogeneous on a finer scale of 10 µm scale.

### 2.2.3 Melt size and reaction time to homogenize

We found the melt homogenized in only 6h (fig. 16a) while the 2 gram melt took 168 h
Fig. 16 Raman profiling data on a Ge$_{19}$Se$_{81}$ melts (a) 2 gram melt reacted for 6h, (b) 2 gram melt reacted for 168h and (c) 1/4 gm melt reacted for 6h. Smaller size melts homogenize much quicker than larger ones.

At two compositions (x = 19% and 25.5%) we investigated the effect of rocking on melt homogenization. Quartz tubes were positioned horizontally in a muffle furnace, and the furnace rotated continuously in a vertical plane by 45 degrees at a rate of 1/10 cycles per second. After reaction of the elements at 950°C for 48 hours, Raman profiling data on these rocked melts showed that the appropriate local structures had formed, i.e., no crystalline phases were observed suggesting that the 1st step of homogenization had been speeded up (Fig. 17a and d). However, a significant variation in Ge stoichiometry across the batch composition still persisted. At that point samples were transferred to a box furnace and kept vertical and reacted further. At $t_R = 120$ h, melts were profiled and found still not to be completely homogeneous (Fig. 17 b and e).

2.2.1 Rocking of melts and homogenization

For comparison, in Fig. 16, we compare Raman profiling results on a 2 gram melt with the ¼ gram melt both reacted for 6h. It is abundantly clear from these data that melt sizes play a crucial role in the kinetics of homogenization, and we discuss the issue in Chapter 3.
However, at $t_R = 168\text{h}$, melts did homogenize completely as shown in Fig. 13c and f. Note that the lineshape spread near the Se-chain mode (250 cm$^{-1}$), in the region of the low frequency band (100-180 cm$^{-1}$) and near the ES mode (320 cm$^{-1}$) disappeared after 168h. It is this slow step 2 of homogenization of chalcogenides melts that is a recurring theme in the equalization of melt stoichiometry across batch compositions globally. We discuss it in chapter 3.

![Fig. 17](image-url)  

**Fig. 17** Raman profiling data on Ge$_{19}$Se$_{81}$ melts shown in the left panel after (a) being rocked for 48h (b) held stationary for 120h (c) held stationary for 168h. Parallel results are shown in the right panel for Ge$_{25.5}$Se$_{74.5}$ melts. Rocking melts assists homogenization incrementally.
2.3 Dispersive Raman scattering in glasses

All Raman scattering measurements on glasses made use of a dispersive system (Model T 64000, Horiba, Jobin Yvon Inc). A 5mW quantity of 647 nm radiation from a Kr-ion laser with a 50 μm spot size was brought to a line focus on a glass samples contained in evacuated quartz tubes used in their synthesis. The typical laser power density on samples was at 10W/cm². The back scattered radiation was analyzed in the triple subtractive mode using a CCD Detector. An accumulation typically lasted 2 mins.

The observed Raman lineshapes in glasses were analyzed as a superposition of Gaussian profiles using Peak Fit software. Examples are provided later. Our experience has also shown that deconvolution of FT Raman lineshape on glasses using the same Peak fit software in terms of a superposition of Gaussian profiles does not work as well as it does on the Dispersive Raman lineshapes. The issue is addressed in detail in Appendix I.

2.3.1. Water as a dopant in glasses

We synthesized a pair of samples (x = 19% and 33.33%) of 2 gram in size, this time using finely powdered (< 5μm) elemental Ge and Se, which were left in the laboratory ambient environment (45% Relative Humidity) for 24 hours. These starting materials were encapsulated in evacuated (10⁻⁶ Torr) quartz tubing and reacted at 950°C the usual way. Melts were homogenized and Raman profiled. Surprisingly, after reacting the melt at x = 19% for tᵣ= 42h, it completely homogenized as illustrated in Fig. 18.a. The behavior is in sharp contrast dry melts that took 168h to completely homogenize (Fig. 7). Melt at x = 33.33%, took a 72 h to completely homogenize as illustrated in Fig. 18.d. These data unambiguously show that traces of water speeds up the kinetics of melt homogenization rather remarkably, an issue we will discuss in chapter 3.
Fig. 18. Raman profiling data on (a) a wet Ge$_{19}$Se$_{81}$ melt reacted for 42h; a wet GeSe$_2$ melt reacted for (b) 6h (c) 48 h (d) 72h, showing the more dramatic effect of homogenization assisted by water traces in melts. Results on corresponding dry melts are given in Fig. 3 and 8.
Dispersive Raman scattering on these wet melts when compared to their dry counterparts show presence of *residual scattering* as shown in Fig. 19. For example, at $x = 19\%$ (Fig. 19a) we observe that modes of the CS and ES tetrahedra and CM sit on a baseline that is measurably higher than the corresponding modes in the lineshape of dry samples. A parallel behavior is noticed at $x = 33.33\%$ (Fig. 19b). Furthermore, in Fig. 19a, we note that the Se chain mode scattering strength in the wet sample is lower than in the dry sample (Fig. 19a). Presence of water impurities in melts leads to residual scattering of the laser light. We return to discuss these Raman data along with those on calorimetric and molar volumes to elucidate the role of water impurities in chalcogenides in chapter 3.

![Fig. 19](image.png)

**Fig. 19** Dispersive Raman scattering of a wet melt compared to a dry one (a) at Ge$_{19}$Se$_{81}$ and (b) at GeSe$_2$. Note that the residual scattering in the wet melt exceeds that in the dry one.
2.3.2. **Raman scattering of “as quenched” melts compared with “T<sub>g</sub> cycled” glasses**

Once melts were found to be homogenized in Raman profiling experiments, we undertook to compare Raman scattering of the *as-quenched melts* with those of the *T<sub>g</sub>-cycled glasses* slow cooled to room temperature making use of the Dispersive system. The *T<sub>g</sub>-cycled glasses* were obtained by taking the *as-quenched melts* in quartz tubes, and heating to T<sub>g</sub> for 10 min., and then slow-cooling to room temperature at 3°C/min. in a box furnace. It is useful to mention that samples were always retained in the same quartz tubes used in their synthesis until the glasses were thermally relaxed and brought to 23°C, i.e., they were not exposed to the laboratory environment. The purpose in undertaking such Raman scattering investigations was to establish in what way, if any, does glass molecular structure of the *as-quenched* samples differ from their *T<sub>g</sub> cycled* counterparts, hopefully shedding some light on changes of structure accompanying a cool down across T<sub>g</sub>. The results are summarized in Figures 20-22. These dispersive macro-Raman scattering measurements used 647 nm radiation, with samples contained in original quartz tube used for synthesis, to avoid photo-oxidizing or degrading samples due to exposure to humid laboratory environment. Each panel in these figures compares two lineshapes, the *as-quenched* melt with the *T<sub>g</sub>-cycled* glass, at a total of 9 compositions.

Starting at x = 15% (Fig. 20), we find that the scattering strength of the Ge centered CS and ES tetrahedra decrease in going from the melt to the glass, a feature also observed in T-dependent Raman measurements by Murase<sup>17</sup>. But as x increases to 19%, close to the onset of the IP, lineshapes become quite similar, and in fact vanish as one goes across the IP glass compositions (x = 22%, 23% and 24%, Fig. 21), only to grow again as x increases to 29%, 31% and 33%. Remarkably, the absence of a change in the scattering strength ratio of the CS mode to the Se chain mode across T<sub>g</sub> at x = 25% was also noted by Murase in T-dependent Raman
experiments\textsuperscript{17}. These data show that molecular structure changes across \( T_g \) are minuscule for IP glass compositions, demonstrating that these represent the optical analogue of the reversibility window (see below). Raman profiling scans at 18 of the 21 melt compositions synthesized in the present work appear in Fig. 23. At each composition, 9 Raman spectra were recorded, and they completely overlap into a single lineshape, which is truly representative of these melt compositions, and we discuss these in chapter 3.

\textbf{2.3.3. Raman scattering results on dry homogeneous glasses}

Dispersive Raman data on \( T_g \)-cycled homogeneous glasses appear in Fig. 24 at select compositions. As mentioned earlier, these data were acquired using a macro-Raman configuration with glass samples in the original evacuated quartz tubes used for synthesis to avoid hydrolysis. Furthermore use of the curved surface of a quartz tube brings laser light to a line focus and thereby reduces the laser power density on samples, and suppress photostructural effects. These \( T_g \) cycled samples, as mentioned earlier, were obtained by \( T_g \) cycling the homogenized melts in a box furnace and slow cooling to RT at 3C/min. Lineshape evolution with \( x \) show a characteristic pattern, which is qualitatively similar to earlier reports\textsuperscript{17, 21}. There is broad agreement on mode assignments; Se-chain mode near 250 cm\(^{-1}\), the Corner-sharing Ge tetrahedral mode (200 cm\(^{-1}\)), the ES GeSe\(_2\) mode (217 cm-1, 320 cm-1), the ethanelike\textsuperscript{22} mode (180 cm-1), outrigger\textsuperscript{17} Se-Se mode (245 cm-1). The pair of modes (arrow locations), one at 245cm\(^{-1}\) and another at 180 cm\(^{-1}\) both appear first once \( x > 31.5\% \), and both grow simultaneously as \( x \) increases to 33.33%. We will discuss these data in chapter 3.
**Fig. 20** Dispersive Raman scattering lineshape in quenched melts compared to $T_g$ cycled ones (a) $x = 15\%$ (b) $x = 17\%$ and (c) $x = 19\%$. Note that changes in lineshape between the two types of samples decreases considerably at $x = 19\%$. 
Fig. 21 Dispersive Raman scattering lineshape in quenched melts compared to $T_g$ cycled ones (a) $x = 22\%$ (b) $x=23\%$ and (c) $x= 24\%$. Note that changes in lineshape between the two types of samples is minuscule for these compositions in the thermally reversing window, suggesting that the melt and glass molecular structures are nearly the same in each case.
Fig. 22 Dispersive Raman scattering lineshape in quenched melts compared to T_g cycled ones (a) x = 29% (b) x=31% and (c) x= 33.33%. Note that changes in lineshape between the two types of samples increases as x > 26%. Note that the residual scattering in the as quenched melts is greater than in Tg cycled ones for all these compositions in the stressed-rigid phase.
Fig. 23 A summary of FT Raman profiling data on 18 of the 21 As-quenched Ge$_x$Se$_{100-x}$ melt compositions homogenized in the present study. The glass compositions are indicated as Ge content in %. We can see the growth in scattering strength of the ES and CS tetrahedra at the expense of the Selenium chain mode as $x$ increases from top left to bottom right.
Fig. 24 Dispersive Raman scattering in indicated $T_g$ cycled $\text{Ge}_x\text{Se}_{100-x}$ glass compositions showing evolution of lineshapes with increasing $x$ from the bottom to the top. Of special interest are the modes near 247 cm$^{-1}$ and 180 cm$^{-1}$ at the arrow locations once $x > 31.5\%$. These are associated with Se-rich and Ge-rich moiety in the glasses once they segregate.
Lineshapes were deconvoluted to extract mode-centroids, widths and scattering strengths. An example of a typical lineshape fit appears in Fig. 25, corresponding to a glass sample at x = 20%. A plot of the CS mode frequency, $v_{CS}(x)$, with glass composition x (Fig. 26) displays three distinct regimes; at low x ($15% < x < 20%$) $v_{CS}(x)$ variation is rapid, at intermediate x ($20% < x < 26%$) the $v_{CS}(x)$ variation is slower than at low x and almost quasi-linear, and finally at high x ($26% < x < 33.3%$), we observe a power-law variation in x.

![Fig. 25 An example of Dispersive Raman lineshape deconvolution of a glass sample at x = 20% in terms of requisite number of Gaussian profiles using Peak Fit software. The corner sharing mode is shown in green, the edge sharing in yellow and the Selenium chain mode is identified in brown.](image)

The frequency and scattering strength of the Se-Chain Mode (CM) appear in (Fig. 27). On these plots we have included corresponding data obtained by Mingji Jin et al.\textsuperscript{23} on samples that were reacted at 950C for 4 days.
The samples used by Mingji Jin et al\textsuperscript{23}. appear to homogenize on a 250 micron landscale in FT Raman profiling experiments, and we now know were not as homogeneous as the present ones. The CM frequency, $v_{CM}(x)$, blue shifts steadily with $x$, but at $x > 31.5\%$ the behavior is reversed- the mode starts to red-shift. The scattering strength of CM normalized to the CS mode, $I_{CM}(x)/I_{CS}(x)$ (Fig. 27b) decreases steadily with increasing $x$ and , as expected, approaches zero when $x$ increases to 33.33\%.

