Glimpses into the Dynamics and Static Ever Evolution in Ge-Se Glasses

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Abstract

The article investigates the evolution of glass transition temperature (T_g) with variation of chemical compositions in Ge-Se chalcogenide glasses, focusing on the correlation between dynamical parameter T_g and static parameter compactness (δ). We experimentally measure T_g for various Ge-Se compositions and explore different fitting models. The author initially fit the log (T_g) against the average coordination number. This paper provides valuable insights into the kinetic and static properties of Ge-Se glasses, showcasing an innovative application of the modified Gibbs-Di-Marzio equation. Through this analysis, we are able to ascertain that the constant β in the Gibbs-Di-Marzio equation is dependent on the ratio of two temperatures and that the value of β (0.74) derived from the fit, while the value of β = 0.72134 derived from the theory for the Ge-Se binary system. We are extending this empirical Gibbs-Di-Marzio form in another way to enrich our scientific research for Ge-Se binary system.

Keyword: Chalcogenide glasses; Glass transition temperature; Compactness; Chemical compositions; Glass dynamics

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Introduction

Chalcogenide glasses have considerable interest due to potential applications in the advancement of technology. Their promising applications are in the area of phase change memory devices in computing, fiber laser, as well as in the optical fiber communications. Additionally, glasses don't possess long range orders. Alloys of group IV and group VI based chalcogenide glasses allow the modification significantly in their structural and thermal properties. Hence, the composition dependent study of thermal properties, such as glass transition temperature is of great importance to understand the structural relaxation phenomena and viscous nature of the glass, to improve their applications in technology. Ge-Se is a typical binary chalcogenide system which is widely studied. Beyond its dynamical properties its static properties are significantly important. Understanding thermal properties such as glass transition and crystallization is important to improve switching characteristic for phase change memory devices. Thus, chemical compositions-based variations in static and dynamic property correlation is not studied yet. This system is, therefore, ideal for analysis and correlation studies between dynamic and static property is to address in this paper. The author initially fit log (T_g) against the average coordination number <r>, our findings are different from the quasi-linear dependence of past studies to ensure consistency with the data.

Experimental

Bulk glassy compositions were prepared by taken elemental Germanium (Ge) and elemental selenium (Se) 5N purity. In a batch 10gm of compositions were prepared. Weighed chunks of elemental (Ge) and Selenium were crushed in a pestle mortar. These crushed powders were mixed up and transferred into silica ampoule. Sample powders in the ampoule were evacuated at a pressure of 10^{-6} Torr by using diffusion pump. Hence, silica ampoules were sealed. Sealed ampoules were kept into rotating furnace. Temperature of the furnace

was gradually increased up to 950 °C. This temperature was monitored at the glass ampoule with the help of thermocouple tip. After 24 hours, melt was rotated for two days at this temperature to ensure make it homogenous. After two days sample was quenched into mixture of ice water in a bucket. Melt quenched samples were retrieved from the ampoule. Samples were annealed for seven days and after that thermal measurements were performed by Modulated Differential Scanning Calorimeter (MDSC) TA Instrument 2910. Measurements were performed from room temperature by ramp the temperature, at a heating rate of 5 °C/min. Glassy nature of the sample was characterized and glass transition temperature was determined.

Results and Discussion

Figure 1 shows a typical thermal curve for the glassy Ge20Se80 composition that was produced by using an MDSC instrument. At the glass transition temperature, an endothermic peak for structural relaxation was observed, which is also displayed in Figure 1. The glass transition temperature was estimated from the heat capacity versus temperature curve shown in Figure 1.
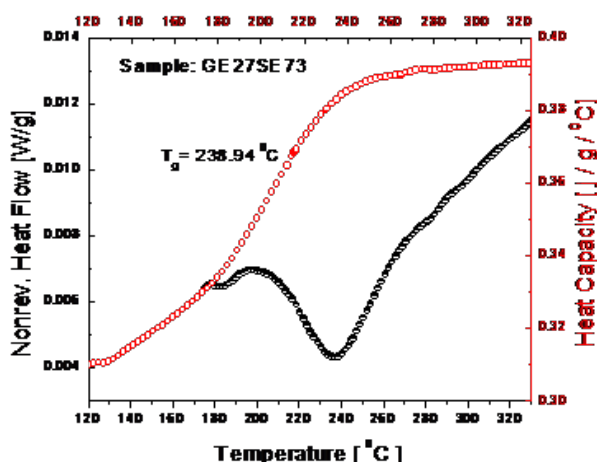

Figure 1: Structural relaxation in non-reversing heat flow and glass transition in heat capacity curve.

