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Optical characterization of $Ge_{0.15}Se_{0.85-x}Ag_x$ (0<x>0.20) Glasses

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ABSTRACT

In the present work we have predicted the optical and some physical parameters viz. coordination number (r), number of constraints (Ncon), no. of lone-pair electrons(L), heat of atomization (Hs) and the compositional effect on the optical gap theoretically. It has been found that <r>, Hs, ΔE_g and the energetic parameter (A). An attempt has been made to explain the varying trends of various parameters with increasing Ag content. Spectral dependence of the absorption coefficient is verified by the energetic parameter relation Vs composition.

Keywords:- Chalcogenides Glasses, Optical gap, Spectral dependence of Absorption coefficient.

INTRODUCTION

Chalcogenide glasses are the promising candidates for photonic applications due to their attractive optical properties such as high refractive index, high photo sensitivity and large optical nonlinearity [1]. Se has been found to have tremendous potential in device technology [2], since it exhibit a unique properties of reversible transformation. These properties like make these glasses very useful in memory devices [3-4]. Among the different families of chalcogenides glasses, the Ge-Se-Ag system is of particular for two main reasons: the system has a broad glass forming region and the optical nonlinearity of the glasses in this system.[5].These glasses are optically highly non-linear and useful for all optical switching(AOS) to the absorption of electromagnetic radiations and shows a variety of photo induced effect as a result of illumination.

Present work is based on bi-chalcogen (Ge-Se) glassy system containing Ag as the third substitute. The present paper concerned with the theoretical prediction of the optical parameters related to compositions for $Ge_{0.15}Se_{0.85-x}Ag_x$ (0<x>0.20) Glassy system.[6,7]

RESULTS AND DISCUSSION

(a) Calculation of Coordination number<r> and No. of Constraint(Nc):-

The average no. of coordination is calculated by the equation-

$$<r> = XZ_{Ge} + YZ_{Se} + ZZ_{In} \quad (1)$$

The idea of rigidity percolation was introduced by Phillips [8-10], and subsequently modified in detail by Thorpe [11]. Consider a network consisting of $N = n_i$ atoms. If no bonds are formed there are3N translational degrees of freedom. However, the translational mobility is reduced by the formation of covalent bonds among these atoms. The glassy networks are influenced by mechanical constraints(N_{con})due to bond stretching forces 'á ' and bond bending force 'â ' .The residual mobility can be expressed by the number of zero frequency modes M_0 , normalized by3N , according to

$$M_0 = (3N - N_{con}) / 3N \quad (2)$$

The total number of bond stretching and bond bending constraint are calculated according to

$$N^{\alpha} = \sum_i n_i r_i/2 \quad \text{and} \quad N^{\beta} = \sum_i n_i(2r_i-3) \quad (3)$$

Knowing the average number of constraints (per atom), $N_{con} = N^{\alpha} + N^{\beta}$ and the average coordination number $< r >$ for different composition of a-glassy system, the effective average coordination number $< r_{eff} >$ can be calculated [12] using the formula

$$< r_{eff} >= (2/5)(N_{con} + 3) \quad (4)$$

The calculated value of N^{α}, N^{β} and N_{con} of $Ge_{0.15}Se_{0.85-x}Ag_x$ (0<x>0.20) glassy system are listed in table-(1) and the variation of <r> with Ag content is illustrated in Fig.-(1).

(b) Correlation of Lone-pair electron and Glass forming Ability:-

The number of lone pair electrons in a chalcogenide glass system can be calculated by using the relation (3)

$$L = V - r \quad (5)$$

Where L and V are the lone pair electrons and valence electrons, respectively. The number of lone pair electrons obtained by using equation (5) is listed in table – (1). A graphical representation of L and Ag composition is given in figure (2). It is clear from Fig.(2) 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 [13-16].

(c) Correlation of Heat of Atomization and Optical band 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 [17], 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.

$$H_s\,(A\text{-}B) = \Delta H + (H_s{}^A + H_s{}^B)/2 \qquad (6)$$

The first term in equation (6) is proportional to the square of the electro negativity difference of two atoms involved i.e.

$$\Delta H\ \alpha\ (X^A - X^B)^2 \qquad (7)$$

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

$$H_S = (\alpha H_S{}^A + \beta\ H_S{}^B + \gamma\ H_S{}^C)\ /\ (\alpha + \beta + \gamma) \qquad (8)$$

Equation (8) 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 increases with the partial substitution of Ge for Se. Average single bond energy H_S/<r> which is a measure of cohesive energy decreases with increase of Ag content may cause increasing of optical band gap. The values of average single bond energy are tabulated in table-(2).

It is therefore interesting to relate the optical gap ΔEg 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[18-19]. According to their study a linear correlation exists for semiconductors of the diamond and zinc blende structure.

$$\Delta E_g = a\ (Hs - b) \qquad (9)$$

Where a and b are characteristic constants. The values of ΔE_g for $Ge_{0.15}Se_{0.85-x}Ag_x$ (0<x>0.20) are listed in table -2. It can be seen that the addition of Ge leads to

Increasing H_s 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[20-22]. A graphical representation of Hs and ΔE_g with Ag content are shown in Fig.-(3) and Fig.-(4).

(d) Spectral dependence of the absorption coefficient:-

Spectral dependence of the absorption coefficient indicates an indirect allowed transition. The result is verified by the energetic parameter relation which is introduced by Angell [23-25], according to which to correlate the optical gap with film composition we used the energetic parameter (A) given by the relation-

$$A = \epsilon \Delta E_g / k \qquad (10)$$

Where $\epsilon = \delta (Z-2)$ and K = Boltzmann constant, δ an independent constant (0.55).The variation of energetic parameter (A) with composition is illustrated in Fig.-(5).

CONCLUSION

The compositional studies have shown that the average no. of coordination <r>, number of constraint (N_{con}), heat of atomization (H_s), optical band gap (ΔE_g) and the energetic parameter (A) increases while the no. of lone-pair electrons(L) decreases with increasing Ag content. The increase in optical band gap with increasing silver concentration may be due to the decrease in the amount of disorder in the materials and decrease in the density of defect states. Spectral dependence of the absorption coefficient indicates an indirect allowed transition. The result is verified by the energetic parameter relation who shows that the parameter A increases with Ag concentration.

Table-(1) Values of<r>, N_{con} and L for the system $Ge_{0.15}Se_{0.85-x}Ag_x$

Composition	<r>	N_{con}	L
$Ge_{0.15}Se_{0.85}$	2.30	2.75	2.95
$Ge_{0.15}Se_{0.78}Ag_{0.07}$	2.44	3.10	2.25
$Ge_{0.15}Se_{0.76}Ag_{0.09}$	2.475	3.18	2.07
$Ge_{0.15}Se_{0.75}Ag_{0.10}$	2.50	3.25	1.95
$Ge_{0.15}Se_{0.70}Ag_{0.15}$	2.60	3.50	1.45
$Ge_{0.15}Se_{0.65}Ag_{0.20}$	2.70	3.75	0.95

Table-(2) Values ofHs, ΔE_g and A for the system $Ge_{0.15}Se_{0.85-x}Ag_x$

Composition	Hs(kj/mol)	Hs / <r> (eV/bond)	ΔE_g (eV)	A X 10^4/°K
$Ge_{0.15}Se_{0.85}$	248.99	1.1231	2576	1.2323
$Ge_{0.15}Se_{0.78}Ag_{0.07}$	253.022	1.0758	2.616	1.834
$Ge_{0.15}Se_{0.76}Ag_{0.09}$	254.174	1.0654	2.627	1.990
$Ge_{0.15}Se_{0.75}Ag_{0.10}$	254.750	1.0572	2.633	2.012
$Ge_{0.15}Se_{0.70}Ag_{0.15}$	257.630	1.0237	2.661	2.546
$Ge_{0.15}Se_{0.65}Ag_{0.20}$	260.510	0.9963	2.690	3.002

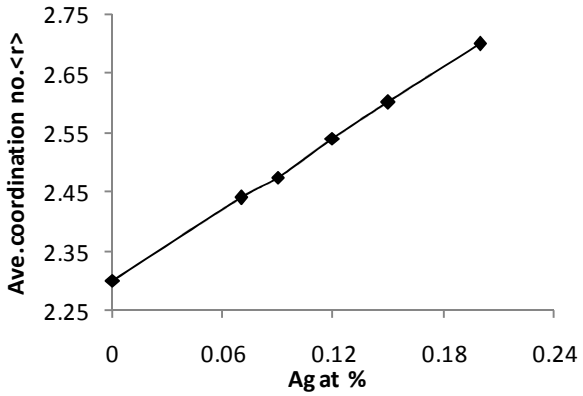

Fig.-(1), Variation of <r> with Ag at %

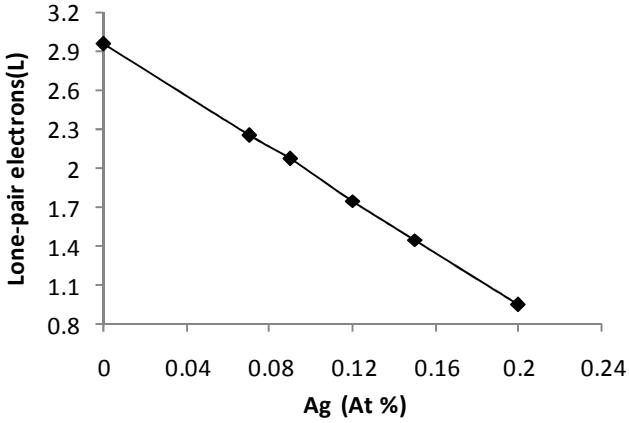

Fig.-2, Lone-pair electrons versus Ag content (At%)

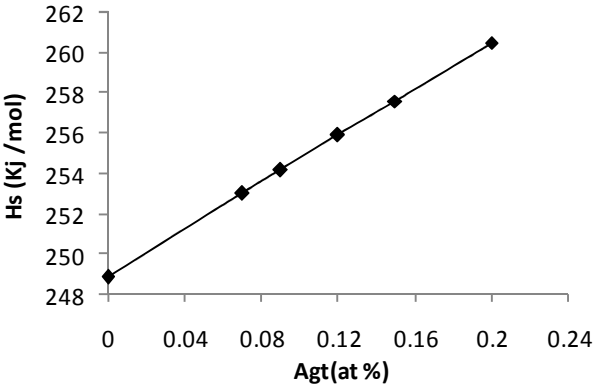

Fig.-3, Variation of Hs with Ag content (at%)

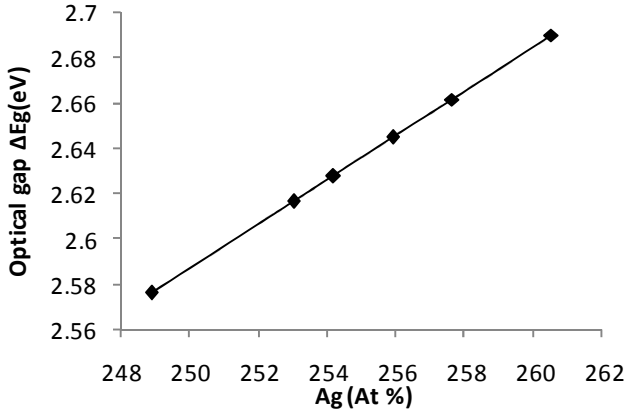

Fig.-4, Variation of ΔEg with Ag content (At%)

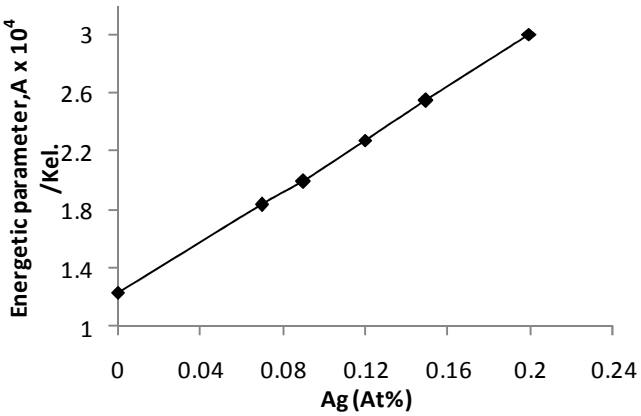

Fig.-5, Variation of A with Ag content (At%)

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