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As corresponding author, I Sabyasachi Sen, hereby confirm on behalf
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3. All authors listed have made a significant contribution to the research reported and have read and approved the submitted manuscript, and furthermore, all those who made substantive contributions to this work have been included in the author list.

Response to referee and editorial comments:

Editor:

Please ensure that all tables and plots of data include uncertainty estimates, and a discussion of how the uncertainties are determined.

Response: Error determination for T_g and molar volume were already there. We have now also mentioned error in the G' and G'' data in the experimental section and in the figure caption.

Reviewer 1

I recommend to publish the paper in its present form.

Response: Thank you.

Reviewer 2

1. The introduction need to list the previous study of binary Se-I melts, which will make the article more innovative.

Response: We already did- but npw we have explicitly mentioned it. These are references 2-4.

2. The bending modes located in the 50-150 cm^{-1} range was mentioned in the Structure by Raman Spectroscopy, but not discussed.

Response: bending modes are very broad and lack resolution. Their assignment is extremely challenging without detailed density functional theory calculations and is outside the scope of the present work. No changes are made.

3. The temperature-dependent G' and G'' spectra of Se and Se97I3 should be given.

Response: We now have included these spectra in Fig. 3a.

4. The symbols and legend in Figure 3 are very confusing.

Response: We have now corrected this.

5. The Se97I3 supercooled liquid is susceptible to iodine loss and surface crystallization. How to avoid this kind of structural change in the process of rheological testing?

Response: This was already given in the original manuscript at the end of the experimental section on p.6 – the reviewer may have overlooked it. No changes are made.

Abstract

The structural evolution and shear relaxation behavior of binary $\text{Se}_{100-x}\text{I}_x$ ($0 \leq x \leq 3$) glasses and supercooled liquids are investigated using Raman spectroscopy and parallel plate rheometry, respectively. The spectroscopic results indicate cleavage and termination of Se polymeric chains by I atoms via the formation of Se-I bonds, leading to shortening of the average chain length with progressive addition of I atoms. Moreover, at I contents of $\geq 2\%$, a fraction of the I atoms forms I_2 dimers. The results from rheometry demonstrate that the structural relaxation rates associated with the fast segmental chain motion and the slow bond scission/renewal dynamics in $\text{Se}_{100-x}\text{I}_x$ liquids increase upon addition of I, with the shortening of the chain length. The increased configurational degrees of freedom of shorter selenium chains leads to a decrease in the isothermal viscosity, T_g and the packing efficiency and an increase in fragility in liquids with higher I content.

Structure and Rheology of Se-I Glasses and Supercooled Liquids

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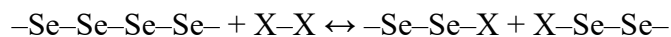
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Abstract

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Introduction

Amorphous chalcogenides have been studied extensively in the past because of their optical transparency in the infrared range. Selenium is one of the chalcogens known for its excellent glass forming ability in its elemental form and its stability against crystallization. It is now well established in literature that the structure of vitreous Se consists practically exclusively of twofold coordinated Se atoms forming polymeric chains [1]. The average coordination number $\langle r \rangle = 2$ of vitreous Se is conventionally taken to signify the lowest limit of nearest-neighbor structural connectivity in chalcogenide glasses. However, the introduction of halogens (X= Cl, Br, I) is known to result in the scission of intrachain Se-Se linkages and the formation of terminal Se-X bonds [2] through the following reaction:



Previous studies based on extended x-ray absorption fine structure spectroscopy and neutron scattering of binary Se-I melts have indicated that such a mode of incorporation of I atoms into Se chains is limited and at high I content ($\sim 80\%$) a large fraction of the I atoms form I₂ dimers. This observation was ascribed to the fact that the Se-I and I-I bonds are characterized by comparable bond strength [3]. On the other hand, previous studies of binary Se-I melts also showed that the decrease in Se chain length with increasing I content would result in a concomitant lowering of viscosity [2-4].

Recent studies of the shear relaxation behavior of supercooled Se demonstrated the existence of two relaxation processes, namely the slow bond scission/renewal dynamics and the fast segmental chain motion [5,6]. The slow process was shown to be closely related to shear relaxation and viscous flow, while the fast relaxation process remains temporally decoupled from

shear relaxation until the temperature closely approached glass transition from above. This scenario remains unchanged upon addition of cross-linkers such as Ge or As, as long as the average length of the selenium chain segments in between the crosslinking points remains longer than 3 to 5 Se atoms. As the network connectivity increases beyond this point with further addition of Ge or As, the segmental chain motion cannot be sustained and the fast process disappears [7]. Although binary Se-I melts have been studied in the past, the relationship between the structure and the rheological behavior of supercooled Se-I liquids, including the effect of shortening of the Se chains via their termination with halogen atoms on the shear relaxation behavior, remains unknown to date. Here we report the results of the first systematic Raman spectroscopic study of the structure of binary $\text{Se}_{100-x}\text{I}_x$ ($0 \leq x \leq 3$) glasses, as well as a rheological study of the shear relaxation behavior of select supercooled Se-I liquids. The correlations between the composition-dependent structural evolution and viscosity, molar volume and glass transition temperature are discussed.