The frequency and scattering strength variation of the ES mode with $x$ (Fig. 27) shows a rather rich behavior. The mode frequency variation, $v_{ES}(x)$, displays three distinct of variation- at low $x$ ($15\% < x < 20\%$), the mode frequency increases rapidly, at intermediate $x$
(20% < x < 26%), we observe a quasi-linear behavior, and at high x (26% < x < 33.33%) the mode frequency increases as a power-law in x. The variation $\nu_{ES}(x)$ is reminiscent of the variation in $\nu_{CS}(x)$ (Figure 26) discussed above.

Fig. 27 Variations in (a) Se$_n$ chain mode frequency (b) scattering strength ratio of CM/CS (c) ES mode frequency and (d) ES/CS mode scattering strength as a function of Ge$_x$Se$_{100-x}$ glass composition. The neutron structure factor determined$^{13}$ ES/CS fraction (▼) at x = 20% and 33.33% are plotted in panel (d).

A plot of the ES mode integrated scattering strength normalized to the CS one, $I_{ES}(x)/I_{CS}(x)$, appears in Figure 27d. In the low x range, i.e., 10% < x < 20%, the ratio starts out
near 0.222) and decreases to 0.18 (2) near 20%. At higher x, 20% < x < 26% range, the ratio increases as a power-law in x. To deduce the ES/CS fraction, \( N_{ES}/N_{CS} \), from the Raman scattering strength ratio, \( I_{ES}(x)/I_{CS}(x) \), one must fold in matrix element effects\(^{24} \) as we discuss in chapter 3.

It is useful to mention here that the \( N_{ES}/N_{CS} \) fraction has been deduced from neutron structure factor measurements\(^{25} \). On the plot of Fig. 27, we project these data and find that they are in reasonable agreement with the Raman \( I_{ES}(x)/I_{CS}(x) \) mode scattering strength ratio. The neutron results were obtained by a first principles modeling of the glass structure at two stoichiometric composition GeSe\(_4\) and GeSe\(_2\), and fitting the observed neutron structure factors to deduce the concentration of these species\(^{26} \). The \( N_{ES}/N_{CS} \) fraction has also been reported recently by \(^{73}\)Ge NMR\(^{12} \) and those data are also quite similar to the present Raman scattering strength ratio. On the other hand, analysis of the electronic density of states from XPS measurements\(^{27} \) reveal the \( N_{ES}/N_{CS} \) fraction to be at 3/7 and to be independent of x in the 20% < x < 30% range. We will discuss these data in chapter 3.

**2.4. Calorimetric measurements on homogenized glasses**

A model 2920 MDSC from TA Instruments Inc., operated at 3° C/min scan rate, 1°C T-modulation, and 100s modulation period was used to study the enthalpy of relaxation at T\(_g\). In these experiments one deconvolutes the total heat flow into reversing- and non-reversing heat flow components\(^{28, 29} \) (Fig. 28). The reversing heat flow captures quasi-equilibrium thermodynamic properties of the metastable glass state, specifically its heat-capacity jump (\( \Delta C_p \)), and from the inflexion point of the heat flow the T\(_g\). Compositional trends in T\(_g\)(x) and \( \Delta C_p(x) \) appear in Fig. 29 (a) and (b) respectively. We find T\(_g\) increase monotonically as x increases,
while $\Delta C_p(x)$ terms remains fixed near 0.35 cal/gm in the present set of samples. Data on $\Delta C_p(x)$ on the Ge$_x$As$_x$Se$_{100-2x}$ ternary also reveal a similar behavior and are included in the plot.

We have fit the $T_g(x)$ variation in our homogeneous glasses to a polynomial and the results are given by equation (2) below.

$$T_g(x) = 39.781 + 8.702x - 0.271x^2 + 0.011x^3 \quad (2)$$

The smooth line in the plot of fig. 29a is a plot of the above equation X, and it reproduces the observed $T_g$s to an accuracy of typically 2°C in most cases except near the composition $x = 31.5\%$. The slope $dT_g/dx$ reaches a maximum near $x = 31.5\%$ (Fig. 29a) and has a bearing on the misfit near that composition. We also observe a cusp in the $\Delta H_{nr}(x)$ term near the same composition $x=31.5\%$. These data are signatures of nanoscale phase separation of the present glasses at $x > 31.5\%$, and we will comment on the issue in chapter 3.

The non-reversing heat flow captures non-equilibrium effects, including network configurational changes that occur upon softening of a glass. This component usually shows a peak as a precursor to $T_g$. By subtracting the integrated area under the peak observed upon cooling (exotherm) from the peak observed upon heating (endotherm), one obtains the frequency corrected $\Delta H_{nr}(x)$ term. For glasses in the composition range, $20\% < x < 26\%$, we find the $\Delta H_{nr}(x)$ term to show a global minimum ($\sim 0$) (Fig. 29c), and to abruptly increase at $x < 20\%$ and $x > 26\%$, displaying a square well like behavior. The global minimum in $\Delta H_{nr}(x)$ term in the $20\% < x < 26\%$ range, is the reversibility window, and it is a feature associated with isostatic networks.

We also examined the effect of aging samples at room temperature and at 240°C. For these measurements samples hermetically sealed in Al pans were rerun after 2 weeks of aging at
**Fig. 28** Typical mDSC scans of bulk Ge$_x$Se$_{100-x}$ glasses obtained at (a) $x = 10\%$, (b) $x = 19\%$ (c) $x = 20\%$ and (d) $x = 33.33\%$ aged for 2 weeks at room temperature. Each panel shows 4 signals; the total, reversing and non-reversing heat flows in the heating cycle, and the non-reversing heat flow in the cooling cycle. Note that the enthalpy of relaxation, $\Delta H_{nr}$ term at $x = 20\%$ is minuscule (0.02 cal/gm).
Fig. 29 Summary of mDSC results on all samples showing variations in (a) Tg(x) and dTg/dx (▼) (b) ΔC_p(x) and (c) non-reversing heat flow ΔH_{nr}(x). In panel (a) Tg(x) from the work of Feng et al.\textsuperscript{21} (○), Sharma et al.\textsuperscript{33} (□) are included for comparison. T_g of wet samples (▼) at x = 19% and x = 33.33% are included. In panel (b) ΔC_p(x) trends from Feng et al. (○) and Wang et al.\textsuperscript{30} on the Ge\textsubscript{x}As\textsubscript{1-x}Se\textsubscript{100-2x} ternary (○) are included. In panel (c), ΔH_{nr}(x) trends in fresh (F) glasses (▼), glasses aged (A1) for 2 weeks at RT (○), glasses aged (A2) at 240°C for 2 weeks (□) are included. Trends in ΔH_{nr}(x) reported by Feng et al. (◊), displaying a near triangular variation with x is included for comparison. The increase in ΔH_{nr} term in wet (▼) glasses compared to dry ones is shown by an arrow. See text.
room temperature, and these data (A1) appear in Fig. 29c as the open circles (red). All compositions except those in the $20% < x < 26\%$, show a general increase in the $\Delta H_{nr}(x)$ term upon aging, with the step near $x = 19.5\%$ becoming abrupt, but not the one near $26\%$. Samples at higher $x$ ($26\%$) possess a $T_g$ that exceeds $260^{\circ}C$. These glasses were aged at $240^{\circ}C$ for two weeks, and the data (A2) reveal the $\Delta H_{nr}(x)$ term to now show an abrupt increase near $x = 26\%$.

Some glass compositions, particularly at $x = 29\%$, $30\%$, $31.5\%$, $32\%$, partially crystallized upon aging at $240^{\circ}C$. These sample compositions were examined in XRD investigations and we shall comment on these data in Appendix II.

The thermal properties of wet glasses differ remarkably from their dry counterparts. Thus, for example, $T_g$’s of wet samples are found to be lower than dry ones; Furthermore, the $\Delta H_{nr}(x)$ term for wet samples is measurably larger than for dry ones. These data are illustrated in Table 1. These variations in calorimetric and optical data (discussed elsewhere) between wet and dry samples are part of a general behavior that can be traced to bonded water in the network producing dangling ends as we discuss in chapter 3.

### 2.5 Molar volumes of homogenized glasses

Molar volumes of the homogeneous bulk glasses (Fig. 30) were measured using a Mettler Toledo model B154 (with 0.1mg resolution) and a quartz fiber suspended from the pan. Bulk glasses were weighed in air and Ethyl alcohol (200 Proof, Anhydrous ACS/USP grade) and the density obtained using Archimedes principle. In these experiments use of samples greater than 200 mg was sufficient to achieve an accuracy of $1/4\%$ in density. A silicon wafer was used to calibrate the Alcohol density and a single crystal of Ge used to ascertain the accuracy of the density measurements. Molar volumes were calculated from the measured density, and show a
rather striking variation with glass composition: in the $20\% < x < 26\%$ range, the *reversibility window*, we observe a broad minimum, while outside this window molar volumes increase precipitously by about 4% in the present homogeneous samples. We have also displayed in the plot of Fig. 30, the $V_m(x)$ data for the two wet samples synthesized at $x = 19\%$ and $33.33\%$, and find that, in general, $V_m(x)$ decrease in wet samples, a behavior noted earlier in oxides as well. In the case of the composition, $x = 33.33\%$, the $V_m(x)$ reduction is about 2.6%. At the composition $x = 19\%$, close to the reversibility window, the reduction in $V_m(x)$ is much smaller, about 0.3%.

We are aware of three previous studies\textsuperscript{7, 35, 36} where rather complete $V_m(x)$ trends on the present binary are reported. Broadly speaking our $V_m(x)$ trends bear similarity to previous reports with some caveats. In two cases\textsuperscript{7, 36} a broad minimum in $V_m(x)$ is observed in the reversibility window, except the increase of $V_m(x)$ observed for glass compositions outside the window is nearly halved. The latter, most likely, is a manifestation of an *intrinsic* heterogeneity of glass samples used in the previous reports. The $V_m(x)$ data of Feltz et al.\textsuperscript{36} is about 2% lower than the Mahadevan data\textsuperscript{7} across the board.
Fig. 30 Variation in molar volumes ($V_m(x)$) of present dry (●) and wet (○) Ge$_x$Se$_{100-x}$ glasses is compared to earlier reports by Mahadevan et al$^7$. (▼), Feltz et al$^{36}$ (■), and Senapati et al$^{37}$ (▲). Note the larger variation in $V_m(x)$ at $x > 26\%$ and $x < 20\%$ in the present set of samples than in earlier reports, probably related to sample homogeneity.
CHAPTER 3.

Discussion

Binary Ge\textsubscript{x}Se\textsubscript{100-x} Glasses

3.1. Variation of glass transition temperature

Glass transition temperatures, T\textsubscript{g}, of bulk materials are determined by several factors including melt quench rates, network connectivity\textsuperscript{38}, sample purity\textsuperscript{39} and the scan rates used to measure them. In the present study all 21 melt compositions, after a water quench, were cycled through T\textsubscript{g} and then cooled at 3°C/min to room temperature. Clearly factors other than quench rates contribute to the observed increase of T\textsubscript{g} with Ge content “x” of the glasses. As mentioned earlier, the T\textsubscript{g}’s were established from the inflexion point of the reversing heat flow in mDSC experiments, and the values reported (Fig. 29a) are the average of T\textsubscript{g} measured scanning up and then scanning down in temperature at a rate of 3°C/min. At these low scan rates, kinetic shift in T\textsubscript{g} due to finite scan rates are minuscule. Furthermore, by scanning up and then down in T, we have obtained the mean T\textsubscript{g}, which is independent of scan rate.

The compositional variation of T\textsubscript{g} (Fig. 29a) observed in our experiments directly reflects the increased connectivity of the network backbones. The idea first emerged from Stochastic Agglomeration theory\textsuperscript{40} which has been used to quantitatively establish T\textsubscript{g}(x) trends in the stochastic or low Ge alloying regime in the present binary. Previous work\textsuperscript{41} in the field has demonstrated that at x < 10\%, the measured slope, dT\textsubscript{g}/dx, is in excellent agreement with the parameter free SAT prediction of this slope. In this range of composition the crosslinking of Se\textsubscript{n} chains by Ge atoms proceeds in a random fashion. At higher x (> 10\%), new building blocks
contribute to the agglomeration process, with the result that the slope changes and the agglomeration process ceases to be stochastic. In the composition interval, $20\% < x < 26\%$, $T_g$ become thermally reversing as glasses self-organize (see below), and the variation $T_g(x)$ cannot be described adequately by SAT. And as $x$ increases to $31.5\%$, the slope $dT_g/dx$ maximizes corresponding to a network that is fully polymerized. At $x > 31.5\%$, excess Ge first begins to segregate as Ge-Ge signatures first appear and the backbone becomes partially polymerized (see below). The variation of $T_g(x)$ in the $10\% < x < 33.33\%$ range can be well described in terms of a third order polynomial (equation 2). The nature of $T_g$ changes with composition however, and this is an issue that comes to the fore as established by the enthalpy of relaxation, which displays characteristic regimes, which have emerged from an interplay between rigidity theory$^{32}$ and mDSC experiments$^1$.

