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Extended aging of Ge-Se glasses below the glass transition temperature.

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Abstract: Germanium selenide glasses of compositions spanning the whole glass-formation range are aged at room temperature for up to twenty years. A prominent enthalpy relaxation process is observed in all glasses and its structural origin is analyzed by Raman spectroscopy. The structural relaxation is manifested in the Raman spectra as a decrease in the ratio of edge to corner-sharing GeSe_{4/2} tetrahedral units. This structural evolution can be explained in terms of configurational entropy and density changes. Changes in Raman features and enthalpy follow an identical stretched exponential relaxation function characteristic of ageing in glasses. The compositional dependence of enthalpy relaxation after twenty years is in agreement with kinetic considerations based on the glass transition temperature of each glass. The relaxation behavior and heat-capacity curves are consistent with standard glass relaxation models for all compositions. These results indicate that the non-reversing enthalpy obtained by modulated differential scanning calorimetry (MDSC) which suggests the existence of non-aging glasses is not a reliable measure of the ability of a glass to relax. Instead, it is suggested that an interpretation of MDSC data in terms of complex heat capacity provides a more complete and reliable assessment of the relaxation properties of glasses.

I. INTRODUCTION

Sub- T_g relaxation is an important problem in glass technology due to the unwanted property changes that can take place in glassy components over time. Volumetric changes are detrimental for glass substrates used in consumer electronics¹ while changes in refractive index are harmful

for optical applications². Chalcogenide glasses are particularly exposed to these issues due to their relatively low glass transition temperature (T_g) which can lead to significant relaxation even at room temperature^{3,4}. Among these amorphous chalcogenides, germanium selenide glasses are of interest due to their complex structural dynamic⁵⁻⁷ and their precedent as testbeds for topological constraint theories^{8,9}. The structure of Ge-Se glasses is composed of Se chains and GeSe₄ tetrahedra that exhibit notably distinct dynamics as shown by Nuclear Magnetic Resonance (NMR)⁵⁻⁷. These two structural elements can in turn be related to the floppy and rigid domains that constitute the basis of topological constraint theories^{8,10,11}. Indeed, Ge-Se glasses have long been used to test topological constraint theories due to their covalent network structure. The well-defined number of bonds and bond angles provides a convenient testbed for constraint counting principles which are thought to help predict some physical properties of the glass. For example, it has been observed that some properties such as density show a broad maximum near the so-called rigidity percolation threshold where the number of atomic degrees of freedom ($d=3$) is exactly compensated by angular and bond constraints^{12,13}. In this region the glass network is expected to undergo a floppy (under-coordinated)-to-rigid (over-coordinated) transition. Constraint counting shows that this transition should occur when the average coordination number (average number of bonds per atom) is $\langle r \rangle = 2.4$ ¹¹.

More recently this theory has been extended to suggest that covalent networks can be optimally constrained over a broader compositional region where they are stress-free¹⁴. Experimental observation of this compositional window has been claimed mainly by invoking a quantity called the non-reversing enthalpy ΔH_{nr} measured by Modulated Scanning Differential Calorimetry (MDSC)^{9,15-17}. In MDSC, the sample is subjected to a linear heating ramp superimposed with a sinusoidal oscillation. The resultant heat flow is often decomposed into a “reversing” heat capacity component and a “non-reversing” kinetic component permitting to separate non-reversible processes such as cold crystallization from the total heat flow¹⁸. This method was in turn applied to analysis of the glass transition with the goal of characterizing relaxation processes¹⁹. In chalcogenide systems, it was observed that the non-reversing enthalpy decreases to zero in certain compositional ranges (0.20 to 0.25 Ge% in Ge-Se); thus, dubbed “reversibility window”. It was further suggested that the self-organized nature of the network within this window would lead to glasses that do not age^{9,15-17}. This observation was derived from measurements of ΔH_{nr} on glasses annealed at room temperature for up to several weeks. It was found that chalcogen-rich glasses exhibited significant change in ΔH_{nr} , while glasses in the “reversibility window” with lower chalcogen content exhibited minimal or no change^{9,15-17}. However, one issue with this interpretation is that glasses with broadly different T_g could have relaxation times spanning multiple orders of magnitude since the enthalpy relaxation time is exponentially dependent on T_g ^{20,21}. Hence, annealing series of glasses with different T_g at a common temperature for the same duration cannot provide a systematic measure of their ability to relax but merely a broad assessment of their relative relaxation times. In other words, low- T_g glasses may relax within a few weeks even at room temperature while relaxation may be too slow to observe for high- T_g glasses within the “reversibility window”. Therefore, more extensive

analyses are needed to assess the ability of glasses from the so-called “reversibility window” to undergo aging.

In this study we analyze glasses across the floppy to rigid range that have been aged over 20 years at room temperature. Furthermore we analyze the time dependent relaxation of two glasses, one outside and one inside the “reversibility window”, for up to five years at room temperature. It is found that all glass compositions exhibit significant relaxation in a way consistent with their relative T_g . Glasses outside and inside the “reversibility window” undergo a large stretched-exponential enthalpy relaxation characteristic of traditional glassy systems. Furthermore, the structural origin of this relaxation process is found to be identical in all glasses and shown to involve a conversion from edge to corner-sharing tetrahedral units that is consistent with a decrease in configurational entropy and an increase in density, as expected from conventional glass relaxation.

II. BACKGROUND

Sub- T_g glass relaxation – also called aging – has been extensively studied over the years²²⁻³⁴ and it has been shown that the relaxation process depends on multiple factors including the non-exponentiality β , the non-linearity x , the fictive temperature T_f and the fragility index m . The fragility is of particular interest as it affects the relaxation process in multiple ways that may appear contradictory. For example glasses located within the “reversibility window” are generally found to correspond to compositions exhibiting lower fragility index³⁵ so that prior suggestions that these glasses do not age, may appear to indicate that low fragility is associated with a resistance to relaxation. On the other hand, recent energy landscape simulations have shown that high-fragility glasses are more resistant to relaxation during linear heat treatments due to the higher free energy barriers below the glass transition³². This apparent contradiction stems from the fact that fragility affects the relaxation process in two distinct ways: (i) higher fragility increases the thermodynamic driving force for relaxation and leads to greater relaxed enthalpy, (ii) higher fragility increases the relaxation time and leads to slower relaxation process.

The first case can be illustrated using a configurational entropy plot as in Fig. 1. As demonstrated by Martinez & Angell³⁶, the scaled entropy of glass-forming liquids follows the same pattern as the viscosity on a fragility plot and constitute a thermodynamic signature of fragility. The scaled entropy of three hypothetical glass-formers is therefore plotted in Fig. 1(a) using a modified Vogel-Tamman-Fulcher equation with fragility index $m = 16, 55$ and 200 . The equilibrium lines are extended below T_g while the glassy state is represented by the thick dashed line where excess entropy is frozen in. The part of the curve below T_g is of particular interest here and is replotted in Fig. 1(b) as the normalized entropy versus normal temperature in a way similar to a Kauzmann plot³⁷ but normalized by T_g . It is clear from Fig. 1(b) that the entropy of the fragile glass diverges much more rapidly from the equilibrium line than the strong one. Consequently, a much greater thermodynamic driving force for relaxation builds up, while that of the strong

system remains minimal for an equivalent departure from T_g . This indicates that fragile systems are prone to greater structural relaxation, once sufficient time is allowed to reach equilibrium.