Experimental

Glass synthesis and physical characterization.

Binary $\text{Se}_{100-x}\text{I}_x$ glasses with $x = 0.5, 1, 1.5, 2$, and 3 were synthesized in 10 ~12 g batches using the conventional melt-quench method. Mixtures of elemental Se (Alfa Aesar, 99.999%) and I_2 (Sigma-Aldrich, $\geq 99\%$) were loaded in quartz ampoules (8mm inner diameter) that were subsequently evacuated (10^{-4} Torr) and flame-sealed. The bottom of the ampoules containing the batched iodine was submerged in liquid nitrogen during flame sealing in order to avoid iodine sublimation. The ampoules were then loaded into a rocking furnace, slowly heated to 673K over

8 hours and held at this temperature for 12 hours to ensure melt homogeneity. The melts were subsequently quenched by dipping the ampoules in water.

The density of $\text{Se}_{100-x}\text{I}_x$ glasses was measured using a Micrometric Accupyc II gas expansion pycnometer under helium (6N purity) environment. For each measurement, approximately 1.0 g of glass sample was loaded into a 1 cm^3 cup. The reported densities in this study are averages of 10 consecutive measurements at room temperature.

The glass transition temperature T_g was measured using a Mettler-Toledo DSC1 differential scanning calorimeter. Approximately 20 mg powdered glass sample was loaded into a hermetically sealed 40 μL aluminum crucible. Scans were performed with a heating rate of 10K/min under a continuously flowing of nitrogen environment. T_g was determined to within ± 1 K as the onset of the glass transition. The activation energy of the glass transition and, hence, of structural relaxation was determined from the cooling and heating rate q dependence of the DSC profile of the glass transition. In particular, the samples were first heated to 338K, which is well above T_g , and then cooled to 273K, which is well below T_g , at a specific cooling rate q and subsequently held at that temperature for 5 min, followed by an upscan at the same rate back to 338K and the fictive temperature T_f was taken to be $\sim T_g$ [8,9].

Raman Spectroscopy. The Raman spectra of all glasses were collected in backscattered geometry using a Brucker RFS 100/S Fourier-transform Raman spectrometer equipped with a Nd:YAG laser operating at a wavelength of 1064 nm. Each Raman spectrum was collected using a laser power level of 30 mW, and is an average of 64 scans taken with 2 cm^{-1} resolution.

Parallel Plate Rheometry. The small amplitude oscillatory shear (SAOS) rheological measurements reported in the present study were carried out on an Anton-Paar MCR92 parallel

plate rheometer equipped with a Peltier heater under a constant flow of nitrogen gas. All measured samples were first heated above their softening point, then trimmed into a disc geometry with ~ 1 mm thickness that was sandwiched between the 8 mm oscillating upper plate and the stationary lower plate. For each measurement, an oscillatory strain within the linear viscoelastic range of the material with angular frequency ω varying between 1 and 600 rad/s was applied and the induced torque was measured simultaneously to obtain the storage and the loss moduli G' and G'' as a function of probing frequency. Multiple measurements were carried out at various temperatures for each composition and master curves of $G'(\omega)$ and $G''(\omega)$ were constructed using time-temperature superposition (TTS). It may be noted here that TTS is only approximately obeyed by these liquids. The viscosity master curves were then calculated from the relation $\eta(\omega) = \frac{\sqrt{G'^2 + G''^2}}{\omega}$. Details of the experimental setup and procedure can be found in a previous publication [10]. Additionally, Newtonian viscosity measurements on the supercooled Se_{97}I_3 liquid were carried out under steady shear condition, using a 25 mm diameter upper plate and a stationary lower plate, on a sample with a disc-like geometry with ~ 0.8 mm thickness. Although the duration of each measurement is only a few minutes, the Se_{97}I_3 supercooled liquid is susceptible to iodine loss and surface crystallization. Therefore, fresh samples were used for rheological measurements at each temperature to avoid thermal cycling and each measurement was repeated on multiple samples to ensure reproducibility and estimate experimental error. The physical appearance of the samples was checked immediately after the end of each measurement, which indicated the lack of any discernible surface crystallization.

Results and Discussion

Physical properties

The density and molar volume of these $\text{Se}_{100-x}\text{I}_x$ glasses are listed in Table 1. The molar volume of these glasses increases monotonically with increasing iodine concentration (Fig. 1a). When considering the effect of introducing I atoms, which exhibit similar atomic size but significantly heavier molar mass than Se atoms, it is intuitive that the density would increase with increasing I content. On the other hand, the I atoms are monovalent and act as Se chain terminators so that the average chain length is expected to decrease with addition of I. Therefore, the increase in molar volume with increasing I concentration suggests a decreasing efficiency in the packing of the selenium chains in the structure as the average length of these chains progressively shortens. This hypothesis suggests a scenario where long chains are more likely to exhibit chain folding and entanglement and therefore, a more efficient packing compared to short chains. Moreover, by the same token, the shortening of Se chains would lead to a less rigid structure that is capable of undergoing more rapid structural relaxation, which would result in a lowering of T_g with increasing addition of I. Such a trend is indeed observed experimentally for these $\text{Se}_{100-x}\text{I}_x$ glasses, where T_g decreases nearly linearly in a monotonic fashion with increasing x . (Fig. 1b).

