Journal of Non-Crystalline Solids

Viscosity, enthalpy relaxation and liquid-liquid transition of the eutectic liquid Ge15Te85

--Manuscript Draft--

Manuscript Number:	NOC-D-20-01151R1
Article Type:	Full Length Article
Keywords:	viscosity; enthalpy relaxation shear relaxation; Ge15Te85 eutectic liquid; parallel plate rheometry; conventional and modulated differential scanning calorimetry
Corresponding Author:	Sabyasachi Sen, Ph.d. University of California, Davis Davis, CA United States
First Author:	Weidi Zhu
Order of Authors:	Weidi Zhu
	Ozgur Gulbiten
	Bruce Aitken
	Sabyasachi Sen, Ph.d.
Abstract:	The viscosity and enthalpy relaxation in the Ge15Te85 eutectic liquid are investigated using parallel plate rheometry and conventional and modulated differential scanning calorimetry (DSC). The results of these measurements provide evidence for similar temperature dependence of enthalpy and shear relaxation timescales in this liquid. However, the enthalpy relaxation is found to be more than an order of magnitude slower than the shear relaxation. The temperature dependence of the viscosity of the Ge15Te85 liquid in the supercooled state and above its melting point can be described using a single fragility index, except over a narrow temperature region in the vicinity of the melting point where the viscosity abruptly increases, signifying a liquid-liquid transition. This anomalous viscosity jump coincides with the onset of an exothermic event observed in the DSC cooling curve. Together, these results are consistent with a transition that involves incipient liquid-liquid immiscibility that can be bypassed via rapid supercooling.
Response to Reviewers:	

Journal of
Non-Crystalline Solids

Confirmation of Authorship

Please save a copy of this file, complete and upload as the "Confirmation of Authorship" file.

As corresponding author, I Sabyasachi Sen, hereby confirm on behalf of all authors that:

1. This manuscript has not been published, was not, and is not being submitted to any other journal. If presented at a conference, the conference is identified. If published in conference proceedings, substantial justification for re-publication must be presented.

2. All necessary permissions for publication were secured prior to submission of the manuscript.

3. All authors listed have made a significant contribution to the research reported and have read and approved the submitted manuscript, and furthermore, all those who made substantive contributions to this work have been included in the author list.

Response to reviewer's comments:

1. As for MDSC, I miss the figure of measured spectra, which are the key to understanding the results. I am surprised that the authors determined the Tg from conventional DSC. As is known, MDSC clearly separates fast kinetic effects from slow thermodynamic ones, so the Tg determined from the reversible component (Cp vs T) would certainly be the correct value. If it does not correspond to a viscosity value of 12 Pa.s, the MDSC measurement parameter settings should be checked.

Response: We are using MDSC as straightforward heat capacity spectroscopy and not attempting the controversial separation of fast kinetic and slow thermodynamic effects. In this regard we draw the referee's attention to the heat capacity spectroscopy paper by Birge and Nagel (Physical review Letters, 54, 2674 (1985)). Conventional DSC using 10 or 20 K/min heating rate is a globally accepted standard method for Tg determination. Also, the corresponding timescales from the measurement oscillations period after converting to angular frequencies are in the range of ~ 14-28s. We cannot directly obtain the Tg from these measurements as Tg correspond to an enthalpy relaxation time of 100s. We have also stated why Tg may not correspond to a viscosity of 10^12 Pa.s as enthalpy and shear relaxation timescales may be different. The referee must have overlooked this discussion on p. 9 and p.10 of the manuscript. This issue is also addressed in J. Chem. Phys. 135, 214502 (2011). No changes are made in response to this comment.

2. Fig.4 : It seems to me that the shape of the curve measured at 40 K / min shown in the inset does not correspond to the shape of the same part of the curve shown in the figure. The explanation in the text does not seem to correspond to the picture. Moreover, it doesn't seem to me that the sentence "The positions of all endothermic (exothermic) peaks obtained on heating (cooling) at different rates coincide and have a similar width" describes the reality of the picture.
   There are peaks on the heating curve (black curve) that correspond to a relatively complicated crystallization. I miss the discussion of these effects in the text.

Response: It is exactly the same figure- it may appear different due to scale magnification! The location of the extrema in the inset all coincide as shown by the dashed vertical line. The crystallization events are not the focus of this paper, but the two crystallization peaks likely correspond to the crystallization of GeTe and Te as part of the eutectic process. This is already mentioned in the original manuscript and no further changes are made.

3. Similarly, the curve in the insert of Fig. 3 does not appear to correspond to the Tp values in the figure. Their change seems too uneven to result in such an ideal dependence.
I would recommend to the authors that the key values obtained experimentally be listed in the table.

Response: The referee may have overlooked the different temperature scales in the main figure (in ºC) vs. the inset (in K) and the conversion from modulating period to frequency, which involves a factor of 2π. We have now added a table of these data, which should clear up the confusion.

*Abstract

Abstract

The viscosity and enthalpy relaxation in the $Ge_{15}Te_{85}$ eutectic liquid are investigated using a combination of parallel plate rheometry and conventional and modulated differential scanning calorimetry (DSC). The results of these measurements provide evidence for similar temperature dependence of enthalpy and shear relaxation timescales in this liquid. However, the enthalpy relaxation is found to be more than an order of magnitude slower than the shear relaxation process. The temperature dependence of the viscosity of the $Ge_{15}Te_{85}$ liquid in the supercooled state and above its melting point can be described using a single fragility index, except over a narrow temperature region in the immediate vicinity of the melting point where the viscosity abruptly increases, signifying a liquid-liquid transition. This anomalous viscosity jump coincides with the onset of an exothermic event observed in the DSC cooling curve. Together, these results are consistent with a transition that involves incipient liquid-liquid immiscibility that can be bypassed via rapid supercooling.

