Stress Induced Alignment of Se Chains in Supercooled Ge₅Se₉₅ Liquid

Derrick C. Kaseman¹, Ivan F. Hung², Zhehong Gan², and *Sabyasachi Sen¹

¹ Department of Materials Science & Engineering, University of California at Davis, Davis, CA
95616, USA

² Center of Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory,
1800 East Paul Dirac Drive, Tallahassee, FL 32310, USA

*Corresponding Author, Tel: 530-902-2802, email: sbsen@ucdavis.edu

Abstract

The structural modifications in Ge₅Se₉₅ supercooled liquid under the application of a uniaxial compressive load are investigated using one- and two- dimensional ⁷⁷Se nuclear magnetic resonance spectroscopy. The spectroscopic results clearly demonstrate a stress-induced alignment of selenium chains in the structure of the liquid in planes perpendicular to the loading axis. The topological modifications due to this selenium chain alignment result in inefficient atomic packing in the liquid structure that is manifested in a decrease in the glass density and may have important implications in understanding the pronounced non-Newtonian shear thinning behavior observed in Se-rich chalcogenide glasses/liquids.

Introduction

Numerous studies in the literature have established detailed equilibrium structure-property relationships in glasses.¹⁻² However, little is known regarding such relationships in glasses derived from parent melts when these melts are subjected to large stress or strain rate relevant to various industrial forming processes, including but not limited to molding, extrusion, embossing and fiber drawing.³ Most importantly, the non-Newtonian flow response of a supercooled glass-forming liquid, when it is driven out of equilibrium via mechanical deformation, is intimately linked to its viability for various processing techniques and is of key significance in industry in controlling and optimizing the corresponding processing parameters. Inorganic glass-forming liquids typically display this non-Newtonian behavior in the form of shear thinning where the viscosity of the liquid decreases when the shear rate is increased beyond some threshold value.³⁻¹²

Chalcogenide glass-forming liquids, in particular sulfides and selenides, have been shown to display shear thinning behavior at low strain rates that are characteristic of polymers and well below those characteristic of oxide liquids.^{3,10-12} Systematic time-dependent indentation measurements on $\text{Ge}_x\text{Se}_{100-x}$ glasses were also shown to be consistent with the non-Newtonian shear thinning behavior where the strain-rate sensitivity monotonically increased with increasing Se content.⁴⁻⁷ This composition dependent strain-rate sensitivity was ascribed to the network topology and packing density.¹¹ For pure selenium, the localized plastic deformation due to nanoindentation is assumed to proceed via Se chain alignment and slippage. Increasing Ge concentration results in cross-linking of Se chains, which increases shear resistance and lowers strain-rate sensitivity.¹¹ Although the atomistic mechanism for shear thinning remains unclear, it has been argued that viscous flow at high stress or strain-rate is facilitated by the alignment and

displacement of Se chains, at least in glasses with high Se content.⁴ Nevertheless, direct structural evidence supporting the shear-induced alignment of the Se chain elements in selenide glasses/liquids remain lacking to date. Here we present the results of a ⁷⁷Se nuclear magnetic resonance (NMR) spectroscopic study of the structural response of Ge₅Se₉₅ supercooled liquid quenched under uniaxial compression from immediately above its glass transition temperature T_g. The observation of partial alignment of Se chains under compression is correlated to the atomic packing in the glassy state via density measurements. This chain alignment is hypothesized to be the atomistic mechanism for shear thinning in the liquid state.

Experimental

Synthesis and uniaxial loading

Ge₅Se₉₅ glass was synthesized by the melt quenching method. A mixture of the constituent elements (99.999% metals basis purity) was melted under vacuum in a sealed quartz ampule and held at 1073K for 24 hrs before quenching in water. The resulting glass was then annealed in a furnace at 343K. The quartz tube containing the glass was cut into ~10 mm sections using a diamond saw and placed in 48 wt% HF acid for 48 hrs to etch away the quartz glass. 10mm long rods (4mm diameter) of Ge₅Se₉₅ glass were recovered from the acid, rinsed with water and dried in air. The T_g of this glass was measured using a Mettler-Toledo DSC1 calorimeter. Scans were performed in a flowing nitrogen environment on 15 mg of sample loaded into a 40 μ L aluminum crucible. The T_g was determined to be ~77°C, as the onset of the glass transition region, when heating at a rate of 10 °C /min.

