

Compositional effects on the thermo dynamical properties of Ge_{40-x}Se₆₀In_x Chalcogenide Glasses

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Abstract: The influence of compositional variations on the thermal properties viz: glasses transition temperature, mean bond energy and thermal relaxation with the variation in Ge content, has been studied theoretically for Ge-Se-In glassy chalcogenides. In the present work we have analyzed the thermal properties relatives to the given composition with theoretical predictions.

Keywords: Chalcogenide Glasses, Glasses Transition Temperature, Thermal Relaxation.

I. Introduction

The study of the thermal, structural and physical properties of chalcogenides such as magnetic, mechanical and thermodynamic behavior of these glasses has gained considerable attraction for several years. Recently extensive studies had been carried out on the thermal expansion technology, optical and electrical properties of these materials [1-5]. Chalcogenide glasses are the interesting members of the amorphous solids, due to their use in optical waveguide, biosensors, chemical sensors, thermal imaging detectors and opto-electronic devices [6-8]. Multi-component glasses were found to be more useful for many of these applications [9-10]. Depending upon the composition, the chalcogenide glasses are stable against crystallization and are chemically inert. They have excellent thermal stability and are relatively easy to fabricate. The present paper is concerned with the theoretical prediction of the thermal parameters related to composition, viz: mean bond energy, glass transition temperature and thermal relaxation for Ge-Se-In glassy system. It has been observed that partial substitution of Ge for Se leads to the densification of the system [10].

II. Analysis Of Various Theoretical Parameters

[A] Coordination Number and Constraints:-

The average coordination number r , for the system is calculated using the expression,

$$\langle r \rangle = Z_A X_A + Z_B X_B + Z_C X_C \quad (1)$$

where $Z_A = 4$, $Z_B = 2$, $Z_C = 4$, are the coordination numbers for Ge, Se, and In, respectively, the average coordination number being situated in the range $2.40 \leq r \leq 2.70$. In a glassy system covalent networks can be mechanically constrained by interatomic valence forces such as bond stretching and bond bending. Optimal glass formation is attained when the network is at a mechanically critical point. This point is reached when the number of constraints (N_{con}) per atom is equal to the degrees of freedom (N_d) per atom i.e. for ideal glass $N_{con} = N_d$. The enumeration of mechanical constraints in this system gives $\langle r \rangle / 2$ bond stretching constraints (N_α) and $2\langle r \rangle - 3$ bond bending constraints (N_β) [9]. The average coordination number $\langle r \rangle$ and the average number of constraints, given by $N_{con} = N_\alpha + N_\beta$ for various compositions with In are listed in table 1.

[B] Heat of Atomization and Mean Bond Energy:-

Heat of atomization $H_s(A-B)$ at standard temperature and pressure of a binary semiconductor formed from atoms A and B, as proposed by Pauling [11], is the sum of the heat of formation, ΔH , and the average of heat of atomization H_s^A and H_s^B , that corresponds to the average non polar bond energy of two atoms.

$$H_s(A-B) = \Delta H + (H_s^A + H_s^B) / 2 \quad (2)$$

The first term in equation (2) is proportional to the square of the electro negativity difference of two atoms involved i.e.

$$\Delta H \propto (X^A - X^B)^2 \quad (3)$$

In order to extend this idea to ternary and higher order semiconductor compounds, the average heat of atomization H_s is defined for the compounds $A_\alpha B_\beta C_\gamma$ as a direct measure of cohesive energy and the average bond strength is given by

$$H_s = (\alpha H_s^A + \beta H_s^B + \gamma H_s^C) / (\alpha + \beta + \gamma) \quad (4)$$

Equation (4) is applicable to this ternary system. The value of H_S obtained by using the values of H_S for Ge, Se, and In (the H_S values in units of kJ / mol are 377 for Ge, 226.4 for Se and 243 for In). It is clear that value of H_S decreases with the partial substitution of Ge for Se. The properties of chalcogenide glasses are related to overall mean bond energy <E>, which is a function of average coordination number <r>, the type of bonds and the bond energy. Using the correlation proposed by Tichy [12], for a chalcogenide rich system we can determine the value of <E>. The overall mean bond energy for the system Ge_aSe_bIn_c is given by

$$\langle E \rangle = E_{cl} + E_{rm} \quad (5)$$

where E_{cl} is the mean bond energy of average cross linking per atom and is given by

$$E_{cl} = P_r \cdot D_{hb} \quad (6)$$

Here P_r is the degree of cross linking given by

$$P_r = (aZ_{Ge} + cZ_{In}) / (a+b+c) \quad (7)$$

D_{hb} is the average heteropolar bond energy and is suggested to be

$$D_{hb} = [aZ_{Ge}D_{Ge-Se} + cZ_{In}D_{Se-In}] / [aZ_{Ge} + cZ_{In}] \quad (8)$$

The average bond energy per atom of the “remaining matrix” E_{rm} is given by

$$E_{rm} = 2D_{In-In}(0.5\langle r \rangle - P_r) / \langle r \rangle \quad (9)$$

