

## COMPOSITIONAL TREND OF THE GLASS TRANSITION TEMPERATURE IN $\text{As}_x\text{Se}_{1-x}$ NETWORK GLASSES

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The compositional trend of the glass transition temperature ( $T_g$ ) in  $\text{As}_x\text{Se}_{1-x}$  network glasses ( $x = 0$  to  $0.4$ ) is investigated using differential scanning calorimetry. The variation of  $T_g$  with As content and the mean coordination number of aged and rejuvenated samples are discussed in terms of proposed theoretical and empirical models. Critical assessment of the applicability of various models to explain the compositional variations of  $T_g$  is presented. Evidence of multiple rigidity transitions in the present network glasses is reported and the influence of the long-term physical aging is discussed.

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### 1. Introduction

$\text{As}_x\text{Se}_{1-x}$  chalcogenide glasses are typical examples of covalent glass network that received extensive theoretical and experimental investigations [1-8]. For example, the pioneer works of Phillips and Thorpe [9-11] on glass forming ability and rigidity percolation transitions in covalent glass networks has remarkably improved our understanding of the glass transition and glassy state. Numerous efforts were devoted to the understanding of the compositional dependence of the glass transition temperature and its relation to the different elastic phases and rigidity transitions observed in a variety of covalent glasses. Further insight on the nature of the glass network connectivity can be provided by investigating the correlation between the  $T_g$  and the average heat of atomization of glassy systems.

In this work, we investigate the compositional trend of  $\text{As}_x\text{Se}_{1-x}$  glasses using different theoretical and empirical models. The applicability of various empirical and theoretical relationships was tested. The compositional trend of the present glasses was also used to monitor rigidity transitions in the glass network. The effect of prolonged physical aging of the samples on the variation of  $T_g$  with  $x$  was also discussed.

### 2. Theoretical background

One of the key physical parameters characterizes the glassy materials is the glass transition temperature,  $T_g$ . The variation of  $T_g$  with glass composition is proved to be a useful probe of the topological glassy structure of the network. It is a well established experimental fact that  $T_g$  increases with the increase of the connectivity of the covalent glass network. The glass network connectivity can be described by the mean coordination number  $\langle r \rangle$  of glassy alloys which according to Phillips [9] can be determined for a covalently bonded binary alloy  $A_aB_b$  using

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$$\langle r \rangle = \frac{ar_A + br_B}{a + b} \quad (1)$$

where  $r_A$  and  $r_B$  are the coordination numbers of the constituent atoms. Thus, for  $\text{As}_x\text{Se}_{1-x}$  glasses,  $\langle r \rangle$  is given by:

$$\langle r \rangle = x r_{As} + (1 - x) r_{Se} \quad (2)$$

Since  $r_{As} = 3$  and  $r_{Se} = 2$ , the above equation becomes

$$\langle r \rangle = x + 2 \quad (2a)$$

Therefore, the mean coordination number (and the network connectivity) can be changed in a controlled manner by varying the composition of the glass.

Numerous theoretical models were introduced to explain the compositional trend of  $T_g$  in many network glasses.

### Gibbs-DiMarzio theory

One of early prediction of the compositional trend of  $T_g$  was provided by the Gibbs-DiMarzio theory of the glass transition and glassy state [12]. According to this theory,  $T_g$  varies with the degree of cross-linking of polymeric chains as [12,13]:

$$T_g = \frac{T_o}{1 - Kx} \quad (3)$$

where  $T_o$  is glass transition temperature of the linear chain, i.e., pure selenium in our case, and the constant  $x$  is the cross-link density incorporates the effects of crosslinks and  $K$  is a constant.

### Modified Gibbs-DiMarzio equation

Sreeram et al [14] have modified Eq. 3 by replacing the cross-linking parameter by the mean coordination number as:

$$T_g = \frac{T_o}{1 - \beta(\langle r \rangle - 2)} \quad (4)$$

where  $\beta$  is a system dependent parameter. In fact for  $\text{As}_x\text{Se}_{1-x}$  glasses and using Eq. (2a), we can write Eq. (4) in the following form

$$T_g = \frac{T_o}{1 - \beta x} \quad (5)$$

### Tanaka's Equation

The following empirical correlation between  $\ln T_g$  and the mean coordination number was suggested by Tanaka [15]:

$$\ln T_g \cong 1.6 \langle r \rangle + 2.3 \quad (6)$$

A possible justification of the above relationship is based on the temperature dependence of the viscosity  $\eta$  which is assumed to follow Arrhenius law:

$$\eta = \eta_o \exp(E/k_B T) \quad (7)$$

where  $\eta_o$  is a constant and  $E$  is the activation energy of the viscous flow. It is assumed that the glass transition occurs when  $\eta \approx 10^{13}$  poise. The temperature corresponding to this particular value of viscosity is the glass transition temperature,  $T_g$ . Moreover,  $E$  was assumed to depend on  $\langle r \rangle$  in such a way that Eq. (6) was obtained [15].