To facilitate a more direct comparison of the present results with earlier DSC work in the field, we have also performed DSC measurements on the present homogeneous samples using a $10^\circ C/min$ scan rate. We find that the DSC derived $T_g(x)^{DSC}$ (Fig. 31) to be about $6^\circ C$ lower than the mDSC derived $T_g(x)^{mDSC}$ ones of Fig. 29a. These $T_g(x)^{DSC}$ data along with several earlier reports are displayed in Fig. 31. The data of Guin et al.$^{42}$ are about $19^\circ C$ lower than the present results, while those of Sreeram et al.$^{35}$ are much closer to the present work at $x = 10\%$ and $22\%$ but much less so at other compositions where data are available. On Fig. 31 we have also plotted $T_g(x)$ for a wet sample at $x = 19\%$ synthesized in the present work. Our $T_g(x)$ data for the wet sample nicely agrees with the trends reported by Guin et al.$^{42}$. These data suggest the possibility that samples of Guin et al. may have traces of water impurity.
Within Rigidity Theory other descriptions of the variation of $T_g(x)$ have emerged. Naumis et al\textsuperscript{43} have shown the Lindemann melting criteria in conjunction with the mean-squared displacement of atoms can be used to account for the variation in $T_g(x)$ in the present binary.

\textbf{Fig. 31} Variation in DSC measured $T_g(x)$ in present dry (▼) and wet (▼) glasses compared with those reported earlier by Guin et al\textsuperscript{42} (●), Sreeram et al\textsuperscript{15} (■). The DSC scan rate in all measurements was $10^\circ$C/min. The $T_g(x)$ of Guin are 19C less than our dry samples but coincide with our wet sample.
3.2 Melt homogenization and nanoscale mixing

The Raman profiling data presented earlier (Figures 6-13) provides new insights into physical processes that lead to homogenization of chalcogenides melts. The reaction of elemental Ge with Se in evacuated quartz tubing at 950°C is broadly consistent with two steps that underlie the homogenization process of melts.

3.2.1. First step: Formation of characteristic melt local structures.

In the initial stages, when Ge-Se mixtures are heated to 950°C, the sloshing liquid running up and down the reaction tube is predominantly molten Se, ($T_m = 221°C$), and with increasing reaction time one expects steadily increasing amounts of Ge to be alloyed. Because of the higher density of Ge (5.323 g/cm$^3$) compared to Se (4.81 g/cm$^3$), molten Ge, in the initial stages resides largely at the tube bottom. In melts containing low Ge content, such as Ge$_{15}$Se$_{85}$, we observe a small amount of $\alpha$-GeSe$_2$ to form at the tube bottom (Fig. 6) in the initial stages ($t_R = 24-48$ h). With increasing Ge content of melts (as in Ge$_{19}$Se$_{81}$), more of the $\alpha$-GeSe$_2$ forms (Fig. 6) in the initial stages as expected. In melts of GeSe$_2$ composition (Fig. 9), new Ge-richer crystalline phases appear in the initial stages. Thus, for example, in the spectra of GeSe$_2$ melts reacted for 6h (Fig. 9) we observe modes near 175 cm$^{-1}$ and near 220 cm$^{-1}$, which are replicas of the $A_g$ (170 cm$^{-1}$) and $B_2g$ (230 cm$^{-1}$) phonons of the distorted rocksalt structure of $c$-GeSe$_{44}$. More exactly the feature near 175 cm$^{-1}$ is really a composite of two vibrational modes—one from the distorted rocksalt structure (170 cm$^{-1}$) and the other from ethanelike Ge$_2$Se$_6$ local structures (180 cm$^{-1}$). These phases form near the tube bottom (loc 1,2,3). Moving up along the tube, we then observe a mode near 180 cm$^{-1}$ of ethanelike units (Ge$_2$Se$_6$) at locations 5, 6, 7 and a sharp mode near 210 cm$^{-1}$ from $\alpha$-GeSe$_2$. Towards the top of the tube, we observe a broad mode
near 200 cm\(^{-1}\), which is the CS symmetric breathing mode of Ge(Se\(_{1/2}\))\(_4\) tetrahedra. Clearly, the phases formed in the initial stages of reaction in these Ge-Se melts particularly the Ge-rich phases(\(\text{Ge}_2\text{Se}_6\), GeSe,GeSe\(_2\)) formed at the lower end of the tube are controlled by the equilibrium phase diagram (Fig. 4). These phases contribute to melt heterogeneities in the early steps of reaction of the starting materials as shown by the Raman profiling data (Fig.7, 8, 12).

As these Ge-rich crystalline and/or amorphous phases dissolve in melts upon progressive reaction, appropriate local structures of glasses evolve. These local structures include CS-, ES-, Ge-tetrahedra and Se\(_n\) chain fragments, and their vibrational signatures are well established\(^8,45\). At the end of step 1, melts are not homogeneous however, as is illustrated in the data of Figs. 7c, 8c and 12c. Melt stoichiometry, measured in terms of Ge content \(x\), typically varies anywhere from 3 to 6% across the length of the liquid column. In Raman scattering (Fig. 7c, 8c and 12c) evidence for such heterogeneity is deduced from the scattering strength ratio of the Se\(_n\) chain mode to the CS mode. In Fig. 7c, for example, we find melt stoichiometry varies from \(x = 21\)% at location 1 (tube bottom) to \(x = 17\)% at location 9 (tube top). The 4% spread in Ge content across the length of the tube for the melt of Ge\(_{19}\)Se\(_{81}\) average stoichiometry is a typical result. Parallel results are observed for Ge\(_{15}\)Se\(_{85}\) and GeSe\(_2\) melts in Fig. 8c and 12c. In dry melts, the first step usually entails reaction times, \(t_R\), of up to 96 hours.

### 3.2.2. Second step: Nanoscale mixing & global homogenization of a melt composition.

We visualize the second step of homogenization to involve nanoscale mixing as Ge atoms diffuse up and Se atoms down and melts globally homogenize. The process must involve a sequence of bond breaking and forming as Ge diffuses and the Ge/Se fraction across a batch composition equalizes. The case of GeSe\(_2\) melts is diagnostic (Fig. 11, location 4,5,6) in this
respect. We observe growth in scattering near 110 cm$^{-1}$, which is surely due to quasi-elastic scattering caused by melt heterogeneity at intermediate and extended range scales. Here we have to remember that in these FT-Raman data, the spectral response cuts off near 100 cm$^{-1}$ because of notch filters, and the peak observed at the arrow location near 110 cm$^{-1}$ (Fig. 11) is not a vibrational mode but it is evidence of increased quasi-elastic scattering as one approaches the laser line. Melts in the lower-half of the tube, and especially at locations 3, 4 and 6 display significant quasi-elastic scattering, which we suppose is due to heterogeneity on an extended scale. In sharp contrast, as melts are reacted for $t_R = 192$ h, not only does the quasi-elastic scattering but also the spread in lineshape at higher frequencies all vanish as melts homogenize (compare Fig. 12c with d) as all 9 spectra completely coalesce to yield a solitary spectrum. The result is not peculiar to GeSe$_2$ melts, it is observed in Ge$_{15}$Se$_{85}$ melts (compare Fig. 8c and d) and also in Ge$_{19}$Se$_{81}$ (compare Fig. 7c and d). Our experiments show that in dry melts, nanoscale mixing of Ge with Se typically takes about 96h of reaction time (192h–96h), as the Ge/Se fraction across the 2 gram batch composition globally homogenizes. From these data we can estimate a diffusion constant ($D_{\text{exp}}$) of Ge and Se atoms in liquid GeSe$_2$ at 950°C by using the Diffusion equation,

$$D = \frac{1}{6} \left( \frac{2}{t} \right)$$

Taking a path length ($d$) of 2.5 cm for Ge and Se atoms to diffuse in an amount of time ($t$) of 96h in the reaction tube, one obtains a $D = 3 \times 10^{-6}$ cm$^2$/s. From MD simulations, the viscosity data on liquid GeSe$_2$ have obtained a Diffusion constant of Ge and Se of $10^{-5}$ cm$^2$/s in liquid GeSe$_2$ at 950°C. In bulk glasses realized by $T_g$ cycling such homogeneous melts, we have found that the calorimetric properties are quite
uniform. In particular $\Delta H_{nr}$ data do not display variations across a batch composition. Such is not the case in glass samples that are not homogeneous.

**3.2.3. Wet melts homogenize much quicker than dry ones.**

An important finding of the present work is that wet melts synthesized at $x = 19\%$ and $33.33\%$ homogenize much quicker than their dry counterparts. In synthesizing the wet melts, the starting elements (Ge, Se) were finely powdered and left in laboratory environment for just 24 hours prior to sealing them in evacuated quartz tubes. It is widely known that in such powders the large surface to volume ratio of the micron sized particles will lead to adsorption of water on the surface of particles, and it is difficult to remove water from such starting materials by merely pumping even with a high vacuum line at room temperature.

The viscosity of pure Se reduces upon alloying chain terminators such as halogens\textsuperscript{48} but increases upon alloying chain cross-linkers such as Ge as networks polymerize. Melts containing traces of water vapor will transform bridging Se sites, i.e., Ge-Se-Ge signatures to Ge-[OH] .... [H]-Se-Ge ones, creating [OH] and [H] dangling ends. Monovalent [OH] and [H] species will also serve as Se\textsubscript{n} chain terminators and assist Ge to react with Se\textsubscript{n}. For this reason a wet 19\% melt completely homogenizes in only 42h (Fig. 18a), while its dry counterpart (Fig. 7d) took nearly 168h to homogenize. A parallel circumstance occurs at $x = 33.33\%$, where a wet melt completely homogenized in 72h (Fig. 18(d)) while its dry counterpart took 192h to completely homogenize (Fig. 12d). These data underscore the crucial role of water impurities in promoting melt nanoscale mixing.

While it is tempting to add traces of water vapor to accelerate homogenization of melts in the present chalcogenides, the fact is that the presence of trace water impurities
measurably alters the thermal, optical and mechanical properties of wet melts/glasses from those of their dry counterparts. Thus, we find $T_g(x = 19\%)$ of a dry sample of 171.6°C, is 13.6°C higher than the $T_g$ of its wet counterpart (158°C). A parallel circumstance occurs at $x = 33.33\%$, where $T_g$ of a dry sample (425.7°C) exceeds that of its wet counterpart ($T_g = 420.6 \, ^\circ C$). The lower $T_g$s of the wet samples compared to dry ones is due to a loss in connectivity of the Ge-Se cross-linked polymeric network by the creation of dangling ends and is consistent with interpretation of $T_g$ as revealed by stochastic agglomeration Theory\textsuperscript{40}. A perusal of the data of Table 1 (see page 8) also shows that the $\Delta H_{nr}$ term at $T_g$ in wet glasses are significantly larger than in dry glasses. We attribute the increased enthalpy of relaxation near $T_g$ in wet samples to the rocking of dangling [OH] and [H] ends, an entirely non-ergodic process, as a glass softens near $T_g$, and is therefore manifested in the $\Delta H_{nr}$ term exclusively. Molar volumes of wet glasses (Table 1) (see page 8) are found to be lower than dry ones most likely because of a loss in network structure due to slicing of the network. The behavior has also been observed in oxide glasses elsewhere\textsuperscript{39}. Thus the physical properties of wet glasses are distinctly changed from their intrinsic value observed in dry glasses. These findings lead naturally to the notion that if Ge-Se melts of 2 gram in size were reacted as we have described here, and should they homogenize in less than 68h of reaction time then such melts would undoubtedly be wet.

It is useful to reiterate that in the Raman profiling experiments use of a 250 µm spot size is not a sufficient requirement to establish melt homogeneity. Although melts appear to homogenize more quickly using a coarse spatial resolution (Fig. 14), calorimetric investigations on $T_g$ cycled glasses show\textsuperscript{49} a reversibility window with walls that are broad (5% wide) compared to walls that are only 0.5% wide in the present set of glasses (Fig. 26c). Dry melts take much longer to homogenize on a finer spatial resolution (50 µm) (Fig. 7, 8, 12) than on a
coarser one (250 µm). Furthermore, such samples are found to be homogeneous even on a finer scale of 10 µm (Fig. 15). The sharper reversibility window in the present glasses (Fig. 32b) is direct evidence of the crucial role of sample homogeneity in determining the sharpness of the rigidity and stress transitions than in the glasses homogenized on a scale of 250 µm.