Highlights:

- Viscosity and enthalpy relaxation in the $Ge_{15}Te_{85}$ eutectic liquid are investigated
- Enthalpy relaxation is an order of magnitude slower than the shear relaxation
- Liquid-liquid transition is consistent with an incipient liquid-liquid immiscibility

Viscosity, enthalpy relaxation and liquid-liquid transition of the eutectic liquid $Ge_{15}Te_{85}$

[1]Weidi Zhu, [2]Ozgur Gulbiten, [2]Bruce Aitken, [1]Sabyasachi Sen*

[1]Department of Materials Science & Engineering, University of California at Davis,

Davis, CA 95616, USA

[2]Science & Technology Division, Corning Incorporated, Corning, NY 14831, USA

Abstract

The viscosity and enthalpy relaxation in the $Ge_{15}Te_{85}$ eutectic liquid are investigated using a combination of parallel plate rheometry and conventional and modulated differential scanning calorimetry (DSC). The results of these measurements provide evidence for similar temperature dependence of enthalpy and shear relaxation timescales in this liquid. However, the enthalpy relaxation is found to be more than an order of magnitude slower than the shear relaxation process. The temperature dependence of the viscosity of the $Ge_{15}Te_{85}$ liquid in the supercooled state and above its melting point can be described using a single fragility index, except over a narrow temperature region in the immediate vicinity of the melting point where the viscosity abruptly increases, signifying a liquid-liquid transition. This anomalous viscosity jump coincides with the onset of an exothermic event observed in the DSC cooling curve. Together, these results are consistent with a transition that involves incipient liquid-liquid immiscibility that can be bypassed via rapid supercooling.

1. Introduction

A eutectic liquid upon cooling undergoes simultaneous freezing and decomposition, which begs the question as to whether such liquids may undergo structural rearrangement near and above the melting/freezing point, which could act as a precursor of simultaneous crystallization of two solid phases with significantly different compositions and structures. Previous studies have shown that a wide variety of eutectic liquids display anomalous superliquidus non-Arrhenius viscosity behavior, which is often accompanied by anomalies in density and electrical conductivity and relatively sharp structural changes [3–8]. Particularly noteworthy in this regard is the behavior of the eutectic composition $Ge_{15}Te_{85}$ in the binary Ge-Te system that crystallizes into a mixture of two phases with rather different chemical compositions, namely GeTe and pure Te, below the eutectic temperature T_m located near 661 K [9]. The $Ge_{15}Te_{85}$ liquid has been studied widely for the anomalous temperature dependence of many of its physical properties above T_m. Tsuchiya reported a minimum in both the molar volume near 773 K and the thermal expansion coefficient near 673 K, the former being reminiscent of the well-known molar volume anomaly in water [2,10]. Further investigations revealed an anomalous broad maximum in the heat capacity centered around 673 K, which spans approximately 100 K [3,11]. Anomalous behavior was also reported in the transport properties of $Ge_{15}Te_{85}$ liquid as its viscosity and electrical resistivity were found to rise abruptly when the temperature approached T_m upon cooling [5,12,13].

A number of recent studies have suggested the possible association of these anomalies with a fragile-to-strong transition (FST) in the supercooled liquid state [14] of the $Ge_{15}Te_{85}$ liquid. The fragility index m of a glass-forming liquid is defined as $m = \left.\frac{d\log\eta}{d(T_g/T)}\right|_{T=T_g}$, where η is the viscosity of the liquid and T_g is its glass transition temperature. A 'fragile' liquid is characterized by a large

m, while the opposite is true for a 'strong' liquid. The temperature dependence of viscosity of a wide variety of glass-forming liquids can be described reasonably well, over the entire range of supercooling, by the MYEGA equation [15]:

$$\log_{10}\eta(T) = \log_{10}\eta_\infty + \left(\log_{10}\eta_{T_g} - \log_{10}\eta_\infty\right)\frac{T_g}{T} exp\left[\left(\frac{m}{\log_{10}\eta_{T_g} - \log_{10}\eta_\infty} - 1\right)\left(\frac{T_g}{T} - 1\right)\right]$$

In this equation $\log_{10}\eta_{T_g}$ and $log_{10}\eta_\infty$ correspond to the logarithm of viscosity at T_g and at infinite temperature, respectively. Therefore, the $log_{10}\eta$ vs. $\frac{T_g}{T}$ behavior of a glass-forming liquid over the entire range of supercooling is expected to be approximately characterized by a single value of m. However, a number of studies have claimed that a variety of glass-forming liquids violate this behavior as they are characterized by a low value of m, i.e. behave as a strong liquid at low temperatures near T_g, while their viscosity near the liquidus is characteristic of that of a fragile liquid with high m[12,16,17]. For $Ge_{15}Te_{85}$, it has been found that the fragility index m obtained via calorimetric methods based on the cooling rate dependence of the fictive temperature (T_f) (m ~ 50) differs significantly from that (m ~ 98) corresponding to the η(T) behavior well above T_m, measured using oscillation viscometry. However, direct estimation of m based on viscosity measurements in the supercooled liquid state near T_g has remained lacking.

Additionally, irrespective of the existence of an FST, anomalies in the thermophysical and transport properties of $Ge_{15}Te_{85}$ liquid near T_m suggest the existence of a liquid-liquid structural transition. Previous X-ray and neutron scattering experiments across the transition indicated the formation of ordered structures in the $Ge_{15}Te_{85}$ liquid as T_m is approached from above [5,7,8]. Neumann further introduced the idea that the liquid forms different associates or structural moieties at temperatures immediately above T_m, which possess precursor structures similar to those of the crystalline phases α-GeTe and pure Te that form during eutectic crystallization [5]. This hypothesis is intriguing as it can explain how a eutectic liquid crystallizes into domains of such drastically different chemical compositions as GeTe and Te. Such a scenario has been corroborated by the results of the *ab initio* molecular dynamics (MD) simulation by Kalikka et al. that has shown the formation of clusters of GeTe network interconnected by Te domains in the liquid [18]. This incipient clustering in a liquid at the immediate vicinity of T_m is somewhat akin to conventional phase separation, which normally results in an abrupt and concomitant rise in the melt viscosity and a broad heat capacity anomaly [19,20].

Here we report direct viscosity measurements of the $Ge_{15}Te_{85}$ liquid in both supercooled and superliquidus states using parallel plate rheometry to analyze the fragility of this liquid. We also present results of conventional (linear) and modulated differential scanning calorimetry (DSC) to investigate the enthalpy relaxation behavior of the supercooled liquid near its glass transition. Finally, we isolate the enthalpy signal corresponding to the liquid-liquid transition and demonstrate complete reversibility of the latter.

