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Aging-Induced Structural Evolution of a $GeSe_2$ Glass Network: The Role of Homopolar Bonds

Bing Yuan, Hao Chen, and Sabyasachi Sen*

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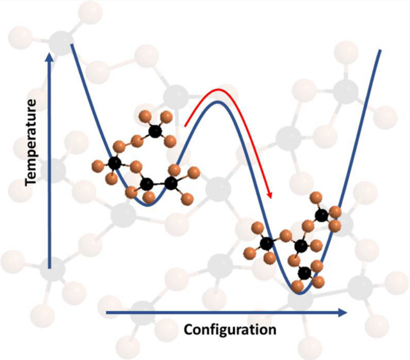
ABSTRACT: The structural evolution of $GeSe_2$ glass during aging is studied using Raman spectroscopy and density relaxation measurements. The Raman spectra indicate volume- and entropy-driven changes in the relative concentrations of the corner-sharing (CS) and edge-sharing (ES) $GeSe_4$ tetrahedra and in the degree of chemical order of the tetrahedral network during aging at 65 °C below the nominal glass transition temperature. The attendant structural changes involve a progressive increase in the CS:ES ratio and in the chemical order that can be expressed in the form of a reaction Ge−Ge + Se−Se → 2 Ge−Se, which shifts to the right, with lowering of fictive temperature. The isothermal relaxation of both the structure and density during aging displays rather similar stretched exponential kinetics with a stretching exponent β ∼0.54 and an average relaxation time of ∼13.5 h. *In situ* high-temperature Raman spectroscopic measurements indicate that structural relaxation does not affect the anharmonicity of the vibrational potential wells in the energy landscape of $GeSe_2$ glass.



1. INTRODUCTION

Chalcogenide glasses display unique optical properties in the infrared region, which make them attractive candidates for various applications in photonics, telecommunication, and remote sensing.[1−4] Therefore, the structure of these glasses, especially those in the Ge−As−Se system, was studied in detail in the past using a wide variety of spectroscopic and diffraction techniques to establish the structure−property relationships as a function of composition.[5−11] However, the glassy state not being in thermodynamic equilibrium, the atomic structure, and hence the properties of a glass may also depend on its thermal history and consequently on the resulting fictive temperature T_f. A knowledge of this dependence is therefore key in optimizing the processing conditions of glasses to obtain the desired properties. Furthermore, fundamental understanding of temperature-induced structural changes in a glass-forming liquid or of such changes during annealing of the derived glass below its glass transition temperature T_g, i.e., aging, can shed light on the nature of the configurational entropy S_{conf} of the liquid and its temperature dependence. It may be noted that S_{conf} (T) has been related in a number of theoretical models to the temperature-dependent evolution of the relaxation time-scale associated with the transport properties of glass-forming liquids in the transition range.[12,13]

Previous studies of temperature dependence of the atomic structure of oxide glasses and glass-forming liquids have demonstrated that the bond scission-renewal dynamics between the network-forming cations (e.g., Si, P, and B) and oxygen are primarily responsible for the reconfiguration and relaxation of the structural network in response to any change in temperature or in T_f.[14,15] However, the structural mechanisms of relaxation remain less clear for chalcogenide glasses and liquids, even for those in the archetypal Ge−Se and As−Se systems. A recent ^{77}Se dynamical nuclear magnetic resonance spectroscopic study of supercooled $As_{10}Se_{90}$ liquid[16] has demonstrated the coexistence of a slow process of chemical exchange between the various Se environments via bond scission/renewal and a fast process of Se chain segmental motion, and both processes were found to be coupled to viscous flow and shear relaxation near T_g. On the other hand, spectroscopic studies on $As_{30}Se_{70}$ glass have indicated that prolonged (20 years) aging at ambient temperature results in a net conversion of two As−Se−Se−As linkages into one As−Se−As and another As−Se−Se−Se−As linkage.[17] In the case of the Ge−Se system, previous Raman spectroscopic studies have shown that the most prominent aging-induced T_f -dependent structural change in glasses with excess Se (70−90% Se) involves the conversion of the edge-shared $GeSe_4$ tetrahedra into corner-shared tetrahedra.[18,19] The timescale of this conversion process was shown to be consistent with that of enthalpy relaxation and to be an important source of S_{conf} in supercooled $Ge_{20}Se_{80}$ liquid near the glass transition range.