### Stochastic Agglomeration Theory

The compositional trend of  $T_g$  has been analyzed using the stochastic agglomeration theory (SAT) [16-17]. The theory relates an increase in melt viscosity to agglomeration of specific local structural configurations, and  $T_g$  is identified with the temperature where the agglomeration process freezes. The variation of the glass transition temperature with chemical composition (or mean coordination number) was addressed by Micoulaut and Naumis [17]. On the basis of the stochastic agglomeration theory, and considering the modified Gibbs-Di Marzio equation [Eq.4], Micoulaut and Naumis [17] derived the following formula for the constant  $\beta$  as

$$\beta^{-1} = (r_{As} - 2) \ln\left(\frac{r_{As}}{2}\right) \quad (8)$$

or  $\beta^{-1} = \ln(3/2)$  which gives  $\beta = 2.47$  for As-Se glasses.

### 3. Experimental

The materials in a glassy state were prepared by the well known melt quench technique. High purity elements (99.999% Sigma Aldrich) of Se and As in the proper atomic wt% proportions were sealed in an evacuated ( $10^{-5}$  Torr) quartz ampoule. The contents were heated to around 750 K for 24 h. The ampoule was regularly shaken to ensure good homogeneity. The melt was quenched in ice water. The DSC experiments were performed using a TA Q-2000 instrument under dry nitrogen gas supplied at a rate of  $50 \text{ ml min}^{-1}$ . The temperature accuracy is  $\pm 0.1 \text{ }^\circ\text{C}$ , and a sensitivity of  $0.2 \text{ } \mu\text{W}$ . To minimize the temperature gradients, a small weight (5 mg) and uniform fine powder from the samples was spread as thinly as possible and encapsulated in standard aluminum sample pans. The temperature and enthalpy calibrations were validated using indium ( $T_m = 429.75 \text{ K}$ ,  $\Delta H_m = 28.55 \text{ Jg}^{-1}$ ) as a standard material. To remove the previous thermal history, the samples were rejuvenated by heating them to a temperature higher than the glass transition temperature with a holding time of 5 minutes. The samples were subsequently cooled at a cooling rate of  $10 \text{ K/min}$ . to  $T \sim 20 \text{ }^\circ\text{C}$  and immediately heated at heating rates of  $10 \text{ K/min}$ .

### 4. Results and discussion

Fig.1 shows a typical DSC scan recorded at heating rate of  $7 \text{ K/min}$  for a rejuvenated  $\text{As}_{0.4}\text{Se}_{0.6}$  glass. The glass transition, crystallization and melting processes along with their characteristics temperatures ( $T_g$ ,  $T_p$ , and  $T_m$ ) are shown in the graph. The endothermic events representing the glass transition regions of the  $\text{As}_x\text{Se}_{1-x}$  network glasses are shown in Fig. 2. The temperature of the endothermic peak is used as an assignment for the glass transition temperature ( $T_g$ ).

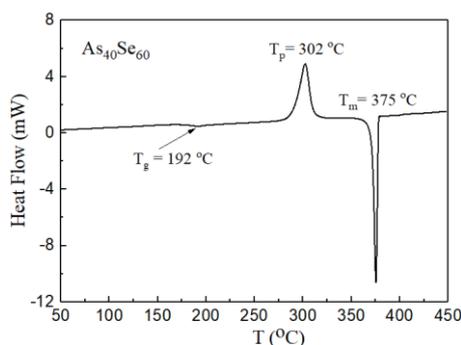


Fig. 1 DSC scan for  $\text{As}_{40}\text{Se}_{60}$  glass recorded at heating rate of  $7 \text{ K/min}$ .