2. Experimental Details

2.1. Synthesis and rheometry

The $Ge_{15}Te_{85}$ glass was synthesized using the conventional melt-quench method from constituent elements (≥99.999% purity, metal basis) in an evacuated quartz ampoule. Details of the synthesis are reported elsewhere [21]. The viscosity near T_m in the temperature range of 659-754 K was measured by an Anton Paar MCR302 rheometer with a parallel-plate setup. The temperature of the experiment environment was controlled by a convection oven with flowing N_2 as the heating agent. The sample was confined in a 0.5 mm gap between two plates in parallel with a diameter of 25 mm. During the measurement, a constant shear rate of 10 s^{-1} was applied to the sample, while the corresponding torque was monitored as a function of time. The viscosity of the sample was taken as the average viscosity value within a 2 min observation window. The chemical composition of the sample was analyzed before and after the experiment with electron probe microanalysis, and no significant change was observed.

The viscosity of the supercooled $Ge_{15}Te_{85}$ liquid near T_g was measured using an Anton Paar MCR92 rheometer with a parallel-plate setup (8 mm diameter). The temperature of this rheometer was controlled by a Peltier heater under constant N_2 flow. The sample was first quickly heated to 453K, followed by pressing and trimming to form a sandwich-like geometry (1-1.5 mm thick) with both plates. The temperature was then rapidly lowered to each measurement temperature. A constant shear stress was applied to the sample, while the creep compliance was monitored as a function of time. The viscosity was calculated from the compliance slope in the steady shear flow regime, where the compliance increases linearly with time. A fresh sample was used for measurement at every temperature. The creep compliance $J(t)$ can be related to the viscosity η via the classical equation:

$$J(t) = \frac{\gamma(t)}{\sigma} = J_g + J_d\Psi(t) + t/\eta$$

where J_g and $J_d\Psi(t)$ are the glassy compliance and delayed compliance, respectively [22]. At long times where the steady state is reached, $\Psi(t)$ approaches unity, and therefore the contribution to $J(t)$ comes entirely from the viscous flow t/η, i.e. $J(t)$ scales linearly with time. The viscosity was calculated as the inverse of the slope of this linear region at every temperature.

2.2. Differential scanning calorimetry

The linear DSC experiments were performed on a Mettler-Toledo DSC1 calorimeter under constant N_2 flow. Powder samples (5-10 mg) were packed and sealed in a 40 μL aluminum crucible. The T_g was taken as the onset of the endothermic glass transition signal while heating the sample at a constant rate of 10 K/min, following cooling at the same rate from T_g +30K to T_g −50K. The fragility of the sample was also determined using the calorimetry method [3], where the T_g was monitored as a function of heating rate. Before every heating scan for T_g measurement, the sample was first heated to and cooled from T_g +30K to T_g −50K where the cooling rate was the same as the following heating rate.

The modulated DSC (MDSC) experiments were performed on a Mettler Toledo DSC2. Before the measurement, a thin piece of the sample was loaded into a hermetically sealed 40 μL aluminum pan and was subsequently heated to 425.15 K, isothermally held for 1 min to erase the thermal history, and then cooled to 298.15 K at the cooling rate of 2 K/min. Subsequently, the MDSC scan was performed during heating from 298.15 K to 425.15 K in a flowing nitrogen environment where a sinusoidal temperature profile was superimposed onto a linear cooling rate. The overall temperature profile had an oscillating amplitude of 1 K and an average heating rate of 2 K/min. Four measurements were carried out with P = 90, 120, 150, and 180 s, where P is the periods of the oscillations during the sinusoidal temperature profile. Under a modulated heating/cooling profile, the heat capacity can be represented as a complex quantity C_p^* where the real (C_p') and the imaginary (C_p'') parts can be calculated as: $C_p' = |C_p^*| \cos\theta$ and $C_p'' = |C_p^*| \sin\theta$, with θ being the phase angle between the modulated heat flow and the modulated heating rate [23].

The constant phase angle introduced by the thermal lag in the system was corrected to yield a flat baseline for C_p' and C_p'' curves.

3. Results and Discussion

The viscosity data for the $Ge_{15}Te_{85}$ liquid in both supercooled and superliquidus states are shown in Fig. 1. These directly measured viscosity data in both the molten state as well as the supercooled liquid state near T_g grant the opportunity to test whether a single fragility index m is sufficient to describe the temperature dependence. It is clear from Fig. 1 that the low-temperature viscosity data and the high-temperature data above 673 K (before the abrupt viscosity increase) can be well described by a standard MYEGA equation with $m \sim 46$. The availability of viscosity data near 10^{12} Pa.s (Fig. 1) allows for a more accurate estimation of m for $Ge_{15}Te_{85}$ liquid using the mathematical definition of this parameter, which is related to the activation energy E_η of viscosity in this temperature range near the glass transition as: $m = E_\eta / RT_g \ln 10$. Such an analysis yields E_η = 404 kJ/mol and correspondingly m ~ 52. It can be seen from Fig.1 that there is a significant discrepancy between the superliquidus viscosity data measured by parallel plate rheometry in the present study and by oscillating-cup viscometry in previous studies.[7,12,13] A similar discrepancy in viscosity measured by the conventional and oscillatory techniques was also observed in our previous work on Ge-Se liquids and was ascribed to a possible underestimation of viscosity measured by the oscillation technique, especially at high temperatures [24]. This questionable reliability of the oscillating-cup viscometry data for the $Ge_{15}Te_{85}$ liquid is further evidenced by the recently reported viscosity data for liquid Te by Li et al.[25], measured by a transient torque method (see Fig. 1). The viscosity of Te and that of $Ge_{15}Te_{85}$ measured by the oscillation technique are found to be surprisingly similar, while our data from parallel plate rheometry show a higher viscosity for the latter liquid, which is to be expected upon addition of Ge, a known cross-linker, to Te.

We have carried out conventional DSC measurements to determine the fictive temperature T_f of the $Ge_{15}Te_{85}$ glass as a function of the cooling rate q varying over nearly two orders of magnitude following the method reported by Wei et al.[3] The accuracy of the fragility was estimated using the Frenkel-Kobeko-Reiner (FKR) relation[26] : $q\tau_R$ = constant, where τ_R is the characteristic shear relaxation timescale, given by the Maxwell relation: $\tau_R = \eta / G_\infty$ with G_∞ being the high-frequency glassy modulus (~ 1 GPa). A comparison between the temperature dependence of q and $1/\tau_R$ in Fig. 2 shows good agreement, which clearly proves the validity of the FKR relation and corroborates the fragility estimation from viscosity data.