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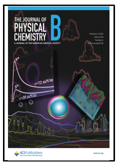

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Similarly, T_f -dependent tetrahedral speciation was reported in a recent Raman spectroscopic study to be responsible for the structural relaxation of $Si_{25}Se_{75}$ glass during aging at 40 K below T_g.[20] This tetrahedral speciation was shown to involve a conversion of two doubly edge-shared $SiSe_{4/2}$ tetrahedra (E^2) into a singly edge-shared (E^1) and another corner-shared (E^0) tetrahedra upon lowering of T_f with aging, which can be expressed as $2E^2 \rightarrow E^0 + E^1$.

Besides the heteropolar Ge−Se bonds associated with the corner- and edge-shared $GeSe_4$ tetrahedra, the Ge−Se glasses with Ge contents close to the stoichiometric $GeSe_2$ composition also contain a significant fraction of homopolar Ge−Ge bonds, indicating a violation of chemical order in glasses with ≤33.33% Ge.[18,21] Such violation of chemical order is likely entropically stabilized in these glasses and possibly more so in their parent liquids. However, to the best of our knowledge, the role of these homopolar bonds in the structural relaxation of these glasses during aging has never been investigated in the past. Here, we report the results of a Raman spectroscopic study of structural relaxation in the three-dimensionally connected tetrahedral network structure of nominally stoichiometric $GeSe_2$ glass consisting of corner- and edge-sharing $GeSe_4$ species (denoted as CS and ES, respectively, in the subsequent discussion for the sake of brevity) as well as ethane-like Se_3−Ge−Ge−Se_3 units as a function of T_f. Furthermore, the structural relaxation of this glass is compared with the corresponding relaxation of its density and thus of the atomic packing.

A second objective of this study is the investigation of the nature of the anharmonic properties of the vibrational excitations in the potential energy landscape (PEL) of $GeSe_2$ glass and whether structural relaxation during aging exerts any influence on this anharmonicity. In the PEL theory, the metabasins in the energy landscape represent the “inherent states”, i.e., the stable atomic configurations in the liquid/glass.[22] The viscous flow and primary (α) structural relaxation involve thermally activated jumps between these metabasins, while secondary (β) relaxation processes are attributed to localized structural rearrangements represented by smaller sub-basins inside the metabasins. On the other hand, vibrations are extremely localized high-frequency excitations that reside deep within these metabasins or sub-basins. It is generally assumed that these excitations remain essentially unchanged as the supercooled liquid/glass sinks into metabasins with progressively lower energy on cooling (for $T > T_g$) or on aging (for $T < T_g$), though the validity of this assumption remains to be confirmed in network glasses and liquids. In the present study, we have utilized *in situ* high-temperature Raman spectroscopy to investigate the effect of aging on the anharmonicity of the vibrational potential wells in the PEL of $GeSe_2$ glass.

2. EXPERIMENTAL DETAILS

2.1. Sample Synthesis. The $GeSe_2$ glass was synthesized in a 5 g batch by mixing the constituent elements Ge and Se with ≥99.995% purity (metals basis) in an evacuated (10^{-6} Torr) and flame-sealed fused silica ampoule. The mixture was first heated to 930 °C over 20 h followed by 15 h of rocking to ensure homogeneity of the melt. The ampoule was subsequently quenched in ice water. Several pieces of the as-quenched $GeSe_2$ glass with individual sample sizes of approximately 1.0 g were subsequently sealed in separate evacuated fused silica ampoules and were annealed at 345 °C (T_g = 410 °C) for durations ranging from 1 h to 1 week followed by quenching in air to study the relaxation kinetics during aging.

2.2. Density Measurements. The densities of as-quenched and annealed/aged $GeSe_2$ samples were measured using a Micromeritics Accupyc II gas expansion pycnometer under a helium environment of 6 N purity. Each measurement was carried out on ~1.0 g of the sample loaded into a 1 cm^3 cup. Density values reported in this study are averages of 10 consecutive measurements at room temperature.

2.3. Raman Spectroscopy. A Bruker RFS 100/s Fourier-transform (FT) Raman spectrometer equipped with a Nd:YAG laser operating at 1064 nm was used to collect the unpolarized Raman spectra of the as-quenched and annealed $GeSe_2$ glass samples at ambient temperature in backscattering geometry. A power level of 30 mW was used, and the experimental resolution was configured to 3 cm^{-1}. A total of 128 scans were collected and averaged to obtain each Raman spectrum.