Structure by Raman Spectroscopy

The Raman spectra of all $\text{Se}_{100-x}\text{I}_x$ glasses are shown in Fig. 2. The three major high-frequency bands in the $150\text{-}300\text{ cm}^{-1}$ range can be assigned to I-I ($\sim 172\text{ cm}^{-1}$), Se-I ($\sim 210\text{ cm}^{-1}$), and Se-Se ($\sim 250\text{ cm}^{-1}$) stretching modes [11,12]. The bending modes are located in the $50\text{-}150\text{ cm}^{-1}$ range. The Se-Se stretching band is the most intense, which indicates the abundance of the

Se chains in glasses. The intensity of the Se–I stretching band increases monotonically with increasing I content, which is consistent with the increasing concentration of the terminal Se–I bonds and corresponding shortening of the average Se chain length. This observation is in agreement with the thermophysical property trends discussed above. On the other hand, the I–I stretching band starts to appear at relatively high I concentration ($I \geq 2\%$) and increases in intensity with addition of I. This finding suggests that, beyond a threshold of $\sim 2\%$ I, not all I atoms are incorporated in Se chains and a fraction of these atoms form I_2 dimers. This propensity for I to form both Se–I and I–I bonds is consistent with the fact that Se and I exhibit similar electronegativity, which suggests similar bond strength for Se–Se and I–I bonds. Moreover, previous studies of Se–I melts reported interchange of Se–I and I–I linkages and the formation of I_2 molecules in the molten state [3].

Viscosity, shear relaxation and fragility

The frequency dependence of $G'(\omega)$ and $G''(\omega)$ at various temperatures and the corresponding master curves for pure Se and $Se_{97}I_3$ supercooled liquids obtained from the TTS of the SAOS rheometry data are shown in Fig. 3. The two relaxation processes corresponding to the low- and high- frequency crossovers between $G'(\omega)$ and $G''(\omega)$ in pure Se were shown in previous studies to represent, respectively, the slow Se–Se bond scission/renewal process and the fast segmental chain motion [5]. Correspondingly the viscosity $\eta(\omega)$ displays two onsets of frequency dependence. In contrast with Se, the $Se_{97}I_3$ supercooled liquid displays a clear high-frequency $G'(\omega)$ - $G''(\omega)$ crossover. However, in the low-frequency terminal region $G'(\omega)$ and $G''(\omega)$ display only a kink due to the changes in the relative strength and degree of temporal coupling between the two relaxation processes. Nevertheless, the two-step onset of the frequency dependence of $\eta(\omega)$ remains clear. Such behavior was ascribed in previous studies to

the terminal modes in short-chain polymers [13]. Therefore, similar to pure Se, two relaxation processes also exist in the Se_{97}I_3 supercooled liquids. The similarity in the activation energy E_a of the fast and the slow processes (Fig. 4), estimated from the temperature dependence of the corresponding relaxation times for the two liquids ($\sim 337 \pm 23$ kJ/mol and $\sim 179 \pm 5$ kJ/mol, respectively, for Se and $\sim 308 \pm 10$ kJ/mol and $\sim 145 \pm 8$ kJ/mol, respectively, for Se_{97}I_3) is a further corroboration of this hypothesis [5,14,15]. However, and more importantly, a comparison of the relaxation timescales between the two liquids shows that, compared to Se, the Se_{97}I_3 liquid has faster and more similar timescales for both processes (Fig. 4). It is tempting to hypothesize that further shortening in the selenium chain length at higher I concentration would lead to an eventual collapse of the two processes into a single relaxation process. According to the Maxwell relation, viscosity can be estimated as $\eta = (G_f - G_s)\tau_f + G_s\tau_s \approx G_f\tau_f + G_s\tau_s$, where the G and τ are the plateau shear moduli and relaxation time, and where the subscripts f and s correspond to the fast and slow processes, respectively. Since both shear moduli are found to have insignificant temperature dependence in the Se_{97}I_3 liquid, the temperature dependence of viscosity should be reflected in that of the relaxation times. Therefore, the results shown in Fig. 4 suggest a decrease in viscosity of $\text{Se}_{100-x}\text{I}_x$ liquids with progressive addition of I. This expectation is in agreement with the experimental viscosity data obtained in this study for the Se_{97}I_3 liquid using steady shear measurements (Fig. 5). Therefore, when taken together, these results indicate that the viscosity and the timescale of shear relaxation processes both decrease with the shortening of Se chain length as intuitively expected, since shorter chains should have more degrees of freedom and thus faster structural rearrangement compared to longer chains.