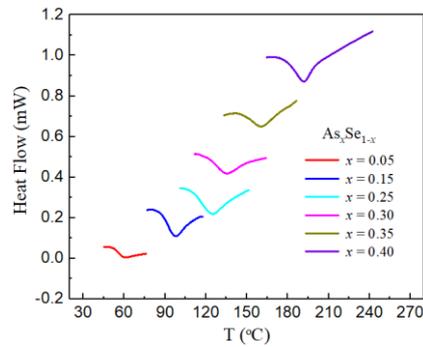


Fig. 2. Glass transition regions of the  $As_xSe_{1-x}$  glasses at different As contents

The variation of the glass transition temperature,  $T_g$ , is a useful probe for the glass network connectivity. Fig. 3 shows the variation of  $T_g$  with composition,  $x$ , as observed in the DSC measurements of  $As_xSe_{1-x}$  glasses. Several important features in the compositional trend of  $T_g$  is evident from Fig. 3. Initial monotonic increase of  $T_g$  with increasing As content  $x$  is observed up to  $x = 0.10$  in aged glasses and up to  $x = 0.20$  in the rejuvenated glasses followed by further linear variations but with different slopes in the composition region up to  $x = 0.30$ . Different compositional dependence occurs for  $x > 0.3$  in aged as well as rejuvenated glasses. This progressive increase of  $T_g$  with  $x$  indicates that adding As atoms into the Se matrix increases the connectivity of the glass network. The change in slope at  $x = 0.30$  marks the first elastic threshold of the reversibility window (also known as the intermediate phase) in  $As_xSe_{1-x}$  glasses.

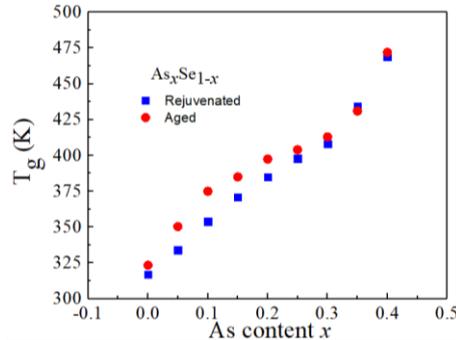


Fig. 3. Compositional trend of the glass transition temperature,  $T_g$  of  $As_xSe_{1-x}$  glasses.

The change in slope of the  $T_g(x)$  trend is a clear indication of a significant change in network connectivity in the  $As_xSe_{1-x}$  glasses. These are additional topological thresholds of the glass network that appears at  $\langle r \rangle = 2.1$  and  $\langle r \rangle = 2.3$ , which are lower value than the widely observed rigidity percolation threshold at  $\langle r \rangle = 2.4$ . These multiple transitions in the glass structure reveal the complexity of the microscopic structural units and their connectivity of the glass network. A similar behavior was observed by Myers and Felty [1] who reported the existence of inflection points in the variation of  $T_g$  with As composition in glassy  $As_xSe_{1-x}$  at  $x = 0.1$  and  $x = 0.3$  which coincide with observed trend in the present work as shown in Fig. 3. The existence of topological thresholds at low mean coordination numbers were reported by Mikla [18] in  $As_xSe_{100-x}$  and Thiruvikraman [19] in  $As_xS_{100-x}$  glasses.

The deviation from the linear dependence of  $T_g$  with As content in both aged and rejuvenated glasses is an indication of the variation of molecular configuration which is more pronounced in the composition range between  $x = 0.1$  to  $x = 0.2$  due to physical aging as evident from Fig. 3. Within this composition range, the physical aging produces significant changes in the

rigidity of the glass network in the aged samples leading to different compositional trends of the  $T_g$ . This effect of physical aging is also responsible for the significant shift of  $T_g$  to higher temperatures and the pronounced enthalpic loss reported by many authors [5,7]. It is also worth noting that above  $x = 0.30$ , the effect of physical aging becomes insignificant as the glass network enters a more stable structural configuration.

Since the  $T_g$  values of the rejuvenated glasses represent the true glass transition temperatures because of the removal of thermal history, we investigate the applicability of the theoretical models and empirical relations describing the compositional trends of  $T_g$  using the experimental data of the rejuvenated As-Se glasses.