Variable temperature Raman spectra were collected using the same spectrometer and laser along with a confocal microscope (Olympus BX51M) attachment. As-quenched and annealed $GeSe_2$ glass samples of dimensions ~1 × 1 mm and thicknesses of ~100 μm were heated on a commercial hot stage (THMS600, Linkam Scientific Instruments Ltd.). Temperature control was achieved through the use of a TMS94 temperature programmer connected to the stage. The temperature of the stage was calibrated using known phase transitions in crystalline standards.[23] Laser light was focused on the sample using a long working distance objective (Olympus LMPlanFL, magnification of 20×, numerical aperture of 0.4, and working distance of 12 mm). Spectra were collected at 50 °C intervals between 20 and 300 °C. The samples were equilibrated at each temperature for several minutes before data collection. A power level of 400 mW was used, and 512 scans were collected and averaged (~30 min) at each temperature to obtain the Raman spectrum.

3. RESULTS AND DISCUSSION

The temporal evolution of density ρ of the $GeSe_2$ glass upon aging is shown in Figure 1. As expected, with decreasing T_f, the density increases monotonically with time t and tends to approach equilibrium at long times. The time dependence $\rho(t)$

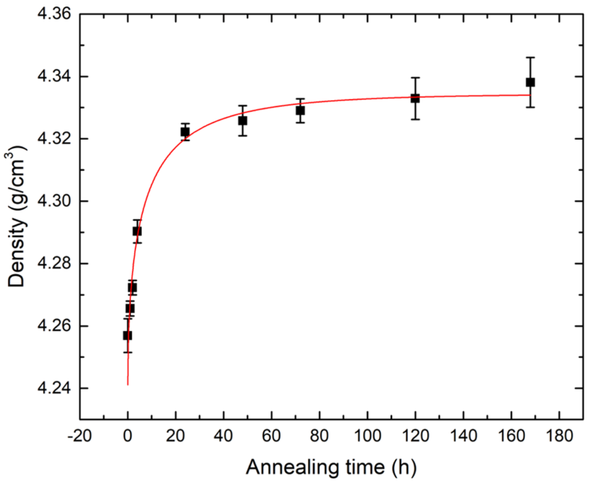

Figure 1. Temporal evolution of the density of $GeSe_2$ glass during aging at 345 °C.

can be fitted to a stretched exponential function $\rho(t) = A + B\exp\left(-\frac{t}{\tau}\right)^{\beta}$, where A and B are constants, τ is a relaxation timescale, and $0 \leq \beta \leq 1$ is the stretching exponent (Figure 1). The parameter β is related to the width of the distribution of relaxation timescales in a system such that a lower value of β corresponds to a larger width of the distribution.[24] The corresponding average relaxation time $\langle\tau\rangle$ can be obtained from the relation[24] $\langle\tau\rangle = \left(\frac{\tau}{\beta}\right)\Gamma\left(\frac{1}{\beta}\right)$, where Γ is the gamma function. Such a fit of the stretched exponential function to the data in Figure 1 yields $\beta = 0.54$ and $\langle\tau\rangle = 13.3$ h (Figure 1).

A representative Raman spectrum of the as-quenched $GeSe_2$ glass sample collected at room temperature is shown in Figure 2. A detailed analysis of this Raman spectrum in terms of the structural assignments of the constituent vibrational bands can be found in a recent density functional theory (DFT)-based study of Ge−Se clusters by Holomb et al.[25] Here, we follow their analysis and show a representative simulation of the Raman spectrum in Figure 2 using these bands. The spectrum displays three main regions: (a) a broad, low-intensity band between 50 and 170 cm^{-1} with main peaks at ∼100 and 140 cm^{-1} corresponding to inter-tetrahedral bending modes; (b) prominent bands centered at ∼180, 200, and 215 cm^{-1} corresponding, respectively, to Ge−Ge stretching in Se_3−Ge−Ge−Se_3 ethane-like units and symmetric Ge−Se stretching of CS and ES units; and (c) a broad band spanning from 220 to 320 cm^{-1}. This broad band in the high-frequency region contains strongly overlapping signals from several symmetric and asymmetric stretching modes of $GeSe_{4/2}$ tetrahedra in four- and six-membered Ge−Se rings that includes a relatively sharp peak at ∼248 cm^{-1}, and a broad peak centered at ∼285 cm^{-1}, which corresponds to the stretching of Se−Se bonds shared between two $GeSe_{4/2}$ tetrahedra, i.e., in Ge−Se−Se−Ge linkages (Figure 2). It is important to note here that the Se−Se stretching mode in Se−excess glasses containing −Se−Se−Se− linkages is located near 250 cm^{-1}, and its frequency is influenced by the inter-chain interaction in these glasses.[18,25]

