

Compositional Trends of the Optical Properties in Chalcogenide Ge-Se-Ag Glasses

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Abstract

Chalcogenide glasses of $[\text{Ge}_{(0.5-0.33x)}\text{Ag}_{0.33x}\text{Se}_{0.5}]$ systems with $x = 0.6, 0.7, 0.8, 0.9$ at Ag% were investigated. Lone-pair electrons(L), Heat of atomization(Hs), Mean bond energy<E>, Optical gap (Eg), Glass transition temperature(Tg) were calculated. The increasing in Ag content leads to a structural change due to a gradually replacement of Ge atoms by Ag atoms. The number of constraints per atom (N_{con}) as a function of average coordination number is calculated. The lone-pair electrons, mean bond energy, optical gap, the Glass transition temperature decreases with the addition of Ag to the Ge-Se matrix. The optical gap increases with the increase in Ag content.

Keywords: Amorphous materials, Chalcogenide glasses, Optical properties.

Introduction

Chalcogenide glasses have been investigated intensively as they exhibit electrical and optical properties which make them useful for several potential applications. They are used in memory devices and fiber optics [1, 2] as they exhibit the threshold and memory switching behavior as well as infrared transmission. They have been, also, applied in xerography [3], photolithography [4], and in the fabrication of inexpensive solar cells [5]. Multicomponent glasses were found to be more useful for many of these applications [6, 7]. 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.

Chalcogenide glasses are often called lone pair semiconductors. The chemical bonds with lone pair electrons are characterized by flexibility. It is easier to distort a

bond with lone pair electrons than a bond with no unshared electrons. By increasing the number of lone pair electrons, the strain energy in a system decreases. The structure with large number of lone pair electrons favor the glass formation.

In this paper we have reported results from measurements of glasses in $[\text{Ge}_{(0.5-0.33x)}\text{Ag}_{0.33x}\text{Se}_{0.5}]$ system. The relation between the glass transition temperature and the optical gap and the basic physical parameters of the glass is an essential demand for any comprehensive theory relating their properties.

Analysis of various physical parameters

Various parameters *viz* coordination number and constraints, number of lone pair electrons, heat of atomization, optical gap and mean bond energy has been theoretically predicted for Ge-Se-Ag glassy system.

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 Ag, respectively, the average coordination number being situated in the range $2.95 \leq r \leq 3.00$. 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 $N_{\text{con}} = N_d$. 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 $N_{\text{con}} = N_\alpha + N_\beta$ for various compositions with In are listed in table 1.

Role of lone pair electrons

The number of lone pair electrons in a chalcogenide glass system can be calculated by using the relation [1]

$$L = V - r \quad (2)$$

where L and V are the lone pair electrons and valence electrons, respectively. The number of lone pair electrons obtained by using equation (2) is listed in Table 1. A graphical representation of L and Ag composition is given in Fig.1-

It is clear from Fig. 1 that the lone pair electrons, L , decrease continuously with the increase in Ag content. We can conclude from these results that some lone pair electrons in the structure of a system are a necessary condition for obtaining the

system in vitreous state. For a binary system the value of L must be larger than 2.6 and for a ternary system it must be larger than 1 [11].

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.

$$H_S(A-B) = \Delta H + (H_S^A + H_S^B)/2 \quad (3)$$

The first term in equation (3) is proportional to the square of the electro negativity difference of two atoms involved i.e.

$$\Delta H \propto (X^A - X^B)^2 \quad (4)$$

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

$$H_S = (\alpha H_S^A + \beta H_S^B + \gamma H_S^C) / (\alpha + \beta + \gamma) \quad (5)$$