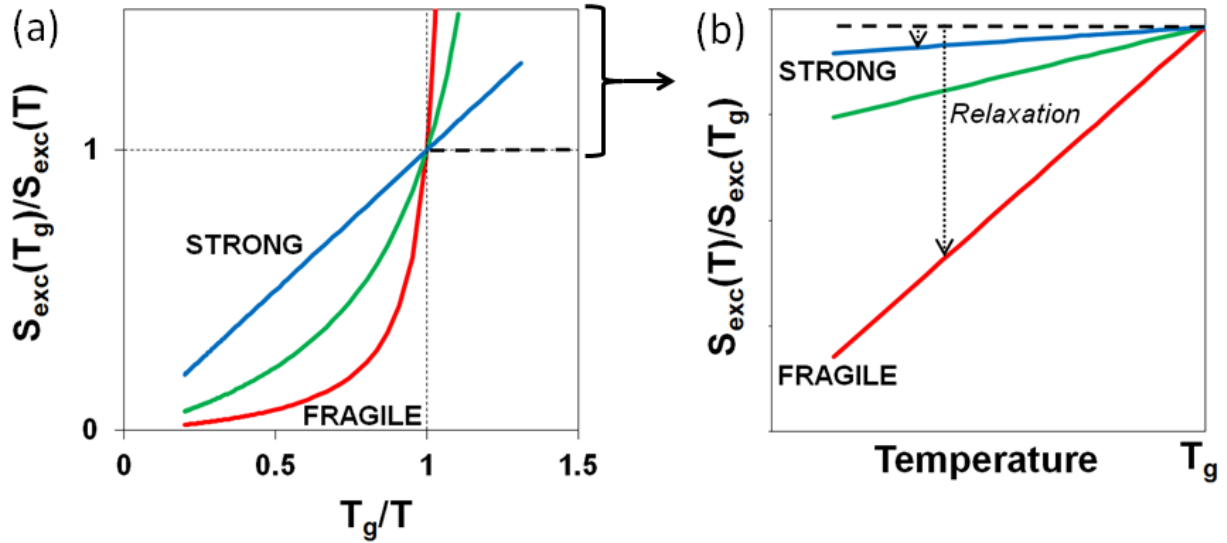


Fig. 1: (a) Scaled entropy (inverse excess entropy normalized by its value at T_g) for three hypothetical glass-formers with fragility ranging from $m = 16$ to 200. Thick dashed lines indicate the idealized glass state where configurational entropy is frozen in. (b) Variation of the equilibrium entropy with temperature relative to the glassy state for the same three glass-formers.

The second case can be simply derived from the Tool-Narayanaswamy-Moynihan (TNM) equation for the structural relaxation time τ ^{20,25} and the equation for the fragility index m ³⁸ where the activation energy for enthalpy relaxation ΔH^* is considered equivalent to the activation for viscous flow as suggested by Moynihan³⁹.

$$\tau = A \exp \left[\frac{x\Delta H^*}{RT} + \frac{(1-x)\Delta H^*}{RT_f} \right] \quad (1)$$

$$m = \frac{\Delta H^*}{RT_g \cdot \ln 10} \quad (2)$$

It is then obvious that when the fragility index m increases, the relaxation time τ increases exponentially. Therefore, when all other parameters are kept constant, relaxation is considerably slower in the fragile systems than in the strong ones.

In summary, fragile glasses have a greater thermodynamic potential for relaxation during aging, but their relaxation rate is much slower compared to that of the strong ones.

III. EXPERIMENT

A. Glass samples:

Two sets of Ge-Se glasses were produced for this study. All Ge-Se samples were high purity glasses used for the preparation of optical elements. Syntheses were performed in evacuated silica tubes in a rocking furnace as detailed in ref [40] and [41]. As shown in ref [41] these glasses were fully homogenized and were free of impurities such as water, which may affect their structural and dynamic behavior as implied in ref [9]. The first set was a series of bulk glasses produced in 1999 with composition $\text{Ge}_{10}\text{Se}_{90}$, $\text{Ge}_{15}\text{Se}_{85}$, $\text{Ge}_{20}\text{Se}_{80}$, $\text{Ge}_{25}\text{Se}_{75}$ and $\text{Ge}_{30}\text{Se}_{70}$ ^{40,42}. This set of glass was stored in air in a thermostated room ($22^{\circ}\text{C}\pm 2^{\circ}$) for 20 years in the LARMAUR lab at the University of Rennes with no light exposure until it was characterized. The second set included samples of two compositions that were drawn into fibers. The first composition was the Se-rich GeSe_9 which lies well outside of the “reversibility window”. The second composition was the archetypical GeSe_4 stoichiometry which corresponds to the rigidity percolation threshold at $\langle r \rangle = 2.4$ and lies within the “reversibility window”. For this study, GeSe_9 and GeSe_4 fibers were fabricated at various times over the course of five years. The fibers were drawn in a He atmosphere at a speed of 1.22 m/min and a tension of 20 g. At this speed and tension, no measurable structural anisotropy could be observed by ⁷⁷Se Nuclear Magnetic Resonance, polarized Raman or X-ray Diffraction along the axis of the fibers. In these conditions, the quench rate was estimated at $\sim 500^{\circ}\text{C}/\text{min}^3$. After fabrication, the fibers were removed from their storage drums and stored in 15 cm long strands in silica tubes, in the dark at room temperature in the laboratory. Small pieces of the stored fibers were then removed from the silica tubes when DSC and Raman experiments were ready to be performed.

B. Raman spectroscopy:

Raman spectroscopy was performed on 20 year old bulk samples of each composition before and after rejuvenation in a DSC (See section C). Raman spectra were collected using a Renishaw InVia spectrometer with a 1200 lines/grating and a diode laser at a wavelength of 785 nm focused with a 10X objective at a power of 15mW to avoid any photostructural changes. Spectra were collected for 120 seconds and averaged over three scans. Raman spectroscopy was also performed on small sections of GeSe_9 and GeSe_4 glass fibers from the same batch as that used for calorimetric measurements. Prior to each measurement, the sample surface was cleaned with alcohol and the fibers were lightly crushed and pressed into aluminum sample holders. Unpolarized Raman spectra were collected at ambient temperature and in backscattering geometry using a Bruker RFS 100/S Fourier-Transform Raman spectrometer equipped with a Nd:YAG laser operating at 1064 nm and a liquid nitrogen cooled solid-state Ge detector. A laser power level of 50 mW was used, and spectra were collected using a resolution of 2 cm^{-1} . Approximately 100 scans were collected and averaged to obtain each Raman spectrum. The low photon energy and the low power level used to collect the Raman spectra, permitted to avoid any photostructural damage during data collection.