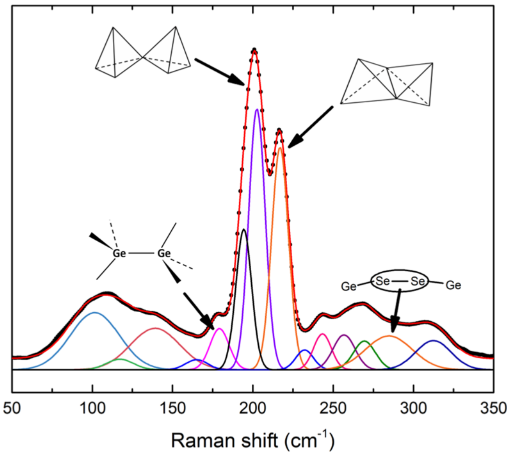

Figure 2. Experimental (black circles) and simulated (red solid line) unpolarized Raman spectra of as-quenched $GeSe_2$ glass. Individual simulation components as proposed by Holomb et al.[25] based on DFT calculations are shown as solid lines, vertically offset for clarity. Vibrational bands corresponding to CS, ES, Se_3−Ge−Ge−Se_3, and Ge−Se−Se−Ge units are shown with arrows.

On the other hand, experimental studies of Se confined in zeolites as well as DFT calculations indicate that this vibrational mode in isolated Se chains is located near 260 cm^{-1}.[25,26] However, previous ^{77}Se nuclear magnetic resonance spectroscopic studies have shown that the Se−Se homopolar bonds in the $GeSe_2$ glass are expected to exist as Ge−Se−Se−Ge linkages between two neighboring $GeSe_{4/2}$ tetrahedra.[10,27] The DFT calculations of Holomb et al.[25] have indicated that, compared to long Se chains, the stretching frequencies of these homopolar Se−Se bonds in Ge−Se−Se−Ge moieties are located at a significantly higher frequency of ∼285 cm^{-1}.

The Raman spectra of the as-quenched sample and of samples annealed at 345 °C for 4 h and for1 week, all normalized with respect to the intensity of the 215 cm^{-1} band, are shown in Figure 3 in the frequency region corresponding to the stretching modes of the Ge−Ge bonds, CS and ES units. A simple visual inspection reveals that the intensities and therefore the relative concentrations of the CS units increase and of the ethane-like units with Ge−Ge homopolar bonds decrease with respect to those of the ES units on annealing and thus on lowering of the T_f. As mentioned above, such an increase in the CS:ES band intensity ratio upon aging below but near T_g was also observed for $GeSe_4$ glass in a previous study.[18] This result indicates conversion of the ES tetrahedra into CS tetrahedra in the glass/supercooled liquid upon the lowering of T_f and is consistent with a concomitant increase in the packing density of tetrahedra as the specific volume of the ES units is larger than that of the CS units in the structure of Ge−Se glasses.[18] More interestingly, however, the spectra shown in Figure 3 provide the first clear evidence of a lowering of the concentration of homopolar Ge−Ge bonds in the glass structure and a corresponding increase in the heteropolar Ge−Se bonds as evidenced in the increase in the sum of CS and ES band intensities, upon lowering of T_f. Since the structure of these glasses is expected to follow the 8-N coordination rule, this result also implies a concomitant lowering of the Se−Se homopolar bonds in the structure. These structural changes can be represented via the schematic reaction:

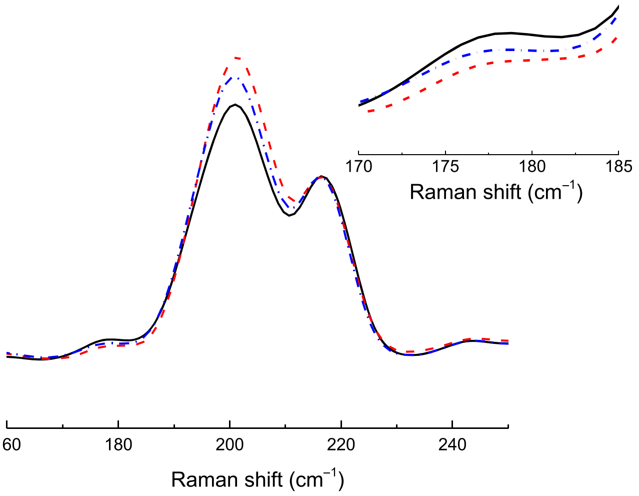

Figure 3. Expanded view of Raman spectra normalized to the intensity of the 215 cm^{-1} band, in the frequency region between 160 and 250 cm^{-1}, of as-quenched (solid line), 4 h annealed (dot-dashed line), and 1 week-annealed (dashed line) $GeSe_2$ glasses. The inset shows a magnified view of the evolution of Ge−Ge homopolar bond stretching mode in Se_3−Ge−Ge−Se_3 units.

$$\mathrm{Ge-Ge + Se-Se \rightarrow 2\,Ge-Se}$$

This reaction moves to the right with lowering of T_f during aging of the glass and presumably with lowering of temperature in the supercooled liquid state. It may be noted that the chemical order also increases in the same direction, as would be expected with lowering of temperature and a concomitant lowering of configurational entropy. To the best of our knowledge, this is the first direct observation of the involvement of homopolar ↔ heteropolar bond conversion in the structural relaxation of chalcogenide glasses. As noted above, the DFT calculations of Holomb et al.[25] on Ge_nSe_m nanoclusters indicated that the band corresponding to Se−Se stretching vibrations in Ge−Se−Se−Ge linkages in the $GeSe_2$ glass would be expected near ∼285 cm^{-1}.[25] Unfortunately, this band cannot be directly distinguished in the Raman spectra due to broadening and severe overlap with the Ge−Se stretching bands in the Raman spectra. Therefore, the time-dependent evolution of this band during aging could only be obtained from full simulation of the Raman spectra, as exemplified in Figure 2.

It may be noted that the abovementioned structural reaction implies a change in the Ge−Se vs Ge−Ge peak areas in a relative ratio of 2:1, which appears to be significantly lower than that displayed by the Raman spectra in Figure 3. This apparent discrepancy can be ascribed to the relatively small Raman scattering cross section of the Ge−Ge stretching mode at 180 cm^{-1} compared to those of the Ge−Se modes at 200 and 215 cm^{-1} as the fractional area under the 180 cm^{-1} band is considerably smaller than what would be expected if nearly 25% of the Ge atoms in this glass participates in Ge−Ge homopolar bonding as indicated by previous diffraction measurements.[21]

The aging-induced temporal evolution of the CS:ES intensity ratio and that of the relative areas under the 180 and 285 cm^{-1} bands corresponding, respectively, to the Se_3−Ge−Ge−Se_3 ethane-like units and Se−Se bonds in Ge−Se−Se−Ge linkages in this glass are shown in Figures 4 and 5, respectively. All spectral quantities display stretched relaxation kinetics with $\beta = 0.54$ and $\langle\tau\rangle = 13.5$ h for the increase in the CS:ES ratio and $\beta = 0.54$ and $\langle\tau\rangle = 13.8$ h for the lowering of the relative concentrations of the Se_3−Ge−Ge−Se_3 units and the Ge−Se−Se−Ge linkages (Figures 4 and 5, respectively).

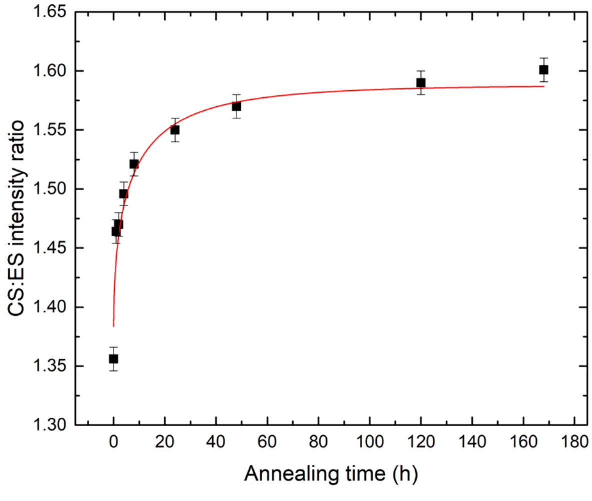

Figure 4. Temporal evolution of the CS (200 cm^{-1}):ES (215 cm^{-1}) band intensity ratio during aging at 345 °C.