Equation (5) is applicable to this ternary system. The value of H_S obtained by using the values of H_S for Ge, Se, and Ag (the H_S values in units of kJ / mol are 377 for Ge, 226.4 for Se and 284 for Ag). 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 $\langle E \rangle$, which is a function of average coordination number $\langle r \rangle$, 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 $\langle E \rangle$. The overall mean bond energy for the system $\text{Ge}_a\text{Se}_b\text{Ag}_c$ is given by

$$\langle E \rangle = E_{cl} + E_{rm} \quad (6)$$

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

$$E_{cl} = P_r \cdot D_{hb} \quad (7)$$

Here P_r is the degree of cross linking given by

$$P_r = (aZ_{\text{Ge}} + cZ_{\text{Ag}}) / (a+b+c) \quad (8)$$

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

$$D_{hb} = [aZ_{Ge}D_{Ge-Se} + Cz_{Ag}D_{Se-Ag}] / [aZ_{Ge} + Cz_{Ag}] \quad (9)$$

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

$$E_{rm} = 2D_{Ag-Ag}(0.5\langle r \rangle - P_r) / \langle r \rangle \quad (10)$$

The values of the overall mean bond energy for the glassy alloy $[Ge_{(0.5-0.33x)}Ag_{0.33x}Se_{0.5}]$ are listed in Table -2 and are found to decrease with increasing Ag content. A graphical representation of Hs with increasing Ag content is given in Fig.-2 and of $\langle E \rangle$ with Ag content is given in Fig-3.

Optical gap and Heat of atomization

In a given chalcogenide system, decreasing the relative atomic mass of chalcogen (Se) or its proportion in the glass increases the average bond strength and hence the T_g also increases [13]. It is therefore interesting to relate the optical gap ΔE_g with the chemical bond energy and the parameters we use to specify the bonding are Hs and Z. The relation between the energy gap and average heat of atomization was discussed by Aigrain and Balkanski[14,15]. According to their study a linear correlation exists for semiconductors of the diamond and zinc blende structure.

$$\Delta E_g = a(Hs - b) \quad (11)$$

Where a and b are characteristic constants. The values of ΔE_g for $[Ge_{(0.5-0.33x)}Ag_{0.33x}Se_{0.5}]$ with $x = 0.6, 0.7, 0.8, 0.9$ are listed in table- 2. It can be seen that the addition of Ge leads to increasing Hs as well as ΔE_g . It is suggested by the above equation that the average heat of atomization are a measure of cohesive energy and represent the relative bond strength, that in turn are correlated with properties like energy gap[16,17]. A graphical representation of Hs with ΔE_g is given in Fig-4.

The Glass transition temperature and the mean bond energy

The covalent bond approach of Tichy and Ticha [18,19] 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 $\langle E \rangle$, 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 $\langle E \rangle$ in the form

$$T_g = 311[\langle E \rangle - 0.9] \quad (12)$$

Which satisfied the Arrhenius relation for viscosity[19,20]. Applying this model in our problem, we have evaluated mean bond energies for various composition of Ge-Se-Ag system, and it can be seen that T_g is proportional to mean bond energy $\langle E \rangle$. This shows that when Ag content increases, T_g of the system decreases with the decrease of mean bond energy $\langle E \rangle$ as shown in Fig- 5.

Table1. The average coordination number $\langle r \rangle$ and the average number of constraints, given by $N_{con} = N^{\alpha} + N^{\beta}$ for various composition of Ag

Compositions	$\langle r \rangle$	Ncon	L	V
Ge _{0.302} Se _{0.5} Ag _{0.198}	2.97	4.497	1.4056	4.4056
Ge _{0.269} Se _{0.5} Ag _{0.231}	2.98	4.490	1.3066	4.3066
Ge _{0.236} Se _{0.5} Ag _{0.264}	2.99	4.485	1.2016	4.2016
Ge _{0.203} Se _{0.5} Ag _{0.297}	3.00	4.479	1.1206	4.1206

Table 2. The value of Hs, $\langle E \rangle$, Eg and Tg for the [Ge_(0.5-0.33x)Ag_{0.33x}Se_{0.5}] glassy system.