The Ge₅Se₉₅ glass rods were placed between flat tungsten carbide dyes after coating each sample end with MoS₂ paste to prevent binding. The sample and dyes were placed in an

Instron® hydraulic tensile tester enclosed in a clamshell furnace. Inert Ar gas was flown over the sample while the temperature was raised to $\sim 79\text{ }^{\circ}\text{C}$ ($T_g+2\text{K}$). A schematic of the experimental setup is shown in Fig. 1. Once the temperature was equilibrated over 10 minutes, the sample was compressed to a disk of thickness $\sim 0.7\text{ mm}$ by advancing the Instron arms at a rate of 0.5 mm/min , corresponding to a maximum stress of 140 MPa . The sample was cooled to room temperature while under compression by increasing the flow of Ar gas over the sample and simultaneously opening the furnace. Pressure was released after cooling and the glass disk was cut into thin strips ($3\text{mm} \times 10\text{ mm}$) using a diamond saw. The amorphous nature of the samples before and after the compression was verified using powder X-ray diffraction measurements. Their amorphous nature is also corroborated by the ^{77}Se NMR results (*vide infra*).

^{77}Se NMR spectroscopy

The static ^{77}Se NMR line shape measurements were performed at a magnetic field 11.7 T (^{77}Se Larmor frequency = 99.3 MHz) using a Bruker AQS spectrometer. The sample strips were placed in a glass tube inside the horizontal *rf* coil of a Bruker 5mm wideline probe and NMR spectra were acquired with two different sample orientations. In one case the strips were oriented such that the compression axis was oriented with respect to the external magnetic field at 0° and in another case at 90° . Spectra were acquired using a Hahn echo sequence, consisting of a $\pi/2$ ($2.2\text{ }\mu\text{s}$) and a π pulse ($4.4\text{ }\mu\text{s}$) separated by an inter-pulse delay of $157.5\text{ }\mu\text{s}$ and a recycle delay of 30 s . For each sample orientation the ^{77}Se spectrum was obtained by averaging and Fourier transforming 1600 free induction decays.

The two-dimensional (2D) magic-angle-spinning (MAS) rotor synchronization experiments⁸⁻
⁹ were performed at the National High Magnetic Field Laboratory at a magnetic field of 19.6 T

(^{77}Se Larmor frequency = 158.8 MHz) using a Bruker DRX console. The rotor-synchronized 2D NMR experiment was originally developed for measuring orientational ordering in liquid crystals and polymers and was subsequently applied to oxide glasses.^{16,17} In this experiment, the NMR spectra are collected by synchronizing the rf pulse with rotor position and a series of spectra/slices are collected while incrementing the rotor phase in the t_1 dimension. For a total of n slices in the second dimension, the rotor phase is advanced by $2\pi/n$ for the collection of each slice. The 2D spectrum is obtained after a second Fourier transformation with respect to the rotor phase. Such a spectrum is quite sensitive to any structural alignment in a sample. For example, in the absence of any alignment, all slices in the t_1 dimension will yield identical spectra and hence, after Fourier transformation only the center slice in the 2D spectrum will have spectral intensity. However, in the presence of structural alignment, signal collected at different rotor phase will be different and after Fourier transformation spectral signature will be observed in other slices besides the center slice in the 2D spectrum.

Two 2D MAS rotor-synchronized ^{77}Se spectra were collected using two different orientations of the sample: in one case the strips were placed in a 4mm ZrO_2 rotor such that the compression axis was oriented parallel to the rotor axis and in the other case it was perpendicular. The samples were loaded into 4mm rotors and spun at 5kHz, while keeping the compression axis of the sample perpendicular or parallel to the rotor axis. A home-built 4mm probe with a Samoson MAS stator was used and the sample was spun at 5 kHz. A Hahn-echo sequence ($\pi/2$ pulse length of 2.0 μs) was employed for collection of each slice in the t_1 dimension. Rotor-synchronized ^{77}Se Car-Purcell-Meiboom-Gill (CPMG) spikelet spectra were acquired with the regular CPMG sequence after t_1 time delay triggered by the TTL signal from the MAS controller. The recycle delay was 60 s. Eight t_1 increments were collected with 512 scans for each slice and

the 2D spectra were obtained after Fourier transformation in the t_1 dimension. All ^{77}Se NMR spectra were referenced externally to a standard of NH_4SeO_3 ($\delta_{\text{iso}}=1040.2$ ppm).