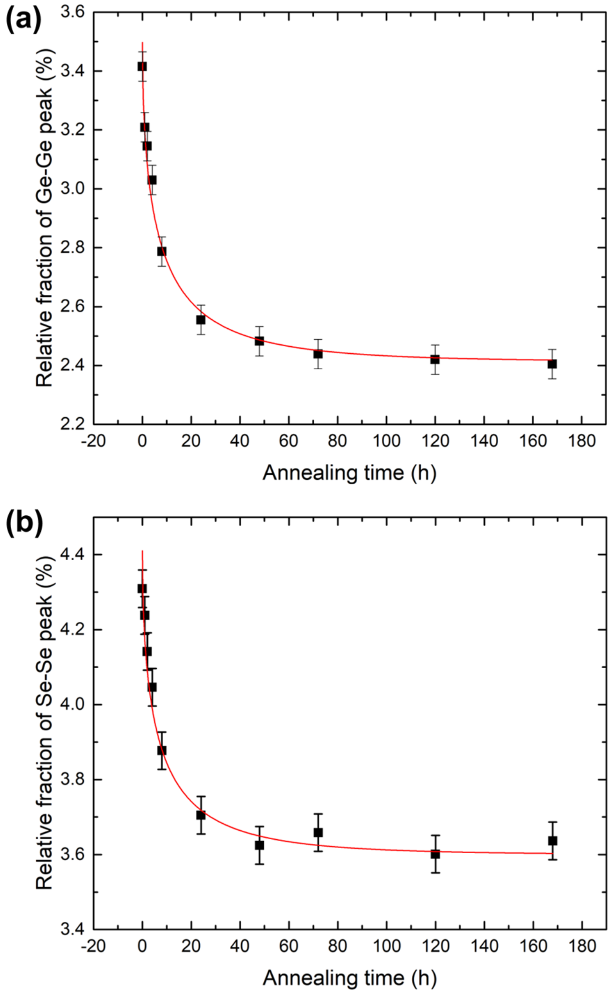

Figure 5. Temporal evolution of the fractional area under a (a) 180 cm^{-1} band corresponding to Se_3−Ge−Ge−Se_3 units and (b) 285 cm^{-1} band corresponding to Ge−Se−Se−Ge linkages during aging at 345 °C.

The remarkable similarity in their relaxation timescales and stretching exponents with that of density relaxation ($\beta = 0.54$ and $\langle\tau\rangle = 13.3$ h) indicates a close mechanistic relationship and corroborates the validity of the proposed structural reaction. This aging-induced structural evolution of the $GeSe_2$ network is shown schematically in Figure 6.

The temperature dependence of the Raman spectra of the as-quenched glass in the range of 20−300 °C is shown in Figure 7. It is clear that the peak frequencies of the strongest bands at ∼200 and 215 cm^{-1}, corresponding to the CS and ES units, respectively, progressively shift to lower values, i.e., they display mode frequency softening with increasing temperature. A similar mode softening behavior is also observed for the annealed sample, and all mode softening are found to be fully reversible upon cooling. It must be noted that, in this temperature range, which is nearly 100−380 °C below T_g, no significant structural relaxation of the glass is likely within the timescale of these experiments. Therefore, the temperature-dependent mode softening behavior can be ascribed entirely to the anharmonicity of the vibrational potential wells that are contained within the metabasins that correspond to the as-quenched and annealed glass structures.