C. Differential Scanning Calorimetry

Enthalpy relaxation measurements were performed on 20 year old bulk samples of each composition using a TA Instrument DSC25 equipped with a refrigerated cooling system RCS90 and calibrated with an indium standard. Small bulk glass pieces were lightly polished to obtain a flat surface to optimize thermal contact with the DSC pan. Samples of mass ~ 10 mg were then hermetically sealed in a Tzero[®] aluminum pan. An identical empty pan was used as the reference. Samples were first heated at $10^\circ\text{C}/\text{min}$ up to 100°C above T_g to measure the heat capacity of the relaxed glass. The sample was then rejuvenated by subjecting it to the same heat-treatment as the original glass through equilibration at T_g (up to 4h) and slowly cooling at $1^\circ\text{C}/\text{min}$ to room temperature⁴⁰. A run of the rejuvenated glass was then immediately collected at $10^\circ\text{C}/\text{min}$ over the same temperature range. The two thermograms were integrated and subtracted to calculate the relaxed enthalpy of the 20 year old sample. Enthalpy relaxation measurements were also performed on glass fibers using a Mettler Toledo DSC1 calorimeter equipped with a FRS5 sensor and sub-ambient cooling unit. DSC was performed on both sets of GeSe₉ and GeSe₄ fibers of varying ages, in standard (non-modulated) mode. Prior to any experiments, both the temperatures and the heat flow were calibrated using indium and zinc standards. Heat capacity values were calculated from the heat flow using the molar mass of the samples. Tested samples consisted of 3 mm long pieces of fiber, placed side by side in the center of an aluminum DSC pan and hermetically sealed. Empty aluminum pans were used as a reference, and sample masses were in the range of 5 to 7 mg. Enthalpy change calculations were completed using two consecutive heating scans of each sample. To perform such a calculation, each fiber sample was placed in the DSC and heated at 10 C min^{-1} to a temperature well above T_g , allowed to equilibrate at this temperature, and subsequently cooled in the DSC using the same 10 C min^{-1} rate to well below T_g . This first temperature up-scan captures the enthalpy of the fiber due to relaxation. Upon completion of cooling, the sample is then reheated, again at 10 C min^{-1} , to obtain the reference DSC curve. Enthalpy change is then determined by the integration of the area between the two heat flow curves.

IV. RESULTS

A. 20 year old bulk samples:

1. Calorimetry

The DSC curves of all Ge-Se bulk glasses after 20 year aging at room temperature are shown in Fig. 2. Each curve is compared with that of the same glass after rejuvenation. Glasses with lower T_g exhibit large endothermic peaks corresponding to the regain of relaxed enthalpy during reheating. The large relaxed enthalpy is consistent with the shorter relaxation time associated with the lower T_g since the A term in the TNM equation (Eq. 1) is exponentially dependent on T_g . Moreover, the large relaxed enthalpy ($>300\text{ J/mol}$) is also consistent with the higher fragility m

of these glasses³⁵. As shown in Fig. 1b, higher fragility leads to steeper departure from equilibrium and greater build up for relaxation. Interestingly, glasses within the so-called “reversibility window” also show rather large relaxed enthalpy (up to 167.5 J/mol) despite their higher T_g and the reduced thermodynamic potential for relaxation associated with their lower fragility. Finally, glasses with T_g values far above room temperature exhibit small but still measurable enthalpy relaxation as shown for $\text{Ge}_{30}\text{Se}_{70}$. Overall, these data clearly indicate that all glasses, including those in the “reversibility window” can undergo significant structural relaxation. As shown in the inset of Fig. 2, the ability to relax at room temperature is directly dependent on the T_g of the glass and therefore appears to be mainly limited by kinetic factors.

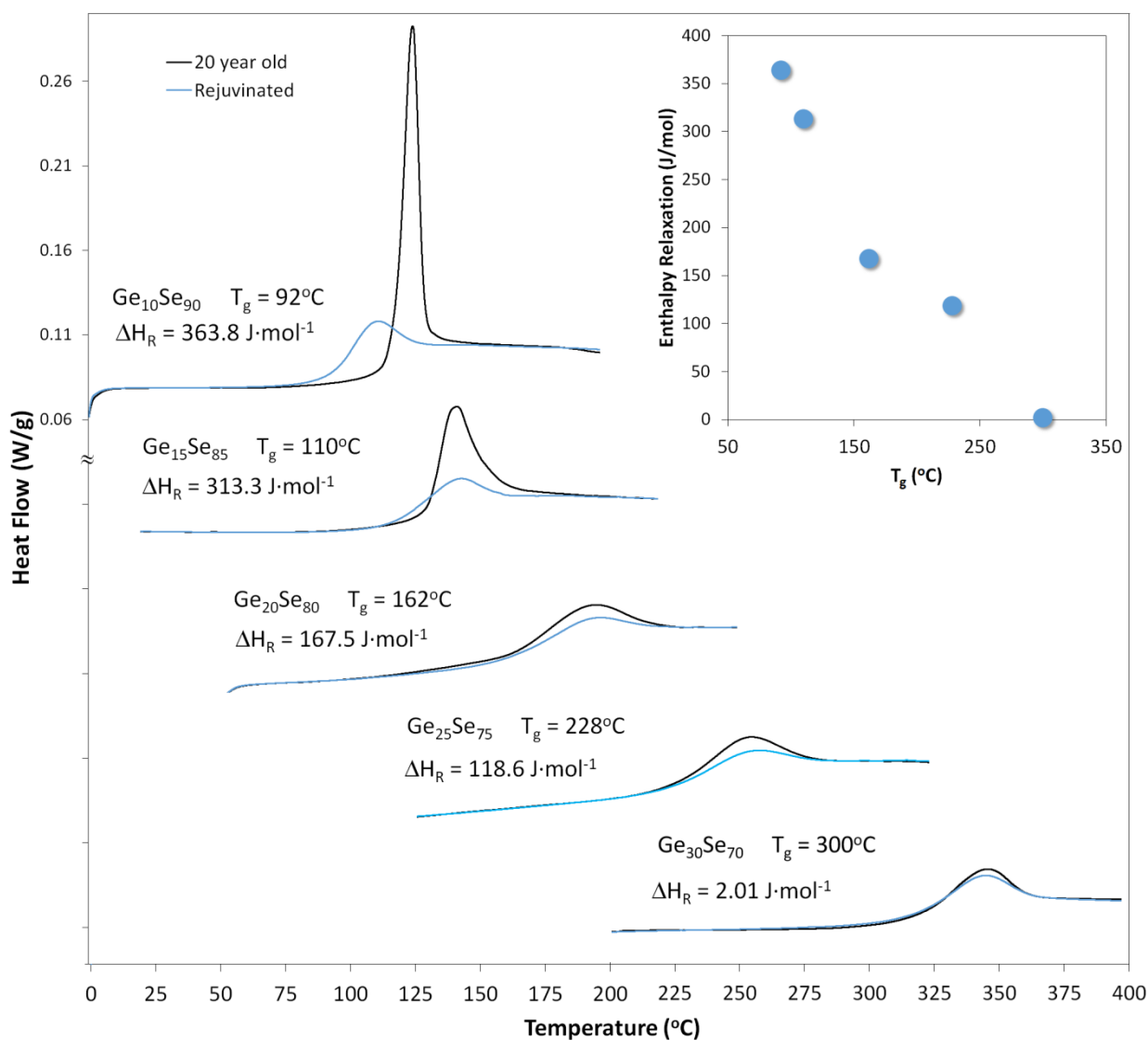


Fig. 2: DSC curves of bulk Ge-Se glasses after 20 year annealing at room temperature (295 K). The relaxed enthalpy ΔH_R corresponds to the difference between the integrated curves of the relaxed and rejuvenated glass. The inset shows the dependence of ΔH_R on the glass transition temperature T_g . (endothermic is up)

