

Fragility of Ge₄₀S₆₀ Glass Forming Liquid

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Abstract

From differential scanning calorimetry (DSC) measurements performed on Ge₄₀S₆₀ chalcogenide glass forming liquid, the values of the apparent activation energy Δh^* , and the fragility index, m , as defined in the strong-fragile glass forming liquid concept, have been determined. The calculated value of m for this glass forming liquid is equal to 82. From this m value, it is suffice to conclude that this glass forming liquid belongs to an intermediate category that exhibits a kinetic behaviour between strong and fragile.

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INTRODUCTION

Structural relaxation is a general phenomenon occurring when a glass is maintained at a temperature lower than its glass transition temperature, $T < T_g$. From the variations of the viscosity, η , or relaxation time, τ , with the normalized reduced T_g/T quantity, a classification scheme of glass-forming liquids has been proposed. This scheme is well known as the strong-fragile glass forming liquid concept [1, 2] and allows the definition of a 'kinetic fragility' index, m [3]. This 'm fragility' is a measure of the rate at which the relaxation time τ decreases with increasing temperature around T_g and is given by [3];

$$m = \left. \frac{d \log_{10}(\tau)}{d \left(\frac{T_g}{T} \right)} \right|_{T=T_g} \quad (1)$$

According to this classification scheme, glass-forming liquids which exhibit an approximately Arrhenius temperature dependence of their τ 's are defined as strong and are characterized with a low value of m ($m \approx 16$) [4]). Those whose τ 's are fitted with a Vogel-Fulcher-Tammann (VFT) equation are referred to as fragile and are characterized by a high value of m ($m \approx 200$) [5]). It is commonly accepted that oxide glass formers with well-formed tetrahedral network rigid structures

and covalent directional bonds belong to the category of strong-forming liquids [2, 6–9]. In contrast, molecular units interacting via isotropic bonds of van der Waals type represent fragile glass-forming liquids [10]. Thus, the concept of fragility in undercooled liquids has often been used as a basis for organizing data on amorphous materials: thermoplastics [8], liquid-crystalline polymers [11], inorganic glasses [12] and polymer networks [13].

However, despite the extensive research on this 'fragility' concept, the factors that determine m for a given liquid or polymer are still unequivocally understood [14]. It is therefore important to obtain new data on any liquid that can be vitrified with the purpose of getting a better insight of the strong-fragile glass forming liquid concept.

Therefore, the aim of this paper is to report new calorimetric data obtained on Ge₄₀S₆₀ glassy alloy, and discuss them in terms of the strong and fragile behaviours.

METHOD

According to equation (1), the fragility index determination requires the definition of the relaxation time, τ , associated with molecular relaxation. This thermally activated relaxation also depends on the glass structure [15–20].

The most frequently used expression for τ is the Tool-Narayanaswamy-Moynihan [17, 18, 21] (referred to as TNM) expression which is given by:

$$\tau = \tau_0 \exp\left(\frac{x\Delta h^*}{RT}\right) \exp\left(\frac{(1-x)\Delta h^*}{RT_f}\right) \quad (2)$$

where, x ($0 \leq x \leq 1$) is the partitioning parameter that defines the degree of non-linearity, Δh^* is the apparent activation energy, R is the ideal gas constant, and T_f is the fictive temperature defined as the temperature at which the structure of the glass would be in equilibrium if instantaneously brought to it (or the temperature of the undercooled liquid with the same structure as that of the relaxing glass). The apparent activation energy, Δh^* , may be determined from the variation of the fictive temperature, T_f , (as defined by Tool [21]) with the cooling rate q^- according to the relation:

$$\frac{d \ln(q^-)}{d(1/T_f)} = \frac{-\Delta h^*}{R} \quad (3)$$

For each cooling rate used, the fictive temperature can be calculated graphically from calorimetric measurements by the so-called 'equal areas' construction method [18] using the following integral form:

$$\int_{T_f}^T (C_{pL} - C_{pV}) dT = \int_{T_1}^T (C_p - C_{pV}) dT \quad (4)$$

where, T is any temperature above the transition region at which C_p is equal to the equilibrium liquid value, C_{pL} , and T_1 is a temperature well below the transition region. Finally, from the knowledge of Δh^* and T_g the fragility index, m , can be evaluated from

$$m = \frac{\Delta h^*}{2.3RT_g} \quad (5)$$

EXPERIMENTAL

Sample preparation

The Ge₄₀S₆₀ glass was prepared by the melt-quenching technique using a mixture of high purity Ge and S. The mixture was introduced into a cylindrical glass silica ampoule and sealed under vacuum of 10^{-5} Torr. The ampoule was then placed in an electric furnace and gradually heated to 900°C. At this temperature the melt was homogenized by continuous agitation of the ampoule. To obtain

the glass, the ampoule was quenched in an ice-cooled water.

