

Fragility of chalcogenide glass in relation to characteristic temperature T_0/T_g

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Abstract. The present study reports the mutual relationship between the fragility index m and the characteristic temperature T_0/T_g . The fragility of the chalcogenide amorphous glass of $\text{Ge}_{10}\text{Se}_{50}\text{Te}_{40}$ is calculated by utilizing glass transition temperature (T_g) measured by DSC (Differential Scanning Calorimetry) at different heating rates (β) in the range 5 to 20 K/min. Vogel-Fulcher-Tammann (VFT) equation is fitted to the data of T_g . In addition to the VFT method, three other methods are also used to evaluate m . The fragility index m of the $\text{Ge}_{10}\text{Se}_{50}\text{Te}_{40}$ system showed the trend of decrease with increasing heating rate but remained stable around 22 for the heating rate 10 K/min. The value of m for the glass is near the lower limit ($m \approx 16$) this indicates the alloy is a strong glass forming material in accordance of Angell's interpretation of fragility. The calculated values of characteristic temperature T_0/T_g is very close to 1 which also indicates that clearly the system is most fragile.

1. Introduction

Chalcogenide glasses are prepared by mixing the chalcogen elements, viz, S, Se and Te with elements of the periodic table such as Ga, In, Si, Ge, Sn, As, Sb and Bi, Ag, Cd, Zn etc. These materials are amorphous materials. $\text{Ge}_{10}\text{Se}_{50}\text{Te}_{40}$ system falls under the category of ternary chalcogenides and easily prepared by doping a suitable additive element in a new binary matrix. Chalcogenide glasses are used in many technological applications like solar cells [1], biosensors [2], optical elements and switching devices [3].

The subject of fragility is pioneered by Angell [4]. Angell categorized glass forming liquids in to three categories. The first category is glass formers which are strong and obey Arrhenian behaviour and the second category is glass formers which are fragile and are viscosity dependent. These are studied by Vogel-Fulcher-Tammann (VFT) relation and the third category are glass formers which are intermediate and lie between the first and the second categories [5]. The fragility index m generally evaluated using viscosity data. However, T_g dependent on heating rate, measured by DSC can also be adequately exploited to understand the fragility [6].



For several glass forming liquids, the characteristic temperature T_0/T_g is correlated with the fragility index m [7]. The fragility index, m and the characteristic temperature T_0/T_g is equivalent measures of m because the ratio T_0/T_g takes the values in between 0 and 1 [8]. Zhao et al. [9] have discussed the association between characteristic temperature T_0/T_g and index of fragility, m for metallic glasses. But these correlations have not been explored for the nonmetallic glasses. The purpose of the present investigation is to test this correlation for the chalcogenide $\text{Ge}_{10}\text{Se}_{50}\text{Te}_{40}$ system.

2. Experimental Methods

Amorphous glass of $\text{Ge}_{10}\text{Se}_{50}\text{Te}_{40}$ were developed by the method of melt-quenching approach. Ultra pure (99.999%) Ge, Se and Te are taken in suitable atomic percentages and weighed, then sealed in a quartz ampoule at a vacuum of 10^{-4} torr. These sealed ampoules are heated in a furnace around 1375 K for one day to ascertain the homogeneity of the mixture. The detailed method of preparation is discussed elsewhere [10] and T_g values scanned from DSC are availed to calculate the index of fragility, m .

3. Results and discussion

Four different independent approaches are deployed to enumerate fragility index m and these are discussed in detail below

3.1 VFT fitting method

The dependence of T_g with β in DSC scans is given in terms of VFT equation [11-13]

$$\beta(T_g) = C \exp [B / (T_0 - T_g)] \quad (1)$$

C , B and T_0 are adjustable VFT parameters and T_0 is called correct glass transition temperature.

This is approximated to the asymptotic value of T_g , when the cooling rate is very slow (i.e. 1 K/min). Here the dimensions of C is heating rate and $B = D T_0$, where D is known as strength parameter. The Equation (1) is written as

$$\ln \beta(T_g) = \ln C + [B / (T_0 - T_g)] \quad (2)$$

fragility index m for a specific T_g can be evaluated from the equation (3), [14]

$$m = [B T_g / 2.303 (T_g - T_0)^2] \quad (3)$$

Inserting T_g and adjusting T_0 value (by checking maximum regression value), plotting $\ln \beta$ versus $1 / (T_g - T_0)$, the slope B is determined (figure 1). Hence, substituting B value in equation (3), the fragility index m is calculated (Table.1). $T_0 = 320$ K for the proper VFT fit is obtained.

3.2 Kauzmann Temperature method

The ideal glass transition temperature T_0 and the Kauzmann temperature T_K are unstable thermodynamically and approximated as $T_K \approx T_0$ for many metallic glasses [15]. The heating rate dependence of T_g and T_c (on set crystallization temperature) are plotted and extrapolated to lower temperature and heating rates which leads to a intersection point (figure 2). This point is well known as Kauzmann Temperature T_K [16]. Here $T_K \approx T_0$ value is found to be 333.5 K. Substituting this value in equation (2) and plotting $\ln \beta$ versus $1 / (T_g - T_0)$ (figure 1), the slope B is determined and substituted in equation 3, and hence the fragility parameter m is calculated (Table 1).

3.3 Lasocka's method

The glass transition temperature T_g is dependent on heating rate, β and is given by Lasocka's relation [17]

$$T_g = A + E \ln \beta \quad (4)$$

Here A and E are constants. Extrapolating the data to $\beta = 1$ K/min, it is possible to obtain a tentative value $A = T_0$, which may be the lower limit of T_g [18]. Plotting T_g against $\ln \beta$, the value $A = T_0 = 362.52$ K is obtained (figure 3). Inserting T_0 value in equation (2), the slope B is obtained. Again putting B in equation (3), m values are determined. The m values are tabulated for the $\text{Ge}_{10}\text{Se}_{50}\text{Te}_{40}$ in Table 1.

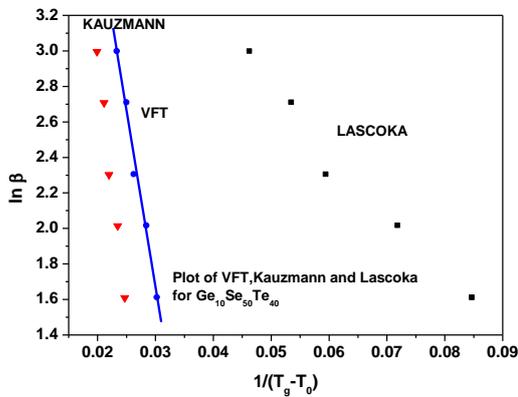


Figure 1 Plot of VFT, Kauzmann and Lasocka

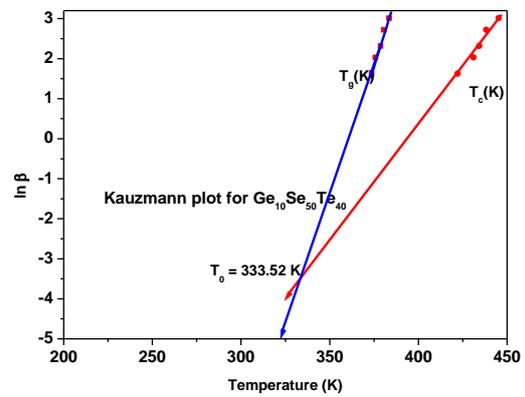


Figure 2 T_g and T_c as a function of ln β

3.4 Ozawa method

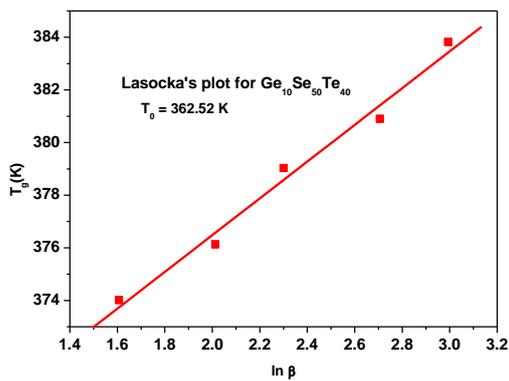


Figure 3 Plot of T_g versus ln β

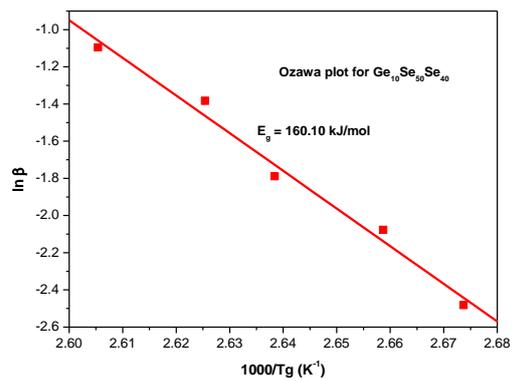


Figure 4 Plot of ln β versus 1000/T_g

Table 1. Fragility parameter, m for Ge₁₀Se₅₀Te₄₀.

Heating rate (K/min)	T _g (K)	T _c (K)	m for Ge ₁₀ Se ₅₀ Te ₄₀			
			VFT	Kauzmann	Lasocka	Ozawa
5	374.00	422.52	29.66	28.43	41.85	22.38
7.5	376.11	431.36	26.35	25.83	30.05	22.26
10	379.01	434.58	22.66	22.82	20.55	22.07
15	380.88	438.65	20.69	21.15	16.66	21.98
20	383.80	445.59	18.10	18.91	12.50	21.81

The fragility index, m is also calculated using the relation [19]

$$m = [E_g / (2.303RT_g)] \tag{5}$$

Here E_g is activation energy of glass transition and R is universal gas constant. Ozawa equation for non isothermal method to evaluate E_g is expressed as

$$\ln \beta = -1.0516 E_g / RT_g + \text{constant} \tag{6}$$

Here β and E_g are the heating rate and activation energy of glass transition, respectively. The plot of

$\ln \beta$ versus $1000/T_g$ (figure 4) yields the activation energy of glass transition $E_g = 160.10$ kJ/ mol and substituting in equation (5), m values are determined (Table 1).

Figure 5 shows the variation of m with the heating rate. $m=22$ is the fragility index for the studied sample at 10 K/min (from the graph and the Table 1 bold values). The value $m=22$ indicates from the Angell's approach $Ge_{10}Se_{50}Te_{40}$ is a strong fragile glass.

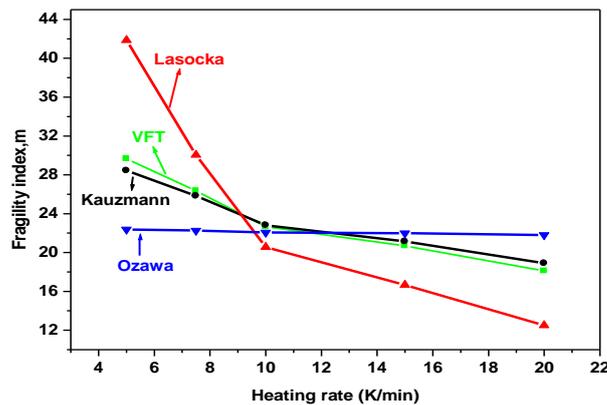


Figure 5 Plot of m versus heating rate (K/min)

Table 2 gives the values of m and T_0/T_g for the studied sample, calculated by three different methods. The characteristic temperature T_0/T_g is very close to 1 which also strongly indicates $Ge_{10}Se_{50}Te_{40}$ is a most fragile material. This fact is also evident from the figure 6 and 7 which followed an equation $m = m_{min} / (1 - T_0/T_g)$. Here m_{min} is a constant and equal to 16. The nature of the graphs in figure 6 and 7 are also obtained by different authors [20] for metallic glasses indicate the correlation between T_0/T_g and m for the nonmetallic chalcogenide glasses.

Table 2. m and T_0/T_g for $Ge_{10}Se_{50}Te_{40}$.

T_g (K)	VFT ($T_0=320$ K)		Kauzmann($T_0=335.5$ K)		Lasocka($T_0=362.52$ K)	
	m	T_0/T_g	M	T_0/T_g	m	T_0/T_g
374.00	29.66	0.91	28.43	0.89	41.85	0.97
376.11	26.35	0.91	25.83	0.89	30.05	0.96
379.01	22.66	0.90	22.82	0.88	20.55	0.96
380.88	20.69	0.90	21.15	0.88	16.66	0.95
383.80	18.10	0.90	18.91	0.87	12.50	0.94

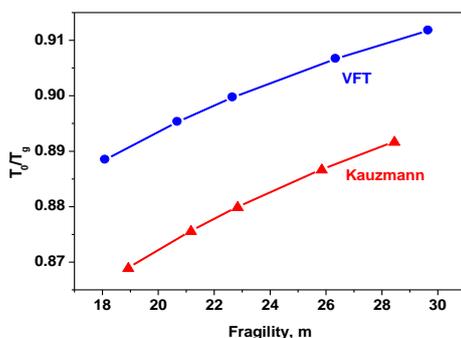


Figure 6 T_0/T_g versus m

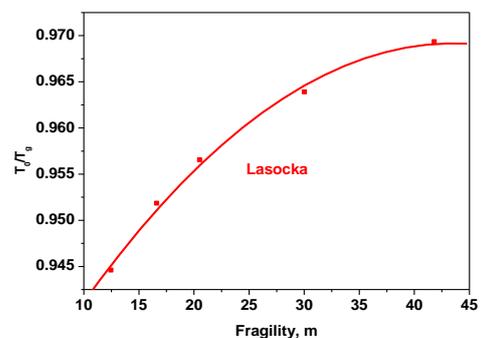


Figure 7 T_0/T_g versus m

4. Conclusion

The present work shows that the characteristic temperature T_0/T_g is mutually correlated with fragility index, m for chalcogenide glass $\text{Ge}_{10}\text{Se}_{50}\text{Te}_{40}$. It also equally emphasizes T_0/T_g is another criterion to elucidate fragility index, m .

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