It is interesting to note that in Fig. 1, at the DSC T_g of 406 K that corresponds to a 10 K/min scanning rate, the viscosity is merely $10^{9.5}$ Pa·s, which is significantly lower than the usual presumed value of ~10^{12} Pa·s at this temperature. The temperature T_{12}, where the viscosity is truly 10^{12} Pa·s, can be estimated by slight extrapolation of the data in Fig. 1, which yields T_{12} = 388 K. The discrepancy between T_g and T_{12} is in fact not uncommon, especially for systems with high fragility indices characterized by wide distributions of the relaxation times at the T_g with enthalpy and shear relaxation sampling different parts of this distribution [27–30]. This is indeed borne out in the frequency dependence of C_p'' of the $Ge_{15}Te_{85}$ liquid near T_g as obtained from the MDSC experiments (Fig. 3). The C_p'' maximum corresponding to the different temperature oscillation periods P provides the characteristic timescale for enthalpy relaxation $\tau_{en} = P/2\pi$ (see Table 1) . [31] The temperature dependence of τ_{en} yields an activation energy E_{en} = 464.7 kJ/mol (Fig. 3) and thus, a fragility index of $m \sim 60$ ($m = E_{en} / RT_g \ln 10$), which is consistent with but somewhat higher than that determined from the viscosity data ($m \sim 52$) in Fig. 1. However, and more interestingly, a small extrapolation of the τ_{en} vs. temperature dependence in Fig. 3 yields a temperature of ~ 401 K for $\tau_{en} = 100$ s. At this temperature the shear relaxation timescale τ_R is ~ 4 s corresponding to a viscosity of $10^{9.6}$ Pa.s (Fig. 1) and $G_\infty \sim 1$ GPa. Thus, for supercooled $Ge_{15}Te_{85}$ liquid $\tau_R \ll \tau_{en}$ at any specific temperature near T_g.

The conventional DSC heating and cooling curves of $Ge_{15}Te_{85}$ at a 40 K/min scanning rate are shown in Fig. 4. When heated above T_g, two distinct crystallization peaks could be observed. With further temperature increase, a sharp endothermic melting peak appears at around ~ 661 K, which agrees with the eutectic temperature T_m of the Ge-Te system [9]. More interestingly, and consistent with previous reports [3], the melting peak has an unusually long tail on the high-temperature side that extends to ~ 100 K above the melting point. Upon cooling, a broad exothermic broad peak was observed near $T_{exo} \sim 673$ K. Similar to the long tail of the melting peak in the heating curve, this exothermic peak spans over 150K, which makes it unlikely for the corresponding heat capacity anomaly to be associated with a first-order liquid-liquid transition. By fast cooling from 773 K to 573 K at 40 K/min, we were able to avoid crystallization and isolate this anomalous event on heating (Fig. 4). The positions of all endothermic (exothermic) peaks obtained on heating (cooling) at different rates coincide and have a similar width, which indicates the liquid-liquid transition process to be fully reversible.

In Fig. 5 we compile the superliquidus viscosity data of Fig. 1 and shift them vertically to overlap at the high-temperature end of our dataset at ~ 750 K. It can be seen that the viscosity activation energy remains the same for all data sets before the onset of the exothermic event observed in the DSC cooling curve. Below the onset temperature, the sharp rise in viscosity by several orders of magnitude coincides nicely with the heat capacity anomaly corresponding to the liquid-liquid transition. Note that in contrast, the viscosity of elemental Te does not display any anomalous trend above its melting point (Fig. 1). These results, when taken together, are consistent with a scenario of structural and chemical clustering or incipient liquid-liquid immiscibility in the $Ge_{15}Te_{85}$ liquid. The difference in the rates of rise in η reported by different groups may represent different experimental durations that would result in different degrees of clustering via a kinetically controlled process. As discussed above, this hypothesis is fully consistent with the unique characteristic of a eutectic liquid, i.e., it undergoes simultaneous freezing and decomposition. This effect of clustering in the vicinity of T_m is expected to be more pronounced in those eutectic liquids such as $Ge_{15}Te_{85}$, which simultaneously crystallize phases with significantly different compositions. Moreover, owing to its relatively slow kinetics, this clustering could be largely avoided in the glassy state during rapid supercooling, which explains why a single MYEGA equation can be fitted to the viscosity data both somewhat above the melting point as well as in the deeply supercooled state as both represent a homogeneous liquid (Fig. 1). The viscosity becomes anomalous only close to the melting point upon the onset of the immiscibility. It may be noted that a viscosity jump associated with liquid-liquid transitions characterized solely by structural clustering is also possible in chemically homogeneous or elemental liquids.

4. Conclusions

The viscosity of the $Ge_{15}Te_{85}$ eutectic liquid in the supercooled state and above its melting point is determined using parallel plate rheometry and can be fitted to the MYEGA equation using a single value of m over the entire temperature range except near the melting point where the viscosity shows an abrupt increase, corresponding to a liquid-liquid transition. Although such a result seems counterintuitive at first as the two temperature ranges that can be fitted to a single *m* are separated by a liquid-liquid transition, this behavior is argued to be consistent with a scenario where the transition involves incipient liquid immiscibility. Results from conventional DSC and MDSC measurements indicate that although the activation energies for the enthalpy and shear relaxation in this liquid near its glass transition are similar, the timescale of the former is slower by more than one order of magnitude.

Acknowledgement

This study was supported by the National Science Foundation Grant NSF-DMR 1855176.

References

[1] F. Herwig, W. Hoyer, in *Mater. Sci. Forum* (Trans Tech Publ, 1996), pp. 297–302.

[2] Y. Tsuchiya, J. Phys. Soc. Japan **60**, 227 (1991).

[3] S. Wei, P. Lucas, C.A. Angell, J. Appl. Phys. **118**, 034903 (2015).

[3] Y. Tsuchiya, H. Saitoh, J. Phys. Soc. Japan **62**, 1272 (1993).