**Fig. 32** (a) Earlier report (2009) of a reversibility window in Ge$_x$Se$_{100-x}$ system taken from Boolchand et al.$^{50}$ (b) In homogeneous Ge$_x$Se$_{100-x}$ glasses, synthesized in the present work, the reversibility window is square-well like, resulting in **abrupt rigidity** and **stress** transitions.
3.3. Rigidity and stress transitions in Ge,Se\textsubscript{100-x} binary

3.3.1 Optical Analog of reversibility window

The first indications that batch compositions in the 19.5% < x < 26% range, behave quite differently from those outside this compositional window emerged in comparing the observed Raman lineshapes of the “as quenched” melts with their “T\textsubscript{g} cycled” glass counterparts (compare Fig. 21 with 20 and 22). In figures 21, we compare the Raman scattering of “as quenched” melts with their “T\textsubscript{g} cycled” glass counterparts at compositions, x = 22%, 23% and 24% (Figure 21), and find that the observed lineshapes of “as quenched” melts to be remarkably similar to those of “T\textsubscript{g} cycled” glasses. These data suggest that melt compositions in the window show little or no change in molecular structure as they undergo structural arrest at T\textsubscript{g}, a feature identified with strong melts\textsuperscript{51}. The behavior is in sharp contrast to the one encountered for melt compositions outside the IP as exemplified by melt compositions at x > 26% (Figure 22), which show not only increased residual scattering and but also systematically higher concentration of ES units compared to their “T\textsubscript{g} cycled” counterparts. In these compositions, upon cooling to T < T\textsubscript{g}, more ordered structures evolve. A similar pattern is noted for glass compositions x < 20%. In particular for the composition at x = 19%, close to 20%, differences in spectra between as quenched melts and T\textsubscript{g} cycled glasses are minuscule. But at x = 17% and at x = 15%, the fraction of the CS mode decreases substantially in the T\textsubscript{g} cycled glass. Melts of these batch compositions that reside outside the IP range clearly undergo substantial configurational changes upon structural arrest at T\textsubscript{g} and are thus fragile\textsuperscript{52}, leading to increased activation energy of viscosity as one goes away from the window.
3.3.2. Three Elastic Phases

The optical elasticity deduced from the square of the Raman CS mode frequency, $v_{CS}^2(x)$, or ES mode frequency $v_{ES}^2(x)$ has served as a useful probe of elastic power-laws in glasses. Theory predictions of elastic power-laws in the stressed-rigid phase of covalent glasses use a Keating potential that has nearest neighbor bond stretching and near- nearest- neighbor bond bending forces only. More distant forces are not considered, and invariably contribute to the bulk elastic constants and smear the elastic phase transition as is documented in Ultrasonic measurements and Brillouin scattering experiments. On the other hand, for optical excitations that are nearly localized\(^5\) such as the the Raman CS and ES vibrational modes ,the Keating potential based elastic power-law predictions, can be expected to work well. These vibrational excitations, furthermore, relate to the optimal and near optimally coordinated building blocks of networks, and have therefore been useful probes of elastic behavior of glasses. The optic mode associated with long Se\(_n\) chains, on the other hand, localized in the flexible part of the network cannot be as useful a probe of network rigidity. These ideas have worked well and are supported by experiments as discussed elsewhere\(^5\).

Corner-Sharing mode. The variation in the CS mode frequency (Fig. 26) has been analyzed to extract optical power-laws in the stressed-rigid (Fig. 33a) and IP (Fig. 33b) using the relation,

$$v^2 - v_c^2 = A (x - x_c)^p$$  \hspace{1cm} (4)

and yields a power $p_2 = 1.50(3)$ in the stressed-rigid and $p_1 = 1.1(1)$ in the IP respectively. In equation (4) $v_c$ represents the frequency at the elastic threshold $x_c$. To reliably ascertain the
power-law we have analyzed the CS mode frequency variation using two methods, a polynomial fit and separately a log-log plot to the $v_{cs}(x)$ data using equation 4.

![Graph](image)

**Fig. 33** Elastic power-law ($p$) and thresholds ($x_c$) in the (a) stressed rigid and (b) the intermediate Phase obtained from the data of Fig 26. Here $v_{cs}(x)$ represents the mode frequency variation of the CS mode. See text for details.

The polynomial fit approach is not sensitive to $x_c$ but the log-log plot approach most certainly is. The starting value of $x_c$ is varied so that the elastic power-law using both approaches converges to the same value. The dual approach to analyzing the $v_c(x)$ gives reliable elastic

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thresholds of $x_c(1) = 19.5\%$ for the rigidity threshold, and of $x_c(2) = 26.0(3)\%$ for the stress transition.

The power-law of $p_2 = 1.50(3)$ in the stressed-rigid phase may be compared to the predicted value of 1.50\textsuperscript{55} and 1.40\textsuperscript{56}. These results strongly support that glassy networks at $x > x_c(2)$ are stressed-rigid. There are currently no theoretical predictions available for the elastic power-law in the IP, although this is not because of a lack of an attempt to obtain them\textsuperscript{57}.

**ES-sharing Mode.** The characteristic features of the ES mode such as mode frequency and mode scattering strength in our homogeneous glasses have been analyzed. The mode scattering strength at a fixed laser-power, is found to display three distinct regimes (Fig. 27(b)), it increases linearly in the $10\% < x < 18\%$ region, shows a plateau in the $19\% < x < 26\%$ range and then increases as a power-law at $x > 27\%$, a behavior that replicates the behavior of the CS mode (Fig. 26).

The ES mode frequency variation, $v_{ES}(x)$ (Fig. 27c), also displays three distinct regimes of variation (Fig. 27c). The data at $x > 26\%$ in the stressed-rigid regime has been analyzed using equation 4 and shows an elastic power-law $p_2$ to be 1.50(3) (Fig. 34 a) from the polynomial plot and $p_2 = 1.47(3)$ from the log-log plot (Fig. 34 b) with both approaches converging to yield the same value of the stress transition $x_c(2) = 25.5(5)\%$. It is thus comforting to see that the Raman mode frequency variation of both CS and ES tetrahedra yield the same elastic power-law ($p_2$) and stress transition ($x_c(2)$) phase boundary, thus confirming the details of the elastic phase transition at $x_c(2)$.
Fig. 34 Elastic power-law (p) and threshold ($x_c$) of ES mode deduced from the data of Fig. 27c. The deduced power-law was obtained using both a polynomial fit and a log-log plot of the ES mode frequency variation $v_{ES}(x)$. 
Variation of the ES/CS fraction in Ge$_x$Se$_{100-x}$ glasses. The Raman Scattering strength ratio of ES/CS (Fig.27d) shows a value of about 0.20 in the 10% < x < 20% range, it increases slowly to 0.22 in the 20% < x < 26% range, and then increases as a power-law in the 26% < x < 33.3% range to acquire a value of 0.39. The Raman scattering strength ratio must be normalized by matrix element effects to obtain the ES/CS fraction in the network. These were estimated by Jackson et al.$^{24}$ using cluster calculations, who found the Raman cross sections to excite the ES and CS mode to be respectively 40.5 A$^4$/amu and 47.9 A$^4$/amu. It is difficult to reliably ascertain the uncertainty in these cross sections, but if one assumes an error of 10%, then these cross-sections are about the same, suggesting that the Raman scattering strength ratio also represent the ES/CS fraction in the glassy networks. We have projected in Figure 27 d the neutron scattering results$^8$ for the ES/CS fraction at x = 20%$^{25}$ and at x = 33.33% from recent ab-initio analysis of the neutron structure factors. The ES/CS fraction has also been inferred from preliminary $^{77}$Se NMR experiments$^{58}$, and the reported results are in reasonable accord with the Raman results.

3.3.3 Intermediate Phase

The power of mDSC in probing thermal transitions in general, and the glass transition in particular has come to the fore in recent years. The variations in $T_g(x)$ and $\Delta H_{nr}(x)$ in the present glasses (Fig. 29), independent of scan rate, provides invaluable information on network structure and dynamics respectively. The $\Delta H_{nr}(x)$ term provides a measure of the hysteretic nature of the glass transition. The vanishing of the term in the 19.5% < x < 26% composition range provides the thermal signature that liquid and glass structures are configurationally very close to each other as one goes across $T_g$, and that the glass transition is thermally reversing in character. Earlier, we had noted that Raman lineshapes of melts and $T_g$ cycled samples show little or no
change across $T_g$ in this special compositional window (hence window). The present calorimetric data confirm the finding that glass compositions in this window possess liquid like entropy.

The square well like variation of $\Delta H_{nr}(x)$ term in the present samples of unprecedented homogeneity, is accentuated by aging. In the present samples, the $\Delta H_{nr}(x)$ term already shows a step-like variation near $x = 20\%$ in the rejuvenated (F) samples, but a more gradual increase of the term at $x > 26\%$. Upon aging the samples at room temperature for 2 weeks (A1 in Fig. 29c), we find that the variation in $\Delta H_{nr}(x)$ near $x = 20\%$ now becomes abrupt, while the increase of the term at $x > 26\%$ continues to remain more or less as in the Fresh samples. This is expected because for these stressed-rigid glass compositions, room temperature $T= 23^\circ C < T_g$ ($> 260^\circ C$, fig. 29c), and one expects the kinetics of aging to be very slow. By aging these glass compositions at $240^\circ C$ for 2 weeks, one can speed up the kinetics, as is observed in the variation of $\Delta H_{nr}(x)$ term, which now becomes abrupt (A2 in Fig. 29c) near $x = 26\%$. It is quite remarkable that glass compositions in the window show little or no aging attesting to the rather special state of matter in the intermediate phase.

Why does the variation of $\Delta H_{nr}(x)$ become abrupt near the rigidity ($x = 19.5\%$) and stress transitions ($26.0\%$)? We do not know the fundamental reason for the behavior but suspect it is related to the isostatic character of networks formed in the Intermediate Phase. Recently Micoulaut$^{59}$ modeled the enthalpy of relaxation at $T_g$ and showed that the term can be expected to be large in flexible and stressed-rigid networks but to show a minimum when networks are optimally constrained.
3.3.4 Variation of $\Delta H_{nr}(x)$ and sample heterogeneity

The nearly triangular variation of $\Delta H_{nr}(x)$ term reported by Feng et al.\textsuperscript{15} in 1997, and the square-well like behavior observed in the present work on the Ge$_x$Se$_{100-x}$ binary deserves a comment. These data highlight the crucial role of sample synthesis, in particular sample homogeneity on the $\Delta H_{nr}(x)$ term.

The source of starting materials, elemental Ge and Se, including purity and lump sizes in the present work and the work of Feng et al. were the same. The batch sizes (2grams) and handling of the starting materials (vacuum sealing) was also the same. In 1997 we used an oxy-acetylene flame to vacuum seal the samples, this time we used an oxy-hydrogen flame. But the principal difference was that melts were reacted for 2 days at 950°C in our 1997 study but they were reacted for at least 7 days at 950°C in the present work (Fig. 29). The triangular $\Delta H_{nr}(x)$ variation in the heterogeneous samples of 1997 can be understood in a natural fashion. The global minimum in $\Delta H_{nr}(x)$ in the window center is quite diagnostic: it suggests that if we were to place a composition spread of plus and minus 2.5% in Ge content for a sample at $x = 22.5$, one would still observe a vanishing $\Delta H_{nr}(x)$ term since the intrinsic value of that term across the window is zero. However, as ones moves to the window edges, one expects contributions to the $\Delta H_{nr}(x)$ term from the Flexible phase on the low side and the stressed rigid phase on the high side to creep in and increase the term because of sample heterogeneity. These data highlight the extreme sensitivity of the $\Delta H_{nr}(x)$ term to sample homogeneity.

Our $T_g(x)$ results also reveal that a small spread of Ge content of plus or minus 2.5% in sample stoichiometry from an average value of $x$ does not lead the magnitude of the glass transition temperature $T_g$ to measurably shift in relation to the $T_g$ of a very homogeneous sample.
This is borne out by the smooth red line $T_g(x)$ variation (Fig. 29a) on our homogeneous samples in the present study that completely tracks the $T_g(x)$ variation ($\circ$) reported by Feng et al. in the 1997 study. On the other hand, doping traces of water impurities in glasses at $x = 19\%$ and $x = 33.33\%$ (Fig. 29a, c) leads to a rather large depression of $T_g$ (171(1)$^\circ$C to 158(1)$^\circ$C at $x = 19\%$, and from 425 (1)$^\circ$C to 420 (1) $^\circ$ C at $x = 33.33\%$) and a measurable increase in $\Delta H_{nr}(x)$ term (0.36(5) cal/gm to 0.55 cal/gm at $x = 19\%$, and 0.52(5) cal/gm to 0.75 cal/gm at $x = 33.33\%$).

The reduction in $T_g$ is the natural consequence of a loss in network connectivity as OH- groups bond to Ge and H to Se replacing bridging Se in the network. On the other hand the same loss of connectivity that produces the Ge-OH and Se-H dangling ends in the network also contribute to the $\Delta H_{nr}(x)$ term as the glass softens upon heating as $T$ approaches $T_g$. The heat intake upon glass softening due to these dangling ends is non-ergodic in nature and contributes to the non-reversing enthalpy as expected. These data underscore the crucial role of melt purity and homogeneity in synthesis of glasses if extrinsic effects are to be minimized. Once care is taken to address these issues in the experiments, the present findings highlight that the intrinsic physical properties of glasses can change abruptly with composition.

