E-ISSN: 3048-6041| www.shodhpatra.org | Volume 1, Issue 8, August 2024

Parameters that depend on Glass Transition Temperature (T_g) in Indium doped Ge-Se Chalcogenide Glasses

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ABSTRACT: - *Glass transition temperature (T_g) dependent properties described the structural configuration of multicomponent chalcogenide glasses briefly. In the present work, Glass transition temperature dependent properties like the creation energy of micro-voids (E_h), the Urbach tail slope energy (Δ) and peak energy in the distribution of hoping barrier (E_m) has been calculated for $Ge_{10}Se_{90-x}In_x$, $Ge_{15}Se_{85-x}In_x$ and $Ge_{20}Se_{80-x}In_x$ chalcogenide glassy systems. From the calculated data we have seen that the values of T_g, E_h, Δ and E_m vary with Indium content.*

Keywords: *- Glass transition temperature, Chalcogenide glasses and temperature dependent parameters.*

INTRODUCTION

Glass transition temperature (T_g) is one of the most interesting parameter material science and engineering. A lot attention has been devoted to the characterization and improvement of the properties of chalcogenide glasses, especially for those materials which are used in the switching memories. Glass transition is one of the most fascinating problems in physics, but also it remains as one of the most challenging ones. Although this transition has considerable practical and technological importance, still there is no consensus about which thermodynamical and structural factors determine the glass transition temperature (T_g). Chalcogenide glasses have the great attention on the correlation of glass transition temperature with their structural and chemical properties. Technological applications of chalcogenide glasses in electrical and infrared transmission field. One of these interesting problems in the change in the properties of the glass as the chemical composition is changed. For example, the glass transition temperature and the specific heat difference can be raised or lowered by adding impurities, and the fragility of the glass can be changed from fragile to strong [1-5]

The Ge-Se glassy system is an interesting system as it is a combination of two different kinds of amorphous semiconductors: a Ge- which contain unpaired electron and a Se – where defects are changed and unpaired electrons are not present as evident from the electron spin resonance and magnetic susceptibility measurement. This difference arises from the dissimilarity in the short-range structure of these two systems: a Ge- has tetrahedral structure which is more rigid than the flexible structure of Se which has chain structure in two-fold coordination [6]. The properties of such Ge-Se glassy chalcogenides are usually affected by the addition of third element. Addition of third element will expand the glass forming area and also creates compositional sand configurationally disorder in the system and has large effect on their structural, physical, electrical and thermal properties. [7-8].

In the present work we study and describe some glass transition temperature dependent parameters for Indium (In) doped Ge-Se chalcogenide glassy systems like $Ge_{10}Se_{90-x}In_x$ (x = 0, 5, 10, 15, 20), $Ge_{15}Se_{85-x}In_x$ (x = 0, 5, 10, 15, 20) and $Ge_{20}Se_{80-x}In_x$ (x = 0, 5, 10, 15, 20).

GLASS TRANSITION TEMPERATURE (T_g)

All glasses are characterized by a glass transition temperature T_g which can be defined as the temperature at which the equilibrium liquid has a viscosity of 10^{13}poise [9]. This value for the viscosity is not universal; the glass transition is not an iso-viscous phenomenon and some liquids have viscosities at T_g as low as 10^{11}poise [10]. The variation of viscosity with glass transition temperature is illustrated in Fig.- (1).