[5] H. Neumann, F. Herwig, W. Hoyer, J. Non. Cryst. Solids **205–207**, 438 (1996).

[6] P. Lucas, S. Wei, C.A. Angell, Int. J. Appl. Glass Sci. **11**, 236 (2020).

[7] H. Neumann, W. Hoyer, M. Wobst, Zeitschrift Fur Naturforsch. - Sect. A J. Phys. Sci. **46**, 739 (1991).

[8] S. Wei, M. Stolpe, O. Gross, W. Hembree, S. Hechler, J. Bednarcik, R. Busch, P. Lucas, Acta Mater. **129**, 259 (2017).

[9] A. Schlieper, Y. Feutelais, S.G. Fries, B. Legendre, R. Blachnik, Calphad Comput. Coupling Phase Diagrams Thermochem. **23**, 1 (1999).

[10] P.G. Debenedetti, F.H. Stillinger, Nature **410**, 259 (2001).

[11] Y. Tsuchiya, J. Non. Cryst. Solids **156–158**, 704 (1993).

[12] H. Weber, J. Orava, I. Kaban, J. Pries, A.L. Greer, Phys. Rev. Mater. **2**, 93405 (2018).

[13] F. Herwig, M. Wobst, Zeitschrift Fur Met. **82**, 917 (1991).

[14] P. Lucas, J. Non-Crystalline Solids X **4**, 100034 (2019).

[15] J.C. Mauro, Y. Yue, A.J. Ellison, P.K. Gupta, D.C. Allan, Proc. Natl. Acad. Sci. **106**, 19780 (2009).

[16] Y. Chen, G. Wang, L. Song, X. Shen, J. Wang, J. Huo, R. Wang, T. Xu, S. Dai, Q. Nie, Cryst. Growth Des. **17**, 3687 (2017).

[17] P. Lucas, G.J. Coleman, M. Venkateswara Rao, A.N. Edwards, C. Devaadithya, S. Wei, A.Q. Alsayoud, B.G. Potter, K. Muralidharan, P.A. Deymier, J. Phys. Chem. B **121**, 11210 (2017).

[18] J. Kalikka, J. Akola, R.O. Jones, S. Kohara, T. Usuki, J. Phys. Condens. Matter **24**, 12 (2012).

[19] J.H. Simmons, P.B. Macedo, A. Napolitano, W.K. Haller, Discuss. Faraday Soc. **50**, 155 (1970).

[20] S. Curiotto, N.H. Pryds, E. Johnson, L. Battezzati, Metall. Mater. Trans. A Phys. Metall. Mater. Sci. **37**, 2361 (2006).

[21] S. Sen, S. Joshi, B.G. Aitken, S. Khalid, J. Non. Cryst. Solids **354**, 4620 (2008).

[22] D.J. Plazek, I. Echeverría, J. Rheol. **44**, 831 (2000).

[23] O. Gulbiten, J.C. Mauro, P. Lucas, J. Chem. Phys. **138**, 244504 (2013).

[24] W. Zhu, M.A.T. Marple, M.J. Lockhart, B.G. Aitken, S. Sen, J. Non. Cryst. Solids **495**, 102 (2018).

[25] C. Li, C.-H. Su, S. L. Lehoczky, R. N. Scripa, B. Lin, H. Ban, J. Appl. Phys. **97**, 083513 (2005).

[26] J.E.K. Schawe, J. Chem. Phys. **141**, 184905 (2014).

[27] Q. Zheng, J.C. Mauro, Y. Yue, J. Non. Cryst. Solids **456**, 95 (2017).

[28] B. Yuan, B. Aitken, S. Sen, J. Non. Cryst. Solids **529**, 119764 (2020).

[29] P. Koštál and J. Málek, Pure Appl. Chem. **87**, 239 (2015).

[30] R. Böhmer, K.L. Ngai, C.A. Angell, D.J. Plazek, J. Chem. Phys. **99**, 4201 (1993).

[31] G. Yang, O. Gulbiten, Y. Gueguen, B. Bureau, J.C. Sangleboeuf, C. Roiland, E.A. King, P. Lucas, Phys. Rev. B - Condens. Matter Mater. Phys. **85**, 144107 (2012).

[32] K. Tanaka, Phys. Stat. Solidi B **2020**, 2000206 (2020).

Table 1. Parameters for MDSC measurements and enthalpy relaxation of $Ge_{15}Te_{85}$ glass near glass transition

Period of oscillation P (s)	Enthalpy relaxation time $\tau_{en} = P/2\pi$	Temperature of C_p'' maximum (°C)	1000/T (K^{-1})	ln frequency, τ_{en}^{-1} (Hz)
90	14.33	133.8	2.457	−2.662
120	19.10	132.9	2.462	−2.950
150	23.87	132.2	2.467	−3.173
180	28.65	131.8	2.469	−3.355

Figure Captions

Figure 1. Viscosity of $Ge_{15}Te_{85}$ liquids measured in this study (filled squares) and reported in the literature (open symbols) as a function of T_g/T. Viscosity data for Te above its melting point (723 K), from [25] is shown for comparison, where T_g is taken to be ~ 350K from extrapolations of data for binary Se-Te, As-Te and Ge-Te systems [32]. The vertical dashed line corresponds to T_g/T = 1. The black dashed curve represents a least squares fit of the MYEGA equation to data points shown as filled squares.