The values of the heat of atomization and overall mean bond energy for the glassy alloy Ge_{40-x}Se₆₀In_x are listed in table - 1 and are found to increase with increasing In content. A graphical representation of H_S with increasing In content is given in Fig.-1 and of <E> with In content is given in Fig.-2

[C] The Glass transition temperature and the mean bond energy:-

The covalent bond approach of Tichy and Ticha [13] may be considered as a first approximation in the case chalcogenide glass. The glass transition temperature is considered to be proportional to the mean bond energy <E>, which depends on factors like mean coordination number, degree of cross linking, bond energy and the nature of bonds. Taking account of all these factors they have examined 186 chalcogenide glasses with T_g ranging from ~320K to 760K, and obtained a good correlation between T_g and <E> in the form

$$T_g = 311[\langle E \rangle - 0.9] \quad (10)$$

Which satisfied the Arrhenius relation for viscosity [14]. Applying this model in our problem, we have evaluated mean bond energies for various composition of Ge-Se-In system, and it can be seen that T_g is proportional to mean bond energy <E>. This shows that when In content increases, <E> of the system increases as shown in Fig.-3 and the value of T_g are listed in table -1.

[D] Thermal relaxation:-

The obtained value of <E> were found to be obeying the equation (10), this behavior means that, the value of the T_g in chalcogenide glasses is mainly determined through bonding arrangement. This does not mean that, intermolecular interactions have no effect on T_g as indicated by many authors. Furthermore this interaction plays a role in relaxation processes in the glass transition region. This correlation is expressed as an Arrhenian relation [15] for the viscosity in the form of:

$$\mu(T_g) = \mu_0 e^{E_\mu/k_B T_g} \quad (11)$$

Where μ₀ = 10⁻³ Pa, E_μ = <E> - 0.9 and k_B is the Boltzmann’s constant. The obtained values of μ(T_g) are listed in table -2 and it found to be in the order of 10¹³ Pa for the studied glasses. In accordance to Eq.(11), the μ(T_g) values are found to decrease with increasing T_g values. The value of μ(T_g) are listed in table-1 and its variation with T_g and <E> are shown in Fig.-4 and in Fig.-5.

III. Conclusion

From above theoretically analyzed thermal parameters of Ge-Se-In glassy system, the following conclusions were drawn. It has been seen that average coordination number, mean bond energy and glass transition temperature increases with increasing In content or decreasing Se content. This behavior is due to the increase of average binding strength. Heat of atomization is found to decrease with increasing In content and the same behavior is exhibited in thermal relaxation.

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Table-1: The value of H_s , $\langle E \rangle$, T_g and $\mu(T_g)$ for the $Ge_{40-x}Se_{60}In_x$ glassy system

Composition	$\langle r \rangle$	$H_s(Kj/mol)$	$\langle E \rangle$ (eV)	$T_g(K)$	$\mu(T_g)(10^{13}Pa)$
$Ge_{30}Se_{60}In_{10}$	2.40	273.240	2.81	594	1.523
$Ge_{20}Se_{60}In_{20}$	2.50	259.841	2.86	610	1.481
$Ge_{10}Se_{60}In_{30}$	2.60	246.442	2.94	635	1.428
$Se_{60}In_{40}$	2.70	233.048	3.06	672	1.401