The temperature-induced mode frequency softening rates for the CS and ES bands are compared in Figure 8 for the as-

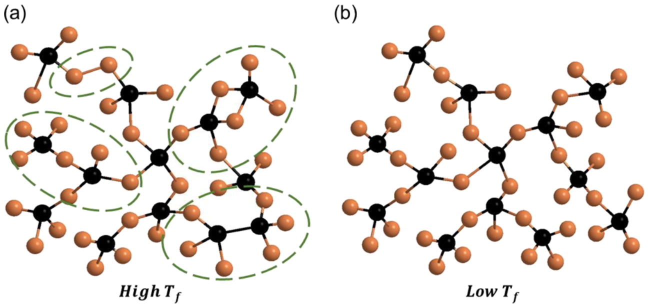

Figure 6. Schematic representation of the $GeSe_2$ glass network at high T_f (left) and low T_f (right). Ge and Se atoms are shown as black and brown spheres. The various structural moieties in the chemically disordered high T_f network with high configurational entropy, including ES and CS tetrahedra as well as Se−Se and Ge−Ge homopolar bonds, are marked by dashed ovals.

quenched and the 1 week-annealed samples. These rates are found to be −0.0085 ± 0.0005 cm^{-1} K^{-1} for the CS band and −0.0115 ± 0.0005 cm^{-1} K^{-1} for the ES band, which do not change significantly upon aging, within the limits of experimental error (Figure 8). The temperature dependence of the vibrational mode frequencies $\left(\frac{\partial \nu}{\partial T}\right)_P$ of a material has two contributions[28] such that $\left(\frac{\partial \nu}{\partial T}\right)_P = \left(\frac{\partial \nu}{\partial T}\right)_\nu - \frac{\alpha}{\beta}\left(\frac{\partial \nu}{\partial P}\right)_T$. Here, α and β are the volume thermal expansion coefficient and compressibility, respectively. The first term on the right-hand side of this equation is the pure temperature effect that represents the explicit anharmonicity related to the phonon−phonon coupling, which is determined by the thermal population of the vibrational levels. On the other hand, the second term corresponds to the implicit quasiharmonic effect related to the thermal volume expansion. A previous high-pressure Raman spectroscopic study of Ge−Se glasses[29] has reported the measurement of the parameter $\frac{1}{\nu}\left(\frac{\partial \nu}{\partial P}\right)_T \approx 0.004$ GPa^{-1} for the $GeSe_2$ glass in the frequency region of ~200 cm^{-1}. Using this parameter, the bulk modulus $1/\beta$ ~14 GPa,[30] and the volume thermal expansion coefficient $\alpha = 45 \times 10^{-6}$ K^{-1},[31] the implicit anharmonic term $\frac{\alpha}{\beta}\left(\frac{\partial \nu}{\partial P}\right)_T$ for the $GeSe_2$ glass can be estimated to be ~0.0005 cm^{-1} K^{-1}. This value is more than an order of magnitude smaller than the observed range of absolute values (0.0085−0.0115 cm^{-1} K^{-1}) for the CS and ES bands, implying that the anharmonicity of the vibrational potentials in these glasses is dominated by the explicit phonon coupling term. It is important to note that the as-quenched and annealed samples do not show any significant difference in the mode softening rates, indicating that the glass structures in the as-quenched and annealed samples occupy metabasins characterized by rather similar explicit anharmonicities of the vibrational excitations within them.

4. CONCLUSIONS

In conclusion, the analysis of the Raman spectra of $GeSe_2$ glasses demonstrates an increase in the CS:ES ratio and a lowering of the Ge−Ge homopolar bond concentration, which give rise to a concomitant increase in chemical order via the reaction Ge−Ge + Se−Se → 2 Ge−Se with lowering of T_f during aging at ~65 °C below T_g. This structural evolution upon aging is shown to be responsible for density relaxation in this glass, and the corresponding kinetics in all cases can be described by the KWW-type stretched exponential function with $\beta = 0.54$ and $\langle\tau\rangle$ ~13.5 h. In addition, the temperature-dependent evolution of the Raman spectra of these glasses at temperatures significantly below T_g provides evidence that the explicit phonon coupling controls the anharmonicity of the vibrational potentials in these glasses. This anharmonicity is shown to be not influenced by the aging-induced structural relaxation.