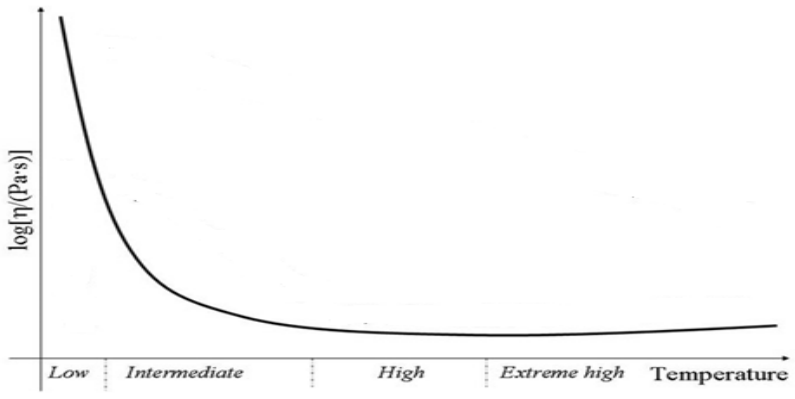

Fig.- (B), The variation of viscosity with glass transition temperature

Above the glass transition temperature, the system is in the rubbery state and bellow T_g, the system is in the glassy state. Thermodynamics properties like isothermal compressibility, specific heat and thermal expansion coefficient changes at glass transition temperature (T_g). These quantity abrupt

changes from values appropriate to supercooled liquid to those typical of the crystalline solid as the temperature is lowered to T_g [11]. Well, known empirical relation of the glass-transition temperature of $T_g \approx 2T_m/3$, where T_m is the melting temperature in glassy materials [12], suggest that T_g is related to the different structural and physical properties. At $T \approx T_g$, glassy network is macroscopically movable due to a sharp decrease in the viscosity. In some extent (while underlying physics is still not clear) above T_g there is a sharp decrease in the viscosity which expected to be due to collapse of glassy network.

For the glassy network systems there is direct consequence between T_g and $\langle Z \rangle$, which correlated by the following relation-

$$\ln T_g = 1.6 \langle Z \rangle + 2.3 \quad (1)$$

is known for wide class of glasses including organic materials [13]. In addition to the coordination number, Tichý and Tichá suggested that the bond energy for each bond should be taken into account for overall network. The average coordination number of any glass system can be calculated from the relation-

$$<Z> = \Sigma\, r_i a_i \quad (2)$$

Where r_i is the covalent coordination number of element i having atomic fraction a_i in the glass [14]. The average coordination number is a measure of connectedness in the network and the average bond energy, which linked with the number of bonds per atom in the network. [15]. The variation of <Z> with In at% and variation of glass transition temperature (T_g) with Indium content are illustrated in Fig. (2) and Fig. (3).

GLASS TRANSITION TEMPERATURE DEPENDENT PARAMETERS

(1) - The creation energy of micro-voids (E_h)-

The creation energy of micro-voids describes the defects in the localized state of energy gap of glassy semiconductors which is related to the glass density and the glass volume. The creation energy of micro-voids also describes the elasticity of a glass sample. According to the free-volume theory Sanditov [16] proposed a following equation for creation energy of micro-voids of glasses-

$$E_h = 3.58\, k_B\, T_g \quad (3)$$

Where E_h is the energy of micro-void creation in a volume V_h and where k_B, the Boltzmann constant (1.38×10^{-23}J/K). The variation of E_h with Indium content is plotted in Fig. (4).

(2)- The Urbach tail slope energy (Δ)-

The dependence of glass transition temperature on the Urbach tail slope describe the temperature dependence of the absorption coefficient. The spectral dependence of temperature is given by the Boltzmann factor. The relation between Urbach tail slope(Δ) and the glass transition temperature (T_g) is given by the relation [17-18]-

$$\Delta = 1.3\ k_B T_g \qquad (4)$$

Where k_B, the Boltzmann constant (1.38×10^{-23}J/K). The calculated value of Urbach tail slope (Δ) for the different Ge-Se-In glass systems are listed in Table-. The Variation of the Urbach tail slope (Δ) as a function of T_g for different Ge-Se-In glass systems are illustrated in Fig. (5).

(3)- Peak energy in the distribution of hoping barrier (E_m)-

Kinetically constrained models consider slow dynamics as of a purely kinetic origin [19-20] where dynamical constraints appear below a crossover temperature T_o, or above a corresponding packing fraction so that above to the dynamics is liquid-like whereas below to the dynamics becomes heterogeneous. According to Hunt the glass as a supercooled liquid. The required time scale for equilibration is a percolation relaxation time. Hunt derived the T_g from equalizing the relaxation time which is known as Hunt's equation [21-23] represented by-

$$E_m = 18\ k_B T_g \qquad (5)$$

The above Hunt's equation correlate T_g with barrier heights (E_m), the peak energy in the distribution of hoping barrier. The variation of hooping barrier energy (E_m) with Indium content is plotted in Fig. (6).