The origin of the linear relationship of  $T_g$  versus arsenic fraction  $x$  was discussed by Micoulaut and Kerner [20] on the framework of the stochastic agglomeration theory. Based on this theory, the following slope equation was proposed for  $\text{As}_x\text{Se}_{1-x}$  glasses at low  $x$

$$\frac{dT_g}{dx} = \frac{T_0}{\ln(r_{\text{As}}/r_{\text{Se}})} \quad (9)$$

where  $T_0$  is the glass transition temperature for glassy Se and  $r_{\text{As}}$  and  $r_{\text{Se}}$  are the coordination numbers for As and Se, respectively. Using  $T_0 = 317$  K,  $r_{\text{As}} = 3$  and  $r_{\text{Se}} = 2$ , Eq. (9) gives  $\frac{dT_g}{dx} = 7.9$ . The slope of the linear part of  $T_g(x)$  at low  $x$  of the rejuvenated data in Fig. 3 is 3.6, much smaller than the predicted value of Eq. (9).

In order to test the validity of the Modified Gibbs-DiMarzio equation to describe the compositional trend of  $T_g$ , fitting the experimental data ( $T_g$  vs.  $x$  shown in Fig. 4) to Eq. (5) was made using  $T_0$  and  $\beta$  as adjustable parameters. We obtain an excellent fit with  $T_0 = 323 \pm 3$  K and  $\beta = 0.74 \pm 0.02$ . The obtained (experimental) value of  $\beta$  is different from the predicted value according to Eq. (8). However, it is within the range of values (0.3 – 0.7) reported for a variety of chalcogenide glasses [20].

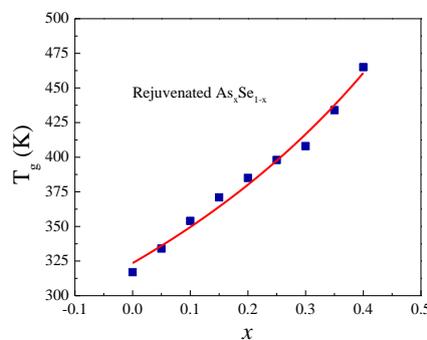


Fig. 4. Variation of  $T_g$  with the mean coordination number for the rejuvenated  $\text{As}_x\text{Se}_{1-x}$  glasses. The solid line is the least squares fit to Eq. (5).

To check the applicability of Tanaka equation (Eq. 6) to  $\text{As}_x\text{Se}_{1-x}$  glasses, experimental and calculated values of  $\ln T_g$  are listed in Table 1 showing a close agreement only for  $x \geq 0.25$ . Fig. 5 shows the plot of  $\ln T_g$  against the mean coordination number. The best fit to the experimental data can be obtained only if Tanaka equation is rewritten in the form

$$\ln T_g \cong a \langle r \rangle + b \quad (10)$$

and treating  $a$  and  $b$  as adjustable parameters. The least squares fit was shown in Fig. 5 as a straight solid line yielding the values of  $a$  and  $b$  as  $0.89 \pm 0.01$  and  $3.96 \pm 0.04$ , respectively indicating the non-universality of Eq. (6).

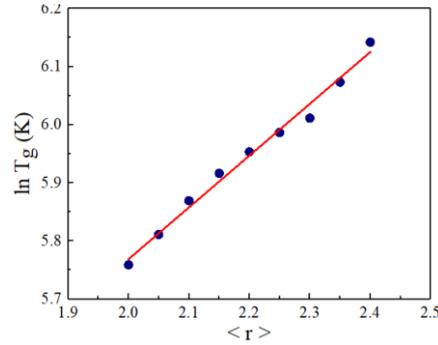


Fig. 5. Variation of  $\ln T_g$  with the mean coordination number for the rejuvenated  $As_xSe_{1-x}$  glasses. The solid line is the least squares fit to Eq. (10).

As pointed out by Sadagopan and Gatos [21], the average heats of atomization is a direct measure of the bond strengths and can be employed to describe the variation of the glass transition temperature with the degree of connectivity of the network glass. The average heat of atomization of the binary  $As_xSe_{1-x}$  glasses  $\langle H_A \rangle$  can be determined by the relation

$$\langle H_A \rangle = xH^{As} + (1-x)H^{Se} \quad (11)$$

Where  $H^{As}$  and  $H^{Se}$  are the heats of atomization of arsenic and selenium. The values of  $H^{As}$  and  $H^{Se}$  are 288.7 and 206.7 kJ/g.at., respectively. The calculated values of  $\langle H_A \rangle$  are listed in Table 1. Fig. 6 shows the variation of the heat of atomization with the mean coordination number. It is evident from the figure that the heat of atomization increases linearly with the increase of connectivity of glass network. This behavior is also indicated by the variation of  $T_g$  with the heat of atomization as shown in Fig. 7.