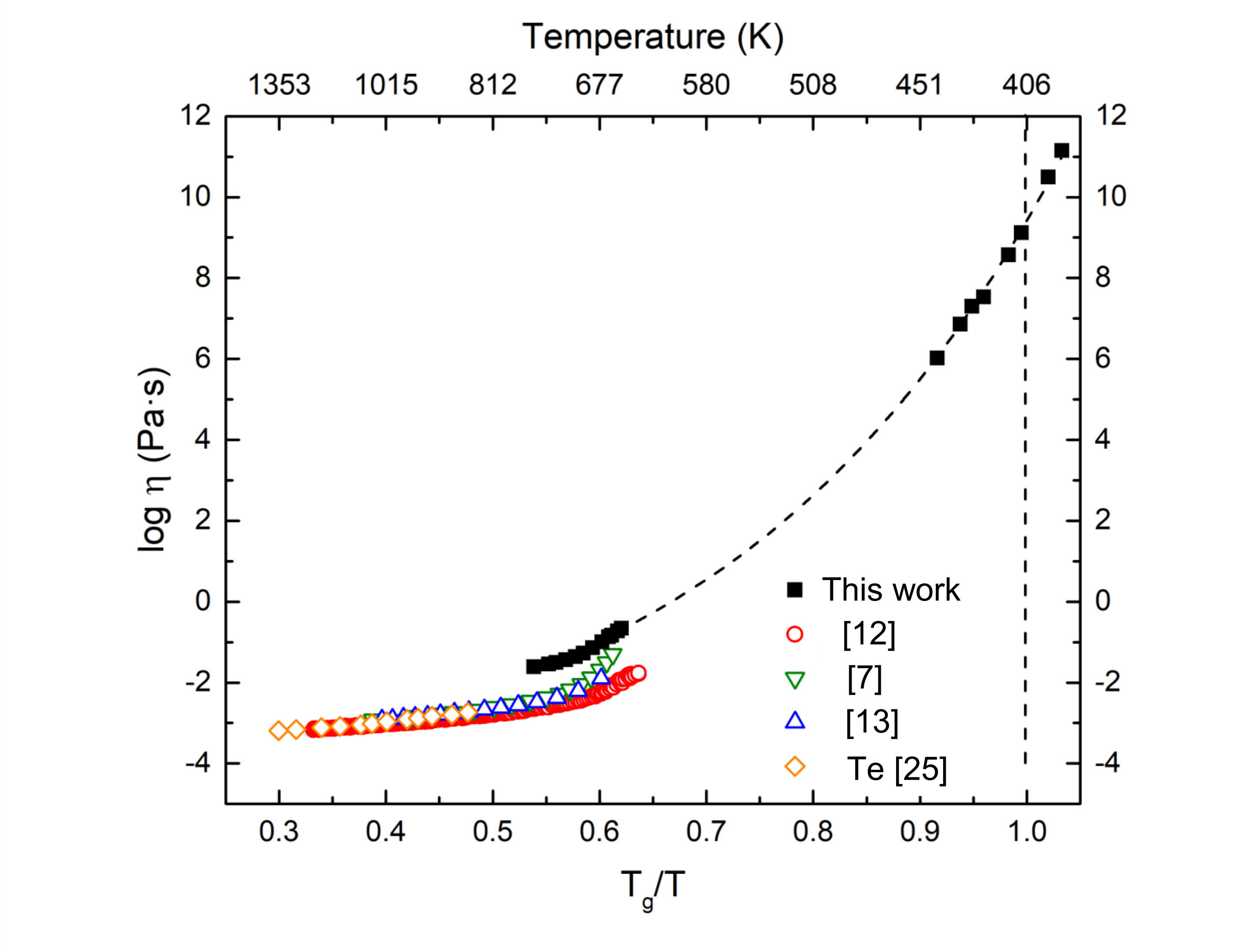
Figure 2. Comparison between natural log of the heating rate q vs. $1000/T_f$ (open squares) and $1/\tau_R$ vs. 1000/T (open circles), where τ_R is calculated from the Maxwell relation: $\tau_R = \eta/ G_\infty$ and G_∞ is taken to be 1 GPa. Dashed line is a guide to eye.

Figure 3. Normalized imaginary heat capacity C_p'' at different modulating periods vs. temperature. Inset shows the natural log of the modulating frequency as a function of the inverse of the corresponding C_p'' peak temperature. The activation energy is calculated from a linear least squares fit (dashed line) to the data points.

Figure 4. DSC heating and cooling curves of $Ge_{15}Te_{85}$ at 40 K/min. Dashed curve is a magnified (5x) view of the cooling curve in the region of the C_p anomaly. Inset shows heating and cooling curves in this region obtained at different scanning rates as indicated alongside each curve. Vertical dashed line in the inset corresponds to the peak position for each curve.

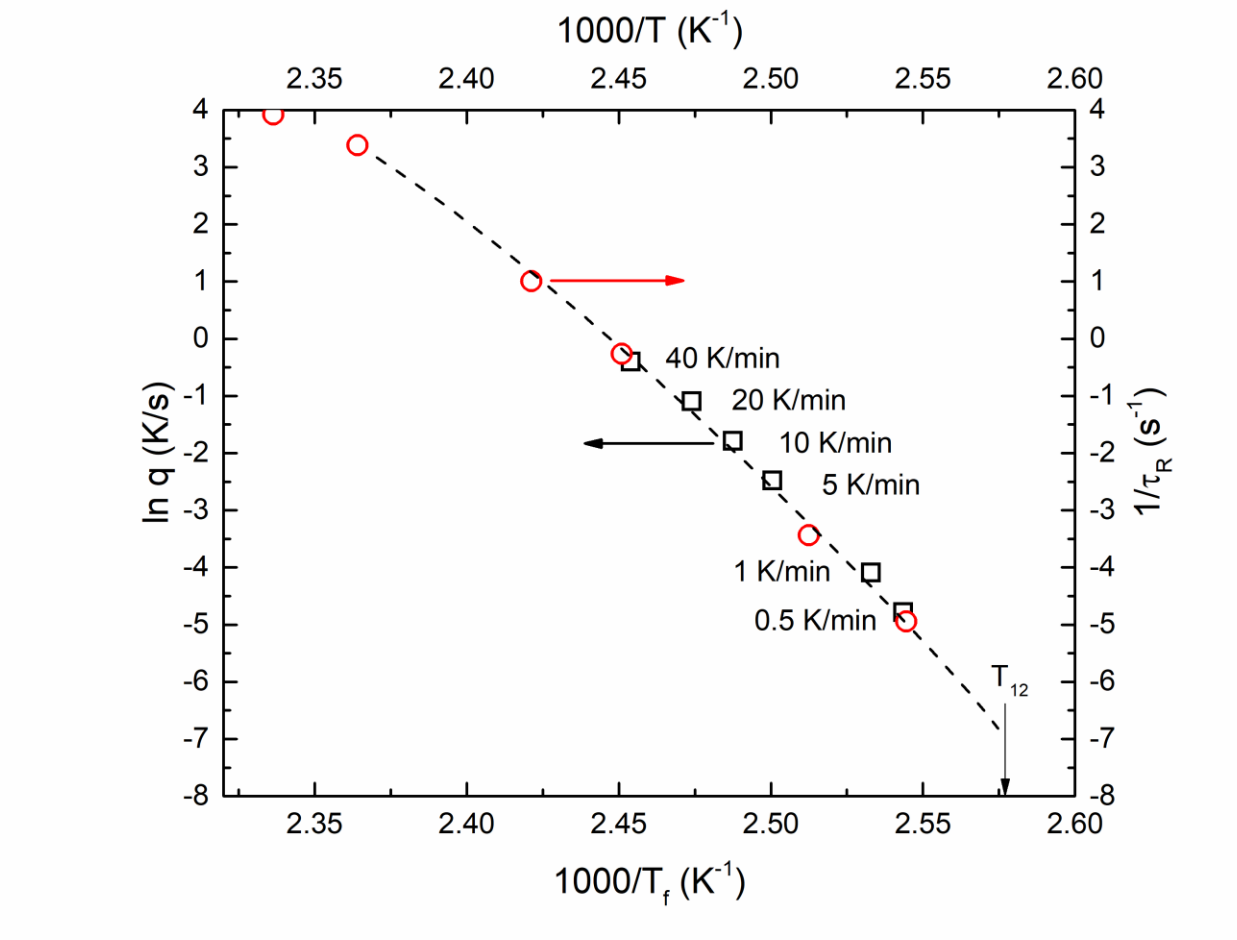
Figure 5. High temperature viscosity data from Fig. 1 shifted vertically to coincide at the high-temperature end of our dataset at ~ 750 K, and DSC cooling curve as a function of T_g/T. Symbols for viscosity data are the same as in Fig. 1. Shaded rectangle highlights coincidence between C_p anomaly and onset of divergence in the viscosity curves along with a departure from Arrhenius behavior.