### 3.3.5 Variation of molar volumes and Intermediate phase

A recurring theme in glass structure is the space filling nature of disordered networks such as proteins and chalcogenide glasses. Molar volumes provide a direct measure of space filling of a glass, and in Fig. 30 we compare data on the present homogeneous Ge$_x$Se$_{100-x}$ glasses with earlier reports. Remarkably, we find the IP glass compositions to possess the lowest $V_m(x)$, and the term to increase both in the stressed-rigid and the flexible phases. In the $V_m$ plot we also include data on two glass compositions at $x = 19\%$ and 33.33\%, which are doped with water traces, and find $V_m$ to decrease drastically, a feature we have noted earlier in oxides as well.
Presence of bonded water in glassy networks cuts or slices the backbone and, in general, lowers the molar volume. Presence of bonded water in these network glasses also lowers Tg and increases ΔH_{nr}(x), and these extrinsic effects pose constraints on synthesis, and must be distinguished from the intrinsic behavior of these materials. The optical, calorimetric and mechanical properties examined in the present work are suggestive of networks that are delicately nanostructured.

In the present chalcogenides the short range covalent forces determine the nature of local structures such as long- and short- Se_{n} chains, ES and CS tetrahedral units and ethanelike Ge_{2}Se_{6} units that form at different Ge content x. In addition, there are long range forces (Coulombic and van der Waals) that come into play as evidenced by the rather systematic variation in V_{m}(x). The global minimum in V_{m}(x) in the IP compositional window is most likely the consequence of a minimal count of floppy modes and redundant bonds that permits the network as a whole to adapt and reconnect and expel stress globally. The stress-free character of glass compositions in the IP was elucidated earlier in Pressure Raman experiments{superscript}61, in which a critical externally applied pressure P_{c}(x) could be identified when Raman modes begin to blue shift. The pressure P_{c}(x) provides a measure of network stress, and displays a trend that closely mimics that of ΔH_{nr}(x), and in particular P_{c} = 0 in the IP range as does the ΔH_{nr} term. These data all strongly point to a new functionality of adaptation acquired by networks in the narrow IP window.

The Molar volume data reported by Mahadevan{superscript}7 are in good accord (Fig. 30) with the present data, and both are measurably higher than those reported Feltz{superscript}36 and Senapati{superscript}37. This could possibly be just an issue of recalibrating the standards used by Feltz and Senapati or simply due to samples that may not have been as dry as the ones used in the present work. Nevertheless, the range of variation in V_{m} outside the IP are measurably higher in the present...
glasses than in the earlier reports, a feature that most likely derives from the intrinsic homogeneity of the present glasses.

### 3.4. Ideal glasses, Melt Fragilities and IP glasses

The correlation between the global minimum in $\Delta H_m(x)$ with the Raman vibrational density of states that show little or no change upon cooling across $T_g$ for the window compositions (Fig. 29c and 21) is a profound result and raises a number of fundamental issues. Both the calorimetric and optical data point to the fact that the configurational entropy change across $T_g$ for these privileged IP compositions is minuscule, i.e., glassy networks in the IP possess liquid-like entropy. Not surprisingly, melt fragilities also reveal a minimum for IP compositions. Here the melt fragility data at $x > 25\%$ is difficult to obtain from viscosity measurements because of the tendency of such melts to crystallize. Melts in the reversibility window range not only display high glass forming tendency$^6$, but also form rigid but stress-free networks that age minimally. We associate these properties with self-organized glasses that are also ideal glasses.

Our calorimetric results on the present binary show that $\Delta C_p(x)$ is independent of $x$ in the $10\% < x < 33.33\%$ range (Fig. 29b). In Fig. 29b, we compare the $\Delta C_p(x)$ data on the present samples with those reported by Feng in 1997, and find that for both sets of data, within the errors of measurement, give $\Delta C_p(x) = 0.035(5) \text{ cal/gm}^0\text{oC}$ or $0.28 \text{ R}$ ($C_p \text{ glass} = 0.56 \text{ R}$ and $C_p \text{ liquid} = 0.84 \text{ R}$) at Ge$_{20}$Se$_{80}$. Where R represents the Gas constant of 8.3 cal/mole/K. A strikingly similar result was noted$^{30}$ earlier in the Ge$_x$As$_x$Se$_{100-2x}$ ternary several years ago. It is useful to emphasize that these $\Delta C_p(x)$ data were obtaining by analyzing the step in the reversing heat flow in mDSC experiments. If, on the other hand we were to deduce the jump in the
specific heat, $\Delta C_p(x)$, from the total heat flow, as one normally does in a DSC experiment, our data shows a shallow minimum (a change from 0.04(2) cal/gm/$^\circ$C to 0.02(2) cal/gm/$^\circ$C) in the reversibility window (Fig. 35). We believe that extraction of $\Delta C_p(x)$ from the total heat flow is polluted by the glass transition endotherm overshoot that is manifested in the total heat flow outside the IP. The large increase in the overshoot of the $T_g$ endotherm$^{62}$ in a DSC experiment, is actually a manifestation of an increasing $\Delta H_{nr}(x)$ term. The presence of this overshoot apparently influences a measurement of the $\Delta C_p(x)$ term in DSC experiments as demonstrated above. These difficulties are circumvented in using mDSC as a method to examine glass transitions, since contributions to the reversing and non-reversing heat flow are completely separated.

The mDSC results are compelling in suggesting that there appears little or no correlation between melt fragilities and $\Delta C_p(x)$ in the present chalcogenides. The $\Delta C_p$ term remains independent of $x$ over a wide composition range ($10\% < x < 33.3\%$), a finding that is at odds with the prevailing view$^{51}$. On the other hand, the present finding strongly suggests that melt fragilities (Fig. 36) correlate well with the $\Delta H_{nr}(x)$ term. The correlation is physically appealing since both $T_g$ and $\Delta H_{nr}$ are of non-ergodic origin, underscoring the non-equilibrium nature of the glass transition. The $\Delta C_p$ term is of ergodic origin and most likely of vibrational in character, which should be distinguished from the $\Delta H_{nr}$ term that is configurational in nature.

The present work on chalcogenides glasses shows that ideal glasses rarely occur in monolithic stoichiometric systems like SiO$_2$, As$_2$S$_3$, B$_2$O$_3$ or GeSe$_2$. They form at non-stoichiometric compositions and particularly in multicomponent systems$^{30, 63, 64}$ where numerous isostatic local structures can open a wide compositional window of self-organization as networks adapt to expel stress from the backbone. These new ideas are in contrast to the prevailing view
of an ideal glass realized by slow cooling stoichiometric melts to approach the configurational entropy that is close to the corresponding crystal at a low temperature, usually identified as the Kauzmann temperature.

Fig. 35 Variation in the jump $\Delta C_p$ at $T_g$ deduced from the reversing heat flow (▲) and the total heat flow (●) in mDSC measurements. The former reveals a variation with x that is almost flat, the latter on the other hand shows increases at x > 26% and x < 20% probably due to the overshoot in the heat flow endotherm for indicated compositions.

3.5. Onset of Nanoscale phase separation in Ge$_x$Se$_{100-x}$ glasses at x > 31.5%

A random cross-linked chain structural description of the present glasses appeared in the early 80s and gained popularity as an attractive model of the present binary glasses. And as physical properties of these glasses were investigated more intensively, non-monotonic compositional behavior of Molar volumes, Mossbauer site intensity ratios, Non-reversing enthalpy of relaxation at $T_g$, was noted. These findings provided first indications that a random
cross-linked chain model may be too simplistic a description at all $x$. The stochastic model also required that Ge-Ge bonds first appear once $x > 33.33\%$, the chemical threshold.

![Graph](graph.png)

**Fig. 36** Variation in melt fragility $m(x)$ (●) reported by Stolen\textsuperscript{16} et al. and the presently reported $\Delta H_m$ term (▼) in the present glasses as a function of $x$. Note that both terms show a minimum in the Intermediate Phase.

The observation of broken chemical order of GeSe\textsubscript{2} glass\textsuperscript{41,67}, which initiates at $x > 31.5\%$ as Ge-Ge bonds first appear in the network, again represent features of experimental data that are difficult to reconcile in terms of a stochastic model.

The maximum in the slope $dT_g/dx$ near $x_c(3)$ in the present glasses is the signature of segregation of Ge-Ge bonds in the network once they first nucleate near $x = x_c(3)$. The
structural evidence first emerged from $^{119}$Sn Mossbauer spectroscopy and Raman scattering experiments, which have revealed signature of homopolar Ge-Ge homopolar bonds to first appear in these glasses once $x > x_c(3)$. These Ge-Ge bonds form part of ethanelike units that apparently decouple or nanoscale phase separate from the backbone. The decoupling is suggested by the sudden decrease of the slope $dT_g/dx$ and the non-reversing enthalpy $\Delta H_{nr}(x)$ once $x > x_c(3)$ (Fig. 29c). Both $T_g$ and $\Delta H_{nr}$ are network topology (polymerization) determined properties, and the lowering of the slope $dT_g/dx$ and the $\Delta H_{nr}$ term at $x > x_c(3)$ reflects loss of network character due to demixing of some of the excess Ge (at $x > x_c(3)$) from the backbone.

In a randomly crossed linked chain model of these glasses, one expects the appearance of Ge-Ge bonds to first appear at $x > 33.33\%$, the chemical threshold, and the stoichiometric glass to be chemically ordered.

Why is the chemical threshold shifted to $x$ less than $33.33\%$? As the Ge content of the binary glasses approaches near $x = 31\%$, a small but finite fraction of Se-Se homopolar bonds form at the edges of a characteristic outrigger raft cluster, a moiety first introduced to account for chemical phase separation of the stoichiometric GeSe$_2$ glass. The evidence for this moiety has come from Raman scattering and $^{129}$I Mossbauer emission spectroscopy. The Raman vibrational signature of these edge Se-Se dimers was first correctly established by Murase et al, who showed the Se-Se stretch mode to be near 246 cm$^{-1}$ in a GeSe$_2$ glass. A perusal of the Raman lineshapes of the present glasses (Fig. 24), shows that this particular mode, and a corresponding mode associated with Ge-Ge bonds simultaneously grow in the $31\% < x < 33.33\%$ range as the network steadily demixes. These optical data confirm the nanoscale phase segregation of these glasses noted earlier in $^{129}$I Mossbauer spectroscopy measurements that showed evidence of a finite concentration of I-Se bonds persisting all the way to $x = 33.33\%$.
In these experiments, $^{129m}$Te tracer alloyed in the binary glass, probes the Se environments and show a bimodal (A,B) site distribution. The most unexpected finding of these experiments was that the $^{129}$Te dopant selects the chemically disordered outrigger Se (B) sites over the chemically ordered bridging Se sites (A) in the cluster interior by a factor of 70 or more. The observed integrated site intensity ratio $I_B/I_A = 1.7$ in the stoichiometric glass, is due to the oversized Te segregating to cluster edges to minimize strain energy. In summary, the present thermal measurements of both $T_g$ and $\Delta H_{\text{inf}}(x)$ along with earlier Raman$^{69}$ and Mossbauer$^{22}$ spectroscopy results provides persuasive evidence for onset of nanoscale phase separation of the present binary once $x > x_c(3) = 31.5\%$. 
CHAPTER 4

CONCLUSIONS

An FT-Raman profiling method is introduced to track structural heterogeneity of \( \text{Ge}_x\text{Se}_{100-x} \) melts along the length of a reaction tube used in synthesis in real time, and shows that 2 gram sized melts take about 196 hours of reaction time at 950°C to homogenize on a scale of 10 \( \mu \text{m} \). The process of homogenization is viewed to consist of two broad steps; in the first step aspects of local structures characteristic of melts/glasses emerge after 72 hours of reaction of the starting materials. At the end of the first step, a systematic variation in Ge stoichiometry across the length of the tube of about 5% persists, with the low end being Ge rich and the upper Ge deficient. An additional 96 hours of reaction time renders melts completely homogeneous across a batch composition as revealed by Raman spectra taken at 9 locations along the tube length completely overlapping. Such homogenized bulk glasses at 21 compositions spanning the 10% < \( x \) < 33.33% range were synthesized, and their physical properties further examined in Dispersive Macro-Raman, modulated DSC and Molar volume measurements. These data, on glasses of unprecedented proven homogeneity, reveal a sharply defined rigidity transition near \( x_c(1) = 19.5(5)\% \) and stress transition near \( x_c(2) = 26.0(5)\% \), with optical elastic power-laws in the Intermediate Phase (IP: 19.5% < \( x \) < 26.0%) of \( p_1 = 1.10(5) \), and in the Stressed rigid phase (\( x > 31.5\% \)) of \( p_2 = 1.50(3) \). These experiments supported by theory show present glasses to be intrinsically nanostructured displaying several distinct regimes of variation; at low \( x \) (< 20%), Ge randomly cross-links \( \text{Se}_n \) chains in the elastically flexible phase. At intermediate compositions (20% < \( x \) < 26%), networks acquire new functionalities including dynamical reversibility and non-aging, physical properties associated with self-organization. At high \( x \) (26% < \( x \) < 31%) networks continue to form fully polymerized networks that are now elastically
stressed-rigid. At still higher $x (> 31.5\%)$ they first segregate into Ge-rich and Se-rich nanophases. Melts containing traces of water homogenize much quicker but their physical properties including $T_g$, $\Delta H_{nr}$, $V_m$ are found to be measurably different from their dry counterparts. Rigidity theory has proved to be a valuable tool to understanding the complex structural behavior displayed by this prototypical binary chalcogenide glass system.
BIBLIOGRAPHY