Differential Scanning Calorimetry Measurements

Variations of the heat capacity changes at T_g were measured by differential scanning calorimetry using DSC 2920 (modulated TA instrument) calorimeter run in the conventional mode. To obtain good reproducibility, the same sample sealed in an aluminium pan was used during all measurements. To avoid any sample oxidation, all measurements were done under a nitrogen gas atmosphere. The calorimeter was calibrated in temperature and enthalpy of melting of pure indium. A small lump of glass (≈ 18.25 mg) was sealed in aluminium pan and referenced to an empty one. To determine Δh^* , cooling experiments were performed. From the rejuvenation temperature, T_r , about 20 K above T_g the sample was cooled down at the cooling rates 100, 50, 20, 10, 5, 1 K/min. Then it was immediately reheated at the constant heating rate $q^+ = 10$ K/min up to T_r . To erase any aging effects in experiments, the sample was kept for 3 min. at T_r before any cooling run to a temperature $T < T_g$. The maximum temperature is limited to about 660 K to avoid any possible contamination of the DSC oven.

RESULTS AND DISCUSSION

Figure 1 displays the set of the DSC scans obtained at the constant heating rate of 10 Kmin⁻¹ on Ge₄₀S₆₀ glass submitted to different cooling rates in the range 1–100 K min⁻¹. In addition to the traditional endothermic step characterizing the glass transition, well known endothermic peaks (overshoots), above the glass transition, are also observed. These are due to the enthalpy relaxation phenomenon (or structural relaxation). The area under these observed peaks, which is used as a measure of enthalpy relaxation, increases with decreasing cooling rate. This is in accordance with the observation in [22]. As commonly recommended, the glass transition temperature, T_g , was determined at the midpoint of the endothermic step of a non-aged sample for $q^+ = q^-$ and its value is found to be equal to 640 K and listed in Table 1. This value compares well with those reported in the literature [23–25]. Also, the value of the width of glass transition, $\Delta T_g = (T_g)_{end} - (T_g)_{onset}$, which

is another parameter to indicate glass transition, is obtained and found to be equal to 45 K (Table 1). The fictive temperature, T_f , for the different cooling rates was calculated according to Moynihan method from Eq. (4). The calculated T_f values are given in Table 2.

From this table, it is seen that with increasing cooling rate, T_f shifts towards higher values. This is to be expected because the lower cooling rate leads to a larger temperature range for which the liquid may be undercooled and hence the lower is T_f [22].

Table 1: Calorimetric Data Concerning the $Ge_{40}S_{60}$ Viterous Alloy.

T_g (K)	ΔC_p (J/g.K)	$\Delta h^*/R$ (kK)	Fragility (m)	ΔT_g	Θ (K ⁻¹)
640	0.32	120.9	82	45	0.3

Values of T_g , ΔC_p , $\Delta h^*/R$, m, ΔT_g , and θ for the investigated glass composition.

Table 2: Fictive Temperatures for the Different Cooling Rates.

T_f (K)	Cooling rate (q) (K/ min.)
634.4	100
632.7	50
630.9	20
631.0	10
627.9	5
620.0	1

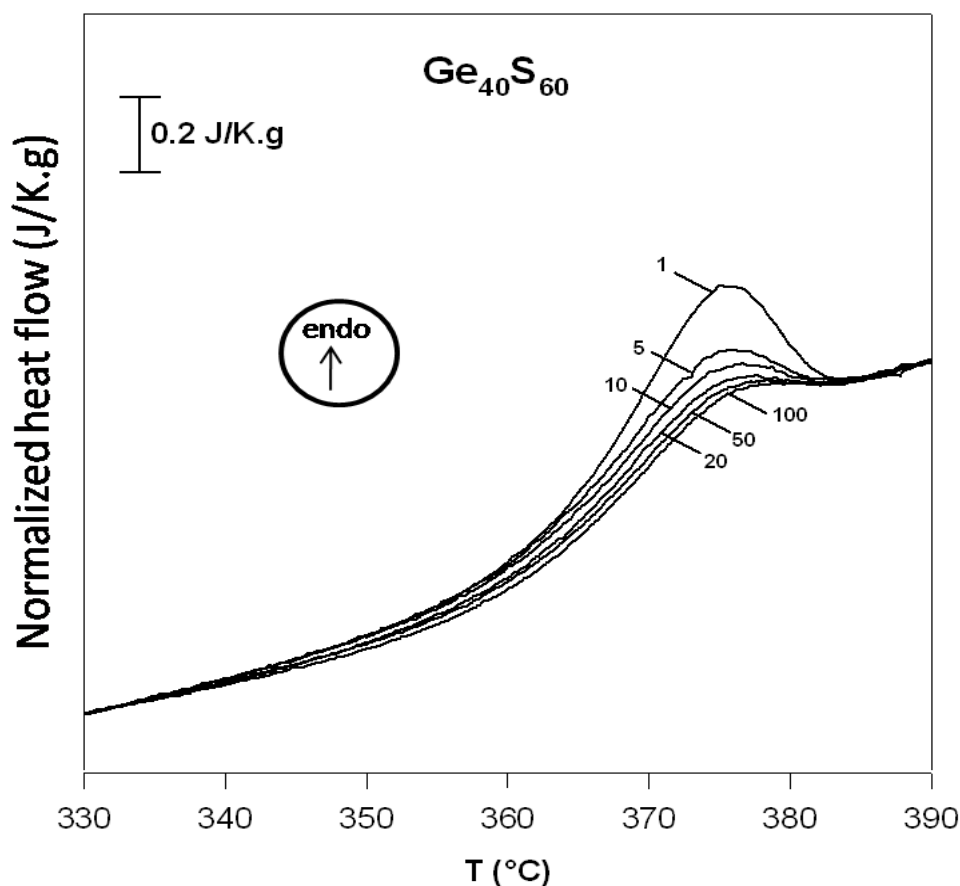


Fig. 1: DSC Curves Obtained on $Ge_{40}S_{60}$ glass. Cooling Rates are indicated on the DSC Curve.

The variation of $\ln q$ versus reciprocal T_f , is depicted in Figure 2 and according to Eq. (3) lead to an apparent activation energy of relaxation, $\Delta h^*/R$. The value obtained for $\Delta h^*/R$ is 120.9 kK and listed in Table 1. Using Eq. (5), one can calculate the fragility index, m , from the measured T_g and evaluated $\Delta h^*/R$ which is found to be equal to 82. Fragility values typically range between $m \approx 16$ for ‘strong’ and $m \approx 200$ for ‘fragile’ glass-forming liquids. The value of m obtained in the present work ($m=82$) lies between strong and fragile pattern and thus it is concluded that this glass-forming liquid belongs to an intermediate category. The values of Kovacs-Aklonis-Huchinson-Ramos (KAHR) parameter θ , estimated from $\Delta h^*/RT_g^2$ [19], where R is the gas constant, are also obtained and listed in Table 1. The parameter θ is a material constant that characterizes the temperature dependence of the retardation times in structural relaxation [26–29] and lies in the range of 0.1 to 1 K⁻¹ for various inorganic glasses [29]. The value of θ for Ge₄₀S₆₀ glass equals to 0.3 K⁻¹ which agrees with the reported values for inorganic glasses.

The value of the heat capacity jump, ΔC_p at T_g [$\Delta C_p = C_{pl} - C_{pg}$, C_{pl} and C_{pg} refer to C_p values of the undercooled liquid and the glassy state, respectively], has also been considered. Its value can be connected to a thermodynamic strength-fragility concept. As discussed by Angell [30], glasses exhibiting a high ΔC_p value ($\Delta C_p \geq 0.3 \text{ J K}^{-1} \text{ g}^{-1}$) are far from their thermodynamic equilibrium [this equilibrium is obtained by extrapolation of the liquid like state in the temperature domain of the glassy state].

These glass-forming liquids and the associated glasses are defined as thermodynamically fragile. On the contrary, a low value of ΔC_p at T_g leads to strong thermodynamic behaviors. Our ΔC_p measurements for Ge₄₀S₆₀ glass-forming liquid give the value of $0.32 \text{ J K}^{-1} \text{ g}^{-1}$ (Table 1) and thus this glass is declared thermodynamically fragile. According to [31] the correlation of a minimum fragility with a minimum of ΔC_p (T_g) follows from the Adam-Gibbs equation [32]

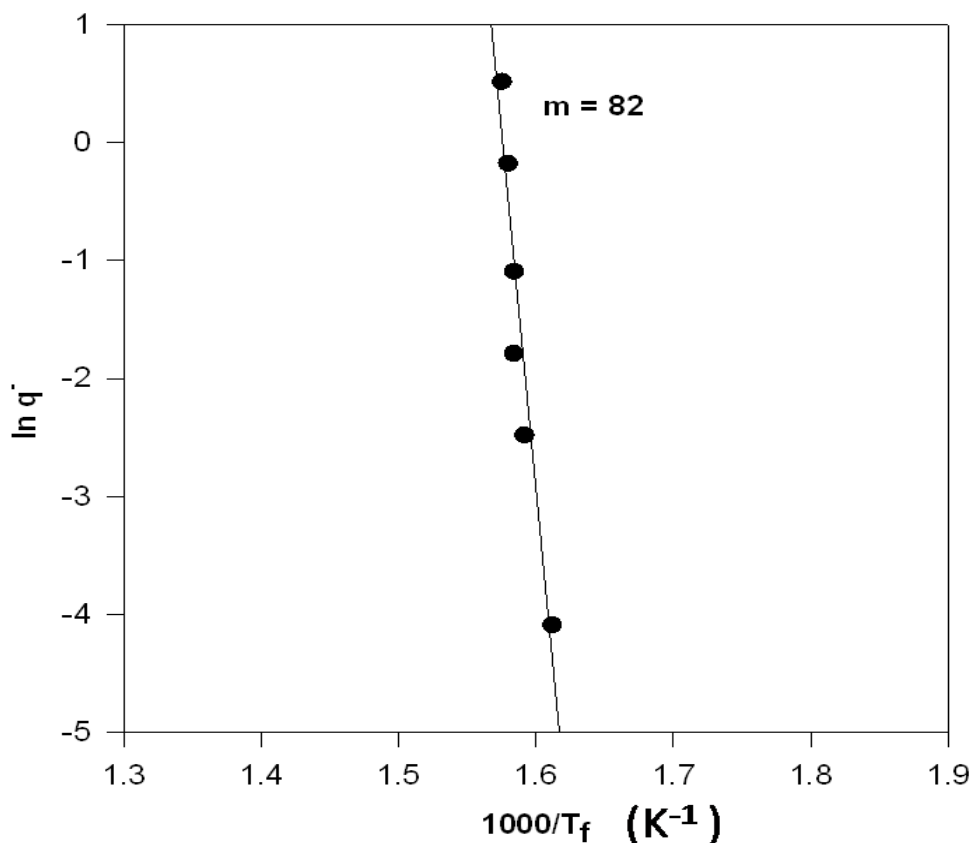


Fig. 2: Variations of $\ln(q)$ with $1/T_f$ for the Ge₄₀S₆₀ Glassy Composition.

$$\eta = \eta_0 \exp \left[\frac{A}{T S_c} \right] \quad (6)$$

where, $A \approx \Delta\mu \ln 2$ ($\Delta\mu$ is the potential barrier hindering rearrangements) and S_c is the configurational entropy given by the relation;

$$S_c = \int_{T_k}^T \left(\frac{\Delta C_p}{T} \right) dT \quad (7)$$

where, T_k is the Kauzmann temperature. Thus, when ΔC_p is very small, S_c is almost temperature independent and Eq. (6) follows an Arrhenius form and when ΔC_p is bigger [33], with a functional dependence of the type D/T [34], the Vogel-Tamman-Fulcher law for viscosity, characteristic of fragile glass forming liquids, is obtained. The high value of ΔC_p for fragile glasses is due to the addition of translational and/or rotational modes made available by the breakage of bonds forming the glass network. An immediate consequence of the high values of ΔC_p at T_g for fragile glasses is that their structures breaks down rapidly with increasing temperature near and above T_g and thus a large number of configurations are made available for the glass (i.e. there is a marked structural rearrangement as the equilibrium liquid transforms to non-equilibrium glass). At the opposite, the low ΔC_p at T_g for strong glasses indicates that their structure resist changes with increasing temperature and undergo fewer configurational changes near and above T_g (i.e. there is not much difference between the structures of the melt and the glass).

The character of the enthalpy relaxation process can also be analyzed by a non-linear relaxation function expressed by the Kohlrausch-Williams-Watts (KWW) equation, (stretched exponential decay function);

$$\varphi(t) = \exp [-(t/\tau)^\beta] \quad (8)$$

where, τ is the mean molecular relaxation time, β is a constant characterizing the width of the relaxation time distribution spectrum ($0 \leq \beta \leq 1$). In this work, the value of ΔT_g is used to estimate the value of β from data presented in [35]. The value of β for $\text{Ge}_{40}\text{S}_{60}$ glassy alloy is found to lie in the range $0.2 \leq \beta \leq 0.4$. This relatively low value of β leads to a wide spectrum of the relaxation function, $\varphi(t)$. This is also indicative of a wide distribution of the

different natures of molecular species responsible for the relaxation phenomenon.

CONCLUSION

From the determined value of the fragility index, m , for $\text{Ge}_{40}\text{S}_{60}$ glass forming liquid, it is concluded that it belongs to an intermediate category that kinetically behaves between strong and fragile. Thermodynamically, the glass forming liquid $\text{Ge}_{40}\text{S}_{60}$ is found to be fragile.

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