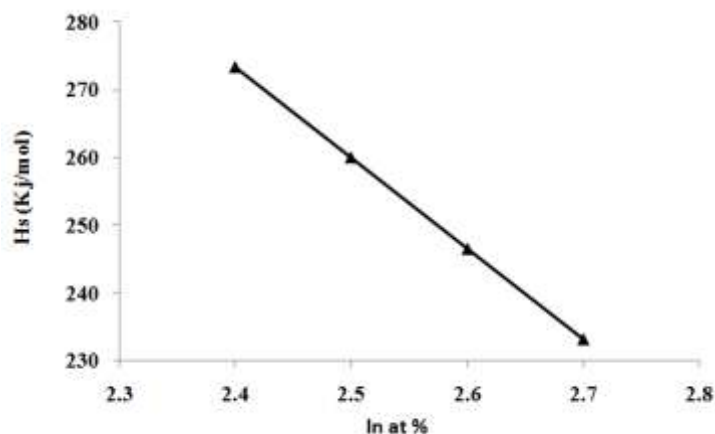


Fig.-1, heat of atomization as a function of In content

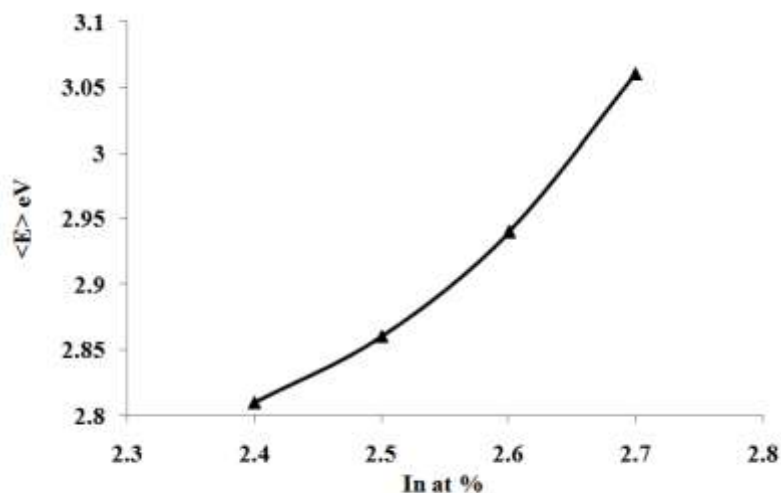


Fig.-2 Mean bond energy as a function of In content

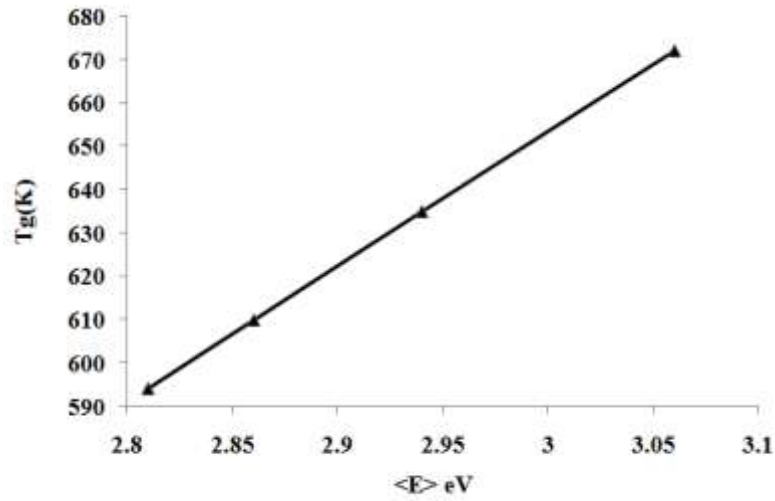


Fig.-3, Tg as a function of $\langle E \rangle$

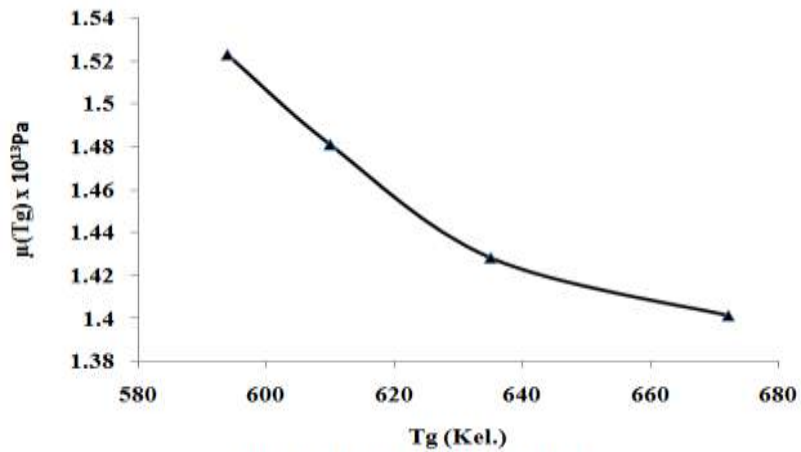


Fig.-4, $\mu(T_g)$ as a function of Tg

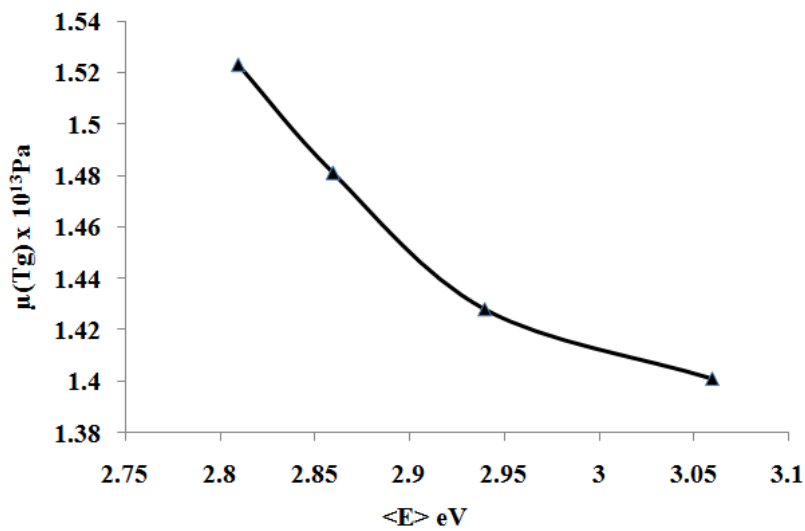


Fig.-5, $\mu(T_g)$ as a function $\langle E \rangle$