Appendix I

Raman lineshape in homogeneous Ge\textsubscript{x}Se\textsubscript{100-x} glasses: FT Raman and Dispersive Raman profiles compared and contrasted

The availability of samples of unprecedented homogeneity from our work permitted us to examine these in both FT-Raman and Dispersive-Raman experiments. Our interest is to understand if both methods give the same result on mode frequencies and widths or are there intrinsic differences and if so what is their origin? Surprisingly, we find the results are different. Here, we present these data and attempt to understand the origin of these differences. FT-Raman measurements were performed in a micro setup utilizing a 1.06 µm radiation from a Nd-YAG laser using 100 mW with a laser spot size of 50 µm. An FT-Raman system has an automated calibration system in which the all the optics and Raman mode frequencies are set by the exciting laser wavelength. Our Dispersive Raman system (model T64000 from Horiba Inc.) was operated in macro-mode using a Kr-ion laser line of 647 cm\textsuperscript{-1} which was brought to a line focus of about 50 µm x 1000 µm with sample wetting a quartz tube of 7mm OD. The system was calibrated using a Neon discharge lamp which is often used as a primary standard. The observed and actual frequencies of Neon atomic transitions are shown in Table 2. The observed lineshapes of Neon atomic transitions were fit to extract the frequencies and compared to the actual values (Fig. 37). Equation (5) gives the relation between \( v_{\text{actual}} \) and \( v_{\text{observed}} \) wavenumber.

\[
\frac{v_{\text{actual}}}{v_{\text{observed}}} = 1.2125 + 0.999 \times \frac{v_{\text{observed}}}{v_{\text{actual}}} \quad (5)
\]

The Neon calibration lines permit one to establish instrument zero frequency offset and CCD nonlinearity in the frequency range of interest. Using the calibration provided by equation
Raman mode frequencies observed in bulk Ge$_x$Se$_{100-x}$ glasses were obtained, and these were used for data analysis to extract mode centroid, width and scattering strengths.

**Table 2. Observed and actual frequencies of Neon atomic transitions**

<table>
<thead>
<tr>
<th>Neon (observed) cm$^{-1}$</th>
<th>Neon (actual) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>83.25</td>
<td>84.38</td>
</tr>
<tr>
<td>145.31</td>
<td>146.38</td>
</tr>
<tr>
<td>298.71</td>
<td>299.63</td>
</tr>
</tbody>
</table>

**Fig. 37** Atomic transitions of Neon discharge lamp observed in dispersive Raman scattering using Kr-ion 647nm line as set up frequency (a). Panel (b) shows a plot of the actual frequency values, against observed frequencies of the atomic transitions. These exhibit a linear variation as expressed in equation (5).
Figures 37 and 38 show the observed Raman lineshape at x = 10% and at x = 20% respectively. The lineshapes are deconvoluted as a superposition of several Gaussians keeping frequency, FWHM and intensity as variables in the fit. In the FT Raman measurements we observe a mismatch in the observed and fitted peak locations as shown at the arrow locations in fig. 38a. On the other hand, in the Dispersive Raman measurements the observed and the fitted lineshape peak locations match well. Table 3 gives us a summary of the results deduced from the lineshape fit. The line width (FWHM) of the CS mode frequency at x = 10% in FT Raman experiments is found to be 30% greater than in the Dispersive Raman measurements. The increased line width as we discuss later is not related to the laser power used.

Figure 40 shows a plot in the variation of the corner sharing (CS) and the edge sharing (ES) mode frequency as a function of Ge content of bulk Ge$_x$Se$_{100-x}$ glasses using dispersive Raman and FT-Raman measurements. Both the CS and ES mode frequencies in the FT-Raman measurements blue shift. However there is an offset of about 2 cm$^{-1}$ between the FT-Raman and dispersive Raman results for both CS and ES mode frequency at low x with the FT-Raman mode frequency being greater than the dispersive Raman mode frequency. Interestingly this offset of 2 cm$^{-1}$ at low x (= 20%) steadily decreases as x increases to 33.33%. This suggests that the offset is not a zero error in frequency measurement but linked to the structural aspect of these glasses. The observed Raman line shapes from the FT and Dispersive measurements at x=20% and x=33% sample are overlaid on top of each other in fig. 42. We find that in general, frequency and line width of the FT Raman lineshape are greater than those of the Dispersive Raman ones.

In FT Raman work by Sen$^{70}$ et al. on bulk Ge$_x$Se$_{100-x}$ glasses, the Raman mode frequencies of CS and ES agree reasonably well with our data shown in fig. 41. In their experiment, Sen et al. used a Bruker RFS 100/S Fourier-transform (FT) Raman spectrometer equipped with Nd: YAG laser
operating at a wavelength of 1.06 µm. Laser power levels were varied between 20 and 50 mW in the experiments. It is interesting to note that when we used 100 mW of laser power for our FT-Raman experiments, we found the same mode frequency variation as Sen et al. We also performed FT Raman experiments at x = 20% in the same setup as described above except we lowered the laser power by using a neutral density filter to 50 mW to excite the scattering and found little or no change in the CS and ES mode frequencies as shown in fig. 40.

Table 3. Fit parameters on the CS mode from FT Raman and Dispersive Raman measurements of a bulk glass at x = 10% and x = 20%.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FT Raman x = 10%</th>
<th>Dispersive Raman x = 10%</th>
<th>% increase in FT Raman lineshape parameters compared to Dispersive Raman for x = 10%</th>
<th>FT Raman x = 20%</th>
<th>Dispersive Raman x = 20%</th>
<th>% increase in FT Raman lineshape parameters compared to Dispersive Raman for x = 20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode Frequency (cm⁻¹)</td>
<td>194.7</td>
<td>192.29</td>
<td>-</td>
<td>196.08</td>
<td>193.79</td>
<td>-</td>
</tr>
<tr>
<td>Modeb Intensity</td>
<td>0.48</td>
<td>.39</td>
<td>23%</td>
<td>0.99</td>
<td>0.88</td>
<td>12.5%</td>
</tr>
<tr>
<td>Mode FWHM (cm⁻¹)</td>
<td>15.23</td>
<td>11.72</td>
<td>30%</td>
<td>16.60</td>
<td>13.75</td>
<td>20%</td>
</tr>
</tbody>
</table>
Fig 38 shows (a) an FT Raman and (b) dispersive Raman spectra of a bulk Ge$_x$Se$_{100-x}$ glass at $x = 10\%$. Lineshape analysis gives a mismatch in the fitted and observed peaks in FT-Raman measurements in (a) but not in the dispersive Raman measurements in (b). In the latter case, the fitted and observed ES mode peaks aligned well (b).
Fig 39 shows (a) an FT Raman and (b) dispersive Raman spectra of a bulk Ge$_x$Se$_{100-x}$ glass at x = 20%. Lineshape analysis gives a mismatch in the fitted and observed ES mode peaks in FT-Raman measurement arrow location in (a), but not in dispersive Raman measurements see (b). In fig. 39b, the fitted and observed peaks aligned well.
Fig. 40 shows (a) an FT Raman spectrum of a bulk Ge$_x$Se$_{100-x}$ glass at $x = 20\%$ taken at a laser power of 100mW and (b) shows a Raman spectrum of the same sample taken at a laser power of 50mW. Lineshape analysis reveals almost similar mode frequency and width for both CS and ES mode upon reducing laser power by a factor of 2.
Fig 41. Variation in (a) the CS and (b) ES mode frequency with Ge content in bulk Ge$_x$Se$_{100-x}$ glasses deduced from FT-Raman (○) and Dispersive Raman (●) measurements. Note that in both the cases mode frequencies blue shift with x, however there is an offset between the two mode frequencies that steadily vanishes as x increases to x = 33.33%. In general, the dispersive measurements yield a lower frequency than the FT-measurement. Results from an FT-Raman study on bulk Ge$_x$Se$_{100-x}$ by Sen et al. are also projected in the fig as (■) data points for comparison to our data. We find that our FT-Raman results are in reasonable agreement with those of Sen et al.
Fig. 42 Comparison of the FT-Raman and Dispersive-Raman lineshapes of bulk Ge\textsubscript{x}Se\textsubscript{100-x} glasses at (a) $x = 20\%$ and (b) $x = 33\%$ glass. Note that at $x = 20\%$ glass the peaks in FT-Raman spectrum are shifted to higher frequency than in dispersive Raman measurements as shown by the arrow locations. On the other hand at $x = 33\%$, two lineshapes, Ft-Raman and dispersive Raman, almost coincide near 180 cm\textsuperscript{-1} but steadily deviate at larger frequency shifts.
Appendix II

Aging of Ge\textsubscript{x}Se\textsubscript{100-x} bulk glasses at T = 240\textdegree{}C and nucleation of crystallites near compositions x = 31\% and x = 33\%

While performing aging measurements of bulk Ge\textsubscript{x}Se\textsubscript{100-x} glasses at 240\textdegree{}C in the stressed rigid phase, we observed evidence of partial crystallization in 30\% < x < 33\% range. Aged glasses at x = 26\%, 27\%, 28\% , 29\% and 33.33\% revealed no evidence of crystallization and we observed a sharp jump in the non-reversing heat flow in going from 26\% to 27\% leading to a sharp jump in \(\Delta H\text{nr}\) across the stress transition. In the equilibrium phase diagram there is a metastable crystalline phase that forms at Ge\textsubscript{4}Se\textsubscript{9} stoichiometry at 350\textdegree{}C. The stoichiometry corresponds to x = 4/13 or 30.76\%. Fig. 43 shows mDSC scans for a \(T_g\) cycled glass at x = 31.0\% and a 3 week aged glass at 240\textdegree{}C. In fig. 43a, the \(\Delta C_p\) and \(\Delta H\text{nr}\) values of the aged glass are somewhat lower than the \(T_g\) cycled glass (fig. 43b). The lowering of \(\Delta C_p\) is attributed to the nucleation of crystallites in the sample. Such nucleation of crystallites leads to a loss of network connectivity which is reflected in a lower \(\Delta H\text{nr}\) value for the aged glass than for the \(T_g\) cycled one (fig. 43a). Note that since the fraction that has crystallized is small, the \(T_g\)'s almost remains the same for both the aged and \(T_g\) cycled glass.

A Rigaku DMAX 2000 XRD machine was used for X-ray measurements. The operating parameters are as follows: High voltage setting was set at 40kV and the operating current at 40 mA. The step size was 0.12 and the step time was 72 seconds. The scan was collected for a total duration of 21 hours between 2\(\theta\) = 10\textdegree{} to 135\textdegree{}. XRD measurements were performed to identify the structures contributing to these crystallites. XRD scans of an annealed glass of x=30\%, and x=31\%, are shown in fig. 44. We find evidence of some narrow peaks sitting on broad peaks (glass), which is a signature for nucleation of crystallites in the glass at a few \% level, we identified the sharp peaks as originating from c-Ge\textsubscript{4}Se\textsubscript{9}\textsuperscript{71} and \(\alpha\)-GeSe\textsubscript{2}. The Ge\textsubscript{4}Se\textsubscript{9} corresponds to x = 30.7\% in Ge\textsubscript{x}Se\textsubscript{100-x} and GeSe\textsubscript{2}, x = 33.33\%. We can see the crystalline peaks grow from x = 30\% to x = 31\% as we get closer to Ge\textsubscript{4}Se\textsubscript{9} stoichiometry (Fig. 44). Fig. 45 Shows XRD data on x = 32\% and x = 33\%. These compositions are closer to \(\alpha\)-GeSe\textsubscript{2}\textsuperscript{17}.
and the crystalline peaks originating from this phase are identified by the arrow locations and their intensity increase as we go from $x = 32\%$ to $x = 33\%$. At $x = 31.5\%$ surprisingly, we don’t see much crystallization (fig. 46), a behavior in sharp contrast to that seen at $x = 31.0\%$ and at $x = 32.0\%$. We see no crystallization at $x = 33.33\%$ as the $T_g$ of the glass increases substantially to 425°C.