Result and Discussion

The values of mean coordination number (<Z>), glass transition temperature (T_g), the creation energy of micro-voids (E_h), the Urbach tail slope energy (Δ) and Peak energy in the distribution of hoping barrier (E_m) are tabulated in Table- 1 for $Ge_{10}Se_{90-x}In_x$ glassy system, in Table- 2 for $Ge_{15}Se_{85-x}In_x$ glassy system and in Table- 3 for $Ge_{20}Se_{80-x}In_x$ glassy system.

Table-1, The values of <Z>, T_g, E_h, Δ and E_m for $Ge_{10}Se_{90-x}In_x$ (x = 0, 5, 10, 15, 20) glassy system

Compositions	<Z>	Tg (Kel.)	E_h x 10^{-23} J	Δ x 10^{-23} J	E_m x 10^{-23} J
$Ge_{10}Se_{90}$	2.20	336.972	1664.777	604.530	8370.385
$Ge_{10}Se_{85}In_5$	2.30	395.440	1953.632	709.422	9822.730
$Ge_{10}Se_{80}In_{10}$	2.40	464.053	2292.608	832.511	11527.077
$Ge_{10}Se_{75}In_{15}$	2.50	544.571	2690.399	976.960	13527.144
$Ge_{10}Se_{70}In_{20}$	2.60	639.061	3157.217	1146.475	15874.276

Table-2, The values of <Z>, T_g, E_h, Δ and E_m for $Ge_{15}Se_{85-x}In_x$ (x = 0, 5, 10, 15, 20) glassy system

Compositions	<Z>	Tg (Kel.)	E_h x 10^{-23} J	Δ x 10^{-23} J	E_m x 10^{-23} J
$Ge_{15}Se_{85}$	2.30	395.440	1953.632	709.42	9822.790
$Ge_{15}Se_{80}In_5$	2.40	464.053	2292.608	832.511	11527.077
$Ge_{15}Se_{75}In_{10}$	2.50	544.571	2690.399	976.96	13527.144
$Ge_{15}Se_{70}In_{15}$	2.60	639.061	3157.217	1146.47	15874.276
$Ge_{15}Se_{65}In_{20}$	2.70	749.945	3705.029	1345.401	18628.634

Table-3, The values of <Z>, T_g, E_h, Δ and E_m for $Ge_{20}Se_{80-x}In_x$ (x = 0, 5, 10, 15, 20) glassy system

Compositions	<Z>	Tg (Kel.)	E_h x 10^{-23} J	Δ x 10^{-23} J	E_m x 10^{-23} J
$Ge_{20}Se_{80}$	2.40	464.053	2292.608	832.512	11527.077
$Ge_{20}Se_{75}In_5$	2.50	544.571	2690.399	976.960	13527.144
$Ge_{20}Se_{70}In_{10}$	2.60	639.061	3157.217	1146.475	15874.276
$Ge_{20}Se_{65}In_{15}$	2.70	749.945	3705.028	1345.410	18628.634
$Ge_{20}Se_{60}In_{20}$	2.80	880.069	4347.892	1578.842	21860.914