Figure 1



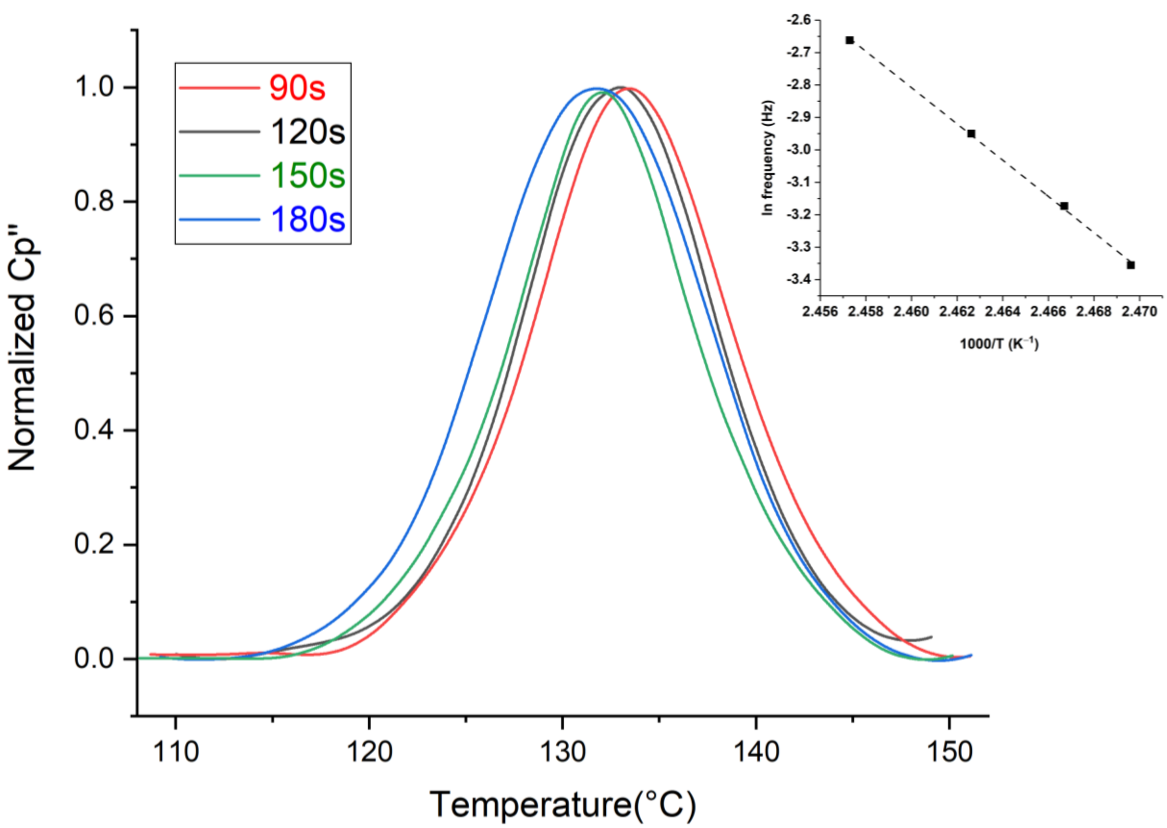
Temperature (K)
1353
1015
812
677
580
508
451
406
12
10
8
6
4
2
0
-2
-4
log η (Pa·s)
This work
[12]
[7]
[13]
Te [25]
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
T_g/T