![Diagram of mDSC scans](image)

**Fig. 43** mDSC scans of bulk Ge$_x$Se$_{100-x}$ glasses obtained at (a) $x = 31\%$, aged at 240°C for 3 weeks and (b) $x = 31\%$ T$_g$ cycled glass. Each panel shows 3 signals; the total, reversing and non-reversing heat flow. In (a) we can see the $\Delta C_p$ value is reduced compared to (b) which indicates nucleation of crystallites in the sample. The $\Delta H_{nr}$ term in (a) also reduces when compared to (b) which is a signature of loss of network connectivity due to partial crystallization.
Fig. 44 XRD scans of (a) x=30% and (c) x=31% along with the reference lines of GeSe$_2$ and Ge$_4$Se$_9$ in panel (b) are shown. The arrow locations in panel (a) and (c) indicate the peaks originating from the Ge$_4$Se$_9$ location.
Fig. 45  XRD scans of (a) x=32% and (c) x=33% along with the reference lines of GeSe$_2$ and Ge$_4$Se$_9$ in panel (b) are shown. The arrow locations in panel (a) and (c) indicate the peaks originating from the GeSe$_2$ location.
Fig. 46 XRD scan of an aged Ge$_x$Se$_{100-x}$ glass at $x=31.5\%$, interestingly not much crystallization is seen.
Appendix III

Raman lineshape in homogeneous Ge\textsubscript{x}Se\textsubscript{100-x} glasses: and the bimodal phase percolation model

In a recent paper\textsuperscript{72}, P. Lucas et al. report NMR and Raman investigations of bulk Ge\textsubscript{x}Se\textsubscript{100-x} glasses. These authors find evidence of the glasses to be composed of intertwined “micro domains” of GeSe\textsubscript{2} and Se\textsubscript{n}. The study claims the absence of Ge-Se-Se linkages in the glass structure. These linkages contribute to rigid but unstressed, isostatic units which form an essential part of the Intermediate phase\textsuperscript{45}. The bimodal phase percolation model of Lucas et al. will be hereafter referenced as BPPM.

To test the validity of BPPM, we performed simulations of the Raman vibrational density of states. Our approach here is to simulate the Raman spectrum of GeSe\textsubscript{4} glass (x=20\%) as made up of a Se-rich (Se glass) and a Ge-rich (GeSe\textsubscript{2} glass) phase. In our approach we use the observed Raman scattering of Se-glass and GeSe\textsubscript{2} glass to simulate the Raman spectrum of GeSe\textsubscript{4} glass. In a BPPM, one may visualize GeSe\textsubscript{4} to be made up of GeSe\textsubscript{2} glass and Se glass according to the following stoichiometric relation,

\[
0.60[\text{Ge}1/3\text{Se}2/3] + 0.40 \text{Se} = \text{Ge}_{0.20}\text{Se}_{0.80}
\]  

(6)

Figure 46a gives a result of this simulation. In this figure we compare the simulated Raman spectrum with the observed Raman spectrum of GeSe\textsubscript{4} glass. A comparison of the spectra reveals a large mismatch of the simulated spectrum with the observed spectrum; the simulations place an ethane like mode at 175 cm\textsuperscript{-1} which is not observed in GeSe\textsubscript{4}. Additionally, the CS and ES mode frequencies are blue shifted and the Se CM is red shifted in the simulations wrt their
counterparts in the observed spectrum of bulk GeSe$_4$ glass. The scattering strength of ES mode in simulation is much higher than the observed scattering strength in GeSe$_4$ glass. Clearly the BPPM is incompatible with macroscopic segregation of the bulk GeSe$_4$ glass into the suggested Se-rich and Ge-rich phases. This result is entirely consistent with a unimodal $T_g$ of 183.2°C for GeSe$_4$. Indeed if the segregation was of mm sized we should have observed 2 glass transitions one at 40°C (Se) and other at 425°C (GeSe$_2$).

If the nature of this bimodal phase separation is microscopic rather than macroscopic, one could expect the nature of Se-rich and Ge-rich phases to be respectively less Se-rich than pure Se and less Ge-rich than GeSe$_2$. So as an alternative we considered the bimodal phase separation to be more like

$$\frac{1}{2}[\text{Ge}_{0.30}\text{Se}_{0.70} \text{(Ge-rich)}] + \frac{1}{2}[\text{Ge}_{0.10}\text{Se}_{0.90} \text{(Se-rich)}] = \text{Ge}_{0.20}\text{Se}_{0.80} \quad (7)$$

In writing (7) we assume that the Ge-rich and Se-rich regions in GeSe$_4$ glass are sub-micron sized rather than being mm sized. Taking then the Raman spectrum of such a bimodal phase separated glass to be made up of the actually recorded Raman spectra of bulk glasses at $x = 30\%$ and $x = 10\%$ in equal proportion we obtain the simulated spectrum of Fig. 47b. Now the simulated spectrum looks closer to the observed spectrum of the $x = 20\%$ glass, but still there are glaring differences. Specifically, the ES mode scattering strength and Se-chain mode scattering strength are overestimated by the simulation, suggesting that even such a model cannot be a viable description of GeSe$_4$ glass.

We carried this step forward next by simulating the Raman spectrum of a bulk $x = 20\%$ glass by adding the actually observed Raman spectrum of a bulk glass at $x = 18\%$ and $x = 22\%$ glass in equal proportion,
\[ \frac{1}{2}[\text{Ge}_{0.22}\text{Se}_{0.78}] + \frac{1}{2}[\text{Ge}_{0.18}\text{Se}_{0.82}] = \text{Ge}_{0.20}\text{Se}_{0.80} \quad (8) \]

Figure 46c shows the simulation result corresponding to equation (8). Clearly now the simulated Raman spectrum looks reasonably close to the observed spectrum of a bulk 20% glass, except for a clear discrepancy on the Se-chain mode scattering strength.

Our final simulation is that of fig. 47d where we carried the step further to compare the simulated Raman spectrum of a bulk \( x = 20\% \) glass as made of \( x = 21\% \) and a bulk \( x = 19\% \) glass. Now the simulation is indeed quite close to the observed Raman spectrum of an \( x = 20\% \) glass.

The simulations of Fig. 47c and Fig. 47d reveal that the bulk \( x = 20\% \) glass is almost chemically ordered. The observed Raman lineshapes in bulk \( \text{Ge}_x\text{Se}_{100-x} \) glasses apparently change almost continuously with composition in a systematic and reproducible fashion. And a Raman spectrum at a given composition cannot be visualized as a superposition of two distinct macro, micro or even nano scale phase separated phases in the \( 0 < x < 31.5\% \) range of Ge. At \( x > 31.5\% \), evidence of nano scale phase separation has been noted in this work as discussed in chapter 3.

This claim of Lucas et al. are in contrast with our findings and probably result from the use of samples that are either segregated or heterogeneous in their \(^{77}\text{Se}\) NMR experiments. They reacted their starting materials in a \( 10^{-6} \) Torr vacuum and kept them in a rocking furnace at 800°C for 12 hours! Our experiments (page 13-23) using Raman profiling clearly demonstrate that 2 gram samples, sealed at \( 10^{-7} \) Torr take 168 hours to fully homogenize at 950°C. This raises possible doubts over the homogeneity of batch preparations used in the NMR experiments by Lucas et al. Unfortunately it is unclear to us how large were the batch sizes used by Lucas et al.
The interpretations of these NMR results are at variance with a similar study by Sen et al.\textsuperscript{12}. The NMR line position in these glasses is recently identified by Massobrio et al.\textsuperscript{73}.

Fig. 47 Simulated Raman spectra (in blue) compared to actual Raman spectra of a homogeneous GeSe\textsubscript{4} (red) glass sample. Note the mismatch in all 4 panels, indicating that GeSe\textsubscript{4} is almost chemically ordered and not phase separated as claimed by Lucas et al.
Appendix IV

MDSC scans of Tg-cycled Ge$_x$Se$_{100-x}$ glasses at different compositions

In this section we provide the actual MDSC scans of Tg-cycled glasses at various compositions. The operating conditions for measurement were same for all the samples. The scan rate was 3°C/min and the modulation rate was 1C/100s. From these scans we were able to extract the values of the glass transition temperature $T_g$, the value of the non-reversing heat flow $\Delta H_{nr}$ and the specific heat $\Delta C_p$. Figures 48-50 summarizes the scans of 18 of the 21 glass samples with each figure displaying scans for 6 compositions respectively.
Fig. 48 MDSC scans of Tg-cycled Ge$_x$Se$_{100-x}$ glasses at different compositions are shown. The green curve denotes the total heat flow. The blue curve denotes the reversing heat flow and the red curve gives the non-reversing heat flow. The T$_g$ is obtained from the inflexion point in the reversing heat flow and the $\Delta$H$_{nr}$ is obtained from subtracting the value of the non-reversing heat flow of the cooling cycle from the value during the heating cycle.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_g$ (°C)</th>
<th>$\Delta$H$_{nr}$ (cal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 10%</td>
<td>104.08</td>
<td>0.25</td>
</tr>
<tr>
<td>x = 19%</td>
<td>171.0</td>
<td>0.36</td>
</tr>
<tr>
<td>x = 15%</td>
<td>137.9</td>
<td>0.52</td>
</tr>
<tr>
<td>x = 20%</td>
<td>183.1</td>
<td>0.03</td>
</tr>
<tr>
<td>x = 17%</td>
<td>156.8</td>
<td>0.42</td>
</tr>
<tr>
<td>x = 21%</td>
<td>196.1</td>
<td>0.00</td>
</tr>
</tbody>
</table>

$\Delta$H$_{nr}$ = 0.25 cal/g

$\Delta$H$_{nr}$ = 0.36 cal/g

$\Delta$H$_{nr}$ = 0.42 cal/g

$\Delta$H$_{nr}$ = 0.00 cal/g
Fig. 49 MDSC scans of Tg-cycled Ge₅₆Se₄₄ glasses at different compositions are shown. The green curve denotes the total heat flow. The blue curve denotes the reversing heat flow and the red curve gives the non-reversing heat flow. The T<sub>g</sub> is obtained from the inflexion point in the reversing heat flow and the ΔH<sub>nr</sub> is obtained from subtracting the value of the non-reversing heat flow of the cooling cycle from the value during the heating cycle.

x = 22%  
T<sub>g</sub> = 208.3°C  
ΔH<sub>nr</sub> = 0.02 cal/g

x = 27%  
T<sub>g</sub> = 283.9°C  
ΔH<sub>nr</sub> = 0.04 cal/g

x = 25%  
T<sub>g</sub> = 249.0°C  
ΔH<sub>nr</sub> = 0.00 cal/g

x = 28%  
T<sub>g</sub> = 299.2°C  
ΔH<sub>nr</sub> = 0.29 cal/g

x = 25.5%  
T<sub>g</sub> = 260.9°C  
ΔH<sub>nr</sub> = 0.00 cal/g

x = 29%  
T<sub>g</sub> = 316.3°C  
ΔH<sub>nr</sub> = 0.40 cal/g
Fig. 50 MDSC scans of Tg-cycled Ge$_x$Se$_{100-x}$ glasses at different compositions are shown. The green curve denotes the total heat flow. The blue curve denotes the reversing heat flow and the red curve gives the non-reversing heat flow. The $T_g$ is obtained from the inflexion point in the reversing heat flow and the $\Delta H_{nr}$ is obtained from non-reversing heat flow of the cooling cycle from the value during the heating cycle.
Appendix V

Ternary chalcohalide Ge$_x$Se$_{83.1-x}$I$_{16.9}$ Glasses

In this section we will discuss the Sample synthesis, Raman scattering, modulated DSC and Molar volumes experiments to investigate the physical properties of Ge$_x$Se$_{83.1-x}$I$_{16.9}$ glasses encompassing a wide range (20.9%<x< 23.38%) of Germanium concentrations in an attempt to understand the evolution of glass structure as a function of composition.

1. Sample synthesis

Fig. 51 The black curve shows the glass forming region in Ternary Elastic phase diagram taken from Fei Wang et al\textsuperscript{74}, which is cut by the line PQ, which defines the elastic phase boundary according to Constraint Theory. Our aim here is to investigate the tri-phase region on the vertex of the red IP triangle along pathway AB.
Constraint Theory with the magic condition $r = 2.40$, was extended to networks containing dangling ends (one fold coordinated atoms) several years ago\textsuperscript{75},

$$r = 2.40 - 0.4(n_1/N) \quad (9)$$

The correction term is due to dangling ends ($n_1/N$) which is the fraction of one fold coordinated sites. The additional term $0.4(n_1/N)$ specifically suggests that the rigidity percolation thresholds depend explicitly on the concentration of one fold coordinated atoms in the network.

