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# High temperature elasticity and viscosity of $Ge_xSe_{1-x}$ glasses in the glass transition range

**Yann Gueguen[1], Tanguy Rouxel[1,€], Pascal Gadaud[2],
Cedric Bernard[1]\*, Vincent Keryvin[1]\*, and Jean-Christophe Sangleboeuf [1]**

[1]LARMAUR ERL-CNRS 6274, Université de Rennes 1, Bat. 10B, Campus de Beaulieu, 35042 Rennes cedex, France.

[2]Laboratoire de Mécanique et Physique des Matériaux, CNRS UMR 6617, ENSMA, 1 Avenue Clément Ader, BP 40109, F-86961 Futuroscope Cedex, France.

[€]Corresponding Author:


Tanguy Rouxel

Professor Tel: + 33-2-23236718

Fax: + 33-2-23236111

E-mail: tanguy.rouxel@univ-rennes1.fr

The viscous flow behavior and the temperature dependence of the elastic moduli of chalcogenide glasses from the germanium-selenium system were studied by means of homemade high temperature indentation setup and resonant frequency technique (1-10 kHz) respectively for temperatures between 0.8 and $1.2xT_g$. The softening rates, both in the elastic and in the viscous flow regimes, were correlated to network de-structuration or re-organization events in the light of previously reported high temperature neutron scattering data. The concomitant change of Poisson's ratio ($\nu$) and the thermodynamics parameters of the thermally activated viscous flow process, were characterized and provide a new basis for the understanding of the sources for the softening in the transition range. The temperature dependence of $\nu$ suggests weak changes of the network cross-linking degree at large Ge-contents. On the contrary, in the case of a-Se a steep fragmentation of the structural units is inferred from the $\nu(T)$ data and the flow process is accompanied by a huge entropy change (activation entropy at saddle point). The entropy contribution at $T_g$ ($T_gx\Delta S_a$) represents more than 50 % of the activation enthalpy for flow ($\Delta H_a$) and increases with the selenium content. Hence the free activation energy ($\Delta G_a$) is much smaller than apparent activation energy as derived from viscosity data.

## I. INTRODUCTION

Glasses from the germanium-selenium system have already been extensively studied both because of their excellent transparency in the far infrared wavelengths range and because they show up as model binary covalent glasses[1-4]. However, the incidence of temperature on their properties is a critical issue, especially for the most chalcogen-rich compositions, which exhibit glass transition temperature below 350 K. It is of paramount interest not only at the processing and shaping stages, but also to evaluate the stability of glass parts in service conditions.

Elastic moduli are intimately related to volume density of energy (as expressed by the $1^{st}$ Grüneisen rule[5]) and to the network connectivity. For instance Poisson's ratio was already found to correlate with the number of bridging oxygen atoms per Si-centered tetrahedron in silicate glasses[6] and to the network connectivity in general[7] and some linear relationships were proposed between $\nu$ and the average coordination number $\langle n \rangle$ (in the case of $Ge_xSe_{1-x}$ glasses, $\langle n \rangle = 2(x+1)$)[8]. As far as $\langle n \rangle$ is less than 2.1, the selenium chains (or rings) are weakly interconnected so that deformation is expected to essentially proceeds through the alignment of the chains in shear planes. In this case properties are believed to be very sensitive to the weak inter-chains Van der Waals forces. A low shear resistance and a high Poisson's ratio follow. As $\langle n \rangle$ increases, covalent bonds come into play. At first sight, $\langle n \rangle = 2.4$ ($GeSe_4$ composition) corresponds to a complete cross-linking of Se and Ge layer units, two neighboring Ge atoms being separated by two Se atoms on average. At $\langle n \rangle = 2.67$ ($GeSe_2$ stoichiometry), homopolar Ge-Ge are present, and a tri-dimensional network is found, leading to a significant increase of the elastic moduli and of the viscosity[9], which can be viewed as a result of stressed rigidity[10]. The structure of these glasses might be slightly more complicated though, as will be further discussed, with Se occurring in at least three different sites[11] and possible "clustering" - at the scale of the structural units[12,13]. $^{77}$Se experimental solid state Nuclear Magnetic Resonance and Raman scattering investigations have suggested a bimodal phase network, where the glass structure is composed of intertwined $GeSe_2$ and $Se_n$ microdomains[14]. This assumption was based on the apparent absence of Se-Se-Ge fragments in the structure. Neutron-diffraction measurements and recent molecular dynamic simulations also suggests that the simple picture based on the $\langle n \rangle$ value is partially valid, as only about half of Se atoms are found in the predicted structural motifs[15,16]. The most recent studies imply that the structure a Ge-Se glasses significantly differs from the one predicted by the

simple chain-crossing and outrigger raft models[17], and very recent ^{77}Se NMR investigations evidence[18,19] the existence of Se-**Se**-Ge sites connecting GeSe$_2$ clusters and Se chains domains. However, whether the Ge-rich units are interconnected by means of Se chains (chain-crossing model) and whether Se form chains or rings (which size) are still matters of controversy. It is noteworthy that elastic moduli (continuum scale measurement) are essentially independent of the fine details of the network structure, provided the atomic coordination remains little affected. Nevertheless, the heterogeneous structure of the glass network at the molecular scale, with the possible coexistence of soft and stiff regions, will surely affect the temperature dependence through a "composite"-like effect which can be probed by means of high temperature measurements. Besides, elasticity data obtained in the temperature range for viscosity measurements allow for the derivation of the actual values for the activation energy and the free activation energy for flow from the directly available (apparent) eat of flow (enthalpy), as will be discussed further. The combination of elasticity and viscosity data provides thus a unique opportunity to get insight into the flow mechanisms and into the composition sensitivity of the rheological behavior.

## II.   MATERIALS AND EXPERIMENTAL METHODS

### A. Materials

Ge$_x$Se$_{1-x}$ glasses, with x between 0 and 0.3 were obtained from high purity elements Ge (99.9999%) and Se (99.999%). Se was further purified of remaining oxygen by the volatilization technique, consisting in heating Se at 523 K under vacuum for 2 hours. This method uses the greater vapor pressure of selenium oxide SeO$_2$ over that of the metal to remove the oxide species. Proper amounts of Ge and Se are subsequently introduced into an amorphous silica tube sealed in vacuum with a better than $10^{-2}$ Pa pressure in order to avoid oxygen contamination. The sealed silica tube was introduced into a rocking furnace and kept at 1023 K during 12 h to ensure a good mixing and homogenization of the liquid. The temperature was subsequently reduced to 923 K and staid constant for 1 h to reduce the gas pressure in the tube[3,12,13]. The obtained glass melt was then quenched in water (293 K) and annealed at T$_g$ during 4 h to reduce the residual stresses resulting from the cooling. The glass rod was sliced and cut to the desired mechanical testing specimen geometry using a diamond saw. Surfaces of the specimens were mirror polished using SiC paper and alumina suspension (1/4 micron particle size).

The glass transition temperature $T_g$ was measured by a TA Instrument differential scanning calorimeter DSC Q20, with a heating rate of 10 K/min, with a better than ±2 K accuracy. The density was measured at 293 K using the Archimedes displacement technique using $CCl_4$. The variability of such a measurement is about ±0.5 %.

## B. Experimental methods

Our laboratory has developed an equipment operating in the micro-indentation range, with applied loads between 0.01 and 15 N, consisting in a hot chamber equipped with an alumina tube and a sapphire indenter, and allowing for a better than 2 K accuracy along a 10 mm testing zone[20,21]. The whole equipment is situated in a vibration-free and air disturbance-free environment. The load is applied using a piezoelectric actuator and the penetration depth is measured with a capacitive sensor having a resolution of 10 nm. The load fluctuation is less than ± 12 mN. The maximum target temperature is 1473 K, with a thermal stability within 1 K variation up to 1323 K.

The shear viscosity coefficient ($\eta$) was estimated from indentation experiments performed at a constant load (P) of 1 to 12.5 N in air using a ball indenter (750 µm radius (R)) and is given by[21-23]:

$$\eta = \frac{3}{16} \frac{P}{\sqrt{R}} \left( \frac{d(u^{3/2}(t))}{dt} \right)^{-1} , \tag{1}$$

where u is the penetration depth.