Density Measurements

Density measurements were performed using a Micromeritics AccuPyc II gas expansion (Helium, 6N purity) pycnometer. Samples of mass 0.5 to 1.0 g were loaded into a 1 cm³ cup. The densities reported are averages of 10 consecutive measurements at 20 °C and are determined to within ± 0.005 g/cm³.

Results and Discussion

The results of the orientation dependence of the static ^{77}Se NMR spectra for the compressed glass sample are shown in Fig. 2. The ^{77}Se NMR spectrum, irrespective orientation of the compression axis with respect to the magnetic field, consists of a broad and somewhat asymmetric line shape extending from 1150 to 400 ppm. Previous analyses of the ^{77}Se static and MAS NMR spectrum of $\text{Ge}_5\text{Se}_{95}$ glass indicated the presence of two peaks at 850 ppm and 550 ppm, corresponding to Se-**Se**-Se and Ge-**Se**-Se environments, respectively, with the dominant peak at 850 ppm.¹⁰⁻¹¹ The ^{77}Se static NMR spectra shown in Fig. 2 are consistent with this observation and display a maximum intensity near 850 ppm with a slight asymmetry on the low frequency side (towards lower ppm values) due to the presence of the Ge-**Se**-Se environments. As these spectra were acquired under static conditions, significant broadening was introduced from the ^{77}Se chemical shift anisotropy resulting in overlapping line shapes. In addition, the relatively short recycle delay used in these NMR experiments is expected to result in preferential enhancement of the peak corresponding to the Se-**Se**-Se chain environments, due to the differential spin-lattice relaxation known to be present in these glasses.¹² On the other hand, the

overlap between the ^{77}Se resonances of the two Se sites and the differential relaxation are inconsequential as no quantitative analysis of the relative fractions of these Se environments is attempted in this study. Rather, in this study we focus on the response of the Se chain environments under uniaxial compressive stress and thus, the preferential enhancement of the Se-Se-Se peak in the ^{77}Se NMR spectra facilitates the structural analyses.

The dependence of spectral intensity on sample orientation is commonly observed in single-crystal NMR spectroscopy where the principal components of the chemical shift tensor yield different chemical shift values and intensities based on the angular orientation of the crystal with respect to the external magnetic field. By the same token, orientation dependence is not observed in powdered crystals or conventional glasses which are isotropic, such that the principal components of the chemical shift tensor of a nuclide randomly sample all possible orientations with respect to the magnetic field and yield an orientation-invariant line shape. However, if alignment of structural units occurs in a melt during the application of pressure and remains preserved in the glassy state after cooling, the NMR spectrum would exhibit an orientation dependent line shape, as is clearly observed in Figs. 2a,b. It is apparent from Fig. 2a that a change in the sample orientation, such that the compression axis rotates from 0° to 90° relative to the external magnetic field, causes significant changes in the ^{77}Se NMR line shape. Near the peak maximum at 850 ppm, the ^{77}Se NMR spectrum collected with the compression axis oriented at 90° has lower (higher) intensity in the region between 1000-850 (850-800) ppm compared to the spectrum collected at an orientation of 0° . This orientation dependence of spectral intensity is particularly apparent in the difference spectrum shown in Fig. 2a. Another difference spectrum in Fig. 2b shows the distinction between the ^{77}Se static spectrum of the compressed glass sample with the compression axis oriented parallel to the magnetic field and

that of the sample, when crushed into a powder. The ^{77}Se static NMR spectrum of the compressed glass sample collected after the sample was crushed into powder is compared with that of the as-made glass in Fig. 2c. The similarity between these two spectral line shapes in Fig. 2c indicates that the crushed powder exhibits no orientation dependence, as expected. When taken together, these results imply that the orientation dependence of the ^{77}Se static NMR spectra of the compressed sample must arise from the structural alignment of the Se-Se-Se chain environments that resulted during uniaxial compression.

