Relaxation dynamics in the strong chalcogenide glass-former of Ge$_{22}$Se$_{78}$

Pengfei Li, Yaqi Zhang, Zeming Chen, Peng Gao, Tao Wu & Li-Min Wang

The enthalpy relaxation is performed in the glassy Ge$_{22}$Se$_{78}$ to understand the dynamic behaviors. The structure of the glass is examined by X-ray diffraction and Raman spectra. The dynamic parameters such as the fragility, stretching exponent and non-linear factor are determined. A low fragility of $m = 27$ is exhibited for the chalcogenide, however, the stretching exponent is found not to have a larger value. The enthalpy relaxation spectra are constructed for various glass formers, and a relationship between the fragility and the symmetry of the spectra is demonstrated. The dynamic results are used to evaluate the structure of the Ge$_{22}$Se$_{78}$ glass.

Ge$_{x}$Se$_{1-x}$ chalcogenide glasses exhibit superior optical properties in the infrared region, and have been considerably applied in the industries such as solar cells and infrared optical fibers$^{1,2}$. Due to the non-equilibrium nature of glassy materials and the tendency moving towards equilibrium states or stable states to release excess energy, the structure and properties might be subjected to variation at a specific temperature, which is initiated by the structural relaxation$^3$. Therefore, the stability of glassy materials is directly related to the structural relaxation dynamics, which is critical to understand the property changes in such materials. The relaxation dynamics of the Se-rich Ge$_{x}$Se$_{1-x}$ glasses have been explored for decades$^{4-6}$, however, a complete interpretation is still needed. In addition, the structure in Ge$_{x}$Se$_{1-x}$ glasses has been a subject of discussion concerning the connection patterns of the basic structural motifs of Ge-Se tetrahedra and (Se)$_{n}$ units$^{7-9}$. Besides the direct structure analyses method such as the diffraction methods$^{10}$ and NMR spectroscopy$^{11}$, dynamic studies have proven to be capable of offering insights into the structure of glasses$^{12,13}$.

Generally, the structural relaxation in glassy materials is largely governed by three dynamic aspects covering non-Arrhenius, non-exponential and non-linear behaviors$^{12}$. The fragility $m$-index reflects how rapidly liquid viscosity or structural relaxation time changes at the glass transition temperature $T_g$, and is quantified by $\log_{10}(\sigma(T)/\sigma(T_g))$ in Angell plot, where $\sigma$ denotes the viscosity or the relaxation time$^{14}$. The stretching exponent (or non-exponential factor) $\beta_{KWW}$ quantifies the degree of the non-exponential dynamics and is usually involved in the isothermal Kohlrausch-William-Watts (KWW) function in the time domain, $\phi(t) = \exp[-(t/\tau_{KWW})^{\beta_{KWW}}]$, where $\tau_{KWW}$ is the structural relaxation time, and $\beta_{KWW}$ is the stretching exponent with $0 < \beta_{KWW} \leq 1$.$^{14-18}$ The non-linear factor defines how much the structural relaxation dynamics in glassy states depends on the thermal history.

Considerable efforts have been made to explore the dynamics in the Ge$_{x}$Se$_{1-x}$ melts and glasses, however, the reported results are not consistent. Based on the viscosity data of the Ge$_{100-x}$ melts, the fragility in the compositions of 10 $< x < 25$ is calculated to range from 22.5 to 32$^{15,19}$. The enthalpy relaxation studies of Ge$_{x}$Se$_{2-x}$ and Ge$_{x}$Se$_{8}$ reported $m = 58-59^{20}$. For the Ge$_{x}$Se$_{100-x}$ alloys with 10 $< x < 33$, the fragility $m$ index was reported to be 14.8–29 using the modulated differential scanning calorimetry (mDSC)$^{6}$. Recent studies of the enthalpy relaxation in Ge$_{x}$Se$_{1-x}$ ($x \leq 15$) presented a continuous decrease in fragility from 68 to 28 measured with a constant ratio between the cooling and subsequent heating rates$^{21}$. Similarly, the $\beta_{KWW}$ values (or the non-linear factor $x$) determined in the enthalpy relaxation measurements are not consistent. It is also found that the values of $\beta_{KWW}$ and $x$ determined by the enthalpy relaxation are notably higher than those determined by the volume relaxation$^{22}$.