The Rouse model for flow in chain polymers predicts that for unentangled chain polymer melts the viscosity η is linearly proportional to the chain length N [16]. Assuming the chain

length in supercooled Se liquid is on the order of ~ 230 atoms, the Se_{97}I_3 glass should have an average minimum chain length of ~ 67 atoms (with 65 Se atoms and two terminal I atoms) if all I atoms participate in selenium chain termination via formation of Se-I bonds [17]. The viscosity of Se and Se_{97}I_3 at $\sim 333\text{K}$ is approximately 2.19×10^7 Pa s and 2.32×10^5 Pa s, respectively (Fig. 5). Therefore, it is clear that the $\eta \sim N$ relation is not satisfied for these two liquids, which suggests the likelihood of significant chain entanglement in supercooled Se liquid. Finally, the effect of addition of I and shortening of the selenium chain length is investigated in this study by comparing the heating and cooling rate dependence of the activation energy of the glass transition of supercooled Se and Se_{98}I_2 liquids. This activation energy E_a for a supercooled liquid at $T \sim T_g$ is related in the literature to its “fragility index” m , which is defined as: $m = \left. \frac{d \log_{10} \eta}{dT_g/T} \right|_{T=T_g}$ and can be obtained using the Wang-Velikov-Angell (WVA) method which relates m to E_a via the expression: $m = E_a / (\ln 10 RT_g)$, where R is the ideal gas constant and E_a/R is the slope of the $\ln(1/q)$ vs $1/T_f$ curve (Fig. 6) [8,9,18]. The Se_{98}I_2 composition was chosen for this experiment instead of Se_{97}I_3 as the latter is significantly more susceptible to iodine loss and surface crystallization during the DSC experiments, which could last for several hours at the slowest cooling/heating rates. It is clear from Fig. 6 that $\ln(1/q)$ for both liquids is not linearly proportional to $1/T_f$ as the E_a is dependent on temperature. Therefore, the slope is taken at the slowest cooling (or heating) rate of 0.2 K/min in this study to ensure that the calculated value of m for pure Se is consistent with the m determined directly from the viscosity data available in the literature at $T \sim T_g$ [19]. This method yields $m \sim 81$ for pure Se, while $m \sim 89$ for the Se_{98}I_2 liquid. This small but significant increase in fragility with addition of I further indicates that the formation of short selenium chains results in a higher degree of motional freedom and

consequently in a larger temperature dependence of the configurational entropy of the chains [20].

Conclusions

When incorporated into amorphous Se, halogens such as I, being monovalent, act as chain terminators. Therefore, progressive addition of I into Se results in the cleavage of Se-Se bonds and the formation of Se-I bonds, which leads to the shortening of Se chains and, consequently, a decrease in isothermal viscosity and T_g as well as an increase in molar volume and fragility. The characteristic timescales for the bond scission/renewal and the fast segmental chain motion associated with structural relaxation become faster and more similar with decreasing chain length. Furthermore, the scaling of isothermal viscosity with chain length indicates the likelihood of significant chain entanglement in supercooled selenium liquid.

Acknowledgement

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Table 1. Density and molar volume of $\text{Se}_{100-x}\text{I}_x$ glasses.

Composition	Density (g/cm^3)	Molar volume (cm^3/mol)
Se	4.270 ± 0.001	18.49 ± 0.01
$\text{Se}_{99.5}\text{I}_{0.5}$	4.277 ± 0.006	18.52 ± 0.02
Se_{99}I_1	4.277 ± 0.003	18.58 ± 0.01
$\text{Se}_{98.5}\text{I}_{1.5}$	4.283 ± 0.009	18.61 ± 0.04
Se_{98}I_2	4.283 ± 0.004	18.66 ± 0.02
Se_{97}I_3	4.287 ± 0.006	18.76 ± 0.03

Figure Captions

Figure 1. (a) Molar volume and (b) glass transition temperature T_g of binary $\text{Se}_{100-x}\text{I}_x$ glasses.

Figure 2. Unpolarized Raman spectra of $\text{Se}_{100-x}\text{I}_x$ glasses. All spectra are normalized with respect to the most intense peak at $\sim 250 \text{ cm}^{-1}$.

Figure 3. (a) Temperature dependence of $G'(\omega)$ and $G''(\omega)$ of (left panel) pure Se [5] and (right panel) Se_{97}I_3 liquids. (b) Master curves of frequency dependence of G' (filled squares) and G'' (open squares), and viscosity η (filled triangles) of (left panel) pure Se [5] and (right panel) Se_{97}I_3 liquids. The reference temperature for TTS is listed alongside the composition in each panel. Experimental errors in $G'(\omega)$ and $G''(\omega)$ are within the size of the symbols.

Figure 4. Temperature dependence of τ_s (squares) and τ_f (circles) for supercooled Se (open symbols) [5] and Se_{97}I_3 liquids (solid symbols).

Figure 5. Temperature dependence of viscosity of pure Se (open squares) [19] and Se_{97}I_3 (solid circles) liquids. The dashed line is a guide to eye.

Figure 6. $\ln(1/q)$ vs $1/T_f$ for (a) pure Se and (b) Se_{98}I_2 supercooled liquids. All experimental errors are within the size of the symbols.

Figure 1.