2. Raman spectroscopy

As shown in Fig. 3, the Raman spectra of all Ge-Se glasses exhibit the characteristic three main spectral lines located at 255 cm^{-1} , 213 cm^{-1} and 195 cm^{-1} which corresponds to the Se-chain modes and the edge-sharing and corner-sharing tetrahedral modes, respectively^{5,43}. The spectra normalized to the Se-chain mode show a systematic decrease in edge-sharing tetrahedra modes with annealing while the corner-sharing mode concomitantly increases. This indicates that a conversion from edge- to corner-sharing tetrahedra is a structural marker of aging in these glasses. In order to further investigate a correlation between this structural evolution and enthalpy relaxation, the aging process was monitored over time in a series of Ge-Se glass fibers as detailed in the following section.

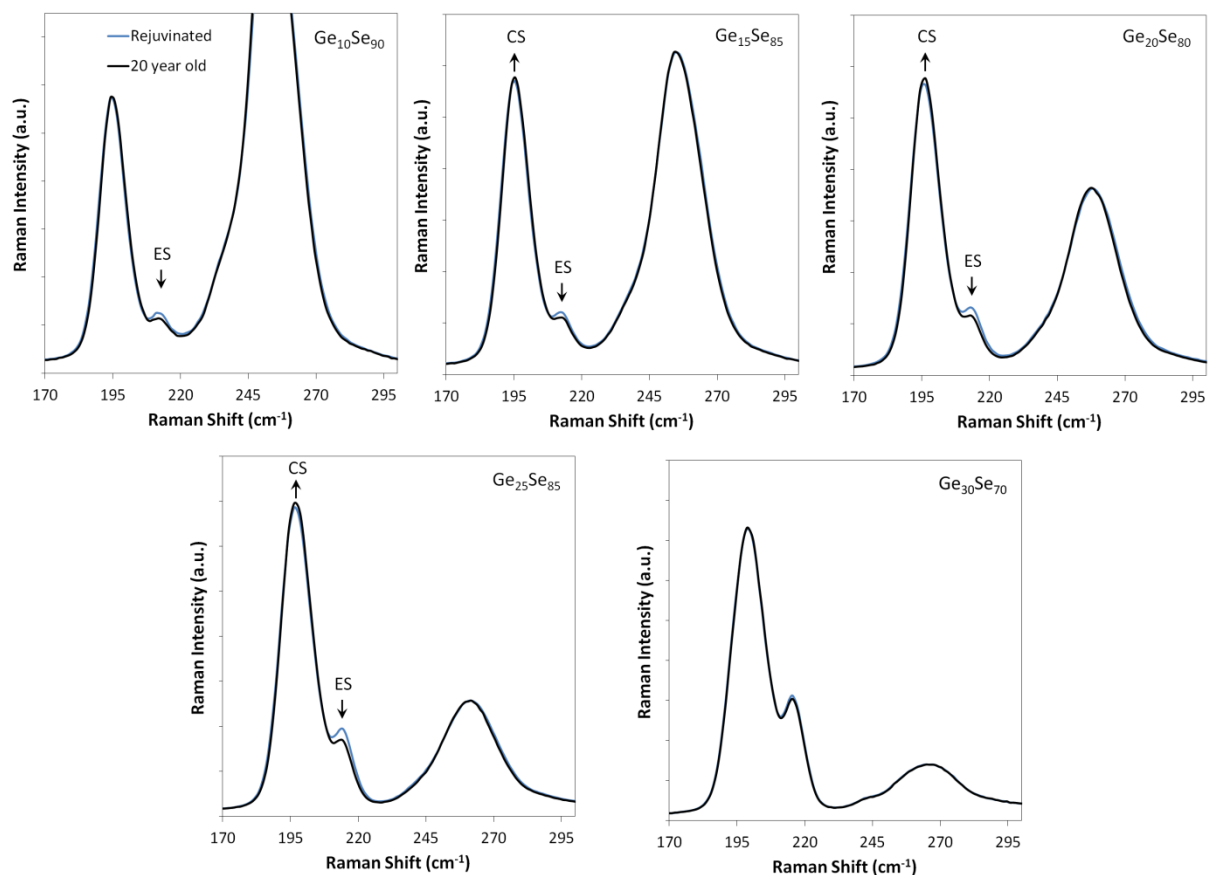


Fig. 3: Raman spectra of bulk Ge-Se glasses after 20 year aging at room temperature (295 K) compared with the rejuvenated glass. The peak intensity ratio between corner- and edge-sharing tetrahedra systematically increases with annealing.

B. 5 year old fiber samples

1. Calorimetry

Figure 4 presents the heat capacity curves of GeSe₉ and GeSe₄ glass fibers collected at several time intervals as they were aging at room temperature for up to five years. The DSC curves reveal notably different evolutions between the two fibers which correspond to the expected behavior of glasses annealed at different temperatures relative to T_g (for GeSe₉ : $T_g - T_a \sim 70^\circ\text{C}$ while for GeSe₄ : $T_g - T_a \sim 140^\circ\text{C}$). The GeSe₉ shows a large C_p overshoot while the GeSe₄ shows the development of a pre- T_g endotherm that slowly grows with aging. The main DSC features of these two glasses can be predictably reproduced using the TNM modeling procedure of Hodge⁴⁴ as shown in Fig. 5. The GeSe₉ and GeSe₄ glasses were modeled using a cooling rate of $500^\circ\text{C}/\text{min}$ ³ and a reheating rate of $10^\circ\text{C}/\text{min}$ after annealing at 25°C (room temperature) for increasing time periods. Modeling parameters were estimated from literature for fragility index m ³⁵, non-exponentiality β ⁴⁵ and non-linearity x ⁴⁶. The modeled and experimental C_p curves show good qualitative match. Figure 4a & 5a shows that, as a result of its low T_g , the GeSe₉ glass can relax rapidly at room temperature and exhibits a large overshoot of C_p after only 3.5 years. This overshoot is indicative of a large relaxed enthalpy enhanced by its higher fragility, as predicted from Fig. 1. In contrast, the C_p of the GeSe₄ glass in Fig. 4b & 5b shows the development of a pre- T_g endotherm that shifts to higher temperatures upon longer annealing. This endotherm is the well-known signature of fast relaxing domains regaining enthalpy upon reheating after a long anneal. Such behaviors have been described in great detail by Hodge both experimentally and theoretically^{44,47-51}. Such pre- T_g endotherms are only observable for a specific range of annealing temperatures far below T_g after a fast quench^{44,47}, which is precisely the case for the GeSe₄ fibers. For glasses with T_g closer to their annealing temperature like GeSe₉, the entire distribution of relaxation times is sufficiently short that relaxation occurs quickly at room temperature, and upon reheating the enthalpy relaxation appears as the conventional overshoot superimposed on the T_g , as shown in Fig. 4a & 5a. Overall, both glasses show the characteristic relaxation behavior predicted by the TNM model.