Recall that the viscous flow regime is associated to the stationary creep regime following the viscoelastic transient one. Consequently, the load was maintained long enough (typically 1 min above $T_g$ to more than 1 hour for points recorded below $T_g$) to insure the occurrence of a stationary creep regime, as evidenced by a constant slope in the $u^{3/2}/P$ versus t curves. This problem is particularly critical as soon as measurements are carried out below $T_g$, i.e. in a range where the characteristic relaxation time increases rapidly and compares with the experimental duration. The specimen and the indentation set-up were kept at each testing temperature for up to 4 hours before loading to ensure a thermal equilibrium.

Young's modulus was determined by means of a resonant frequency technique in bending mode in the kHz range[24]. This method allows to perform experiments at 1 K.mn$^{-1}$ under high vacuum ($10^{-4}$ Pa) up to 1300 K without any harmful contact, the sample beam

being maintained horizontally between steel wires located at the vibration nodes. Furthermore, excitation and detection are insured by an electrostatic device (capacitance created between the sample and a single electrode). The accuracy of this method is better than 0.5% for conducting bulk materials whatever the rigidity range. Young's modulus ($E$) is expressed as[24]:

$$E = 0.9464 \ \rho \, F_B^2 \left[ \frac{L^4(t)}{h^2} T(h/L, \ \nu) \right] ,$$ (2)

where $F_B$ is the resonance frequency in bending mode, $\rho$ the specific mass, $\nu$ Poisson's ratio, h and L, the beam thickness and span length, and $T(h/L,\nu)$ a correcting factor close to 1.

For this work, $20 \times 4 \times 2$ mm$^3$ parallelepipedic bars were plated on one face (AuPd metallic vapor deposition of about 10 nm thick) in order to be electrostatically excited.

A new testing head has been designed in agreement with ASTM recommendations to determine the shear modulus ($\mu$) of plates (typically 30 mm $\times$ 12 mm $\times$ 1.5 mm) in torsion mode[25].

$$\mu = \frac{4\rho}{R L^2 F_T^2} ,$$ (3)

where R is a shape factor equal to 17.51 in the present case, $\rho$ is the specific mass, L is the length of the plate-like specimen and $F_T$ is the torsion resonant frequency.

### III.    RESULTS

Owing to the experimental difficulty to assess high temperature elasticity data, and especially due to the machining of specimens in such brittle glasses (fracture toughness of GeSe glasses is typically below 0.3 MPa.m$^{0.5}$), measurements were limited to a-Se, GeSe$_4$, GeSe$_3$, and Ge$_3$Se$_7$ compositions (Fig. 1). Additional investigations focused on Young's modulus were previously reported by Gadaud et al.[24] for Ge$_{15}$Se$_{85}$ and Ge$_3$Se$_7$ compositions. The raw measurements of E, $\mu$, and $\eta$ are reported in Table I (note that these data might be further used to estimate the vibrational entropy of both the glass and the super-cooled liquids from the classical assumption that S$_{vib}$ is proportional to $d\mu/dT$).

The elastic moduli exhibit only minor changes between room temperature (RT) and $T_g$. Their values at $T_g$ are more than 80 % of their RT values. With regards to the considered temperature interval (0.8 to 1.1$T_g$) data in the super-cooled liquid region exhibit a linear dependence with temperature. The $\left.\dfrac{dE}{dT}\right|_{T \geq T_g}$ and $\left.\dfrac{d\mu}{dT}\right|_{T \geq T_g}$ slopes are reported together with the transition temperatures and the corresponding values of the elastic moduli in Table II. In all cases, experimental data exhibit a change of the softening rate in a temperature range corresponding within fifteen degrees to the glass transition temperature as obtained by classical means such as DSC and dilatometry. In the case of a-Se the transition observed in shear lies about 7 K below that observed in the E(T) curve. For reasons that have not been elucidated yet, the transition as observed from elasticity data is shifted to lower temperature, notwithstanding the fact that frequencies in the 1 to 10 kHz range were used. A similar observation on glasses from various systems and using a different experimental set-up was previously reported[7]. Nevertheless, since a clear transition between two regimes was always observed in a temperature range quite close to the one identified as the $T_g$ range by DSC, this transition was considered in this work to be the glass transition range with respect to the used technique. The softening rate of a-Se above $T_g$ (-115 MPa.K$^{-1}$) is close to the one reported for Zr-based metallic glasses[26] or oxynitride glasses[27], but is ~ twice less than that for glycerol (~ -190 MPa.K$^{-1}$)[28]. The addition of germanium results in a significant reinforcement of the glass. With more than 25 at.% germanium, the softening rate (in absolute value) becomes 3 to 4 times smaller. The viscosity curves as obtained by instrumented indentation are plotted together with previously published data[29-33] on glasses with same compositions in Fig. 2a. The indentation method allows to cover a broad range of viscosity values on both sides of $T_g$, with a unique opportunity to probe the low temperature range associated with viscosities above $10^{13}$ Pa.s. It is noteworthy that the present data are in excellent agreement with those reported in the literature for T>$T_g$. There are 5 to 6 orders of magnitude differences in the viscosity coefficients at a given temperature between adjacent curved, i.e. as the germanium content changes by about 10 %.

In what follows, we will discuss the viscous flow process in the light of general concepts developed in the framework of thermally activated processes, regardless of any structural or microscopical ingredients. With regard to the viscosity range considered here - for $\eta$ between $10^8$ and $10^{15}$ Pa.s - the experimental data could be expressed with a smooth curve-fitting as a function of temperature using a classical Boltzmann term accounting for the probability of a given fluctuation to overcome the relevant energy barrier,

$$\eta = \eta_o \exp[\Delta G_a /(RT)] \ ,\tag{4}$$

where $\eta_o$ is a temperature-independent factor, R is the perfect gas constant and $\Delta G_a$ is the free activation enthalpy for flow.

However, it must be emphasized that $\Delta G_a$ is by essence a temperature-dependent parameter (differentiation of the free enthalpy with respect to T is the negative of the entropy, so that the derivation of Eq.(4) with respect to temperature leads to:

$$R \left.\frac{\partial \ln \eta}{\partial (1/T)}\right|_\sigma = \Delta G_a - T \left.\frac{\partial \Delta G_a}{\partial T}\right|_\sigma = \Delta G_a - T \Delta S_a\tag{5}$$

where $\sigma$ is the stress applied on the specimen (see Refs [34],[35] for further background on this analysis) and is mentionned here to recall that T and $\sigma$ are the two independent external variable in this problem.

By analogy with the formalism introduced in Chemical Kinetics[36], $\Delta S_a$ can be considered as the entropy of activation of the flow process. Hence, it is inferred from Eqs. (4,5) that the only directly available experimental parameter is the activation enthalpy (heat of flow),

$$\Delta H_a = R \left.\frac{\partial \ln \eta}{\partial (1/T)}\right|_\sigma \ ,\tag{6}$$

$\Delta H_a$ values as determined from the slope of the linear intercepts in Fig. 2b are reported in Table III. Following the classical theory of thermally activated flow phenomena, it is possible to estimate $\Delta G_a$ once the temperature dependence of the shear modulus is known (two important assumptions here are: i) the height of the energy barrier is proportional to the shear modulus, and ii) the contribution of the mechanical work to overcome the barrier is small in comparison to that of thermal activation)[34,35,37]:

$$\Delta G_a = \frac{\Delta H_a}{1 - \dfrac{T}{\mu}\dfrac{\partial \mu}{\partial T}}\tag{7}$$

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The activation entropy is then given by: $\Delta S_a = (\Delta H_a - \Delta G_a)/T$:

$$\Delta S_a = \frac{\dfrac{1}{\mu}\dfrac{\partial \mu}{\partial T}}{\dfrac{T}{\mu}\dfrac{\partial \mu}{\partial T} - 1} \Delta H_a \tag{8}$$

Another approach was proposed by Nemilov[38], assuming that all viscosity curves meet in the supercooled liquid region at a given $T_g/T$ ratio corresponding to a viscosity of about $10^{-4.5}$ Pa.s. In this latter approach both $\Delta G_a$ and $\Delta S_a$ are solely estimated from the viscosity data on the basis of Eqs. (5) and (6). For instance at $T_g$ it comes that $\Delta S_a = -316 + \Delta H_a/T_g$ and $\Delta G_a(T_g) = 316 T_g$. The activation volume ($V_a$) associated to the overcoming (saddle point) of the energy barrier for flow is another important parameter. Since $V_a = -\left.\dfrac{\partial \Delta G_a}{\partial \sigma}\right|_T$, it is in principal required to perform temperature jump experiments for different values of the applied stress to estimate the activation volume. However Nemilov[39] proposed a simple estimation for a volume V*, considered to be that of kinetic units overcoming the activation barrier, from the free activation enthalpy for flow and from the shear modulus, $V* = \Delta G_a/\mu$, and concluded that V*/N (N: Avogadro number) can be written as $r_o^3$ where $r_o$ is in excellent agreement (within 10 %) with some interatomic distance (see ref. [35] for details). A similar expression was obtained by Dyre et al.[40] using a volume expansion model, although in this later case the characteristic volume was given a slightly different meaning.