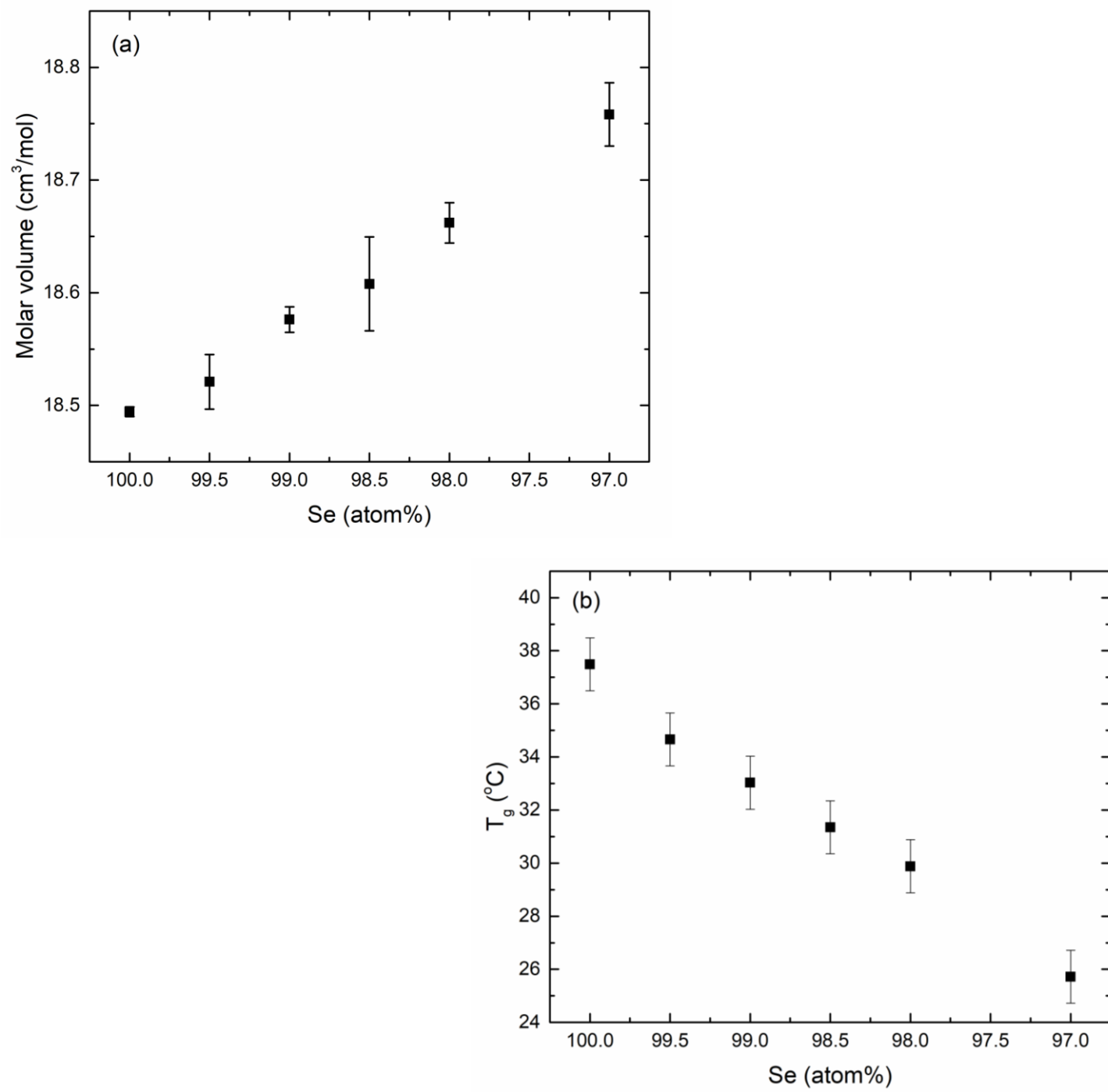


Figure 2.