2. Raman spectroscopy

Figure 6 shows the spectra of the GeSe₄ glass fibers collected by FT-Raman. The spectra show the characteristic Se-chain and tetrahedral modes near 250 cm^{-1} and 200 cm^{-1} respectively as well as the low frequency broadband Se bending modes near 100 cm^{-1} ⁴³ (Fig. 6a). Upon close inspection of the tetrahedral modes, it is found that the relative intensity of the edge-sharing mode progressively decreases as a function of aging, as depicted in Fig. 6b. This change is

observed in both glasses. A similar evolution of edge-sharing mode intensity as a function of temperature has been previously observed in the supercooled liquid of GeSe_4 ⁴³. The edge-sharing mode was shown to decrease with decreasing temperature of the liquid. In the present case the edge-sharing mode intensity is found to decrease with decreasing fictive temperature of the glass as it relaxes towards equilibrium upon aging. This indicates that the structural evolution observed by Raman is related to changes in thermal properties (enthalpy) of the glass. Indeed, a strong correlation between the structural and thermal properties can be revealed by plotting the time evolution of the enthalpy and Raman features as shown in Fig. 7 for GeSe_4 . In Fig. 7(a) the ratio of the intensities of the edge- and the corner-sharing tetrahedral modes is normalized and plotted as a function of aging time. The decay of the spectral ratio is found to follow a stretched exponential function (Kohlrausch function). In Fig. 7(b), the relaxed enthalpy calculated from data in Fig. 4(b) is similarly normalized and plotted as function of time over the same period. It is found that the enthalpy decay can be fitted with the same stretched exponential function with a relaxation time $\tau = 294$ days and a stretching exponent $\beta = 0.686$. This result confirms that the two relaxation processes are strongly correlated.

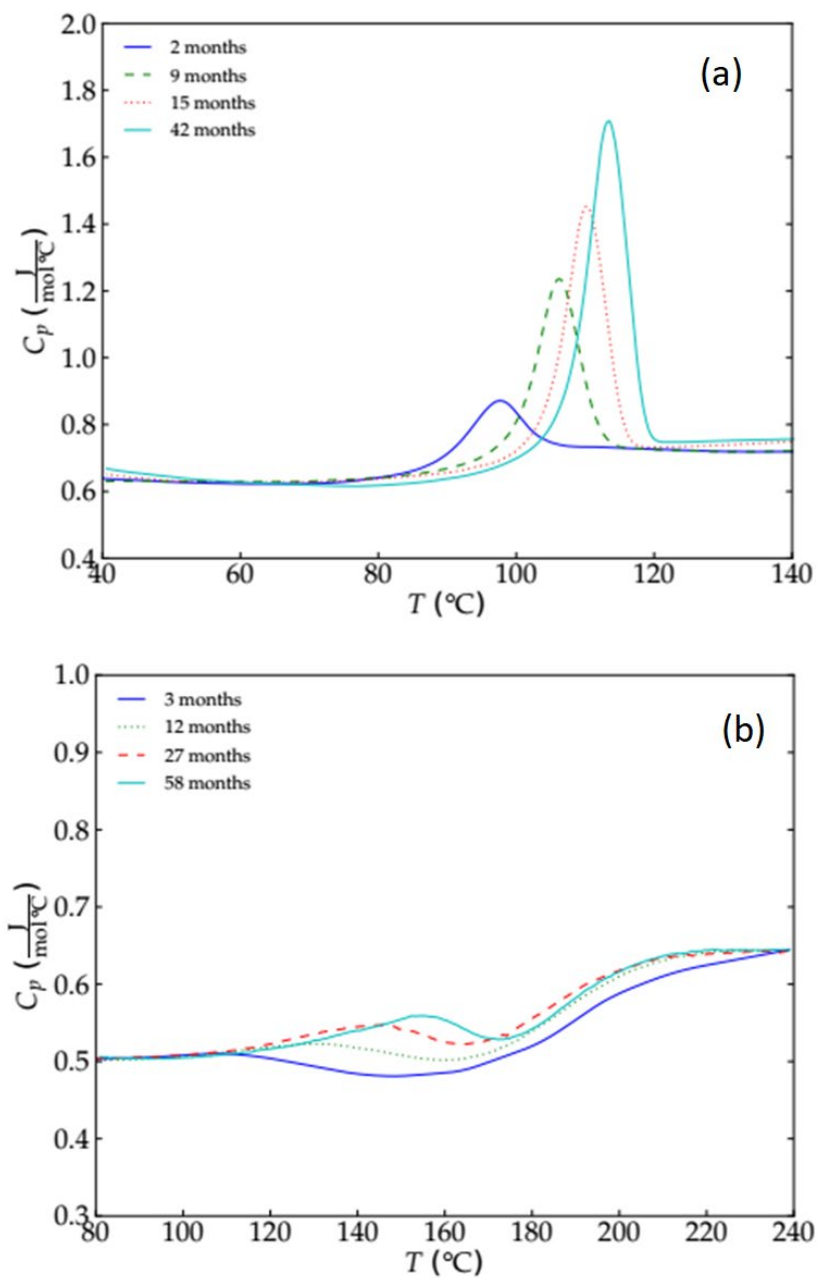


Fig. 4: Experimental heat capacity curves for (a) GeSe_9 glass fibers annealed at room temperature for up to 3.5 years and (b) GeSe_4 glass fibers annealed at room temperature for up to 5 years.