The values for the parameters of the thermally activated viscous flow process are reported in Table III.

## IV.    DISCUSSION

The softening of glasses above $T_g$ is chiefly related to the destructuration of the atomic network. However, the microscopic events at the source for this thermal weakening are quite complicated and differ from one glass to the other. Various scenarios might be invoked depending on the type of structural units and on the inter-units bonding. Generally speaking, the whole network topology comes into play. Interestingly, elastic moduli and shear viscosity coefficient are likely to be primarily sensitive to different microscopic features. For instance, Young's modulus is likely to be affected by the stiffness of the structural units to a normal

stress, whereas the shear modulus is more sensitive to the inter-unit bonding. In principle, elastic moduli are little affected by the size or the length of the structural units (recall that neither the shape nor the size of the phases affect the moduli of a composite mixture; Only the respective volume fractions matter), as far as there is no dramatic structural changes. On the contrary, viscosity is very sensitive to the size and shape of the structural units and to the presence – or absence - of a continuous softer phase. In what follows, we intend to get insight into the softening mechanisms in the light of the abundant literature published on the structure of germanium selenide glasses and on the thermally induced structural changes.

### A. Network cross-linking, average coordination and elastic behavior

The increase of both E and $\mu$ with the germanium content mainly stems from the increase of $\langle n \rangle$. Bridges[6] and Nemilov[39] reported some interesting correlation between Poisson's ratio ($\nu$) and glass network structures, and $\nu$ was found recently to show up as a remarkable index of the cross-linking degree, regardless of the chemical system[7]. For $Ge_xSe_{1-x}$ glasses, a linear relationship (correlation=0.985) is obtained from previously published elasticity data on the same specimens[41]:

$$\nu=0.5135-0.0946\langle n \rangle \qquad\qquad\qquad (9)$$

Where $\langle n \rangle$ is the average coordination number. Note that a very close relationship was also reported in the Ge-Sb-Se system[8].

Although E, $\mu$, and $\nu$ change monotonically with $\langle n \rangle$, their temperature dependences are more interesting. For instance, both dE/dT and d$\mu$/dT (table II) are larger for the $GeSe_3$ composition, in the supercooled liquid range ($T_g^+$), than for the $GeSe_4$ and $Ge_3Se_7$ compositions. It is noteworthy that the $GeSe_3$ composition precisely lies in the so-called intermediate phase range (after Boolchand et al.[10,42]).

Although it receives little attention so far, the temperature dependence of $\nu$ is of paramount interest to probe the thermally induced structural changes in the cross-linking. Recalling that $\nu=E/2\mu-1$, $\nu(T)$ data were calculated from E(T) and $\mu$(T) ones (Fig. 3). A perfectly incompressible body is characterized by $\nu=0.5$ and rubber, glycerol and Pd-based metallic glasses get very close to this upper bound above their $T_g$. On the contrary, a-$SiO_2$ (a tetrahedrally coordinated glass as $GeSe_2$) retains its cross-linked structure well beyond the $T_g$

range[7]. In the present case it seems that the cross-linking remains strong in both GeSe$_3$ and Ge$_3$Se$_7$ compositions up to $1.1 \times T_g$ whereas a-Se experiences a severe depolymerization and approaches the liquid state in a steep manner. It is noteworthy that for a-Se the increase of $\nu$ begins below the $T_g$ range as estimated from E(T) curves. A similar temperature shift was reported earlier on a-Se by Böhmer et al.[9] from ultrasonic investigations in the 1-20 MHz range. The excitation frequencies used here are close to 5 and 8 kHz and the corresponding periods (1-2 $10^{-4}$ s) are thus hundreds of times smaller than the characteristic relaxation time ($\eta/\mu$ from the Maxwell model), which is larger than 5 min below $T_g$. Therefore it doesn't seem reasonable to invoke any dynamic effect, in accord with Böhmer's conclusion[9], nor to account for the dynamic Poisson's ratio[43]. A possible explanation is that the weak inter-chain bonding (major contribution to $\mu$) collapses at a lower temperature than the covalent bonds. The fragmentation of the chains may also weaken the shear resistance more than the uniaxial stiffness. However, the elasticity measurements on a-Se should be taken with caution for the following reasons: i) Dynamic structural relaxation might occur during loading due to a $T_g$ range close to ambient temperature; and ii) The $\pm 2$ K accuracy of our equipment might be a problem for the calculation of $\nu$ of low $T_g$ glasses, because small temperature differences induce large changes in E and $\mu$, leading to a dramatic deviation in $\nu$.

Now, let us summarize what we can learn from the literature about thermally induced structural changes in the studied glasses. a-Se is often considered to consist of a mixture of chain and ring units, with an expected decrease of the amount of rings with rising temperature above $T_g$[44,45]. Dembovsky[46] concluded from quantum chemical data that in addition to 2-fold coordinated atoms there was a growing number with rising temperature of 4-fold coordinated Se (over 10 % at $T_g$). It was suggested that this could play a role in the high temperature range (for $T/T_g<1.3$[46,47]), higher than the temperature range of interest in this study. It has also been concluded from small angle neutron scattering that the chain macromolecules of a-Se, consisting of $10^4$ to $10^6$ atoms, up to $T_g$[42], shorten upon increasing temperature in the liquid range[45,49]. Rings are very likely to give a significant contribution to the resistance opposed to transverse contraction when the material is pulled in tension (recall that foams or cellular solids exhibit very low values for Poisson's ratio). Hence, the disappearance of rings is supposed to be of paramount importance on the increase in $\nu$. The site fraction of Se atoms building rings was estimated to lie about 0.85, 0.78, 0.66 and 0.56 at 293, 300, 350 and 400 K respectively[45]. It is inferred from the abrupt increase in Poisson's ratio that this destructuration is very rapid within 10 K around $T_g$; and the fraction of ring in this

temperature range can not be considered as resulting from a percolation of these units[50,51]. Now, because the inter-chain bonding is relatively weak (Van der Waals type), upon heating a-Se looks more and more like short (-Se-)$_n$ segments embedded in a soft phase, so that shear is enhanced and both shear modulus and viscosity drop sharply.