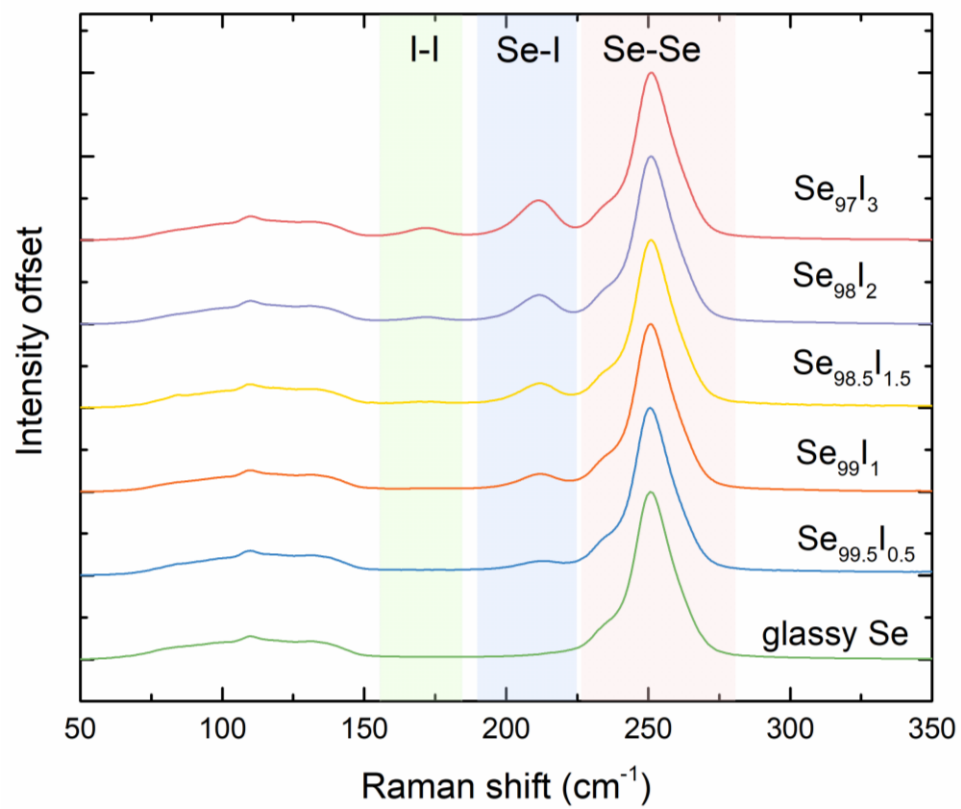


Figure 3.

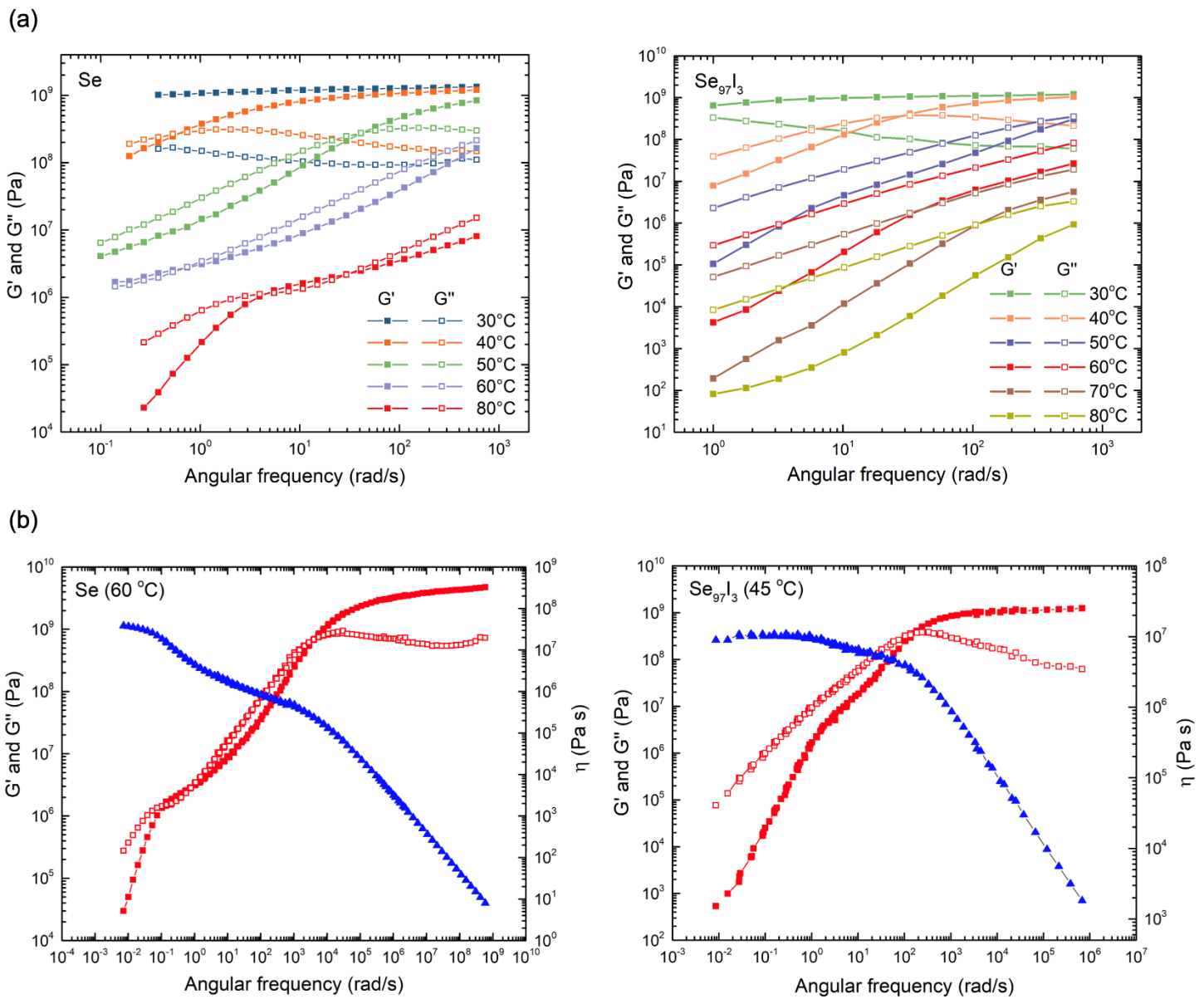


Figure 4.