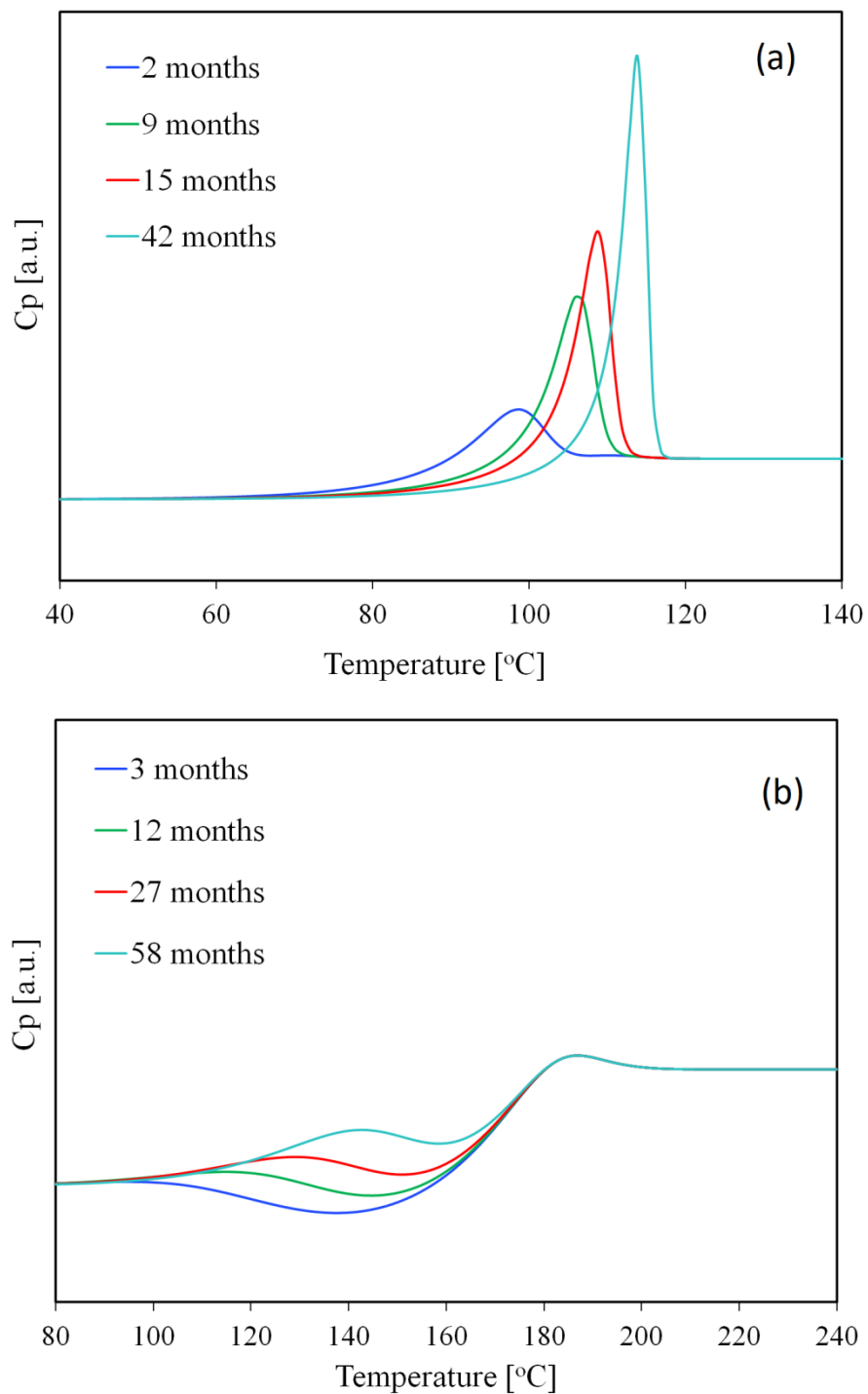


Fig. 5: Calculated heat capacity curves as a function of annealing at room temperature following the TNM modeling procedure developed by Hodge⁴⁴ for (a) GeSe₉ glass using model parameters $\beta = 0.54$; $x = 0.51$; $m = 38$ and $T_g = 365$ K; (b) GeSe₄ glass using model parameters $\beta = 0.60$; $x = 0.57$; $m = 27$ and $T_g = 435$ K.

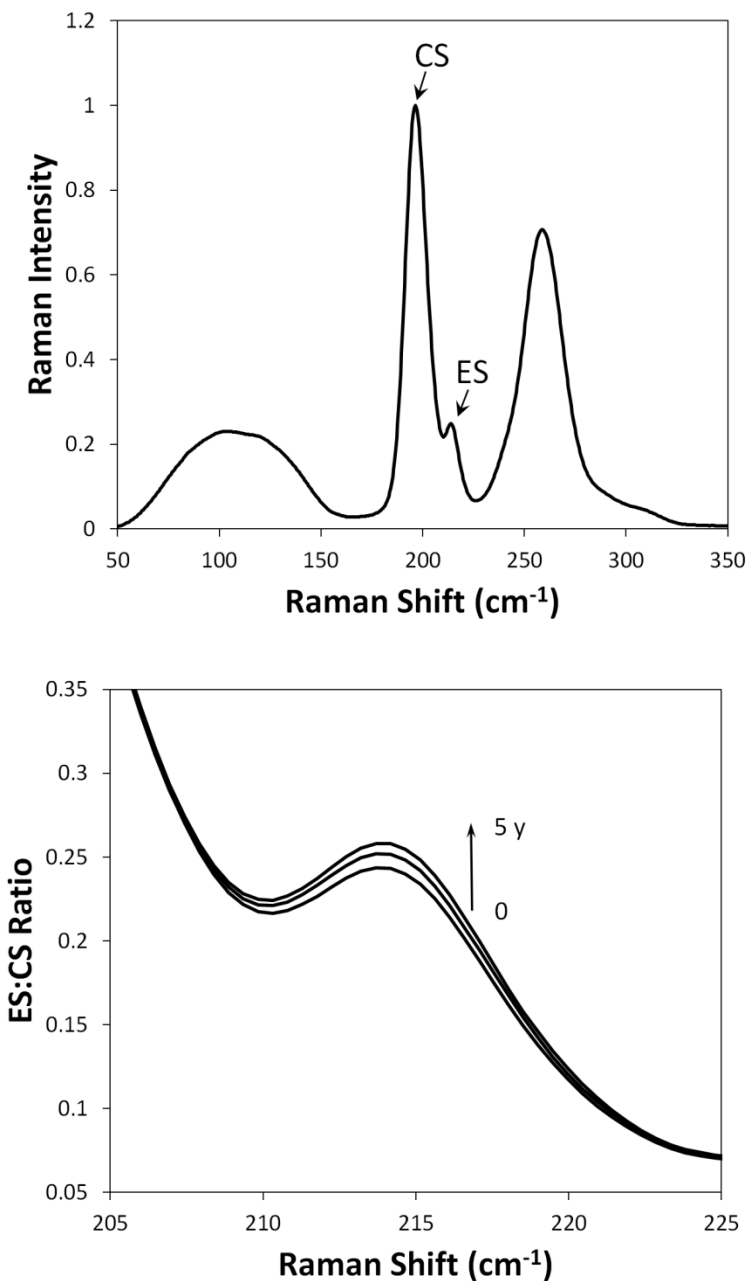


Fig. 6: (a) Typical unpolarized Raman spectrum of GeSe₄ glass showing the two modes associated with corner-sharing and edge-sharing tetrahedra at 195 cm⁻¹ and 213 cm⁻¹ respectively; (b) Increase of the relative intensity of the edge-sharing mode upon aging at room temperature for 0, 2 and 5 years (all spectra are normalized to the intensity of the corner-sharing mode).

The same construction can be performed for the GeSe₉ glass as shown in Fig. 8. Again, Raman features and enthalpy both follow a stretched exponential decay that can be fitted with the same function. In the case of GeSe₉ the relaxation time is $\tau = 118$ days and the stretching exponent

factor is $\beta = 0.424$. As expected, the lower T_g glass has a shorter relaxation time at room temperature consistent with results of Fig. 4(a). The stretching exponent values also show that the non-exponential factor β is notably smaller for the fragile glass (GeSe₉, $m \sim 38$) than the strong glass (GeSe₄, $m \sim 27$). The two glasses are likely still far from equilibrium, hence, these values of β are only estimates, nevertheless they are consistent with expected trend between fragility and non-exponentiality, and the β values obtained in this study are in good agreement with previously reported data⁴⁵.

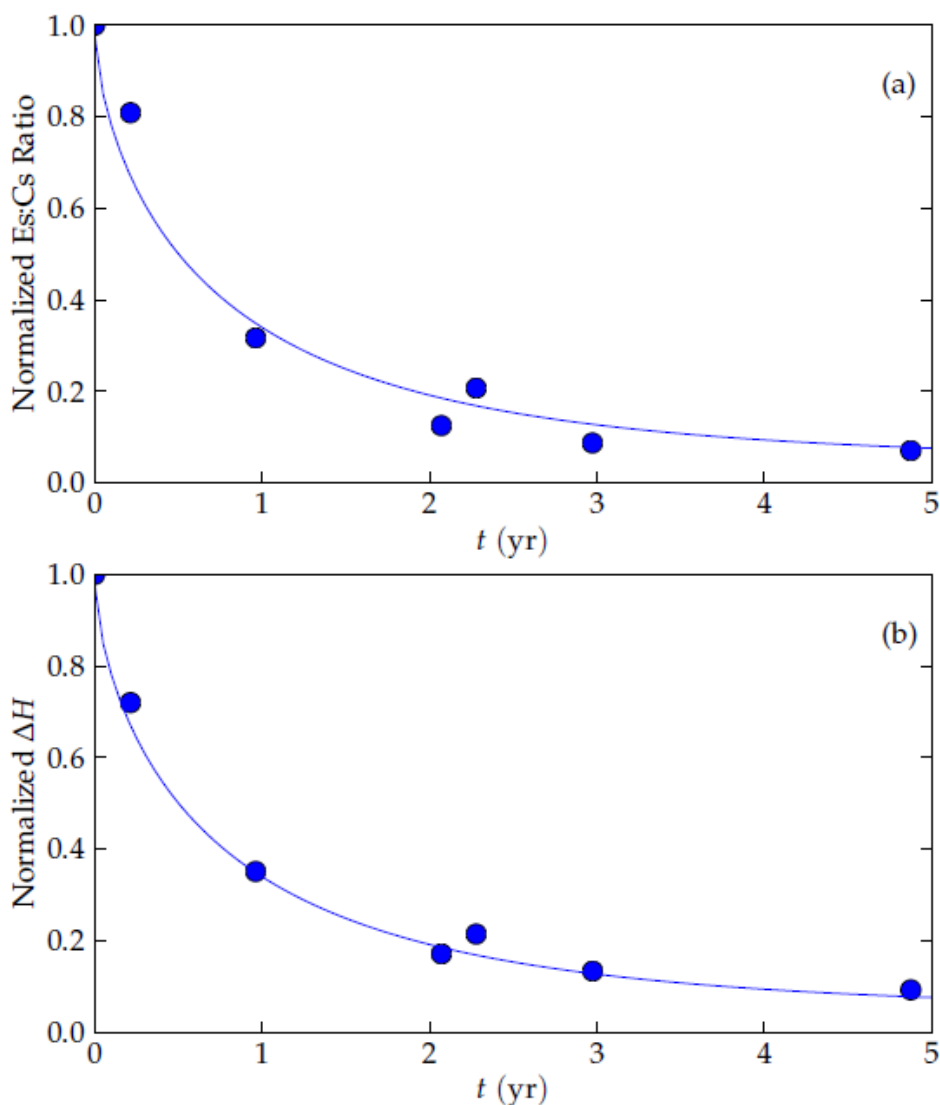


Fig. 7: (a) Normalized ratio of the intensities of the edge- and the corner-sharing tetrahedral Raman modes of GeSe₄ glass as a function of aging time at room temperature; (b) Normalized enthalpy relaxation of GeSe₄ glass as a function of aging time at room temperature. The line in both graphs correspond to the same stretched exponential function with $\tau = 294$ days and $\beta = 0.686$

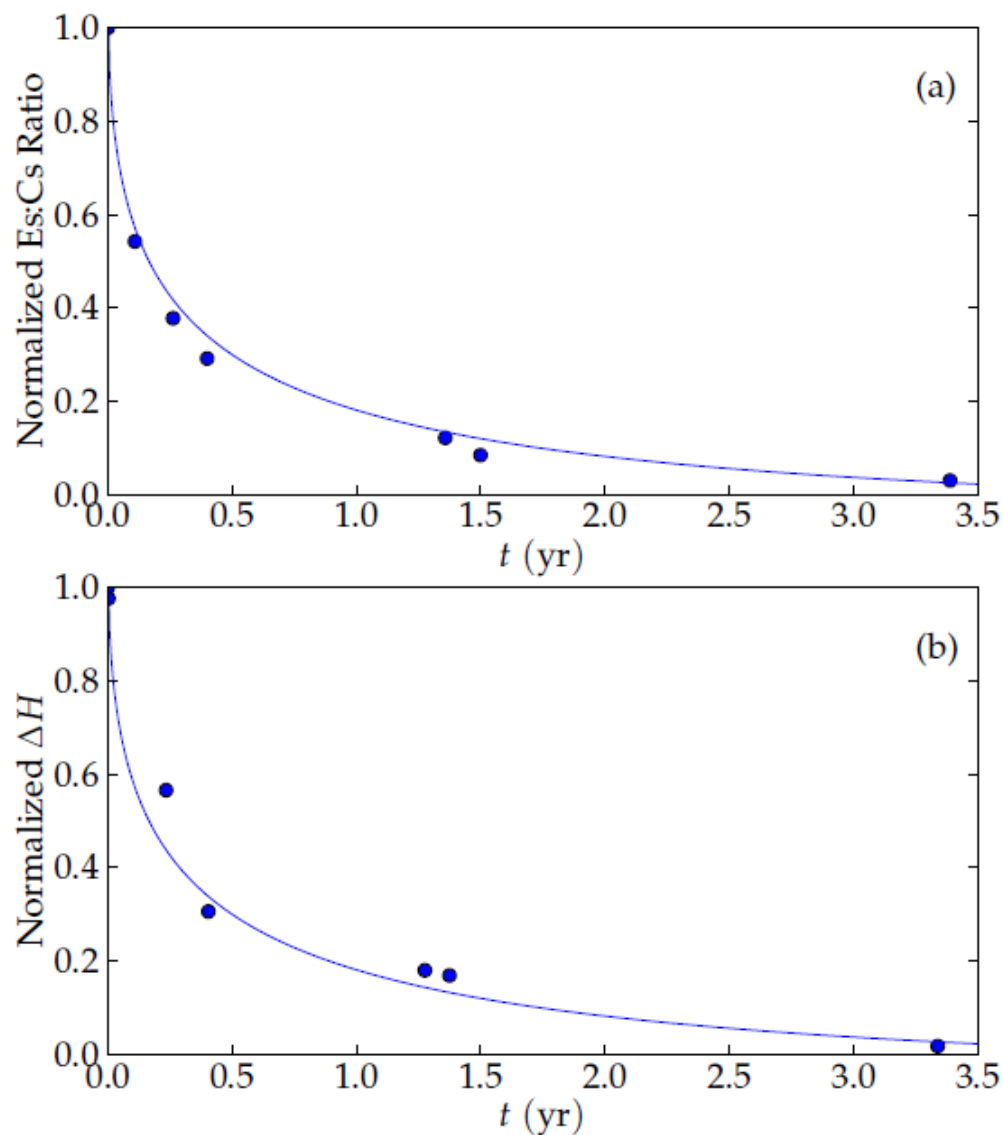


Fig. 8: (a) Normalized ratio of the intensities of the edge- and the corner-sharing tetrahedral Raman modes of GeSe_9 glass as a function of aging time at room temperature; (b) Normalized enthalpy relaxation of GeSe_9 glass as a function of aging time at room temperature. The line in both graphs correspond to the same stretched exponential function with $\tau = 118$ days and $\beta = 0.424$

