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Letter to the editor

Stress induced alignment of Se chains in supercooled Ge₅Se₉₅ liquidDerrick C. Kaseman^a, Ivan F. Hung^b, Zhehong Gan^b, Sabyasachi Sen^{a,*}^a Department of Materials Science & Engineering, University of California at Davis, Davis, CA 95616, USA^b Center of Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, FL 32310, USA

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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.

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1. 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 [3,10–15]. Systematic time-dependent indentation measurements on Ge_xSe_{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 [11]. 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. Nevertheless, direct structural evidence supporting the shear-induced alignment of the Se chain elements in selenide glasses/liquids remains 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.

2. Experimental

2.1. 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 1073 K for 24 h before quenching in water. The resulting glass was then annealed in a furnace at 343 K. 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 h to etch away the quartz glass. 10 mm long rods (4 mm diameter) of Ge₅Se₉₅ glass were recovered from the acid,

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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 μL aluminum crucible. The T_g was determined to be $\sim 77^\circ\text{C}$, as the onset of the glass transition region, when heating at a rate of $10^\circ\text{C}/\text{min}$.

The $\text{Ge}_5\text{Se}_{95}$ glass rods were placed between flat tungsten carbide dyes after coating each sample end with MoS_2 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 $\sim 79^\circ\text{C}$ ($T_g + 2\text{K}$). A schematic of the experimental setup is shown in Fig. 1. Once the temperature was equilibrated over 10 min, the sample was compressed to a disk of thickness $\sim 0.7\text{ mm}$ by advancing the Instron arms at a rate of $0.5\text{ mm}/\text{min}$, 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).

2.2. ^{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 5 mm 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 $\pi/2$ ($2.2\ \mu\text{s}$) and a π pulse ($4.4\ \mu\text{s}$) separated by an inter-pulse delay of $157.5\ \mu\text{s}$ 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 experiments 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 4 mm 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 4 mm rotors and spun at 5 kHz , while keeping the compression axis of the sample perpendicular or parallel to the rotor axis. A home-built 4 mm 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 $2.0\ \mu\text{s}$) 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 ($\delta_{\text{iso}} = 1040.2\text{ ppm}$).

2.3. 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 cm^3 cup. The densities reported are averages of 10 consecutive measurements at 20°C and are determined to within $\pm 0.005\text{ g}/\text{cm}^3$.

3. 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 of 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 [18,19]. 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 [20]. 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

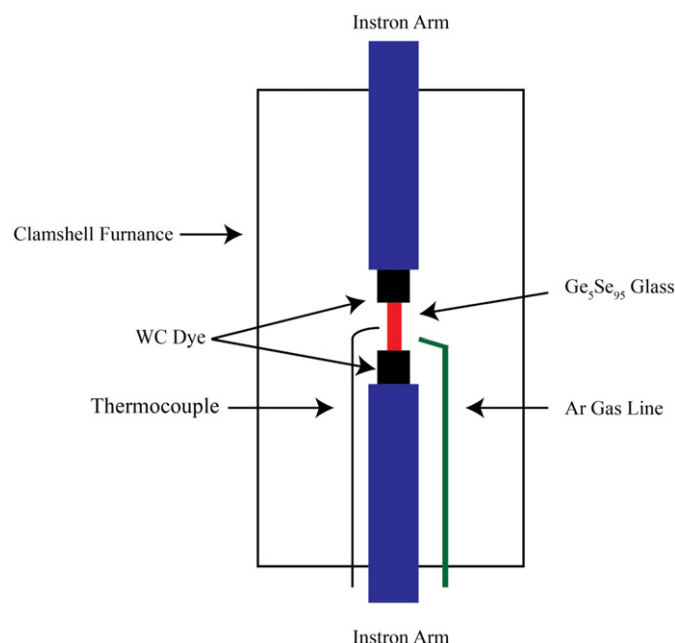


Fig. 1. Experimental setup for uniaxial loading of the $\text{Ge}_5\text{Se}_{95}$ supercooled liquid.

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