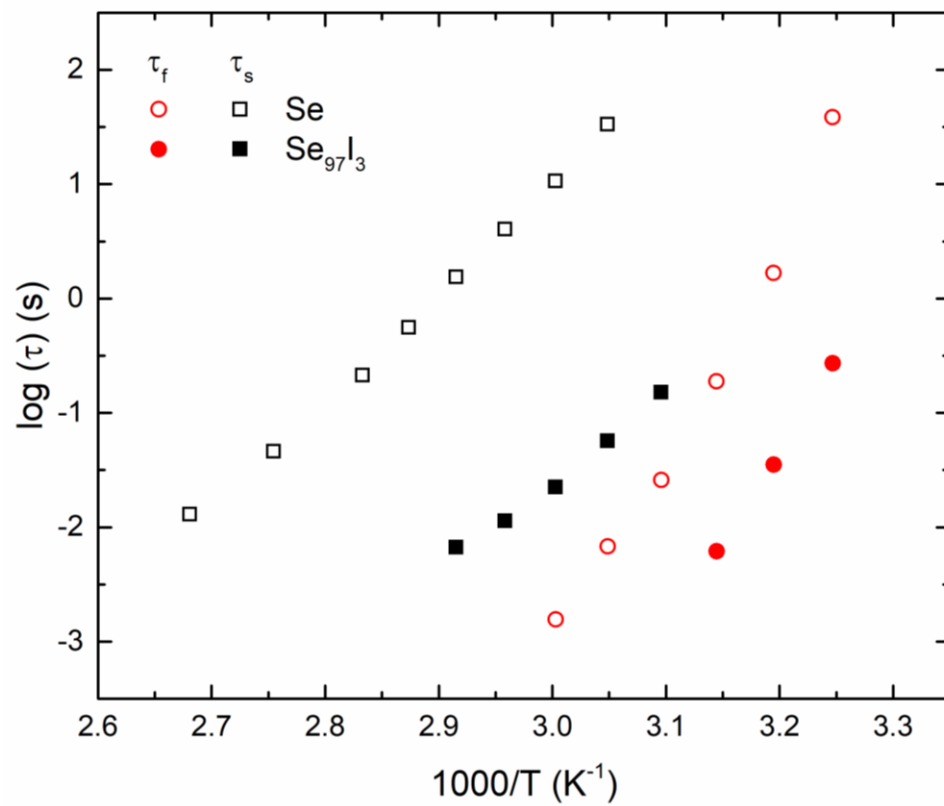


Figure 5.