The glass transition temperatures values were obtained from different chemical compositions by doping germanium into selenium matrix. Coordination number of Germanium (Ge) and Selenium (Se) are 4 and 2, respectively. The Composition dependence of the thermal parameter T_g in terms of average coordination number <r>=2x+2 for Ge_xSe1_{-x} glasses are obtained and shown in Figure 2. Glass transition is the thermal energy that may be considered used as a diffusive motion and the corresponding value of the viscosity or structural relaxation at the glass transition depends upon the glass composition. We have plotted our experimental glass transition data as shown in Figure 2. A previous work [1] showed that the relationship ln(T_g) vs <r> follows lnTg = 1.6<r> + 2.3 is a quasi-linear fit to experimental data. We also tried to find the relation between log (T_g) vs.<r> plotting the dependence of log(T_g) vs. <r> gives a quasi-linear dependence log(T_g) = 0.4734<r>+1.5204 relation. This quasi-linear relationship does not fit well to all experimental data as shown in Figure 2.

To refine this fit on the experimental data, we found a new phase of their relationship with equation y = A +Bx+Cx2 where x represents the average coordination number, now log(T_g) = 5.635-2.92221<r> + 0.69821<r>2 which provides us with better results on the experimental data as shown in Figure 3.
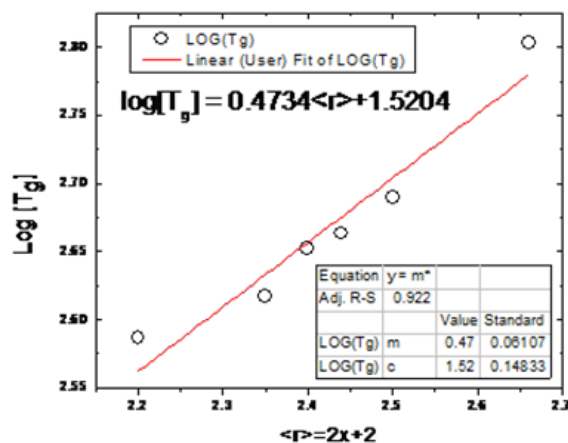
Figure 2: Variation of log (T_g) versus <r> red line is a quasi-linear fit on data points.
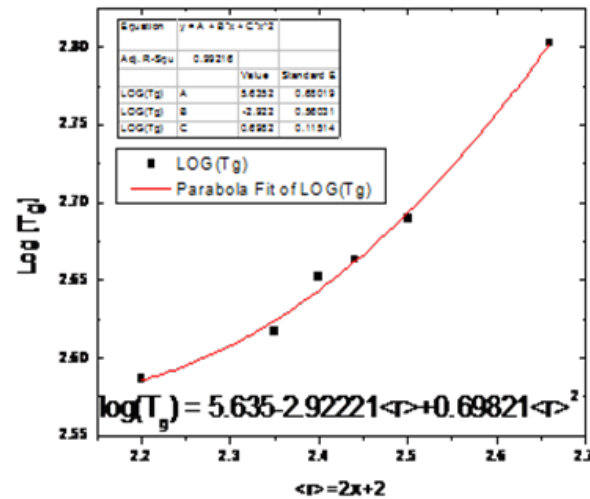
Figure 3: log (T_g) versus < r > red line fitted on experimental data with more accuracy.

It is understandable that glass transition T_g is mainly related to the network rigidity, the number of bonds per atom, and the bond energies between the atoms in the network [2]. Doping Germanium into polymeric selenium chains increases the network rigidity, as evident also from the dynamic /kinetic glass transition values, glass transition temperature increases with germanium doping up to chemical threshold composition $Ge_{33}Se_{67}$. Hence, the glass transition must be proportional to the overall mean bond energy < E > of the glassy sample. Many semi-empirical relationships have been proposed to fit the measured T_g for particular system [3]. Particularly, Gibbs and DiMarzio [4] and DiMarzio [5] have shown that glass transition temperature is given by

$$T_g = \frac{T_0}{1 - \alpha X} \quad (1)$$

where T_0 is the glass transition temperature of non -crossed-link initial polymeric chain, X is the cross linked density and α is a universal constant. Equation (1) is purely on the basis of thermodynamic considerations and therefore, it is suited for the application of chalcogenide glasses.

Sreeram et al. [6] adapted Gibbs DiMarzio equation by redefining the cross-linking density, X, as being equal to the average coordination number <r> and replace the constant α, by a system constant β. Thus, the modified Gibbs DiMarzio equation is rewritten as:

$$T_g = \frac{T_0}{1 - \beta(<r> - 2)} \quad (2)$$

Equation (2) is physically significant when the values of must lie between 0 and 1. In this work, we demonstrate that for the glassy Ge-Se system, the modified Gibbs Di-Marzio equation describes the evolution of the glass transition as a function of the average coordination number, as shown in Figure 4. This equation is in good agreement with the experimental data, and we have estimated the value of T_0 = 316K and the constant β = 0.74, so the modified equation for Ge-Se system is written as follows:

$$T_g = \frac{316}{1 - 0.74(<r> - 2)} \quad (3)$$
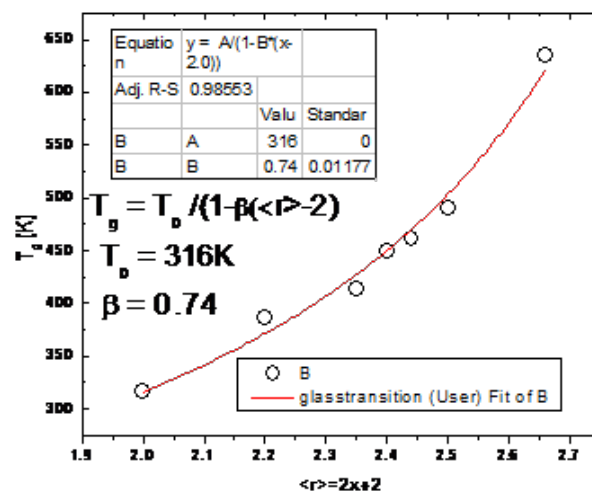
Figure 4: Modified Gibbs- Di-Marzio fit red line on experimental data with constant β = 0.74.

Sreeram et al. [6] investigation of multi-component chalcogenide systems from pure vitreous selenium β is a system dependent parameter and is given by:

$$\frac{1}{\beta} = \sum (m_i - 2)\ln\left[\frac{m_i}{2}\right] \quad (4)$$

Here we computed the value of β from the equation (4), the calculated value of β is 0.72134 for the Ge-Se binary system. The theoretical and experimental aspects of the fitted data are in very good agreement with the modified Gibbs-Di-Marzio equation. However, the data presented by group S. K. Tripathi et al. [7] in the Se-Te-Sb system, the theoretical values of modified Gibbs -Di-Marzio law did not agree with the experimental values. In this article, we also extended the Gibbs-Di Marzio equation proposing a modification for the Ge-Se system. Suppose we don't have data for pure selenium and I have one composition close to pure selenium in Ge-Se binary system, namely Ge2Se98, then we can replace the glass transition temperature of this composition in place of pure selenium. In this case we can extend the modified Gibbs- Di -Marzio equation, which can be written as:

$$T_g = \frac{T_g(Ge2Se98)}{1 - 0.789(<r> - 2.04)} \quad (5)$$

This is shown in Figure 5 with a β value 0.789, which fits very well to the equation (5) for the entire series of the compositions; but the cross linking for Ge_2Se_{98} composition is very small, so the accuracy of the experimental and theoretical results is good. This clearly indicates that T_0 can be easily replaced by composition with very less cross-linking glass transition temperature, which is applicably suitable for the Ge-Se glass series.
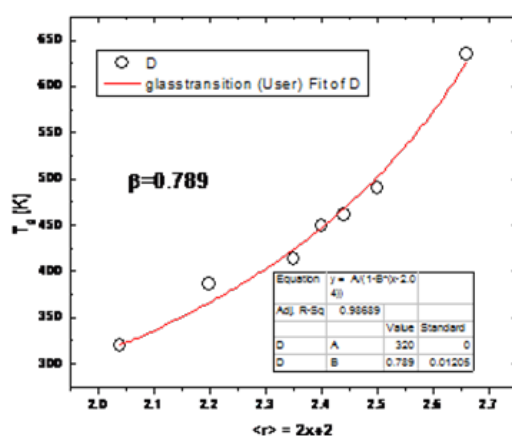

Figure 5: Extended Modified Gibbs-Di-Marzio fit Tg = $T_{Ge2}Se_{98}/(1-\beta(<r>-2.04))$.

We estimated the modified compactness [8] for Ge-Se glasses and are interested in the cross correlation between the variation of the glass transition temperature (dynamic quantity) and the obtained (static) compactness. The quasi-linear fitting of dynamic and static cross-correlation is shown in Figure 6, the fitting relationship is expressed as T_g = 1005.847 ×compactness + 235.28445. The quasi-linear fitting does not show good accuracy for all data points. To overcome this problem, we tried to fit the equation y = A+ Bx + Cx^2 for this cross-correlation, we got a good fitting result as:

T_g =410.0493-598.237×compactness+3314.973× $(compactness)^2$, as shown in Figure 7.
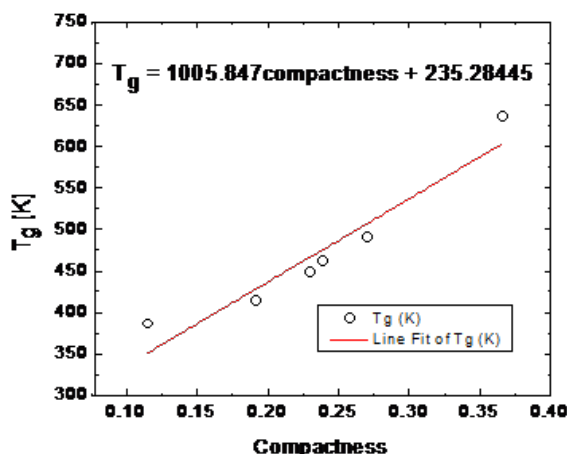
Figure 6: Relationship between glass transition and static compactness by fitted red line.

Conclusion

We are confident that our insights significantly enrich our scientific research and latest advancement in the technological applications; not only in the field of Ge-Se system but it also suggested to explore other multi-component chalcogenide glass system to testify the approach.

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