The 2D MAS rotor-synchronized ^{77}Se NMR spectra collected for the compressed glass with the compression axis being oriented parallel and perpendicular to the rotor axis are compared in Fig. 3 to further confirm the Se chain alignment in the compressed sample and to determine the direction and degree of the alignment with respect to the compression axis. The spectrum in Fig. 3a shows the absence of any significant signal intensities in all slices except in the center slice when the compression axis is parallel to the rotor axis indicating that in case of any orientational ordering in the structure, the compression axis will have to be coincident with the order axis. The existence of orientational ordering becomes clear in the spectrum shown in Fig. 3b, corresponding to the case when the compression axis is perpendicular to the rotor axis, as clear signal intensities can be observed in slices adjacent to the center slice (Fig. 3b). These results, when taken together, therefore provide direct evidence for an alignment of Se chains in the $\text{Ge}_5\text{Se}_{95}$ glass/liquid structure in planes perpendicular to the compression axis.

The effect of this chain alignment on the atomic packing is reflected in the density of these glass samples. The measured density for the uncompressed i.e. as-made glass is 4.32 g/cm^3 , in excellent agreement with a previous study²¹, while that of the compressed glass is 4.25 g/cm^3 . This result is consistent with the expectation that increasing alignment of Se chains would lower

the effective dimensionality and consequently the packing efficiency of the structure, leading to a decrease in the density. The stress-induced alignment of the Se chains can also provide a structural explanation for the non-Newtonian response exhibited by Se-rich $\text{Ge}_x\text{Se}_{100-x}$ glasses under relatively low strain rates. Chain alignment upon shearing is a well-known phenomenon in organic polymer melts that facilitates the sliding motion of chains past one another and lowers the probability of chain entanglement, which can in turn lower the effective viscosity of the liquid resulting in shear thinning. Similar behavior can also be expected in Se-rich chalcogenide liquids where the viscous flow is likely controlled by the sliding of relatively long segments of Se chains. In fact, Aitken and coworkers have shown in a previous study that Se-rich chalcogenide liquids indeed display non-Newtonian response that is comparable to organic polymers.³

Conclusions

Stress induced structural alignment of Se chains is demonstrated in $\text{Ge}_5\text{Se}_{95}$ supercooled liquid immediately above its glass transition. The alignment of Se chains results in inefficient atomic packing and may likely facilitate viscous flow via chain sliding by avoiding chain entanglement. This structural scenario provides an atomistic explanation for the experimentally observed pronounced non-Newtonian response of Se-rich chalcogenide glasses and liquids in the form of shear thinning.

Acknowledgement

This work was supported by a grant from the National Science Foundation (NSF-DMR 1505185) to SS. The National High Magnetic Field Laboratory is supported through the National Science Foundation Cooperative Agreement (DMR-1157490) and by the State of Florida. The authors wish to thank J. Schoenung and H. Yang for assistance with the experimental setup.