V. DISCUSSION

A. Conventional relaxation behavior in the “reversibility window”

Overall, the results of Fig. 2 & 5 reveal that given enough time, all Ge-Se glasses undergo a sizeable enthalpy relaxation even at room temperature. The relative extent of relaxation of all glasses is consistent with expectations for samples annealed at different temperatures relative to

T_g . Hence, it can be concluded that glasses from the so-called “reversibility window” do not exhibit any unusual resistance to relaxation, granted sufficient observation time is allowed for the measurement. The features of the DSC curves and their evolution with aging are also well predicted by the TNM model for glasses inside and outside the so-called “reversibility window”. The multiple features of the DSC curves are fully consistent with their relative fragility and T_g values. Furthermore, the time dependence of the enthalpy relaxation for both glasses exhibit a stretched exponential decay characteristic of conventional amorphous systems during sub- T_g relaxation²⁴. The non-exponential factors β describing the decay are also found to be in good agreement with expectations from glasses with their relative fragilities⁴⁵. Hence, all Ge-Se glasses exhibit a rather conventional relaxation behavior and no abnormal relaxation properties are observed for glasses within the “reversibility window”, in fact these glasses behave exactly as expected from model predictions.

B. Structural origin of relaxation in Ge-Se glasses.

As shown in Fig. 3 & 6, aging of Ge-Se glasses is systematically associated with a conversion of edge-sharing tetrahedra to corner-sharing tetrahedra. The magnitude and kinetics of this structural change is closely related to enthalpy relaxation for each composition studied. This behavior can be explained in two ways, based on considerations of density and configurational entropy. In terms of density, it is expected that the reduced structural dimensionality imparted by edge-sharing tetrahedra leads to poorer packing efficiency and in turn to lower volumetric density. For example, the corner-sharing 3D crystalline polymorph of GeSe₂ is 9.6% denser than the corner- and edge-sharing 2D polymorph consisting of layers⁵². This trend is also broadly observed in tetrahedral liquids such as GeSe₄ and ZnSe₂ where the fraction of edge-sharing units decreases with lower temperature and higher density^{43,53,54}. In the case of Ge-Se glasses, the decrease in edge-sharing units is therefore consistent with the volume contraction associated with lowering of the fictive temperature during aging. In terms of configurational entropy, the relaxation process is associated with a decrease in entropy towards the equilibrium liquid line as illustrated schematically in Fig. 1(b). This entropy loss upon aging can indeed be observed experimentally in the heat capacity curves of Fig. 2 & 4 where the C_p overshoot is representative of the regain in lost entropy upon reheating. This decrease in entropy can also be qualitatively linked to the structural changes observed by Raman using the constraint counting formalism⁵⁵⁻⁵⁷. As previously described⁵⁴, a pair of edge-sharing tetrahedra possess two fewer angular constraints than a pair of corner-sharing tetrahedra. Hence, a decrease in edge-sharing tetrahedra will lead to a decrease in network degrees of freedom f and in turn to a decrease in configurational entropy S_c according to:

$$S_c = fNk \ln \Omega \quad (3)$$

where Ω is the number of accessible microstates per atomic degree of freedom (independent of f)^{55,56}. The structural mechanism for entropy relaxation therefore appears to be related to the backbone of tetrahedral units in the glassy structure. Interestingly, that mechanism is identical in

both glasses, as shown in Figs. 7 & 8. This further confirms that glasses from the “reversibility window” do not exhibit any abnormal relaxation behavior relative to other compositions from the same system.

C. Non-reversing enthalpy and MDSC

The results described above conclusively indicate that glasses within the “reversibility window” can undergo significant enthalpy relaxation. This raises questions regarding the validity of the non-reversing enthalpy ΔH_{nr} as a means of assessing the relaxation behavior of glasses. Indeed it has been broadly suggested that vanishing values of ΔH_{nr} are indicative of a resistance to aging^{9,15-17}. However, the present results clearly indicate that this is not the case. The physical interpretation of ΔH_{nr} therefore remains unclear and in fact it has been highly controversial since the early development of MDSC. In particular, Schawe⁵⁸ emphasizes that ΔH_{nr} is the difference between two quantities that are measured with two different time constants: the underlying heat flow associated with the time constant of the average heating rate and the reversible heat flow associated with the time constant of the superimposed oscillation. Schawe then concludes that “the non-reversing component is determined by subtracting two logically different quantities that are not directly comparable”⁵⁸. Nevertheless, ΔH_{nr} has been tentatively equated to the enthalpy relaxation upon annealing⁵⁹, but Hutchinson *et al.*¹⁹ showed experimentally that this equality does not actually hold. Instead, MDSC signals can be effectively interpreted in terms of complex, in-phase and out-of-phase heat capacities with a real part C' (storage heat capacity) and an imaginary part C'' (loss heat capacity)^{33,60-62}. It should be noted that the use of the complex heat capacity is contingent upon a linear response between the heating rate and heat flow which should be ascertained through construction of a Lissajous plot^{33,63}. When correctly implemented, this approach permits to extract the fragility by measuring the shift of the loss peak with oscillating frequency⁶² and can also provide estimates of the stretching exponent β ⁶⁴. These two parameters provide a more complete and reliable assessment of the relaxation properties of a glass-forming system than ΔH_{nr} .

VI. CONCLUSIONS

In this study, Ge-Se glasses lying outside and inside the “reversibility window” were annealed at room temperature for up to twenty years. The purpose of this experiment was to test whether glasses from the “reversibility window” exhibit any resistance to physical aging as previously claimed. A sizable enthalpy relaxation was observed for all glasses including those within the so-called “reversibility window”. Furthermore, the relaxation process obeys a stretched exponential decay characteristic of amorphous systems. The heat capacity curves of each glass followed the behavior expected from the TNM model for systems annealed far from T_g . The values of stretching exponent β and relaxation time τ were also consistent with expectations. These results demonstrate that glasses from the “reversibility window” do not show any particular resistance to relaxation or aging. In addition, Raman spectra of both glasses reveal that structural relaxation is associated with a conversion of edge-sharing to corner-sharing tetrahedra. This structural

evolution is consistent with an increase in density and a decrease in configurational entropy. The structural mechanism is identical in both glasses and further confirms that glasses from the “reversibility window” do not show any unusual relaxation behavior relative to other compositions in the same system. Finally, these results invalidate the interpretation of a vanishing value of ΔH_{nr} as indicative of a resistance to aging. This is an important consideration in view of the increasing popularity of MDSC and its extension to the characterization of high temperature oxide glasses⁶³.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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