Given accurate dynamic parameters are crucial to understand the relaxation behaviors and the structure in glassy materials$^{12,13}$, here, the structural relaxation dynamics of the Ge$_{22}$Se$_{78}$ chalcogenide glass is studied, referring to earlier studies in Ge$_{x}$Se$_{1-x}$ where a minimum fragility is identified to fall in the compositions of 19 $< x < 26$, preferentially in the range of 21.5 $< x < 23^{4-6}$. The dynamic parameters $m$, $\beta_{KWW}$ and $x$ are determined...
using the enthalpy relaxation, because the method has proven to be capable of producing quite comparable results with the viscosity or dielectric-relaxation measurements. The fragility of the Ge_{22}Se_{78} glass is determined to be low with m = 27. Surprisingly, a low stretching exponent is also revealed. The dynamic results are used to understand the structure of the Ge_{22}Se_{78} glass.

Results
Figure 1(a) and (b) present the XRD patterns and Raman spectra of the glassy Ge_{22}Se_{78} samples synthesized for 24 + 10 hours (details are presented in the Sample preparation section) and 24 + 168 hours. The nature of completely amorphous states is identified for the two samples by the XRD patterns using the wave vector gauged by $q = 4\pi \sin \theta/\lambda$. The intermediate-range order is unambiguously observed by the featured first-sharp-diffraction-peak (FSDP) at $q = 1.09 \text{ Å}^{-1}$, given that the FSDPs in many non-metallic network glassy materials are typically located at $q \sim 1$–2 Å⁻¹. The Raman spectra displayed in Fig. 1(b) show two main regions: (a) a relatively sharp band with high intensity at $\sim$195 cm⁻¹ along with a shoulder located at $\sim$210 cm⁻¹ and (b) a broad band centered at 259 cm⁻¹ with high-intensity, spanning from 225 to 280 cm⁻¹. The 195 cm⁻¹ band in region (a) is assigned specifically to the breathing mode of corner-shared (CS) GeSe₄ tetrahedral units and the 210 cm⁻¹ band is assigned to the vibration of Se atoms involved in edge-shared (ES) GeSe₄ tetrahedral units.

Figure 1. (a) XRD patterns of Ge_{22}Se_{78} with different synthesis time before quenching (b) Raman spectra of Ge_{22}Se_{78} at room temperature. (CS) in the Raman spectrum denotes the corner-shared GeSe₄ tetrahedra, (ES) denotes the vibration of Se atoms in edge-shared GeSe₄ tetrahedra, and (SM) is Se-Se stretching modes in (Se)n units.
work are largely comparable with the reported results based on different methods such as viscosity and DSC measurements.

The cooling/heating capacity curves of the Ge\textsubscript{22}Se\textsubscript{78} glass with synthesis time of 24 + 10 and 24 + 168 hours before quenching into ice water are shown in Fig. 4(a) using the rates of 1, 2.5, 5, 10, and 20 K/min across glass transition (from top). The heating rates are fixed to be 20 K/min. (a) The sample with the synthesis time of 24 + 10 hours before quenching; (b) The sample with the synthesis time of 24 + 168 hours.

Figure 2. Heating heat flow curves of Ge\textsubscript{22}Se\textsubscript{78} glasses quenched from various cooling rates, −1, −2.5, −5, −10, and −20 K/min across glass transition (from top). The heating rates are fixed to be 20 K/min. (a) The sample with the synthesis time of 24 + 10 hours before quenching; (b) The sample with the synthesis time of 24 + 168 hours.

Figure 3. (a) Dependence of fictive temperature on cooling rate, which presents fragility m-indexes to be 23 and 27 respectively for the Ge\textsubscript{22}Se\textsubscript{78} synthesized for 24 + 10 and 24 + 168 hours before quenching. The inset of (a) shows \( C_p \) difference between the glasses quenched from cooling rate of 20 K/min and the glasses quenched at other rates; (b) Fragility curves of glass formers from the Ge\textsubscript{x}Se\textsubscript{1-x} system and the data were adapted from ref. 4. (r) = 2.5, 2.45, 2.4, 2.3, 2.2 and 2.02 correspond to the composition Ge\textsubscript{0.25}Se\textsubscript{0.75}, Ge\textsubscript{0.225}Se\textsubscript{0.775}, Ge\textsubscript{0.2}Se\textsubscript{0.8}, Ge\textsubscript{0.15}Se\textsubscript{0.85}, Ge\textsubscript{0.1}Se\textsubscript{0.9}, and Ge\textsubscript{0.01}Se\textsubscript{0.99}, respectively.