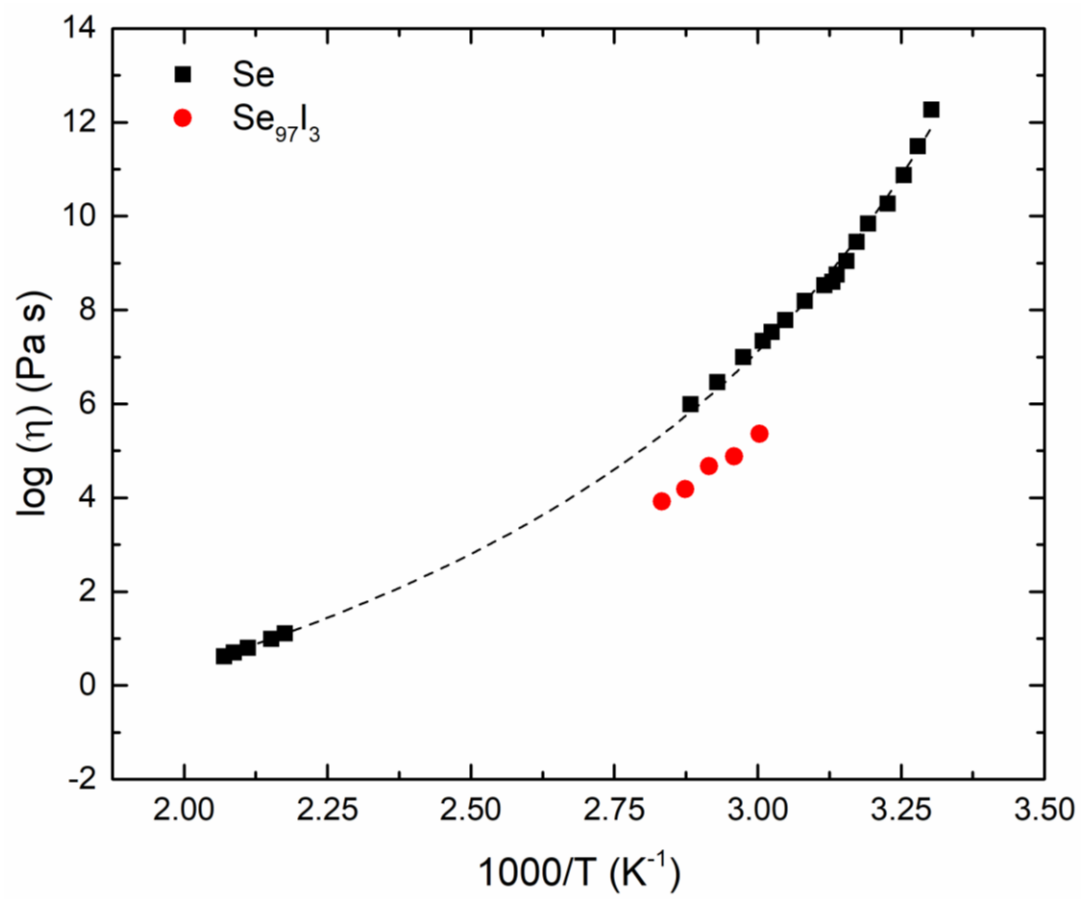
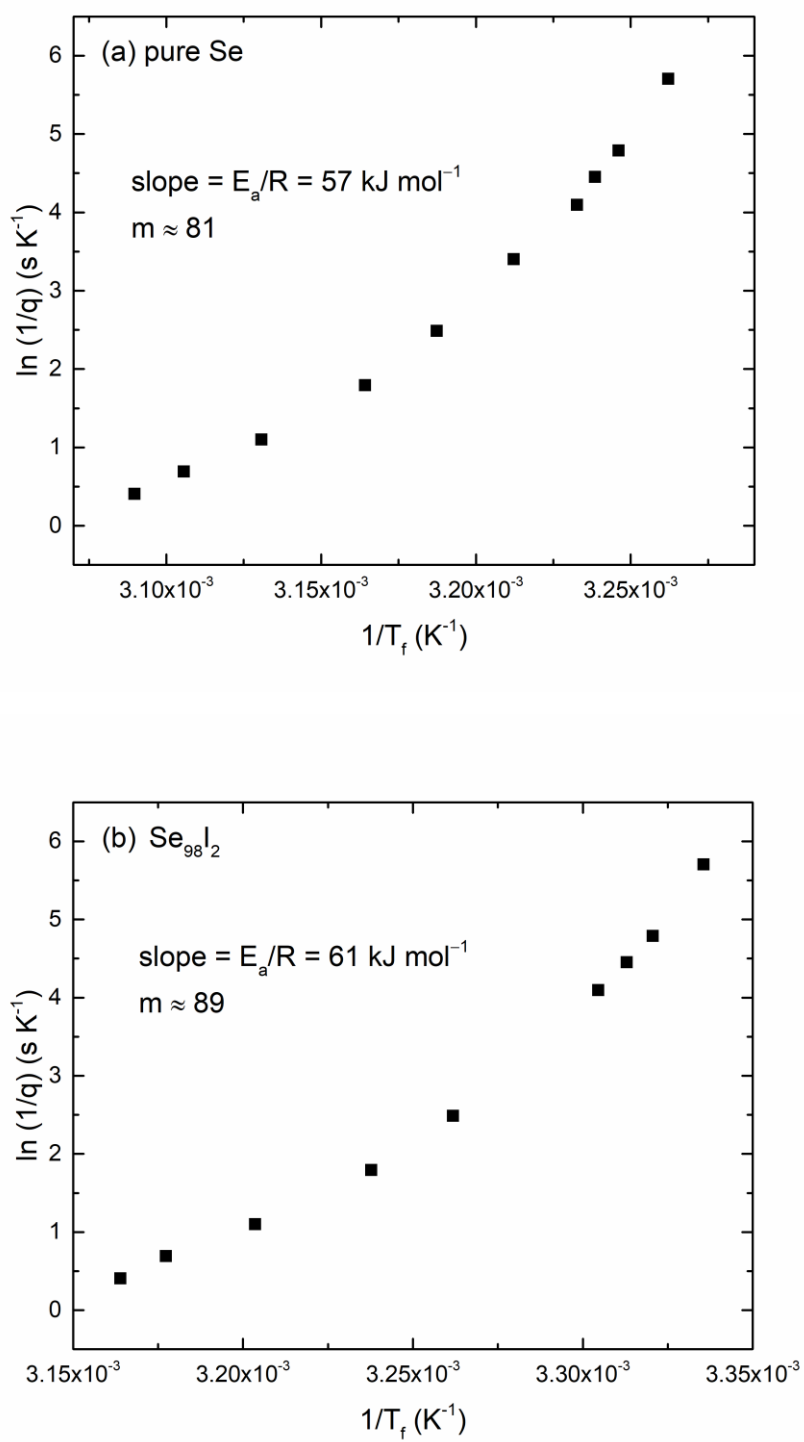


Figure 6.



Credit Author Statement:

Bing Yuan: Experimentation, data processing and interpretation, writing of manuscript. **Sabyasachi Sen:** Conceived the project, provided supervision and help with data interpretation and writing of the manuscript. **Bruce Aitken:** provided supervision and help with data interpretation and reviewing and editing of the manuscript.

Conflict of Interest and Authorship Conformation Form

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