E-ISSN: 3048-6041| www.shodhpatra.org | Volume 1, Issue 8, August 2024

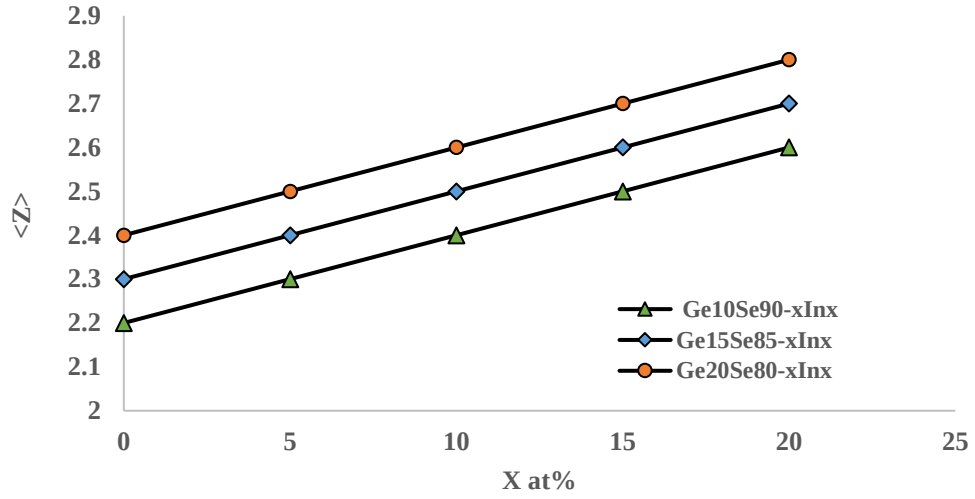

Fig.2:- Variation of <Z> with In content

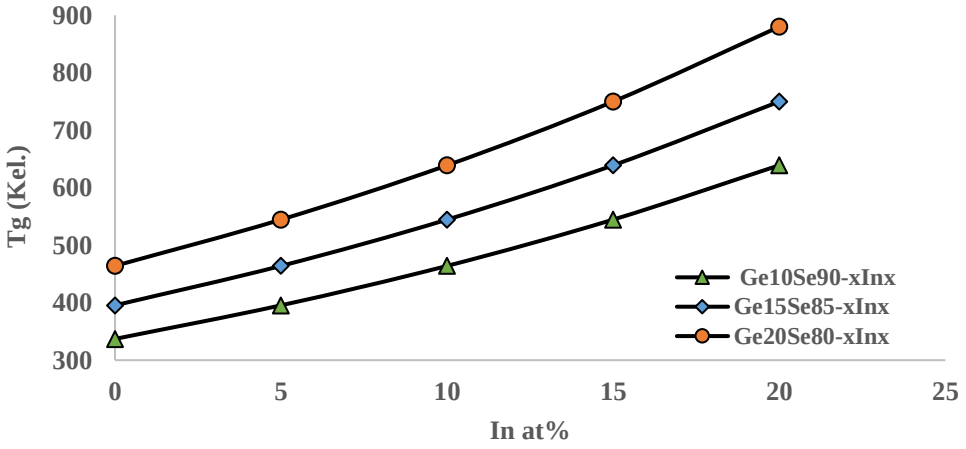

Fig.3:- Variation of Tg with In content

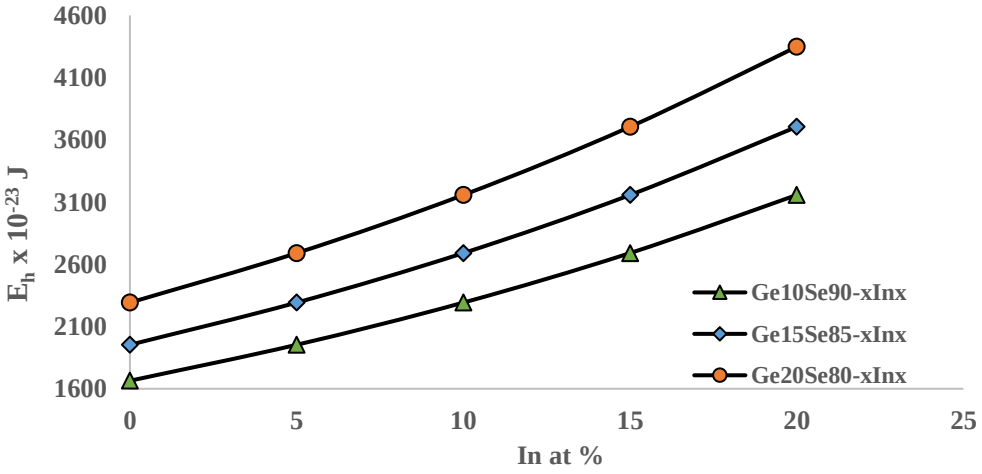

Fig.4:- Variation of E_h with In content

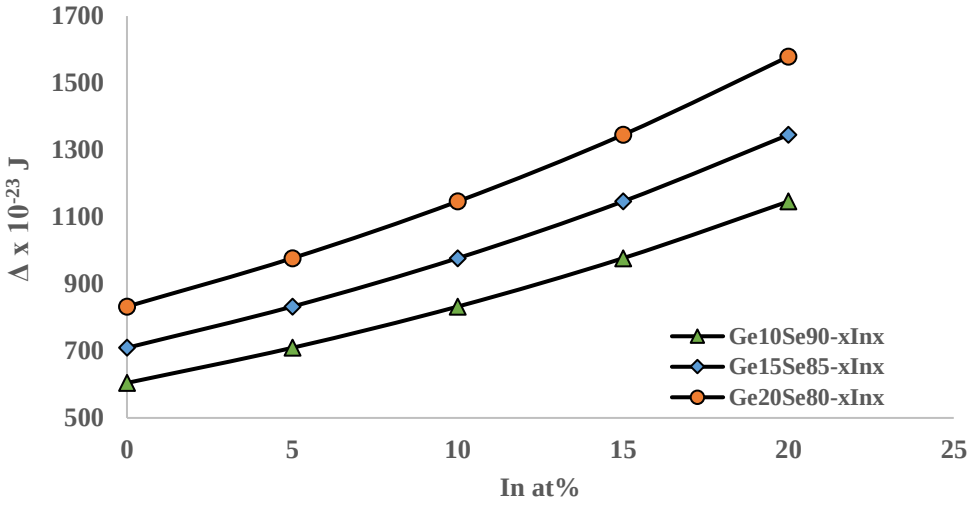

Fig.5:- Variation of Δ with In content

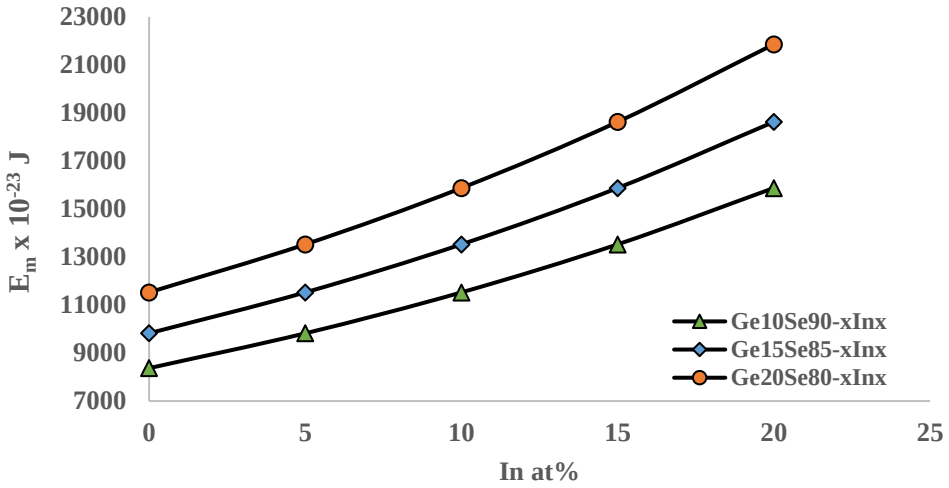

Fig.6:- Variation of E_m with In content

For different Ge-Se-In chalcogenide glassy systems we have seen that the value of <Z> varies from 2.20 to 2.80 which shows that the network transition from an under constrained to an over constrained network has been interpreted. Using equation (1) we calculate the glass transition temperature and we find that T_g increases with increasing Indium content. This is due to the formation of strong bond between Se-In. There is a primary influence of T_g in chalcogenide glasses in short-range chemical-bond arrangement but not an inter-molecular interaction. Also, we calculate the values of the creation energy of micro-voids (E_h) using equation (3) and we find that as the glass transition temperature increases E_h also increases this is due to the formation of wide gap between Ge-Se and Se-In bonds. The Urbach tail slope energy (Δ) and Peak energy in the distribution of hoping barrier (E_m) using equations (4) and (5) and we find that the values of these parameters vary with increase of T_g. The variation of Δ and E_m with increasing of T_g shows the

temperature dependence behaviour of the absorption coefficient. The spectral dependence of temperature is given by the Boltzmann factor.

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