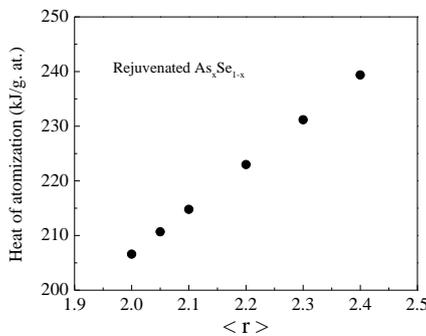


Fig. 6 Variation of the heat of atomization with the mean coordination number for the rejuvenated  $As_xSe_{1-x}$  glasses.

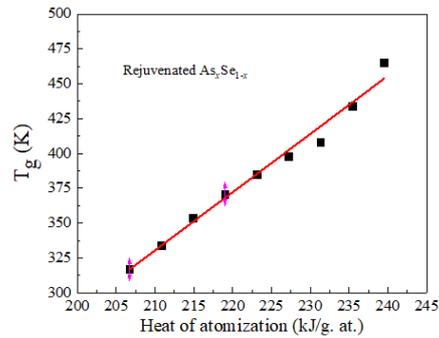


Fig. 7 Variation of  $T_g$  with the heat of atomization for the rejuvenated  $As_xSe_{1-x}$  glasses. The solid line is the least squares fit to the experimental data.

An empirical formula was suggested by Lankhorst [22] to correlate the glass transition temperature with the heat of atomization as

$$T_g = 3.44 \langle H_A \rangle - 480 \quad (12)$$

According to results presented in Fig. 7, we obtain the following correlation between  $T_g$  and  $\langle H_A \rangle$

$$T_g = 4.2 \langle H_A \rangle - 546 \quad (13)$$

showing a qualitative agreement with Lankhorst formula.

The monotonic increase in  $T_g$  with  $x$ ,  $\langle r \rangle$ , and  $\langle H_A \rangle$  in  $As_xSe_{1-x}$  glasses for the composition range  $0 < x < 0.4$  is a clear indication of the progressive increase of rigidity of the glass structure due to the increasing cross linking of Se chains by As atoms as  $x$  increases, in agreement with the chain crossing model [5,6]. It has also been reported from Raman studies [4] that in the range  $0 \leq x \leq 0.1$ , the majority structural building units in  $As_xSe_{1-x}$  glasses are Se chains and  $Se_8$  rings. Further increase of As atoms cause the formation of different structural units such as  $AsSe_3$  pyramids which may explain the crossover behavior of the compositional trend of the glass transition temperature.

Table 1. Mean coordination numbers, glass transition temperatures, and average heats of atomization for  $As_xSe_{1-x}$  glasses.

$x$ (at.%)	$\langle r \rangle$	$T_g$ (K)	$\ln T_g$ (Exp.)	$\ln T_g$ (Calc.)	$\langle H_A \rangle$ (kJ/g.at.)
0.00	2.00	317	5.76	5.50	206.69
0.05	2.05	334	5.81	5.58	210.79
0.10	2.10	354	5.87	5.66	214.89
0.15	2.15	371	5.91	5.74	218.99
0.20	2.20	385	5.95	5.82	223.09
0.25	2.25	398	5.98	5.90	227.19
0.30	2.30	408	6.01	5.98	231.29
0.35	2.35	434	6.07	6.06	235.39
0.40	2.40	465	6.14	6.14	239.49

## 5. Conclusions

Differential scanning calorimetry was used to investigate the compositional trend of the glass transition temperature ( $T_g$ ) in  $As_xSe_{1-x}$  network glasses. The variation of  $T_g$  with  $x$  and the mean coordination number  $\langle r \rangle$  of aged and rejuvenated samples were presented and discussed in terms of proposed theoretical and empirical models. In many cases, the disagreement between the proposed models and the present experimental data arise from the complexity of the structural configurations of the network glasses as  $x$  is varied from 0 to 0.4. Multiple rigidity transitions were observed and the influence of the long-term physical aging was found to be significant at the composition range between  $x = 0.1$  to  $x = 0.2$ .

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