The introduction of germanium adds to the complexity of the problem. When the selenium content exceeds 80 % (GeSe$_4$, GeSe$_9$) anomalous wide angle X-ray scattering and small angle X-ray scattering suggest that the structure is mainly constituted by isolated GeSe$_4$ tetrahedra in an amorphous Se matrix[12]. A recent first principle molecular dynamics simulation on GeSe$_4$ proposes more details to the picture: 88% of Ge atoms are involved in tetrahedral GeSe$_4$ units and a few are not four-fold coordinated to Se, but would form Ge-Se$_2$ and Ge-GeSe$_3$ units, while Se would form Se-Se$_2$, Se-Se-Ge, and Se-Ge$_2$ motifs[16]. At lower selenium content, corner-sharing and edge-sharing tetrahedra are observed[12,18]. This suggests, that there are few – or less[17-19] than expected from the stoichiometry (chain-crossing model) - Se-Se bridges between GeSe$_{4/2}$ tetrahedra, even for the GeSe$_4$ composition. This indicates the presence of Se-rich units in the structure, but not isolated, as suggested by the bimodal model. In addition, due to the relative ease for the dissociation of GeSe$_2$ units[52], it is anticipated that more and more homopolar bonds (Ge-Ge, Se-Se) will form upon heating above $T_g$, giving to the network a more and more chemically heterogeneous nature. Neutron Scattering studies[53,54] conducted on liquid samples from the Ge$_x$Se$_{1-x}$ system at temperature above 900 K confirmed the disappearance of heteropolar Ge-Se bonds with increasing temperature in the liquid range and indicate that the intermediate range order becomes less significant while the average coordination number $<n>$ does not seem to change. Besides, although weak regions develop in the glass network, GeSe$_{4/2}$ tetrahedral units are not much affected. These units clearly oppose to transverse contraction under tensile loading and are responsible for a relatively low value and for a weak temperature sensitivity of $\nu$ in the presence of significant amount of germanium. Our $\nu$(T) data also suggest little change in the network cross-linking degree in the case of GeSe$_3$, GeSe$_4$ and Ge$_3$Se$_7$ compositions and are thus consistent with these structural observations. ***Furthermore, the fact that GeSe$_3$ and GeSe$_4$ compositions behave very similarly (normalized elasticity and viscosity curves are almost superimposed), would support either the existence of an intermediate phase controlling the behavior in this composition range (x=0.2 to 0.25)[55], or the possibility that for Ge content over 20 at%, the Se-rich are progressively taking over the GeSe$_2$ units in controlling the properties of the glasses. This is in agreement with a recent $^{77}$Se NMR study[56] suggesting few bond exchanges between Se rich domains and GeSe$_2$ units, and larger mobility of Se-Se-Se sites.***

## B. Thermal activation parameters and deformation mechanism

The height of the free activation energy, $\Delta G_a$, for the viscous flow process is much lower than any interatomic bonding energy (264, 330 and 484 kJ.mol$^{-1}$ for $U_{oGe-Ge}$, $U_{oSe-Se}$ and $U_{oSe-Ge}$ respectively[51]). This suggests that deformation proceeds by shear along the soft regions in-between stiffer structural units. The larger the selenium content is and the larger the activation entropy ($\Delta S_a$) induced by the flow process and the fragility index (m) become (Fig. 4 and Table II). This is in agreement with the work published by Nemilov[38], which already suggested a strong correlation between $\Delta S_a$ and m. As long as stress effects on viscosity can be neglected (i.e. flow remains Newtonian), $\Delta S_a$ reflects the temperature dependence of the energy barrier and is chiefly related to thermally induced changes of the shear modulus (see Eq. (7)). Therefore the large entropy contribution and the abrupt entropy change above $T_g$ (Fig. 5) in the case of a-Se corroborates the steep softening observed in the same temperature range.

*Amorphous selenium*: There are obviously some dramatic microscopic events responsible of the rapid softening and increase of the activation entropy at $T_g$. Misawa et al.[45] studied the temperature dependence and the energetics of the ring to chain transition in a-Se. In particular these authors intended to estimate the entropy increase associated with the fragmentation of the Se chains. The following expression was derived for the entropy increase:

$$\Delta S = R \ \ln\left[\left(\frac{n_c}{q}\right)^q \frac{1}{f_c^{2q-1} (q-1)! \, \xi^q}\right], \tag{10}$$

where $n_c$ is the number of Se atoms in the chain before fragmentation and q is the number of Se-Se bond disruptions ($n_c/q$: average number of atoms in the fragments), $f_c$ is the fraction of chains (versus rings) and $\xi$ is a constant calculated to be $4.2 \cdot 10^{-3}$. Using their data at $T_g$ ($n_c/q \sim 5 \cdot 10^5$, $f_c \sim 0.22$) an entropy change of $\sim 1100$ J.mol$^{-1}$.K$^{-1}$ (Fig. 5) would correspond to 6 cuts in a chain. At 350 K (T/$T_g \sim 1.12$), with $n_c/q \sim 2 \cdot 10^5$ and $f_c \sim 0.34$, the same entropy change corresponds to 8 cuts. Just below $T_g$, the number of cut falls down to about 4 ($\Delta S = 700$ J.mol$^{-1}$.K$^{-1}$, $n_c/q \sim 10^6$, $f_c \sim 0.15$). It would be very interesting to study the changes of the chain length and chains to rings fraction in situ at high temperature under stress to determine whether

viscous flow affects these processes or not. At higher temperature the activation entropy is expected to decrease as the system gains more and more ergodicity. This is indeed predicted by Eq. (8): As T increases and $\mu$ decreases toward zero, $\Delta S_a$ tends toward 1/T. It is noteworthy that glasses such as glycerol and selenium consisting of chain-like structural units experience a large change in $\Delta S_a$ in the transition range, whereas weak changes are observed in more cross-linked glasses, such as a-$SiO_2$.

*Germanium selenide glasses:* We observed a decrease of the temperature sensitivity of the viscosity ($\Delta H_a$) with an increase of the germanium content up to 20 % ($GeSe_4$). Then $\Delta H_a$ increases and reaches a value for $Ge_3Se_7$ higher than for $GeSe_9$. Our data corroborate previously reported data on similar glasses[30,54] and which concluded to a U-shape curve for $\Delta H_a$ as a function of the germanium content, with a decrease for <n> below 2.4 and an increase above this value and up to the $GeSe_2$ composition. The activation energy for enthalpy relaxation shows also an identical U-shape[14]. However one should keep in mind that the free activation enthalpy $\Delta G_a$ is the relevant parameter of the flow process and is systematically smaller than the apparent energy, $\Delta H_a$. The discrepancy is especially large for a-Se (41 kJ.mol$^{-1}$ and 369 kJ.mol$^{-1}$ for $\Delta G_a$ and $\Delta H_a$ respectively). A monotonic increase of $\Delta G_a$ with the germanium content, from 95 kJ.mol$^{-1}$ for a-Se to 183 kJ.mol$^{-1}$ for $Ge_3Se_7$, is predicted from the simple model proposed by Nemilov[38]. These values are in reasonable agreement with those we obtained taking advantage of our high temperature elasticity data (41 kJ.mol$^{-1}$ and 145 kJ.mol$^{-1}$ respectively). This monotonic trend might simply reflect the fact that an increase of the germanium content results in an increase of the elastic moduli and thus to an increase of the volume density of energy (1$^{st}$ Grüneisen rule). The height of the energy barrier for viscous flow being of an overwhelming part of elastic origin, a monotonic increase of $\Delta G_a$ with the germanium concentration follows. Therefore, the unexpected U-shape curve depicted by $\Delta H_a$ as a function of the germanium content is simply due to a dramatic composition-dependence of the activation entropy. The relatively strong temperature sensitivity of the viscosity at large germanium contents, with a fragility index remaining as large as 27 for both $GeSe_3$ and $Ge_3Se_7$, stems from the fact that the breakdown of the cross-linked network structure (disappearance of the medium range order) above $T_g$ favors shear in-between structural units, which are no more strongly interconnected, so that the microscopic events which cause viscous flow are likely to be very similar in all cases. Eventually, glasses containing at least 40 % germanium ($Ge_2Se_3$) are likely to consist of Ge-rich clusters in a selenium matrix and might show a fragility index close to the one of pure a-Se, as observed

by Senapati et al.[32] Our understanding of the incidence of the composition and structure of germanium selenide glasses on their elastic and viscous deformation is illustrated by the schematic drawings depicted in Fig. 6 and corresponding to the following situations: a) In glassy selenium 8-member rings chiefly predominate over chains. When the temperature approaches the transition range (Fig. 6b) rings progressively disappear to the benefit of chains and Poisson's ratio starts to increase due to the loss of the resistance against transverse shrinkage. Above the transition the fragmentation of the chains becomes more and more significant and some alignment of the fragments may be observed (Fig. 6c). The higher the temperature becomes and the smaller the fraction of rings and the number of atoms per Se chains (Fig. 6d) are. The addition of germanium results in the formation of relatively rigid $GeSe_{4/2}$ tetrahedra. As far as the germanium content remains below 20 at.%, the glass network exhibits weak selenium-rich path for shear in-between Ge-based tetrahedra. The glass network shows up like $GeSe_{4/2}$ tetrahedra clusters with few connections with a soft amorphous selenium matrix (Fig. 6e). When the germanium content is high enough, say for $x \geq 0.20$ ($GeSe_4$), a subnetwork of interconnected tetrahedra forms which brings stiffness to the glass (Fig. 6f). At germanium content over 25 at.% ($GeSe_3$), the cross-linked network provides numerous transverse stressed arms, likely to follow edge-sharing tetrahedra. Hence Poisson's ratio turns out to be quite small and to evolve little with temperature through the transition range. It is noteworthy however than in spite of a highly cross-linked network, there still remain some continuous channels between edge-shared $GeSe_{4/2}$ tetrahedra, which provide paths for the shear deformation (Fig. 6h). Moreover, increasing the temperature could increase the ratio of edge-shared tetrahedra, allowing such weak channels to extend[58]. Edwards et al.[58] even suggest that the corner to edge sharing transition could be the main process involved during shear flow and enthalpy relaxation, because these three processes have similar characteristic relaxation times. Nevertheless, these two latter should involve different structural events, as it is evidenced by their apparent activation energies (~110 kJ/mol for enthalpy relaxation[14], 243 kJ/mol for shear flow, for $GeSe_4$ – table III-). With rising temperature, Ge-rich and Se-rich regions have the tendency to form (a growing amount of homopolar Ge-Ge and Se-Se bonds are found with increasing temperature in liquid $GeSe_2$[52]) due to the ease for dissociation of $GeSe_2$. Thus the shear viscosity drops. The activation volumes (Table III) suggest volumes corresponding to a single atom for a-Se and few atoms for $GeSe_3$ and $Ge_3Se_7$. These values are certainly no more than rough indications due to the simplistic model used for their estimation. Nevertheless, they support the idea that

the relevant scale for flow is typically the chain link in the case of a-Se and the size of the tetrahedron when $GeSe_{4/2}$ units come into play.

## V. SUMMARY AND PERSPECTIVES

We have studied the high temperature elastic behavior and the shear viscosity of germanium selenide glasses in the transition range. Young's modulus and the shear modulus were measured by means of a resonant technique in the 5 to 10 kHz range. Viscosity was measured using a displacement- and load-controlled indentation apparatus. A steep increase in Poisson's ratio ($\nu$) starting slightly below $T_g$ was observed for a-Se whereas little changes were noticed for $GeSe_3$ and $GeSe_7$ compositions. Since $\nu$ was found previously in a couple of independent works[6-8] to be directly correlated to the network cross-linking degree, and to the mean coordination number in chalcogenide glasses, our results strongly suggest that over-constrained Ge-Se glasses experience minor structural changes in the transition range.

The viscous flow behavior could be well described by a pure Arrhenius-type law with a single apparent activation energy, $\Delta H_a$, for the flow process in the temperature range of concern (0.8 to $1.1T_g$). The estimated values for $\Delta H_a$ are in good agreement with those reported by previous investigators in the same temperature range and show a constant decrease with rising Ge content up to 20 at% Ge, that correlate with a minimum in reported heat flows at the glass transition. However for higher Ge contents, $\Delta H_a$ increases. We have applied the theory of thermally activated flow phenomena to analyze our data and derive the activation entropy for flow by means of both elasticity and viscosity data. It turns out that the activation entropy is very high for a-Se and decreases rapidly with rising Ge content. Consequently, the free enthalpy of the flow process is in fact much lower that $\Delta H_a$ for the Se-rich compositions. We propose that the entropy change is of an overwhelming part of elasticity origin and is intimately related to the fragmentation of the chains and probably to a lesser extent to the ring to chain transition. A sketch of the different events occurring in the studied glasses was drawn to describe the structural changes and the deformation mechanisms as a function of the composition. In particular special focus was made to explain the occurrence of easy shear zones in over-constrained Ge-Se compositions, notwithstanding the weak changes of $\nu$ observed in the same temperature range.

Most structural studies on germanium chalcogenide glasses were performed either at room temperature or in the liquid range for $T \gg T_g$. We feel that X-ray and neutron scattering conducted in situ in the transition range under stresses would be invaluable to get insight into

the stress-induced structural changes and thus into the deformation process. For instance this would allow estimating possible effects of the stress on the characteristics of the structural units (namely the Se-chains conformation and length, the inter- and intra-tetrahedral angles, the texturation etc.).

## ACKNOWLEDGMENTS

\*   Present address: LIMATB, EA-4250, UBS-LORIENT, Centre de Recherche, rue de Saint Maudé - BP92116, 56321 Lorient cedex, France.

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**TABLE I.** Measurements of elastic moduli and shear viscosity coefficient as a function of temperature. x: Non-measured.[1] as determined from the E(T) curves (Table II).

| T/T$_g$[1] | a-Se Tg=302 K | | | GeSe$_4$ Tg=416 K | | | GeSe$_3$ Tg=498 K | | | Ge$_3$Se$_7$ Tg=579 K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | E (GPa) | μ (GPa) | log$_{10}$ (Pa.s) | E (GPa) | μ (GPa) | log$_{10}$ η (Pa.s) | E (GPa) | μ (GPa) | log$_{10}$ η (Pa.s) | E (GPa) | μ (GPa) | log$_{10}$ η (Pa.s) |
| 0.930 | x | x | x | 12.45 | 5.06 | 14.69 | 14.07 | 5.60 | x | 16.40 | 6.51 | x |
| 0.935 | x | x | x | 12.41 | 5.04 | 14.56 | 14.02 | 5.58 | x | 16.38 | 6.50 | x |
| 0.940 | x | x | x | 12.37 | 5.03 | 14.43 | 13.96 | 5.56 | x | 16.35 | 6.48 | x |
| 0.945 | x | x | x | 12.33 | 5.01 | 14.30 | 13.90 | 5.54 | x | 16.32 | 6.47 | x |
| 0.950 | x | x | x | 12.30 | 4.99 | 14.17 | 13.84 | 5.52 | x | 16.29 | 6.46 | 13.71 |
| 0.955 | x | x | x | 12.26 | 4.98 | 14.04 | 13.78 | 5.50 | x | 16.26 | 6.45 | 13.61 |
| 0.960 | x | x | x | 12.23 | 4.97 | 13.91 | 13.72 | 5.48 | x | 16.23 | 6.43 | 13.51 |
| 0.965 | x | x | x | 12.19 | 4.95 | 13.78 | 13.65 | 5.46 | x | 16.19 | 6.41 | 13.40 |
| 0.970 | 9.65 | 3.87 | 13.71 | 12.15 | 4.93 | 13.65 | 13.58 | 5.44 | 13.10 | 16.15 | 6.40 | 13.29 |
| 0.973 | 9.60 | 3.86 | 13.51 | 12.13 | 4.92 | 13.57 | 13.54 | 5.43 | 13.02 | 16.13 | 6.39 | 13.22 |
| 0.976 | 9.54 | 3.85 | 13.32 | 12.11 | 4.91 | 13.49 | 13.50 | 5.42 | 12.94 | 16.10 | 6.38 | 13.15 |
| 0.979 | 9.49 | 3.83 | 13.13 | 12.09 | 4.90 | 13.41 | 13.45 | 5.41 | 12.86 | 16.08 | 6.38 | 13.08 |
| 0.982 | 9.43 | 3.82 | 12.94 | 12.07 | 4.88 | 13.34 | 13.41 | 5.40 | 12.78 | 16.05 | 6.37 | 13.00 |
| 0.985 | 9.36 | 3.80 | 12.74 | 12.05 | 4.87 | 13.26 | 13.36 | 5.38 | 12.69 | 16.03 | 6.36 | 12.93 |
| 0.988 | 9.30 | 3.78 | 12.55 | 12.03 | 4.86 | 13.18 | 13.32 | 5.37 | 12.61 | 16.00 | 6.35 | 12.85 |
| 0.991 | 9.23 | 3.76 | 12.36 | 12.00 | 4.85 | 13.10 | 13.27 | 5.36 | 12.53 | 15.97 | 6.34 | 12.78 |
| 0.994 | 9.16 | 3.71 | 12.17 | 11.98 | 4.83 | 13.02 | 13.22 | 5.35 | 12.45 | 15.94 | 6.32 | 12.70 |
| 0.997 | 9.09 | 3.71 | 11.97 | 11.96 | 4.82 | 12.95 | 13.18 | 5.33 | 12.37 | 15.90 | 6.31 | 12.62 |
| **1.000** | **9.00** | **3.67** | **11.78** | **11.88** | **4.81** | **12.87** | **13.00** | **5.30** | **12.29** | **15.89** | **6.30** | **12.54** |
| 1.003 | 8.89 | 3.60 | 11.59 | 11.84 | 4.80 | 12.79 | 12.94 | 5.27 | 12.21 | 15.84 | 6.29 | 12.46 |
| 1.006 | 8.77 | 3.51 | 11.40 | 11.81 | 4.78 | 12.71 | 12.88 | 5.24 | 12.13 | 15.78 | 6.27 | 12.38 |
| 1.009 | 8.65 | 3.40 | 11.20 | 11.77 | 4.77 | 12.64 | 12.82 | 5.22 | 12.06 | 15.73 | 6.26 | 12.30 |
| 1.012 | 8.52 | 3.27 | 11.01 | 11.74 | 4.75 | 12.56 | 12.75 | 5.19 | 11.98 | 15.68 | 6.25 | 12.21 |
| 1.015 | 8.39 | 3.12 | 10.82 | 11.70 | 4.74 | 12.48 | 12.69 | 5.16 | 11.90 | 15.62 | 6.23 | 12.13 |
| 1.018 | 8.25 | 2.97 | 10.63 | 11.66 | 4.73 | 12.40 | 12.63 | 5.14 | 11.82 | 15.57 | 6.22 | 12.05 |
| 1.021 | 8.11 | 2.81 | 10.43 | 11.63 | 4.71 | 12.33 | 12.57 | 5.11 | 11.74 | 15.52 | 6.20 | 11.96 |
| 1.024 | 7.96 | 2.65 | 10.24 | 11.59 | 4.70 | 12.25 | 12.51 | 5.09 | 11.67 | 15.46 | 6.19 | 11.88 |
| 1.027 | 7.80 | 2.50 | 10.05 | 11.55 | 4.68 | 12.17 | 12.46 | 5.06 | 11.59 | 15.41 | 6.17 | 11.79 |
| 1.030 | 7.65 | 2.36 | 9.85 | 11.51 | 4.67 | 12.09 | 12.40 | 5.04 | 11.52 | 15.35 | 6.15 | 11.71 |
| 1.033 | 7.48 | 2.22 | 9.66 | 11.47 | 4.65 | 12.02 | 12.34 | 5.01 | 11.44 | 15.30 | 6.14 | 11.62 |
| 1.040 | x | x | 9.21 | 11.37 | 4.61 | 11.84 | 12.21 | 4.96 | 11.26 | 15.17 | 6.09 | 11.42 |
| 1.060 | x | x | x | 11.08 | 4.50 | 11.32 | 11.84 | 4.80 | 10.77 | 14.78 | 5.96 | 10.85 |
| 1.080 | x | x | x | 10.76 | 4.38 | 10.81 | 11.50 | 4.65 | 10.30 | 14.38 | 5.81 | 10.30 |
| 1.100 | x | x | x | x | x | 10.30 | 11.17 | 4.51 | 9.84 | 13.96 | 5.64 | 9.79 |
| 1.120 | x | x | x | x | x | 9.79 | x | x | 9.40 | x | x | 9.33 |
| 1.140 | x | x | x | x | x | 9.28 | x | x | 8.97 | x | x | 8.95 |
| 1.160 | x | x | x | x | x | x | x | x | 8.56 | x | x | 8.66 |

**TABLE II.** Elastic properties of $Ge_xSe_{1-x}$ glasses. [1]From Differential Scanning Calorimetry; [2]Transition temperature observed in the E(T) measurement with the resonant technique. [3]Softening rates measured in the supercooled-liquid range.

| Glass | $T_g$[1] (K) | $T_g$[2] (K) | $E_{RT}$ (GPa) | $\mu_{RT}$ (GPa) | $\nu_{RT}$ | $E(T_g)$ (GPa) | $\mu(T_g)$ (GPa) | $dE/dT(T_g^+)$[3] (MPa.K$^{-1}$) | $d\mu/dT(T_g^+)$[3] (MPa.K$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| a-Se | 313 | 302 | 10.3 | 3.88 | 0.322 | 9.0 | 3.67 | -115 | -93.8 |
| GeSe$_4$ | 435 | 416 | 14.73 | 5.73 | 0.286 | 11.8 | 4.81 | -35.7 | -14.3 |
| GeSe$_3$ | 501 | 498 | 16.1 | 6.26 | 0.281 | 13.0 | 5.30 | -38.4 | -16.3 |
| Ge$_3$Se$_7$ | 573 | 579 | 17.9 | 7.08 | 0.264 | 15.9 | 6.30 | -30.8 | -11.3 |

**TABLE III.** Viscous flow properties in the transition range of $Ge_xSe_{1-x}$ glasses. [1]Temperature for $\eta=10^{12}$ Pa.s; [2]As defined by $m=dlog_{10}\eta/d(T(\eta=10^{12}$ Pa.s)/T)$=\Delta H_a/(2.303RT_g)$ [43]; and [3] $\Delta G_a$ measured near $T_g$, From the approach proposed by Nemilov [33,34]. nd: non-determined.

| Glass | $T_g$[1] (K) | $\Delta H_a$ (Eq.(6)) (kJ.mol$^{-1}$) | $\Delta G_a$ (Eq.(7)) (kJ.mol$^{-1}$) | $\Delta S_a$ (Eq.(8)) (J.K$^{-1}$.mol$^{-1}$) | $m$[2] | $\Delta G_a$[3] (kJ.mol$^{-1}$) | $\Delta S_a$[3] (J.K$^{-1}$.mol$^{-1}$) | $V*$[3] (m$^3$.mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| a-Se | 301 | 369 | 41 | 977 | 62 | 95 | 910 | 11.10$^{-6}$ |
| GeSe$_9$ | 356 | 249 | nd | nd | 36 | 112 | 383 | nd |
| GeSe$_4$ | 430 | 243 | 102 | 328 | 30 | 136 | 249 | 21.10$^{-6}$ |
| GeSe$_3$ | 492 | 256 | 107 | 303 | 27 | 155 | 204 | 20.10$^{-6}$ |
| Ge$_3$Se$_7$ | 580 | 294 | 145 | 160 | 27 | 183 | 191 | 23.10$^{-6}$ |

**Figure captions:**

FIG. 1a: Temperature dependence of Young's modulus (E).

FIG. 1b: Temperature dependence of the shear modulus ($\mu$). Note the rapid decrease of the shear modulus in a-Se for T>Tg, which contrasts with the decrease found for E.

FIG. 2a: Temperature dependence of the shear viscosity coefficient ($\eta$)

FIG. 2b: Determination of the apparent activation energy ($\Delta H_a$) from the viscosity data.

FIG. 3: Temperature dependence of Poisson's ratio (note that temperature is normalized to $T_g$ as estimated from the E(T) data)

FIG. 4: $T_g$-scaled logarithm of viscosity from which the fragility index is straightforwardly derived from the slope of the linear intercepts in the transition range. The scaling parameter used here is the temperature corresponding to a viscosity of $10^{12}$ Pa.s.

FIG. 5: Activation entropy as calculated from Eq. (7) accompanying the shear viscous flow process in the transition range for glasses with different degrees of network cross-linking.