Figure 2



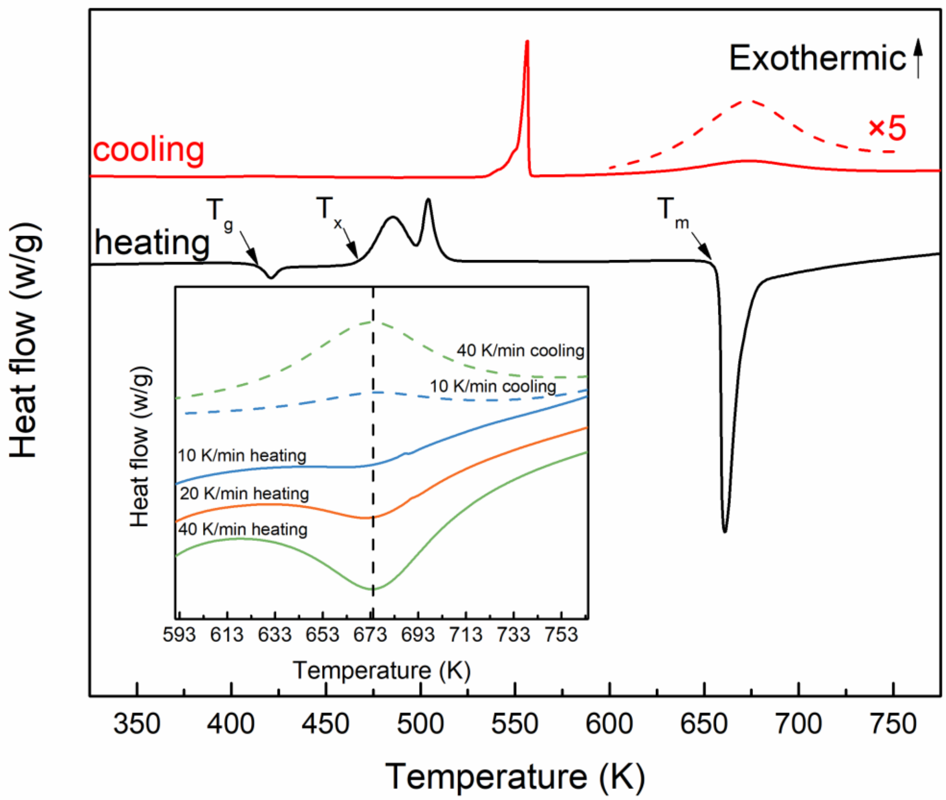
1000/T (K⁻¹)
2.35
2.40
2.45
2.50
2.55
2.60
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
ln q (K/s)
1/τ_R (s⁻¹)
40 K/min
20 K/min
10 K/min
5 K/min
1 K/min
0.5 K/min
T_12
1000/T_f (K⁻¹)

Figure 3



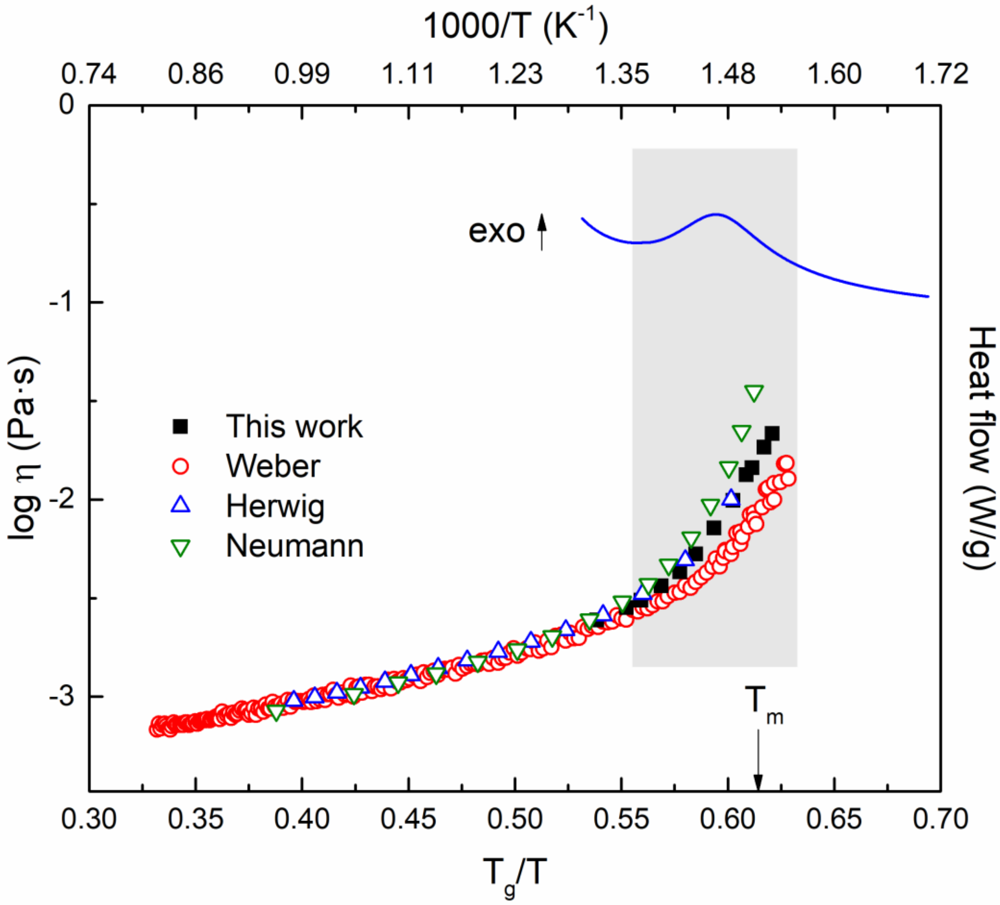
90s
120s
150s
180s
Normalized Cp''
0.0
0.2
0.4
0.6
0.8
1.0
110
120
130
140
150
Temperature(°C)
ln frequency (Hz)
-2.6
-2.7
-2.8
-2.9
-3.0
-3.1
-3.2
-3.3
-3.4
2.456
2.458
2.460
2.462
2.464
2.466
2.468
2.470
1000/T (K⁻¹)

Figure 4



Exothermic
cooling
×5
heating
T_g
T_x
T_m
Heat flow (w/g)
Temperature (K)
350 400 450 500 550 600 650 700 750
40 K/min cooling
10 K/min cooling
10 K/min heating
20 K/min heating
40 K/min heating
593 613 633 653 673 693 713 733 753

Figure 5



1000/T (K^{-1})
0.74
0.86
0.99
1.11
1.23
1.35
1.48
1.60
1.72
0
-1
-2
-3
exo
log η (Pa·s)
Heat flow (W/g)
This work
Weber
Herwig
Neumann
T$_m$
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
T$_g$/T

Credit Author Statement:

Weidi Zhu: Rheometry and linear DSC measurements, manuscript writing. **Sabyasachi Sen**: Conceived the project, provided supervision and wrote part the manuscript. **Bruce Aitken**: Glass synthesis, project supervision and manuscript writing. **Ozgur Gulbiten**: MDSC measurements, manuscript writing.

*Declaration of Interest Statement

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: