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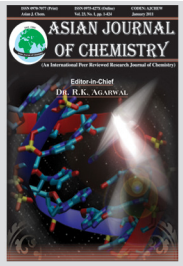

Effect of Silver content on the Optical and Other Physical Characteristics of Ge-Se Glass System†

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The effect on the optical and other physical properties with the addition of Ag content, *viz*, T_g, <E>, H_s, $<r_{eff}>$, Z, N_{con}, L, ΔE_g and energetic parameter A of $Ge_{30-x}Se_{70}Ag_x$ (x = 0, 5, 10, 15, 20 at %) glassy alloy have been examined theoretically. The relationship between the T_g and <E> has been estimated by using Tichy-Ticha approach. The relationship between ΔE_g and chemical composition has been discussed in terms of the H_s and Z. In order to correlate the optical parameter (ΔE_g) with film composition we used the energetic parameter (A). It has been found that <E>, H_s, (ΔE_g), T_g, decreases whereas deviation of stoichiometry R, N_{con} and the energetic parameter A, increases with increasing A_g content in Ge-Se-Ag system.

Key Words: Chalcogenide glasses, Optical gap, Heat of atomization, Energetic parameter.

INTRODUCTION

Recently, great attention has been given to chalcogenide glasses mainly due to their wide range of application in solid state devices both in scientific and technological fields. Optical data storage based on laser induced amorphous to crystalline (a-c) phase transformation of chalcogenide glasses in an ara with on going research activity[1]. Especially Se based alloy exhibit a unique properties of reversible transformation. This properties makes these systems very useful in optical memory devices, X-ray imaging and photonics[2-6]. The Ge-Se-Ag glass system is a superionic conducting glass system and these are the important materials as solid electolytes. The addition of impurity has a pronounced effect on the conduction mechanism of the amorphous glasses and this effect can be widely different for different impurities[7].

The optical properties of amorphous semiconductor has been extensively studied in recent decades because of their wide range of application and storage dependence on composition. In the present paper the effective coordination no. $<r_{eff}>$, no. of constraints (N_{con}), average heat of atomization (H_s), mean bond energy <E>, glass transition temp. (T_g), optical gap (ΔE_g), deviation of stoichiometry (R) and the energetic parameter (A) predicted theoretically for the $Ge_{30-x}Se_{70}Ag_x$ (x = 0, 5, 10, 15, 20 at %) system. From the chemical bond approach, interesting relationship between various parameters has been reported.

Analysis of various theoretical parameter

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:

$$<r> = Z_AX_A + Z_BX_B + Z_CX_C \quad (1)$$

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 $1.98 \le r \ge 2.26$. 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 <r>/2 bond stretching constraints (N_α) and 2 <r>-3 bond bending constraints (N_β)[8]. The average coordination number <r> and the average number of constraints, given by $N_{con} = N_\alpha + N_\beta$ for various compositions which are listed in Table-1 and the variation of mean coordination no. with Ag at % is shown in Fig. 1.

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TABLE-1
AVERAGE COORDINATION NUMBER <r> AND THE AVERAGE NUMBER OF CONSTRAINTS, GIVEN BY $N_{con} = N_\alpha + N_\beta$ FOR VARIOUS COMPOSITION OF Ag

Composition	<r>	N_α	N_β	N_{con}
$Ge_{30}Se_{70}$	1.98	0.988	0.952	1.94
$Ge_{30}Se_{65}Ag_5$	2.04	1.0235	1.094	2.117
$Ge_{30}Se_{60}Ag_{10}$	2.12	1.0588	1.234	2.292
$Ge_{30}Se_{55}Ag_{15}$	2.18	1.0940	1.376	2.470
$Ge_{30}Se_{50}Ag_{20}$	2.26	1.1293	1.516	2.645

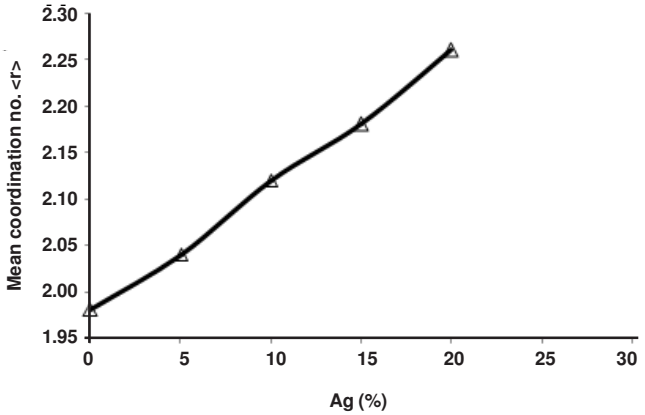

Fig. 1. Mean coordination no. *vs* Ag %

Role of lone pair electrons: The number of lone pair electrons in a chalcogenide glass system can be calculated by using the relation[9].

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

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

TABLE-2
NUMBER OF LONE PAIR ELECTRONS AND R OBTAINED BY RELATION (2, 3)

Composition	<r>	V	L = V-Z	R
$Ge_{30}Se_{70}$	1.98	5.3998	3.4239	∞
$Ge_{30}Se_{65}Ag_5$	2.04	5.2499	3.2029	11.98
$Ge_{30}Se_{60}Ag_{10}$	2.12	5.0999	2.9823	5.50
$Ge_{30}Se_{55}Ag_{15}$	2.18	4.9499	2.7618	3.34
$Ge_{30}Se_{50}Ag_{20}$	2.26	4.7997	2.5410	2.25

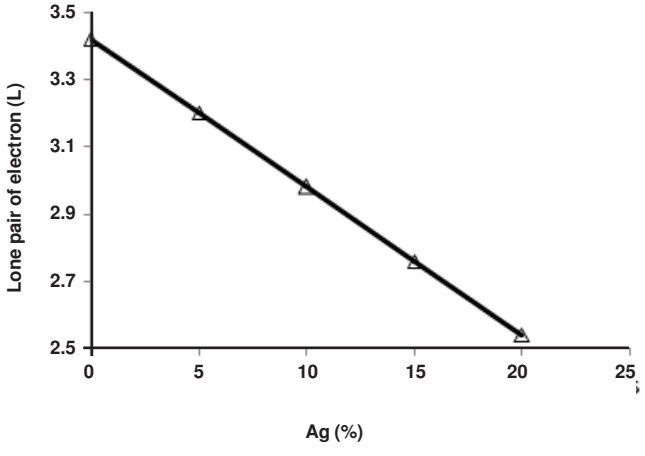

Fig. 2. Variation of L with Ag %

It is clear from Fig. 2, that the lone pair electrons, L, decrease continuously with the increase in Ag content. It is concluded 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[10].

Deviation of stoichiometry (R): The parameter R, which determines the deviation of stoichiometry is defined as the ratio of covalent bonding possibilities of chalcogen atom to that of non-chalcogen atom. The quantity R is given by [10,11]:

$$R = \frac{YN_{Ge} + XN_{Se}}{ZN_{Ag}} \quad (3)$$

where, X, Y and Z are the atomic fractions of Se, Ge and Ag. For R > 1, the system is chalcogen rich and for R < 1, the system is chalcogen poor. The threshold at R = 1 (the point of existence of only heteropolar bonds) is evident. For the $Ge_{30-x}Se_{70}Ag_x$ system the calculated value of R > 1 is listed in Table-2. For the present investing system the value of R > 1, leading the system to chalcogen rich-region. The variation of R with Ag content is illustrated in Fig. 3.

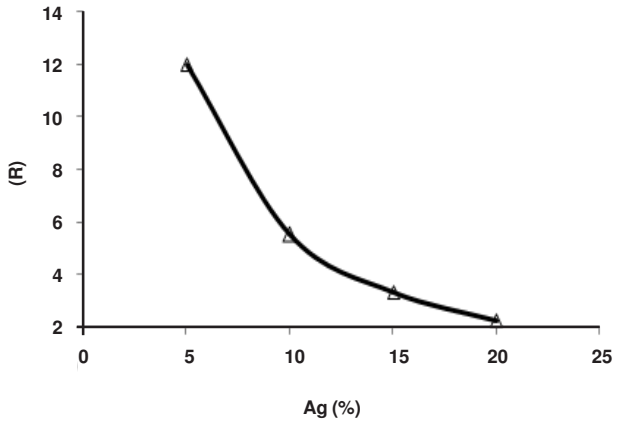

Fig. 3. Deviation of stoichiometry (R) Ag %

Heat of atomization and optical gap: 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[12], 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.

$$H_s(A\text{-}B) = \Delta H + (H_s^A + H_s^B)/2 \quad (4)$$

The first term in eqn. (4) is proportional to the square of the electronegativity difference of two atoms involved *i.e.*

$$\Delta H\alpha (X^A - X^B)^2 \quad (5)$$

In order to extend this idea to ternary and higher order semiconductor compounds, the average heat of atomization Hs 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:

$$Hs = (\alpha H_S^A + \beta H_S^B + \beta H_S^C)/(\alpha + \beta + \gamma) \quad (6)$$

Eqn. (6) is applicable to this ternary system. The value of Hs obtained by using the values of Hs for Ge, Se and In (the HS values in units of kj/mol are 377 for Ge, 226.4 for Se and 284 for Ag. It is clear that value of Hs decreases with the partial substitution of Ge for Se. A graphical representation of Hs with ΔE_g is given in Fig. 4.

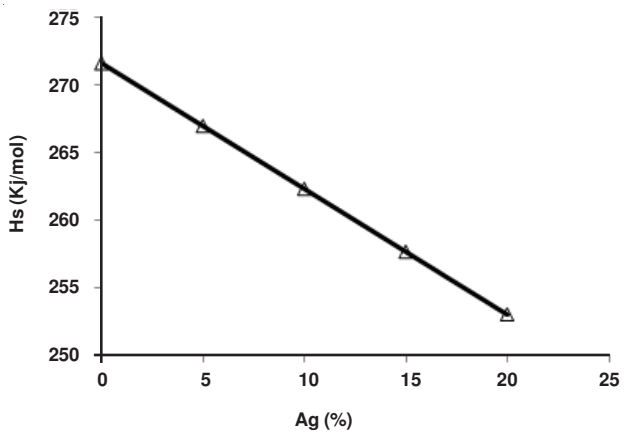

Fig. 4. Variation of Hs(Kj/mol) with Ag %

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.

$$\Delta E_g = a(Hs - b) \quad (7)$$

where, a and b are characteristic constants. The values of ΔE_g for $Ge_{30-x}Se_{70}Ag_x$ with (x = 0, 5, 10, 15, 20) are listed in Table -3. 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. 5 and the value of Hs and ΔE_g are listed in Table-3.

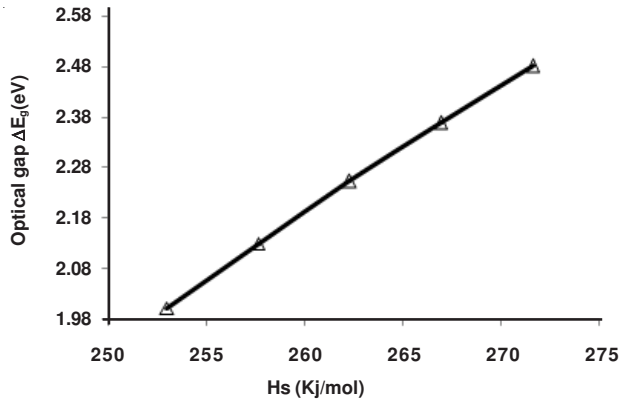

Fig. 5. Variation of Eg(eV) with Hs(Kj/mol)

TABLE-3
VALUE OF H_s, ΔE_g FOR THE $Ge_{30-x}Se_{70}Ag_x$ GLASSY SYSTEM

Composition	<E> (eV)	T_g (kel)	$A \times 10^4$ (kel)
$Ge_{30}Se_{70}$	2.524	505	0.0949
$Ge_{30}Se_{65}Ag_5$	2.482	492	0.1775
$Ge_{30}Se_{60}Ag_{10}$	2.461	485	0.4207
$Ge_{30}Se_{55}Ag_{15}$	2.458	484	0.6383
$Ge_{30}Se_{50}Ag_{20}$	2.452	482	0.8237

Mean bond energy <E> and glass transition temperature (T_g): 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 and Ticha[10], for a chalcogenide rich system we can determine the value of <E>. The overall mean bond energy for the system $Ge_aSe_bAg_c$ is given by:

$$<E> = E_{cl} + E_{rm} \quad (8)$$

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

$$E_{cl} = P_r.D_{hb} \quad (9)$$

here, P_r is the degree of cross linking given by:

$$P_r = (aZ_{Ge} + Cz_{Ag})/(a + b + c)$$

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

$$D_{hb} = [aZ_{Ge}D_{Ge\text{-}Se} + Cz_{Ag}D_{Se\text{-}Ag}]/[aZ_{Ge} + Cz_{Ag}]$$

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

$$E_{rm} = 2D_{Ag\text{-}Ag}(0.5 <r> -Pr)/<r> \quad (12)$$

The values of the overall mean bond energy for the glassy alloy $Ge_{30-x}Se_{70}Ag_x$ are listed in Table-3 and are found to decrease with increasing Ag content. A graphical representation of <E> with Ag content is given in Fig. 6.

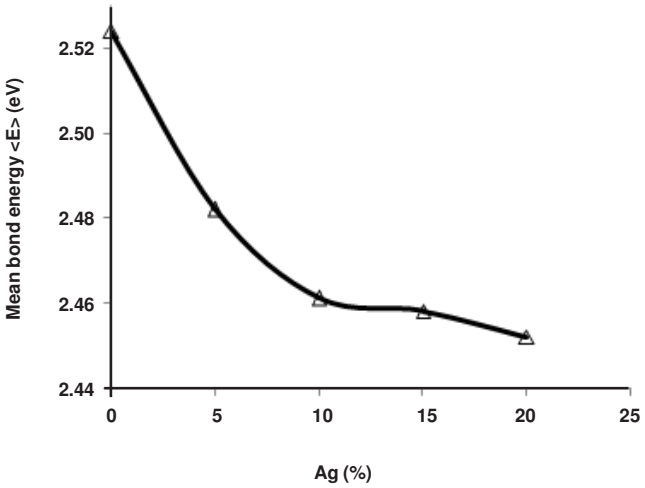

Fig. 6. Variation of mean bond energy <E> with Ag %

The covalent bond approach of Tichy and Ticha[10,11] 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 -320 to 760 K and obtained a good correlation between T_g and <E> in the form:

$$T_g = 11 <E> - 0.9] \quad (13)$$

which, satisfied the Arrhenius relation for viscosity[11,18]. Applying this model in present 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 <E>. This shows that when Ag content increases, <E> of the system increases. The value of T_g, <E> are listed in Table-4.

TABLE-4
VALUE OF <E>, T_g AND A FOR THE $Ge_{30-x}Se_{70}Ag_x$ GLASSY SYSTEM

Composition	H_s (Kj/mol)	ΔE_g (eV)
$Ge_{30}Se_{70}$	271.58	2.482
$Ge_{30}Se_{65}Ag_5$	266.93	2.370
$Ge_{30}Se_{60}Ag_{10}$	262.28	2.254
$Ge_{30}Se_{55}Ag_{15}$	257.63	2.130
$Ge_{30}Se_{50}Ag_{20}$	252.98	2.003

Energetic parameter (A): In order to corelate the optical parameter (ΔE_g) with the film composition we used the energetic parameter(A) introduced by Angell[19].

$$A = \epsilon \Delta E_g/k \quad (14)$$

where $\epsilon = \delta(Z-2)$ and K = Boltzmann constant, δ an independent constant (0.55). Fig. 7 shows the variarion of A with % of composition. The value of A is listed in Table-4.

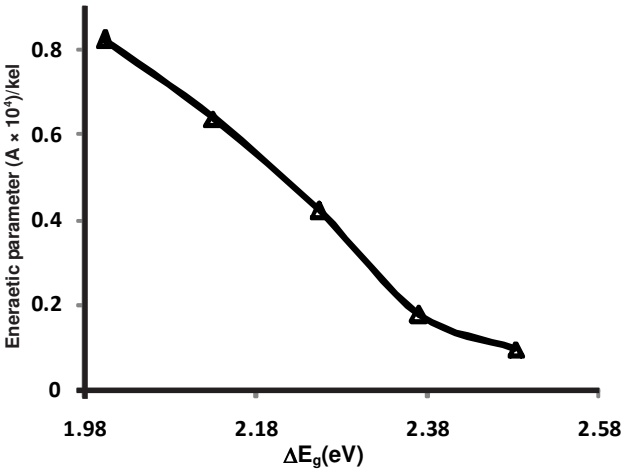

Fig. 7. Variation of A/kel with E_g(eV)

Conclusion

From above theoretically analyzed physical parameters of Ge-Se-Ag glassy system the following conclusions were drawn. It has been found that <E>, H_s, (ΔE_g), T_g, decreases whereas deviation of stoichiometry R, N_{con} and the energetic parameter A, increases with increasing Ag content in Ge-Se-Ag system.

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