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glass and subsequent recovery towards equilibrium supercooled liquid at temperature well higher than $T_g$. The enthalpy relaxation spectrum of the Ge$_{22}$Se$_{78}$ glass is shown in Fig. 4(c), giving the maximum relaxation enthalpy, $\Delta H_R$ to be 0.708 J/g.

Figure 4. (a) Heat capacity curves of Ge$_{22}$Se$_{78}$ synthesized for 24 + 168 hours in the vicinity of glass transition during the cooling and heating measurements at the cooling/heating rates of $-/+20$ K/min. (b) Enthalpy curves in the cooling and reheating cycle. (c) Enthalpy difference involved in the cooling and reheating cycle, indicating the enthalpy relaxation and enthalpy recovery in the quenched glasses upon reheating.

Figure 5. Heat capacity curves measured in the cooling and heating processes for Ge$_{x}$Se$_{1-x}$ and other glass-forming materials with diverse fragility, including small molecules, metals and oxides. All the curves were measured at the cooling/heating rates of $-/+20$ K/min. The materials are Ge$_{22}$Se$_{78}$, B$_2$O$_3$, Pd$_{39}$Ni$_{10}$Cu$_{30}$P$_{21}$, glycerol, di-$n$-butyl-phthallate and decalin.

glass and subsequent recovery towards equilibrium supercooled liquid at temperature well higher than $T_g$. The enthalpy relaxation spectrum of the Ge$_{22}$Se$_{78}$ glass is shown in Fig. 4(c), giving the maximum relaxation enthalpy, $\Delta H_R$ to be 0.708 J/g.
Figure 5 shows the heating and cooling $C_p$ curves for a group of glass forming liquids of diverse fragility with temperature normalized to their $T_f$ values. Five more glass forming systems are used covering inorganic oxide, molecular and metallic glasses. Accordingly, the enthalpy relaxation spectra are plotted in Fig. 6 using the temperature reduced by the fictive temperature and, consequently, the peak values in the spectra read $\Delta H_f/T_f^s$.

To understand the enthalpy relaxation spectra in temperature domain defined by the enthalpy difference curves, we define a parameter of $S = F_2/F_1$ to reflect the symmetry of the spectra as shown in the inset of Fig. 7, where $F_1$ and $F_2$ denote the half width at half maximum of the peak in the left and right flanks, respectively, and therefore, $F_1 + F_2$ defines the full width at half maximum. Figure 7 presents the relation between the symmetry parameter $S$ and fragility. The majority of the data are seen to fall into a master curve, and increased symmetry of the relaxation spectra is evident for strong liquids. Based on the correlation shown in Fig. 7, a complete symmetry might be expected for the strongest liquid of $m_{min} = 16$.

The heating (upscan) $C_p$ curves of the glasses quenched at a cooling rate of 20 K/min are analyzed using the Tool–Narayanaswamy–Moynihan–Hodge (TNMH) equations, which emphasize the effects of fragility, nonlinear parameter $x$ and stretching exponent $\beta_{KWW}$. The application of the TNMH equations requires the equality between the normalized $C_p$ curves and the temperature derivative of the fictive temperature, $dT_f/dT$ (detailed description is available in early studies). The fit of the TNMH equations to the normalized $C_p$ data therefore proceeds with the parameters of pre-exponential ($A$), apparent activation energy ($E_a = \ln10RT_m$), $x$ and $\beta_{KWW}$. With $m = 27$ available for the Ge$_{22}$Se$_{78}$ glass, the fit gives the two parameters, $\beta_{KWW}$ and $x$, to be $0.43 \pm 0.05$ and $0.64 \pm 0.05$ respectively as shown in Fig. 8. It is noted that the mediate glass transition temperature $T_g$ and the marked glass-transition heat capacity increment for the Ge$_{22}$Se$_{78}$ glass are advantageous for the enhanced
accuracy in the DSC measurements and, consequently guarantee the reliable results of the non-exponential and non-linear parameters involved in the enthalpy relaxation. It is a surprise to see such a low $\beta_{KWW}$ value for the Ge$_{22}$Se$_{78}$ glass presents the large deviation from the general correlation between $m$ and $\beta_{KWW}$.

**Discussion**

The determination of the fragility for the Ge$_{22}$Se$_{78}$ glass indicates that the glass former belongs to the category of strong dynamics according to the Angell’s strong-fragile classification scheme. The fragility of various glass formers has been explored for decades and, experimentally, the accessible $m$-index spans from the hitherto strongest SiO$_2$ of $m = 20$ to the most fragile cis/trans-decalin of $m = 145$. The low fragility ($m = 27$) for the Ge$_{22}$Se$_{78}$ alloy is somehow unexpected since, for inorganic substances, the extremely low fragility is generally associated with the network glass-forming materials with the MX$_2$ stoichiometry such as SiO$_2$ and GeO$_2$, where the structures are built predominantly by tetrahedral MX$_4$ motifs. Numerically, the Ge$_{22}$Se$_{78}$ fragility is quite comparable with those of BeF$_2$ ($m = 24$) and ZnCl$_2$ ($m = 30$) glasses, which have strong directional bonds for the network structure.

Studies found that strong glass formers with low $m$ indexes generally have relatively high $\beta_{KWW}$ values (typically higher than 0.6 for the liquids with $m < 40$). Therefore, at a glance, the low enthalpy-relaxation-based $\beta_{KWW}$ of 0.43 is unusual when compared with the strong Ge$_{22}$Se$_{78}$ glass of $m = 27$. In the earlier studies of the $\beta_{KWW}$ data produced by enthalpy relaxation and dynamic measurements such as dielectric and mechanical relaxations for various glass formers, excellent consistency is often exhibited, suggesting the TNMH-based enthalpy relaxation can produce reliable stretching exponents. It appears that the low $\beta_{KWW}$ value of 0.43 makes the Ge$_{22}$Se$_{78}$ glass to be an exception in the strong glass formers with simple compositions.

Dynamic behaviors in glass formers have been recognized to be associated with the structural features of glasses and melts. Our recent studies of binary glass forming mixtures showed that mixing always generates a negative shift of the actual fragility relative to the linear averaging of the fragility values of the two pure components, independent of the sign of the enthalpy of mixing. And in some cases, the minimum fragility can be achieved at an intermediate composition in mixtures. Similarly, the studies of binary glass formers with weak intermolecular interactions detected the lower $\beta_{KWW}$ values than those of pure components, suggesting effective broadening of the relaxation dispersion. In contrast, in the mixtures with strong intermolecular interactions manifested by large and negative enthalpies of mixing, enhanced $\beta_{KWW}$ values are evident. For the Ge$_{22}$Se$_{78}$ glass, it is, consequently, speculated that the low fragility $m$-index and the small $\beta_{KWW}$ value might be partly associated with the mixing effect. This is quantitatively consistent with the random connectivity of the basic structural motifs of GeSe tetrahedra and (Se)$_n$ units in the Ge$_{22}$Se$_{78}$ glass, as involved in the reported models. Due to the unique structure of GeSe (much different from those of GeO$_2$ or SiO$_2$) and Au$_{26}$Cu$_{26}$Ag$_{53}Pd$_{2}Si$_{16}$, similar relations are reached. Further study appears to be necessitated to clarify the unusual behavior.

**Figure 8.** Normalized heat capacity derived in terms of the temperature derivative of the fictive temperature of various glass formers determined using the experimentally measured heating $C_p$ curves of the glasses quenched at cooling rates of 20 K/min. The heating rates are 20 K/min for all the $C_p$ measurements. The fits of the TNMH equations give the nonlinear factor $x$ and the stretching exponent $\beta_{KWW}$.
Methods

Sample preparation. The sample glass GeₓSe₁₀₀ was prepared with the melt-quenching method²⁷. Pure elements of Ge and Se (5N purity, Alfa) mixed according to specific fractions with weight of ~1.5 g are sealed into quartz tubes of 8 mm in diameter under a vacuum of 10⁻³ Pa. The mixtures were heated up to 1230 K, higher than Tᵢ, of two pure components, and kept isothermally for 24 hours in a rocking furnace to promote the degree of mixing. Subsequently, the temperature was set to 1020 K, which is about 100 K above the liquidus temperature for additional 10 hours (24 + 10 hours) and 168 hours (24 + 168 hours), respectively. Glasses were finally obtained by quenching the melt into ice water. The composition of the sample with the synthesized time for 24 + 168 hours was analyzed taken randomly from the bulk using the energy dispersive spectrometer (EDS) analyses (supplemental material).

Sample analyses. The structure of the melt-quenched samples were checked via the x-ray powder diffraction in a Rigaku D/MAX/2500/PC (Cu Kα, λ = 1.54 Å) and Raman measurements on a Renishaw inVia micro Raman spectroscopy with a laser radiation of 514 nm. Heating and cooling heat capacity curves were obtained by using a differential scanning calorimeter (DSC, Perkin Elmer 8000) calibrated by using indium and zinc as references. The sample mass varied from 6 to 10 mg. The calorimetric glass transition temperature Tᵩ was defined as the onset temperature of the heat capacity jump from the glassy to the liquid state. Enthalpy relaxation was performed in two manners. One used a cooling/heating cycle at the same rates of 20 K/min, and the enthalpy difference between the cooling and subsequent heating defines the relaxation enthalpy. The other is based on the identification of the enthalpy difference in the glasses quenched by various cooling rates, of which the enthalpy difference is calculated from the integral of the heating Cₓ difference among the glasses quenched at various cooling rates but fixed heating rate, typically 20 K/min. Usually, the heat capacity curve generated from cooling/heating rates of 20 K/min is set as the reference. This method has been described elsewhere²⁸. The Cₓ measurement temperature spans from Tᵩ to Tᵩ + 50 K, which can guarantee that no relaxation occurs at low temperature regimes, and equilibrium (supercooled liquids) is reached at high temperature regimes.

References

1. Calvez, L., Ma H. L., Lucas, J. & Zhang, X. H. Selenium-Based Glasses and Glass Ceramics Transmitting Light from the Visible to the Far-IR. Adv. Mater. 19, 129–132 (2007).
2. Mukherjee, B. et al. Stepped-surfaced GeSe nanobelts with high-gain photocconductivity. J. Mater. Chem. 22, 24882–24888 (2012).
3. Mauro, J. C. Grand challenges in glass science. Front. Mater. 1, 1–5 (2014).
4. Stolen, S., Grande, T. & Johnsen, H. B. Fragility transition in GeₓSe₁−ₓ liquids. Phys. Chem. Chem. Phys. 4, 3396–3399 (2002).
5. Lucas, P., Doraissamy, A. & King, E. A. Photoinduced structural relaxation in chalcogenide Glasses. J. Non-Cryst. Solids 332, 35–42 (2003).
6. Gunasekera, K., Bhusol, S., Boolchand, P. & Micoulaut, M. Superstrong nature of covalently bonded glass-forming liquids at select compositions. J. Chem. Phys. 139, 164511 (2013).
7. Kaseman, D. C., Oliveira, K. M., Palazzo, T. & Sen, S. Selenium chain length distribution in GeₓSe₁−ₓ glasses: Insights from ⁷⁷Se NMR spectroscopy and quantum chemical calculations. J. Phys. Chem. B 120, 4513–4521 (2016).
8. Lucas, P. et al. Bimodal phase model for the structure of Ge-xSe glasses and the existence of the intermediate phase. Phys. Rev. B 80, 214114 (2009).
9. Boolchand, P., Gunasekera, K. & Bhusol, S. Midgap states, Raman scattering, glass homogeneity, percolative rigidity and stress transitions in chalcogenides. Phys. Status. Solidi. B 249, 2013–2018 (2012).
10. Bouzid, A. et al. Pressure-induced structural changes in the network-forming isostatic glass GeₓSe; An investigation by neutron diffraction and first-principles molecular dynamics. Phys. Rev. B 93, 014202 (2016).
11. Sykina, K. et al. A combined ⁷⁷Se NMR and molecular dynamics contribution to the structural understanding of the chalcogenide glasses. Phys. Chem. Chem. Phys. 16, 17975–17982 (2014).
12. Angell, C. A., Ngai, K. L., McKeown, G. B., McMillan, P. P. & Martin, S. W. Relaxation in glass forming liquids and amorphous solids, J. Appl. Phys. 88, 3113–3157 (2000).
13. Yildirim, C., Raty J.-Y. & Micoulaut, M. Revealing the role of molecular rigidity on the fragility evolution of glass-forming liquids, Nat. Commun. 7, 11086 (2016).
14. Bohmer, R., Ngai, K. L., Angell, C. A. & P hazek, D. J. Nonequilibrium relaxations in strong and fragile glass formers. J. Chem. Phys. 99, 4201–4209 (1993).
15. Ngai, K. L. Predicting the changes of relaxation dynamics with various modifications of the chemical and physical structures of glass-formers. J. Non-Cryst. Solids 353, 4327–4245 (2007).
16. Wang, L.-M. & Richert, R. Measuring the Configurational Heat Capacity of Liquids. Phys. Rev. Lett. 99, 185701 (2007).
17. Trachenko, K., Roland, C. & Casalini, R. Relationship between the Nonexponentiality of Relaxation and Relaxation Time in the Problem of Glass Transition. J. Phys. Chem. B 112, 5111–5115 (2008).
18. Cangialosi, D., Alegria, A. & Colmenero, J. On the temperature dependence of the nonexponentiality in glass-forming liquids. J. Chem. Phys. 130, 124902 (2009).
19. Nemilov, S. V. Z. Viscosity and structure of glasses in the selenium-germanium system. Zh. Prik. Khim. 37 1020 (1964).
20. Cortes, P., Montserrat, S., Ledru, I. & Saiter, J. M. Enthalpy relaxation in GeₓSe; chalcogenide glasses, J. Non-Cryst. Solids 235–237, 522–526 (1998).
21. Svboda, R. & Małek, J. Kinetic fragility of Se-based binary chalcogenide glasses. J. Non-Cryst. Solids 419, 39–44 (2015).
22. Svboda, R., Honcová, P. & Małek, J. Relaxation in GeₓSe; and AsₓSe; glasses. J. Non-Cryst. Solids 356, 447–455 (2010).
23. Wang, L.-M., Velikov, V. & Angell, C. A. Direct determination of kinetic fragility indices of glassforming liquids by differential scanning calorimetry: Kinetic versus thermodynamic fragilities. J. Chem. Phys. 117, 10184–10192 (2002).
24. Wang, L.-M., Tian, Y. J., Liu, R. F. & Richert, R. Calorimetric versus kinetic glass transitions in viscous monohydrosy alcoholic. J. Chem. Phys. 128, 084503 (2008).
25. Elliott, S. The origin of the first sharp diffraction peak in the structure of covalent glasses and liquids. J. Phys.: Condens. Matter 4, 7661–7678 (1992).
26. Sugai, S. Stochastic random network model in Ge and Si chalcogenide glasses. Phys. Rev. B 35, 1345–1361 (1987).
27. Wang, Y. & Murase, K. Floppy modes and relaxation in GeₓSe; glasses. J. Non-Cryst. Solids 326–327, 379–384 (2003).
28. Lucovsky, G., Mooradian, A., Taylor, W., Wright, G. B. & Keezer, R. C. Identification of the Fundamental Vibrational Modes of Trigonal, α-Monoclinic and Amorphous Selenium. Solid State Commun. 5, 113–117 (1967).
29. Giersing, E., Sen, S. & Aitken, B. Structure, Connectivity, and Configurational Entropy of GeₓSe; glasses: Results from ⁷⁷Se MAS NMR Spectroscopy. J. Phys. Chem. C 114, 8601–8608 (2010).
30. Tool, Q. Relaxation of Stresses in Annealing Glass. J. Res. Natl. Bur. Stand. (US) 34, 199–211 (1945).
31. Yue, Y. Z., vanderbeke, R. & Jensen, S. L. Fictive temperature, cooling rate, and viscosity of glasses. J. Chem. Phys. 120, 8053–8059 (2004).
32. Crowdy, K. J. & Zograf, G. The use of thermal methods for predicting glass-former fragility. Thermochim. Acta 380, 79–93 (2001).
33. Wüntgenar, R. & Schmidt, S. J. Phenomenological study of enthalpy relaxation of amorphous glucose, fructose, and their mixture. Thermochim. Acta 369, 95–116 (2001).
34. Barkatt, A. & Angell, C. A. Optical probe studies of relaxation processes in viscous liquids. J. Chem. Phys. 70, 901–911 (1979).
35. Angell, C. A. Calorimetric Studies of The Energy Landscapes of Glassformers by Hyperquenching Methods. J. Therm. Anal. Calorim 69, 785–794 (2002).
36. Chen, Z. M. et al. Dependence of calorimetric glass transition profiles on relaxation dynamics in non-polymorphic glass formers. J. Non-Cryst. Solids 433, 20–27 (2016).
37. Wang, L. M. Enthalpy Relaxation upon Glass Transition and Kinetic Fragility of Molecular Liquids. J. Phys. Chem. B 113, 5168–5171 (2009).
38. Chen, Z. M. et al. Calorimetric determination of fragility in glass forming liquids: Tt vs. Tg-onset methods. Eur. Phys. J. E 37, 1–7 (2014).
39. Hodge, J. M. A Personal Account of Developments in Enthalpy Relaxation: A Tribute to C. T. Moynihan. J. Am. Ceram. Soc. 91, 766–772 (2008).
40. Wang, L.-M., Angell, C. A. & Richert, R. Fragility and thermodynamics in nonpolymeric glass-forming liquids. J. Chem. Phys. 125, 074505 (2006).
41. Salmon, P. S. & Ziedler, A. Identifying and characterising the different structural length scales in liquids and glasses: an experimental approach. Phys. Chem. Chem. Phys. 15, 15286–15308 (2013).
42. Eckert, H. Structural Characterization of Non-Chalcogenide Chalcogenide Glasses using Solid State NMR. Adv. Mater. 12, 423–432 (1999).
43. Angell, C. A. Formation of Glasses from Liquids and Biopolymers. Science (Washington) 267, 1924 (1995).
44. Wei, S., Gallino, I., Busch, R. & Angell, C. A. Glass transition with decreasing correlation length during cooling of Fe50Co50 superlattice and strong liquids. Nat. Phys. 7, 178–182 (2011).
45. Wang, L.-M. & Richert, R. Primary and secondary relaxation time dispersions in fragile supercooled liquids. Phys. Rev. B 76, 064201 (2007).
46. Gao, Y. Q. et al. Anomalous in dielectric relaxation dispersion of glass-forming alkoxy alcohols. J. Chem. Phys. 142, 214505 (2015).
47. Wang, L.-M., Tian, Y. J., Liu, R. P. & Richert, R. Structural Relaxation Dynamics in Binary Glass-Forming Molecular Liquids with Ideal and Complex Mixing Behavior. J. Phys. Chem. B 114, 4216–4222 (2010).
48. Gong, H. X. et al. Kinetic fragility of binary and ternary glass forming liquid mixtures. Eur. Phys. J. E. 34, 1–6 (2011).
49. Rodenburg, B. V. & Sidebottom, D. L. Dynamic light scattering in mixed alkali metaphosphate glass forming liquids. J. Chem. Phys. 125, 024502 (2006).
50. Yang, G. et al. Physical properties of the Ge\textsubscript{x}Se\textsubscript{1-x} glasses in the 0 < x < 0.42 range in correlation with their structure. J. Non-Cryst. Solids 377, 54–59 (2013).
51. Boolchand, P. & Bresser, W. J. The structural origin of broken chemical order in Ge\textsubscript{8}Se\textsubscript{12}. Philos. Mag. B 80, 1757–1772 (2000).
52. Bouchy, M. et al. Angular rigidity in tetrahedral network glasses with changing composition. Phys. Rev. B 84, 054201 (2011).
53. Bureau, B. et al. Germanium selenide glass structures studied by 77Se solid state NMR and mass spectroscopy. J. Non-Cryst. Solids 319, 145–153 (2003).
54. Hodge, J. M. Adam-Gibbs Formulation of Enthalpy Relaxation Near the Glass Transiti. J. Res. Natl. Inst. Stand. Technol. 102, 195 (1997).
55. Hammond, V. H., Houtz, M. D. & O’Reilly, J. M. Structural relaxation in a bulk metallic glass. J. Non-Cryst. Solids 325, 179–186 (2003).
56. Wei, S., Lucas, P. & Angell, C. A. Phase change alloy viscosities down to Tg using Adam-Gibbs-equation fittings to excess entropy data: A fragile-to-strong transition. J. Appl. Phys. 118, 034903 (2015).
57. Saiter, J. M., Chebli, K. & Hamou, A. Enthalpy relaxation and structure in vitreous Ge\textsubscript{45}Te\textsubscript{55}. Physica B 293, 98–107 (2000).
58. Wang, J. Q., Shen, Y., Perepezko, J. H. & Ediger, M. D. Increasing the kinetic stability of bulk metallic glasses. Acta Mater. 104, 25–32 (2016).

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