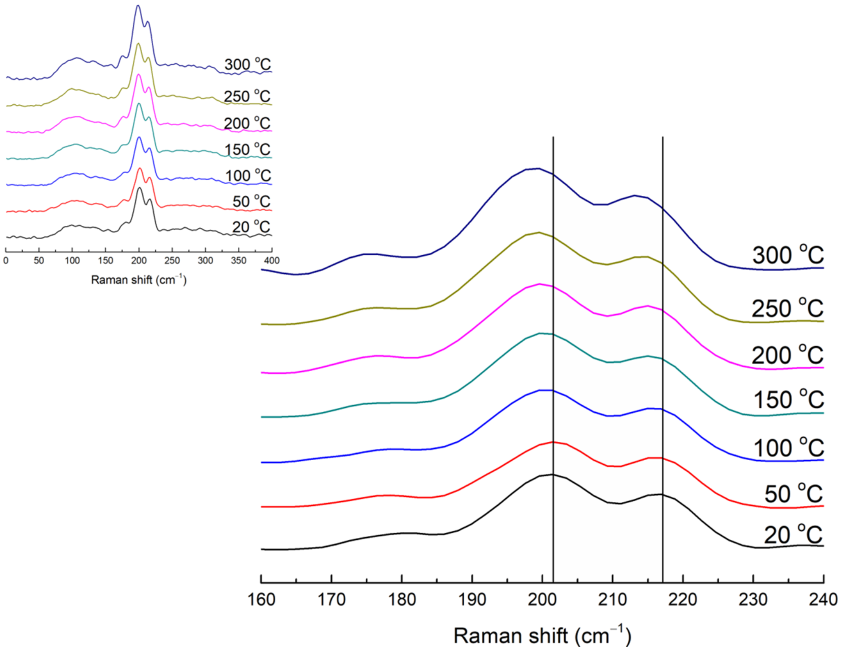

Figure 7. Expanded view in the frequency region between 160 and 240 cm^{-1} of the Raman spectra of as-quenched $GeSe_2$ glass collected at different temperatures displaying mode frequency softening with increasing temperature. Vertical lines are guides to the eye. The inset shows the full spectral range.

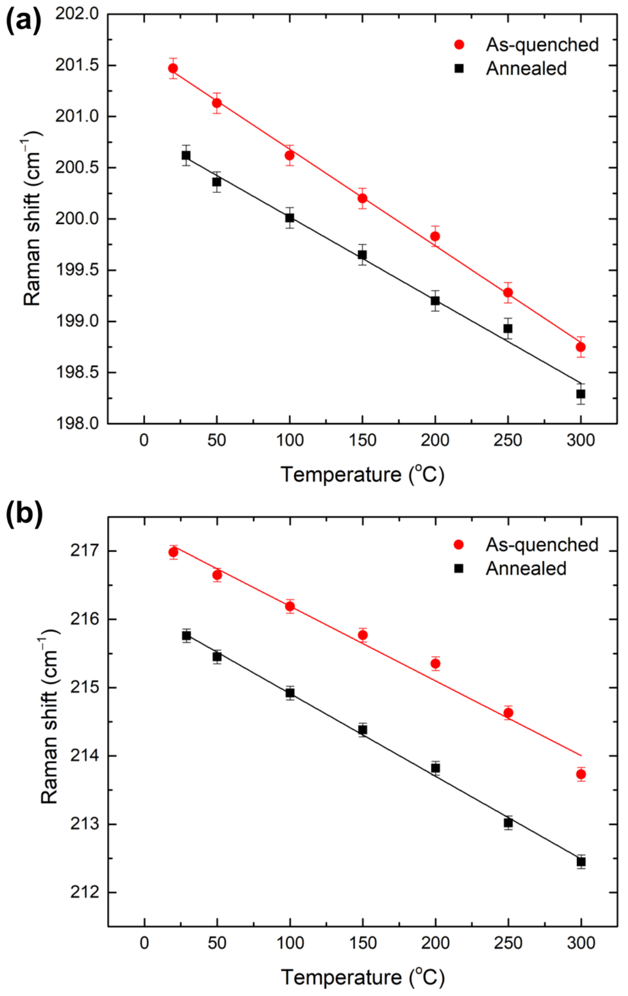

Figure 8. Temperature dependence of the Raman shift for peak positions of (a) CS and (b) ES bands in the Raman spectra of as-quenched and 1 week-annealed $GeSe_2$ glasses.

AUTHOR INFORMATION

Corresponding Author

Sabyasachi Sen − *Department of Materials Science & Engineering, University of California at Davis, Davis, California 95616, United States*; orcid.org/0000-0002-4504-3632; Email: sbsen@ucdavis.edu

Authors

Bing Yuan − *Department of Materials Science & Engineering, University of California at Davis, Davis, California 95616, United States*

Hao Chen − *Department of Materials Science & Engineering, University of California at Davis, Davis, California 95616, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpcb.1c08836

Notes

The authors declare no competing financial interest.

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