FIG. 6: Schematic drawing illustrating the thermally induced changes and the consequences on the elastic and viscous behaviors. Dashed lines show transverse load bearing arms, which oppose lateral contraction upon pulling along a vertical axis. Solid lines show possible regions for easy shear slip. The loading axis has to be imagined vertical in the plane of the figure. a) to d): a-Se, with increasing temperature. e) and f): $Ge_xSe_{1-x}$ glasses with increasing germanium content for x<0.2. g) and h) at high germanium content (x$\geq$0.20), at rest and under stress.
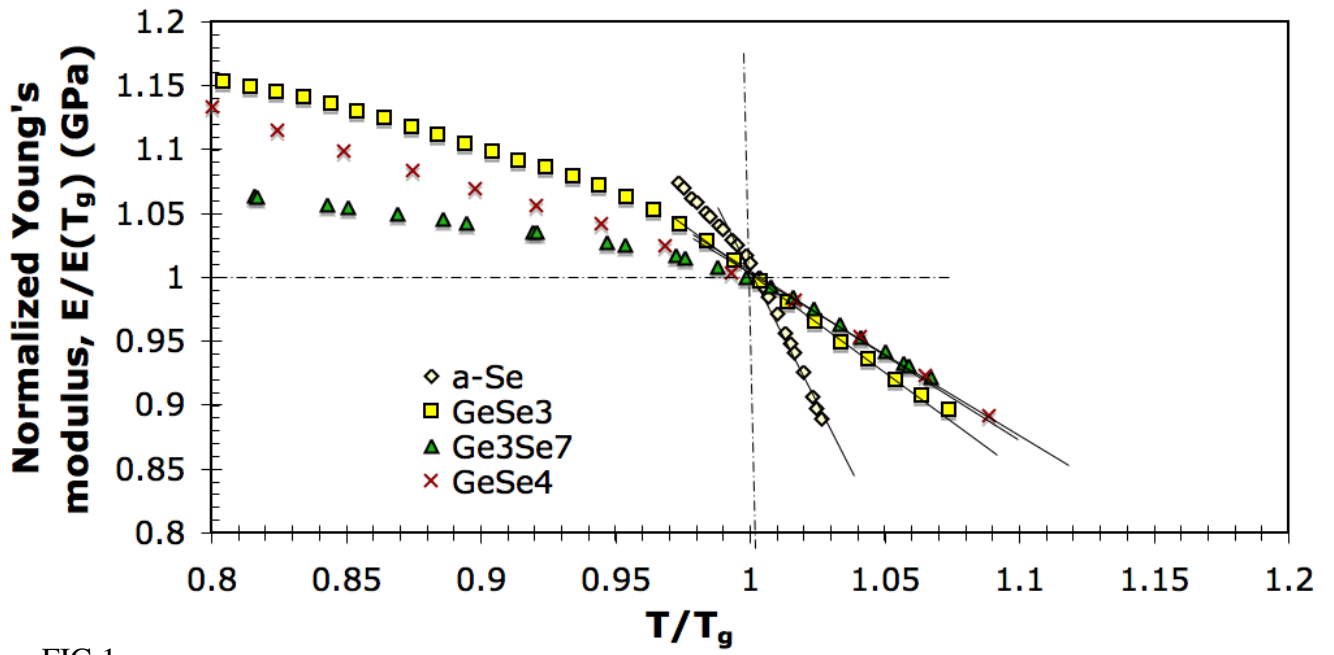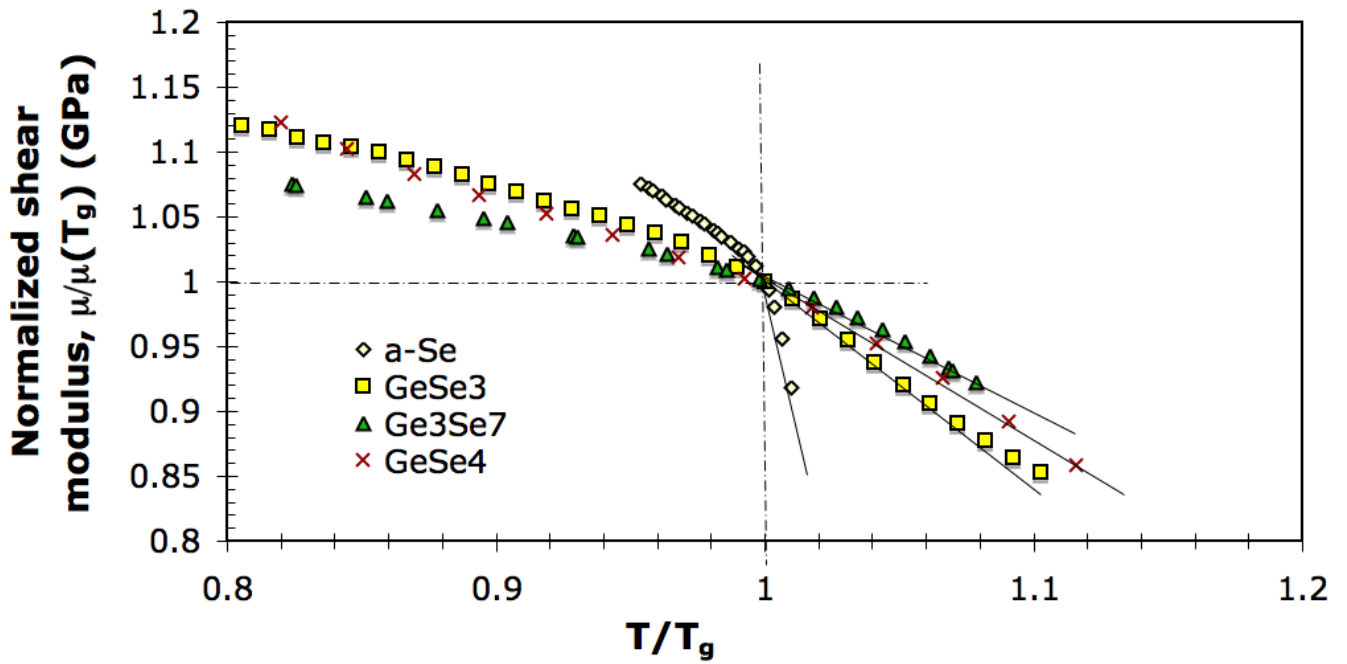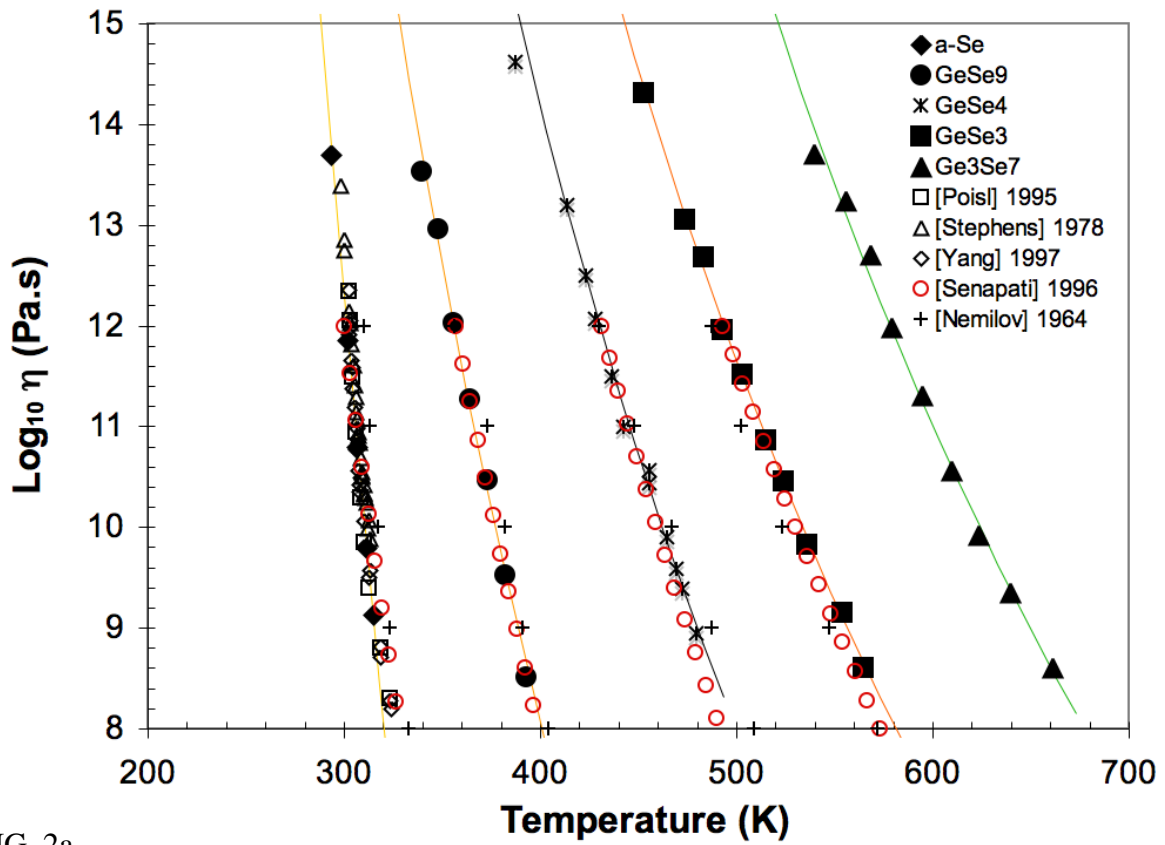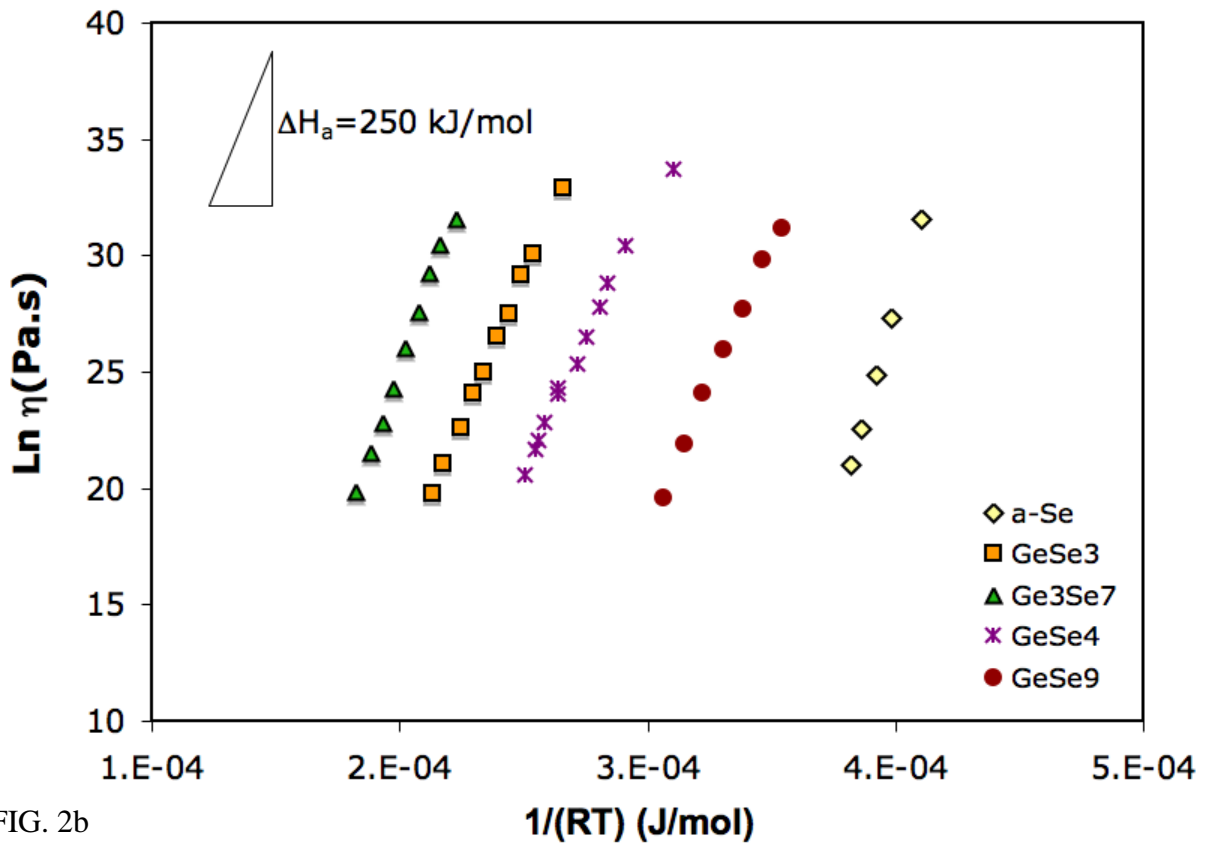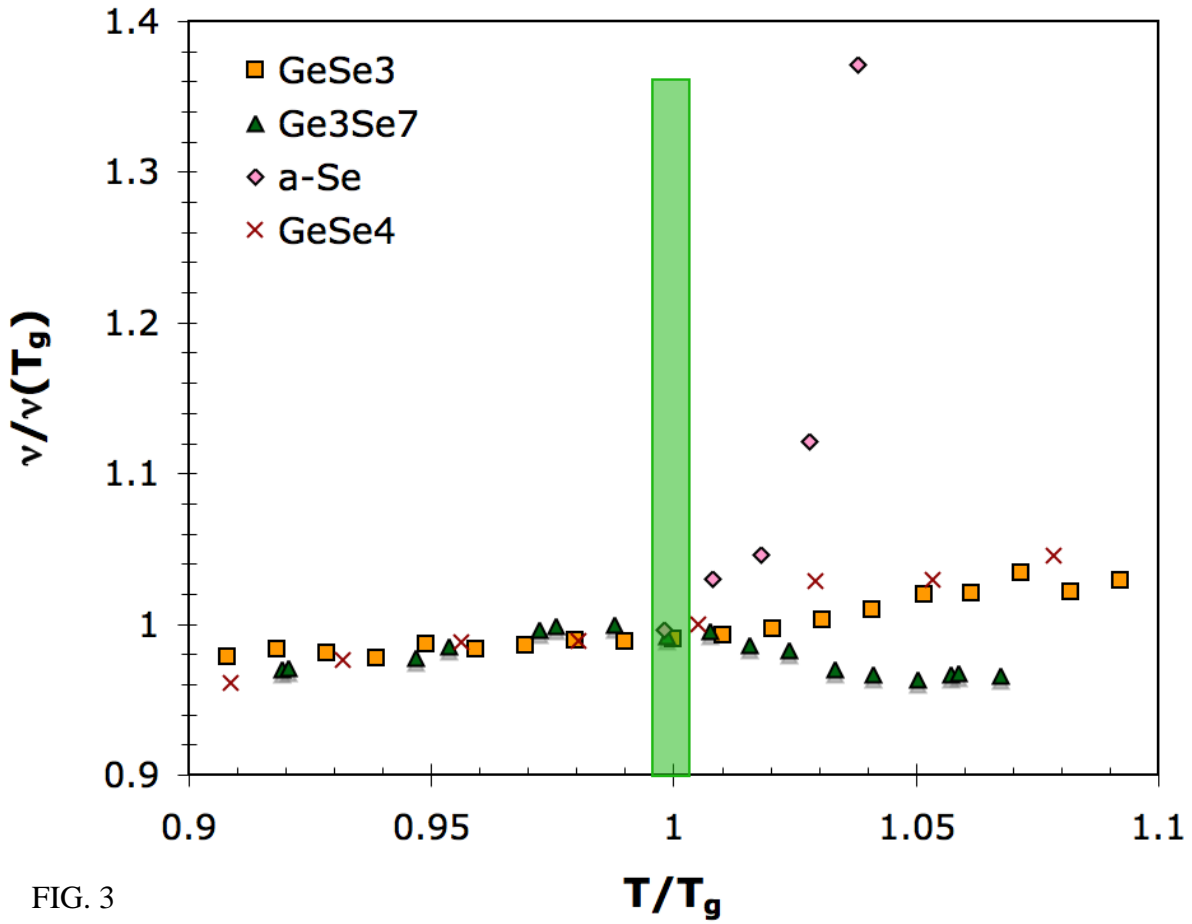
FIG.1a



FIG.1b

FIG. 2a



FIG. 2b

FIG. 3



FIG. 4

FIG. 5



FIG. 6