In the composition triangle of figure 51, we have delineated the glass forming range in the Ge–Se–I ternary\textsuperscript{74} from earlier work\textsuperscript{76}. The thin red line PQ defines the mean-field phase boundary between the floppy phase ($n_c < 3$) on the left and the stressed–rigid phase ($n_c > 3$) on the right of this line. The line PQ is the elastic phase boundary which is identified from the above equation for one fold coordinated atoms (ex: Iodine) in a network. The IP region encloses a hash marked red triangle. The blue line is the path along which samples were synthesized in our earlier work by F. Wang et al. In the Ge\textsubscript{25}Se\textsubscript{75}–I ternary, an IP was observed in the $15.5\% < y < 16.5\%$ Iodine range. In this work we cut through path AB as shown just above the vertex of the triangle to study the structure of these glasses at the triphase region and investigate the nature of the Intermediate Phase.

Ge\textsubscript{x}Se\textsubscript{83.1–x}I\textsubscript{16.9} melts of 4 grams in size were synthesized using 99.999% Ge, 99.999% Se pieces (3-4 mm diam) from Cerac Inc and 99.999% GeI\textsubscript{4} lumps from Strem Inc. The starting materials were mixed in the desired ratio by weight, sealed in evacuated ($10^{-7}$ Torr) quartz tubing (5mm ID) using a hydrogen/oxygen torch. The vacuum line consisted of a liquid nitrogen trapped High Vacuum pumping system. Prior to sealing, quartz tubes were held in a vacuum
oven at 80°C for 24 hours. A total of 13 sample compositions spread in the 20.9% < x < 23.38% range of Ge were prepared. The quartz ampoules were held vertically in a T-programmable box furnace for varying time periods, t_R, ranging from 168 hours to 336 hours at 950 °C. Upon heating melts to 950°C, liquid column was noted to reflux vigorously. Periodically melts were quenched from 260°C and examined in Raman profiling experiments (see below). Once homogenized, the as-quenched melts in quartz tubes were taken to T_g + 20°C in the box furnace, held there for 10 minutes, and then slow cooled to room temperature at 3°C/min to realize homogeneous bulk glasses.

![Elemental lumps of Germanium, Selenium and Germanium iodide used in synthesis of samples. Picture of a 21.8% sample in quartz tube after alloying.](image)

**Fig. 52** Elemental lumps of Germanium, Selenium and Germanium iodide used in synthesis of samples. Picture of a 21.8% sample in quartz tube after alloying.
After alloying Raman profiling was used to track sample homogeneity. Shown below are 9 Raman spectras taken along the length of tube after 168 hours of reaction. We can see every location yields distinct spectra indicative of the fluctuation in stoichiometry of the batch. The vertical lines indicate the various modes: the Selenium chain mode (CM), edge sharing mode (ES), m=0, m=1, m=2, m=3 and m=4. We can see that after 168 hours of reaction all the local structures have evolved and there is absolutely no existence of the crystalline phases associated with Ge-Se and Ge-I but we as we go from the bottom of the tube to the top the intensity of the m=0 mode decreases indicating that the batch stoichiometry becomes Germanium deficient. The Selenium chain mode concentration shows inverse behavior to that of Germanium tetrahedra (m=0) clear from figure 53.

**Fig. 53** Raman scattering taken along the quartz tube length on the right containing a x=21.8% batch preparation showing variations of glass molecular structure at the 9 points. 168 hours after reacting the starting materials at 950°C. The vertical lines are used to identify mode locations.
With increasing $t_R$ from 168 h to 336 h hours range (Fig.53), we can observe a spread in the Selenium chain mode, edge sharing mode, $m=0$, $m=2$, $m=3$ and $m=4$ in panel a. The absence in the variation of the $m=1$ mode strength is due to normalizing spectra at that mode. At this point the local structures have all evolved and further reaction of melts leads intermediate and extended range structures to form. But a fully homogeneous glass, on a spatial resolution of 50μm (set by laser spot size) is obtained only near $t_R = 336$ hours, when all 9 Raman line shapes completely overlap as in fig. 54 b. In the binary Ge-Se system there exists 3 main modes: the corner sharing (CS), edge sharing (ES) and Selenium chain mode (CM). Alloying fixed amount of Iodine produces new features as discussed above. The figure 55 shows pictorial representation of the various mixed tetrahedral modes as a result of incremental substitution of Selenium atom by the Iodine atom.

**Fig. 54** A coalesced view of the 9 Raman spectra of Fig.46 appears in panel (a). Prolonged reaction of the 21.8% melt for (b) 336h show melts homogenizing.
Fig. 55 Schematic view of the molecular structure of various m-units\textsuperscript{74} taken from Wang et al. Here m indicates the number of iodine near neighbors of Ge.

2. Raman scattering experiments

Raman lineshape analysis was done in terms of superposition of Gaussian peaks. Fig. 56 illustrates an example of an observed spectrum that was analyzed as a superposition of several Gaussian profiles. We extract the frequency and scattering strengths of the modes which are then used to study the variation with respect to composition to understand the compositional dependence and the evolution of these modes.

Fully homogenized samples on a scale of 50 microns are shown in fig. 57. Probing the batch preparation at different locations of the quartz tube yield identical spectra suggestive of the uniform stoichiometry of the batch preparation. Any sample taken out for analysis is a true representative of that particular composition as assured by Raman profiling.
All samples were water quenched. To remove frozen stresses in the samples they were $T_g$-cycled. $T_g$ cycling involves taking the samples to $T_g$ and slowly cooling them down to room temperature. Raman spectra of as-quenched and $T_g$-cycled samples reveal interesting features about the structures of the samples (fig. 58). We can observe at low compositions like $x = 21.8\%$ the corner sharing mode and Selenium chain mode increases whereas as we move to high end as in $x = 23.15\%$ the selenium chain mode decreases. But something remarkable happens at the $x = 22.13\%$ sample which lies smack in between. There is no change in the scattering strengths of the chain mode or corner sharing mode. From these data we became aware that there was something special about this sample composition $x = 22.13\%$ - the liquid and the glassy state looked identical!
Fig. 57 10 of the 13 fully homogenized as quenched $\text{Ge}_{x}\text{Se}_{83.1-x}\text{I}_{16.9}$ samples are shown. We can see all spectra coalesce to give uniform stoichiometry.
Fig. 58 Raman line shapes of as-quenched (Asq) and $T_g$-cycled (Tgc) samples are shown above. Note that at 22.13% there is no change in the scattering strengths of the 3 peaks.

From deconvolution of Raman spectra we extracted the mode frequencies. The Fig. 59(a) shows the variation of the Selenium chain mode; we can see that it increases monotonically with $x$. The corner sharing mode ($m=0$) in Fig. 59(b) shows an abrupt change of slope at $x = 22.13\%$. The $m=0$ mode frequency is of interest to us as it forms the backbone of the network and is crucial in understanding the evolution of the network structure with composition. The $m=1$ unit blue shifts with composition. The vertical line at $x=22.13\%$ is shown to indicate the abrupt change of slope in the $m=0$ frequency.
Fig. 59 The frequency variation of the Selenium Chain mode, Corner sharing (m=0) mode and m=1 mode is shown. We can see an abrupt change in slope at $x = 22.13\%$ for the m=0 mode.
Fig. 60 scattering strength variation of the Selenium Chain mode, Corner sharing (m=0) mode and m=1 mode are shown. We can see an inflexion point at $x = 22.13\%$ for the m=0 mode.
Fig. 61 Elastic threshold compositions ($x_c$) and optical elastic power-law ($p$) in Stressed Rigid Phase deduced from the fitting the Raman mode frequency, $\nu_{cs}(x)$
Fig. 62 Compositional trends of (a) Tg(x) (o) binary and (●) ternary. (b) Molar volumes results from present work (●) and the jump in Specific heat at Tg in (o), ΔH_m(x), in samples in fresh state (o) and after 1 year of aging (●). The blue shaded panel gives the Intermediate Phase.
The normalized scattering strengths extracted from the mode analysis are shown on the left panel. We can see a steady decrease of the Selenium chain mode in Fig. 60(a) with incremental increase of Germanium concentration. The $A_0$ fraction of the $m=0$ mode in Fig. 60(b) shows initial increase and levels off around $x=22.13\%$ (red line) and then takes off as we increase Germanium concentration. The $A_1$ fraction representative of $m=1$ mode in Fig. 60(c) shows a global minimum around $x = 22.13\%$ and rises above and below this composition.

We have extracted the underlying optical elasticity power-law variation in $x$, using equation

$$v_{CS}^2(x) - v_{CS}^2(x_c) = A (x - x_c(2))^p \quad (10)$$

Here $v_{CS}^2(x_c)$ represents the value of $v_{CS}^2(x)$ at the threshold composition, $x = x_c$, and $p$ the elastic power law in the stressed-rigid regime. The data at $x > 22.25\%$ was used to extract $p_2$ this time by an iterative process using both a polynomial fit and separately a log-log fit. The value of $x_c$ was varied so that both fitting procedures yielded the same $p$, and the final result (Fig. 61) gives $p = 1.40(10)$ and $x_c = 22.25\%$. The value of $p$ is in good agreement with a numerical simulation of the power-law.

### 3. Calorimetric and Density experiments

Figure 62 captures all the results of calorimetric experiments. Panel a. shows increase of $T_g$ (●) with composition but its growth is arrested around $x=22.13\%$. The $T_g$’s of the binary (○) sit considerably higher suggestive of the fact that addition of Iodine decreases network connectivity. The $\Delta C_p$ (○) variation shows a narrow glitch as its value decreases with composition. The molar volume experiments reveal a narrow region where the values decrease & show a global minimum at $x=22.13\%$ and the $V_m$ for the samples outside this region is pretty flat.
The $\Delta H_{\text{nr}}$ of fresh samples (○) also shows an extremely narrow window extending from
$22.02 < x < 22.25\%$ and having a global minimum at $x=22.13\%$. This region is identified as the
intermediate phase IP. Upon aging for 1 year (●) at room temperature we see the Hnr values of
samples outside the IP to increase whereas the value of samples in the IP show little or miniscule
change which confirms the finding that glass compositions in this window possess liquid like
entropy.

4. **Raman scattering effects of addition of Iodine on the network connectivity.**

In this work we take a new experimental approach to address the issue of stress in the
base glass of Ge-Se varying Ge concentration in the IP range and alloying fixed concentration of
Iodine at 16.9%. We expect the network to stiffen as oversized Iodine ($r = 1.33\text{Å}$) atoms replace
one or more Selenium ($r = 1.17 \text{Å}$) near neighbors to form mixed tetrahedral units.

![Graph showing m=0 frequency in the ternary, blue shifting with respect to the binary frequency suggesting stiffening of the network on addition of Iodine.](image)

**Fig. 63** shows the m=0 frequency in the ternary blue shifting with respect to the binary frequency
suggesting stiffening of the network on addition of Iodine.
The above figure 63 shows corner sharing frequency of the binary and the corresponding ternary on a compressed scale. We can clearly observe the m=0 (CS) frequency in the ternary to be blue shifted from the CS frequency of the binary. This is a clear indication of stiffening of the mode frequency due to addition of oversized Iodine into the network backbone.

5. Collapse of the Intermediate Phase

Upon addition of a large Iodine atom to the binary system the window collapses and we observe an extremely narrow Intermediate phase (fig. 64a). As 2 fold co-ordinated Selenium atom is replaced systematically by one fold coordinated Iodine atom in the GeSe$_4$ tetrahedra the dangling ends of Iodine in the network contribute to the increase in the non-reversing heat flow. But once we reach the boundary of the reversibility window the non-reversing heat flow reduces and we see a global minimum at $x=22.13\%$ which is the midpoint of the Intermediate Phase. This special composition also exhibits minimal change in Raman scattering data of as-quenched melts and $T_g$ cycled glasses as shown earlier. !! This minimal structural change in melts and Glassy structure of glasses is a recent discovery and optical analog of IP’s by Raman scattering.

Fig. 64 comparison of ternary (a) and binary (b) reversibility windows shows a 40 fold reduction of the window width in ternary.
The IP width in the binary (fig. 64 b) is about $\Delta x=6\%$ and in the ternary it reduces to $\Delta x<0.15\%$ which is about 40 folds less than the binary!

6. Molar volume comparison

Density experiments were performed on the ternary similar to as discussed earlier for the binary. We find that as we add fixed amount of Iodine to the base Ge-Se network the molar volumes move to a higher value. This is because of the addition of the oversized iodine atom to the network which increases packing density. In the ternary $V_m$ data we see a global minimum at $x=22.13\%$. This point corresponds to the minimum in non-reversing heat flow and the glitch that we observe in CS frequency shift of the ternary. The blue band identifies the IP from the non-reversing heat flow. The minimum of the molar volumes data in the ternary lies smack at the mid-point of the IP. In the case of the binary the molar volumes show minimal change in the IP.

**Fig. 65** Comparison of ternary (a) and binary (b) molar volume data shows a global minimum in the ternary. We can see that the ternary data sits considerably higher in comparison to binary.