References

1. J. E. Shelby, Introduction to glass science and technology. 2nd ed.; The Royal Society of Chemistry: Cambridge, 2009.
2. A. K. Varshneya, Fundamentals of inorganic glasses. Elsevier: 2013.
3. B. G. Aitken, S. C. Currie, B. C. Monahan, L. Wu, E. W. Coonan, Chalcogenide glass for low viscosity extrusion and injection molding. U.S. Patent 7116888B1, Apr. 13, 2006.
4. J. H. Simmons, What is so exciting about non-linear viscous flow in glass, molecular dynamics simulations of brittle fracture and semiconductor-glass quantum composites, J. Non-Cryst. Solids 239 (1998) 1-15.
5. J. H. Simmons, R. K. Mohr, C. Montrose, Non-newtonian viscous flow in glass, J. Appl. Phys. 53 (1982) 4075-4080.
6. A. Habek, R. Brückner, Direct connection between anisotropic optical properties, polarizability and rheological behaviour of single-phase glass melts, J. Non-Cryst. Solids 162 (1993) 225-236.
7. J. Li, D. R. Uhlmann, The flow of glass at high stress levels: I. Non-newtonian behavior of homogeneous 0.08 Rb₂O-0.92 SiO₂ glasses, J. Non-Cryst. Solids 3 (1970) 127-147.
8. R. Brückner, Y. Yue, Non-newtonian flow behaviour of glass melts as a consequence of viscoelasticity and anisotropic flow, J. Non-Cryst. Solids 175 (1994) 118-128.
9. R. Brückner, Response and structure of glass melts under extreme forming processes, J. Non-Cryst. Solids 73 (1985) 421-449.
10. J. P. Guin, T. Rouxel, V. Keryvin, J. C. Sangleboeuf, I. Serre, J. Lucas, Indentation creep of Ge-Se chalcogenide glasses below T_g: Elastic recovery and non-newtonian flow, J. Non-Cryst. Solids 298 (2002) 260-269.
11. R. Limbach, B.P. Rodrigues, L. Wondraczek, Strain-rate Sensitivity of Glasses, J. Non-Cryst. Solids 404 (2014) 124-134.
12. S. Wang, C. Jain, L. Wondraczek, K. Wondraczek, J. Kobelke, J. Troles, C. Caillaud, M.A. Schmidt, Appl. Phys. Lett. 106 (2015) 201908.
13. M. Cukierman, D. R. Uhlmann, Viscous flow behavior of selenium, J. Non-Cryst. Solids 12 (1973) 199-206.
14. W. H. Poisl, W. C. Oliver, B. D. Fabes, The relationship between indentation and uniaxial creep in amorphous selenium, J. Mater. Res. 10 (1995) 2024-2032.
15. E. Jenckel, The structural viscosity of softening selenium glass, Kolloid-Z. 84 (1938) 266-268.
16. M. Braun, Y. Yue, C. Rüssel, C. Jäger, Two-dimensional nuclear magnetic resonance evidence for structural order in extruded phosphate glasses, J. Non-Cryst. Solids 241 (1998) 204-207.
17. K. Schmidt-Rohr and H. W. Spiess, *Multidimensional Solid-State NMR and Polymers*. Academic Press: 1994.
18. D. C. Kaseman, I. Hung, Z. Gan, S. Sen, Observation of a continuous random network structure in Ge_xSe_{100-x} glasses: Results from high-resolution Se-77 MATPASS/CPMG NMR spectroscopy, J. Phys. Chem. B 117 (2013) 949-954.
19. E. L. Gjersing, S. Sen, B. G. Aitken, Structure, connectivity, and configurational entropy of Ge_xSe_{100-x} glasses: Results from Se-77 MAS NMR spectroscopy, J. Phys. Chem. C 114 (2010) 8601-8608.

20. S. Sen, D. C. Kaseman, I. Hung, Z. H. Gan, Se-77 nuclear spin-lattice relaxation in binary Ge-Se glasses: Insights into floppy versus rigid behavior of structural units, J. Phys. Chem. B 119 (2015) 5747-5753.
21. G. Yang, Y. Gueguen, J. C. Sangleboeuf, T. Rouxel, C. Boussard-Pledel, J. Troles, P. Lucas, B. Bureau, Physical properties of the $\text{Ge}_x\text{Se}_{1-x}$ glasses in the $0 < x < 0.42$ range in correlation with their structure, J. Non-Cryst. Solids 377 (2013) 54-59.

Figure Captions:

Figure 1: Experimental setup for uniaxial loading of the $\text{Ge}_5\text{Se}_{95}$ supercooled liquid.

Figure 2: A comparison on the ^{77}Se static NMR line shapes of the compressed $\text{Ge}_5\text{Se}_{95}$ glass with the compression axis in different orientations with respect to the external magnetic field. (a) Comparison between spectra obtained with the compression axis at 0° (black solid line) and at 90° (red solid line) with respect to the external magnetic field. (b) Comparison between spectra obtained with the compression axis at 90° (red solid line) with respect to the external magnetic field and after crushing the compressed sample (orange dashed line). (c) Comparison between spectra of the as-made glass (green dotted line) and the compressed glass after crushing (orange dashed line). In each case, the difference spectrum (solid blue lines) is shown below.

Figure 3: 2D rotor-synchronized ^{77}Se MAS NMR spectra CPMG spikelet patterns obtained for the compressed glass sample with the compression axis oriented parallel (a) and perpendicular (b) to the rotor axis. The sample (pink rectangles) orientation inside the rotor (black rectangle) is shown schematically to the left of each spectrum where the external magnetic field B_0 is denoted with vertical arrow and the rotor axis with a dashed line. Compression axis is parallel to the width of the pink rectangles. Spectral intensity of the center slice is scaled down by a factor of 40 for better visualization purposes.

Figure 1

Figure 2

Figure 3