Composition	Hs(Kj/mol)	$\langle E \rangle$ (eV)	Eg(eV)	Tg(K)
Ge _{0.302} Se _{0.5} Ag _{0.198}	283.286	3.09	2.922	681
Ge _{0.269} Se _{0.5} Ag _{0.231}	280.217	3.01	2.890	672
Ge _{0.236} Se _{0.5} Ag _{0.264}	277.148	2.71	2.858	563
Ge _{0.203} Se _{0.5} Ag _{0.297}	274.858	2.62	2.802	535

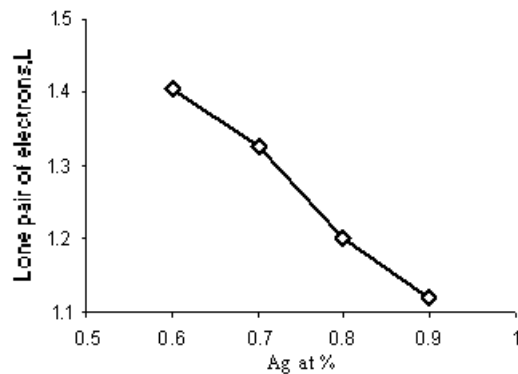


Fig-1 The number of Lone pair electrons as a function of Ag content.

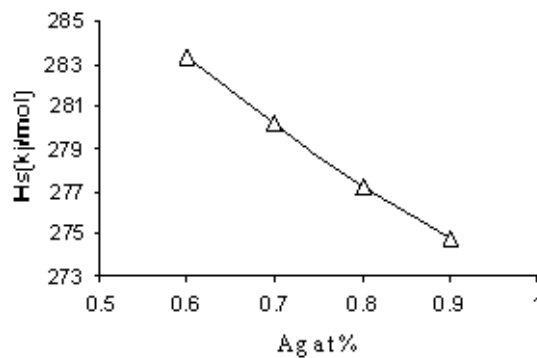


Figure 2 : The heat of atomization as a function of Ag content.

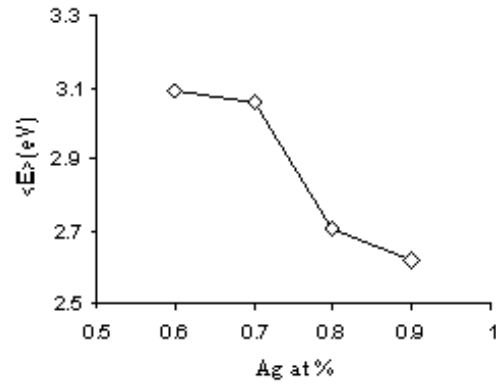


Figure 3 : The mean bond energy as a function of Ag content.

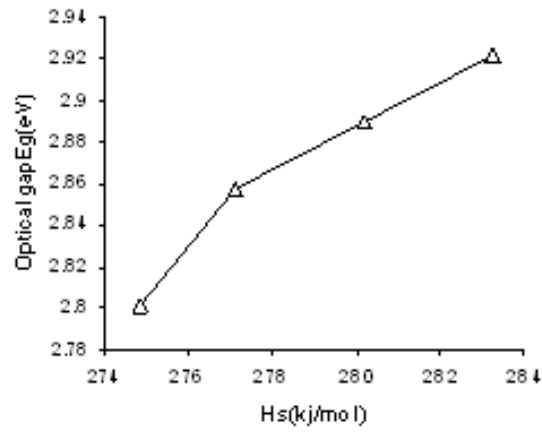


Figure 4 : Optical bandgap Vs H_s .

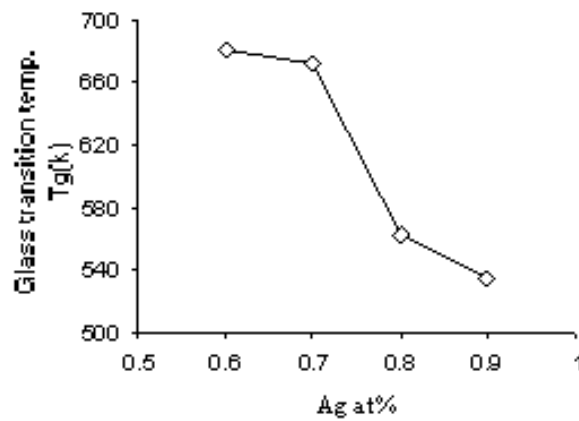


Figure 5 : Variation of glass transition temperature with the increase in Ag content.

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