The Influence of Silver content on the Optical and Other Physical Properties of Ge-Se Glass System

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ABSTRACT

The effect of silver (Ag) content on the optical and other physical characteristics of $(Ge_{0.25}Se_{0.75})_{100-x}Ag_x$ (x = 0, 10, 15, 20, 25 at %) was investigated theoretically. The relation between the optical gap (E_g) and chemical composition has been discussed in terms of the average heat of atomization (Hs) and average coordination number (Z). In order to correlate the optical parameter (E_g) with film composition we used the energetic parameter (A). It was found that the magnitude of (E_g) and Hs increases with increasing silver content. Using the chemical bond approach of Tichy and Ticha the mean bond energy <E> has been calculated and it was found to be proportional to the glass transition temperature T_g and Z of the system.

Key words: Chalcogenide glasses, Optical gap, Energetic parameter.
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INTRODUCTION

Amorphous materials of Ge-Se-Ag system are well known to exhibit super ionic conducting behavior because the super ionic conducting glass is the important material as solid state electrolytes. Since this system has a wide compositional range where amorphous state can be easily obtained by quenching through water or even air [1].The interest in the optical properties of amorphous semiconductors and glasses has been stimulated also by their use as passivating materials for integrated circuits [2]. A great no. of amorphous chalcogen and chalcogenide materials are successfully applied or are of the potential interest for optical storage media[3-5], IR optical windows, sensors[6-8], non-linear optical elements [9] etc.

The role of various metals such as Ag, Cu, Bi etc. as additives in affecting the properties of chalcogenide glasses have been received much attention [10,11]. In this communication we report the compositional effect of Ag on the optical and physical properties of Ge-Se-Ag system.

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Ag is chosen as an additive material because it alloys with most of the metals and modified their physical properties [12].

2. Discussion of various theoretical parameters

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

2.1 Coordination Number and Constraints

For the given system of Ge-Se-Ag average coordination number $<r>$ is calculated using the expression,

$$<r> = Z_A X_A + Z_B X_B + Z_C X_C \tag{1}$$

where $Z_A = 4$, $Z_B = 2$, $Z_C = 4$, are the coordination numbers for Ge, Se, and Ag, respectively[13]. Fig.-(1) shows the variation of average coordination no.$<r>$ with composition of Ag and the value of $<r>$ is listed in table –(1)

2.2 Role of lone pair electrons

In order to calculate the no. of role-pair electrons of a chalcogenide system, the average coordination no. proposed by Phillips [14] was introduced. The lone-pair electrons of the given glass system was obtained according to equation (2) and is listed in table-(1). It is seen from the above table and from the fig.-(2) that the no. of lone-pair electrons decreases continuously with the increase in Ag content.

We can conclude from the results above, 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 $L > 2.6$ and, for a ternary system it must be >1 [15].

2.3 Heat of Atomization and Optical gap

Heat of atomization $H_S(A\text{-}B)$ at standard temperature and pressure of a binary semiconductor formed from atoms A and B, as proposed by Pauling [16], 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.

$$Hs(A\text{-}B) = \Delta H + (Hs^A + Hs^B)/2 \tag{2}$$

The first term in equation (4) is proportional to the square of the electro negativity difference of two atoms involved i.e.

$$\Delta H \; \alpha \; (X^A - X^B)^2 \tag{3}$$

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

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$$H_S = (\alpha H_S{}^A + \beta H_S{}^B + \gamma H_S{}^C) / (\alpha + \beta + \gamma) \qquad (4)$$

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 Ag (the H_S values in units of kj / mol are 377 for Ge, 226.4 for Se and 284 for Ag) are listed in table-(2) As seen forom table –(2) the value of Hs firstly decrease and then increases with the addition of Ag.

It is therefore interesting to relate the optical gap ΔE_g with the chemical bond energy, and rthe parameters we used to specify the bonding are Hs and <r>. The relationship between the energy gap and average heat of atomization was discussed by Aigrain and Balkanski [17]. According to their study a linear correlation exists for semiconductors of the diamond and zinc blendes structure.

$$\Delta E_g = a(Hs - b) \qquad (5)$$

Where a and b are characteristic constants. The value of ΔE_g for $(Ge_{0.25}Se_{0.75})_{100-x}Ag_x$ with x = 0, 10, 15, 20, 25 are listed in table –(2). It can be seen that the addition of Ag leads to the increasing Hs as well as ΔE_g. It is suggested by the above equation that the average heats of atomization are a measure of the cohesive energy and represent the relative bond strength, that in turn are correlated with properties like energy gap[18].Fig.-(3) and (4) represents the dependence of Hs and ΔE_g on the composition. All these parameters are gradually increasing with x.

2.4 The Energetic Parameter(A)
In order to correlate the optical parameter (ΔEg) with the film composition we used the energetic parameter(A) introduced by Angell [19,20].
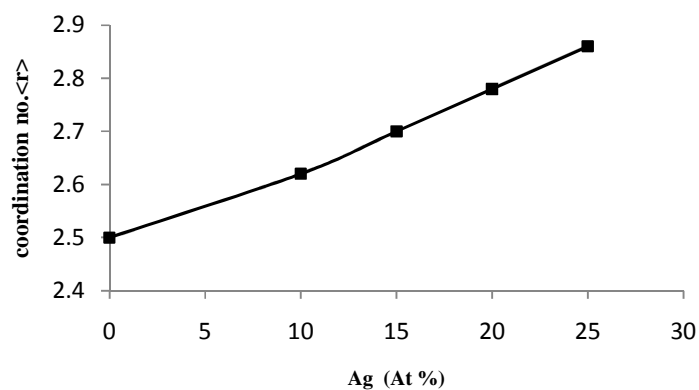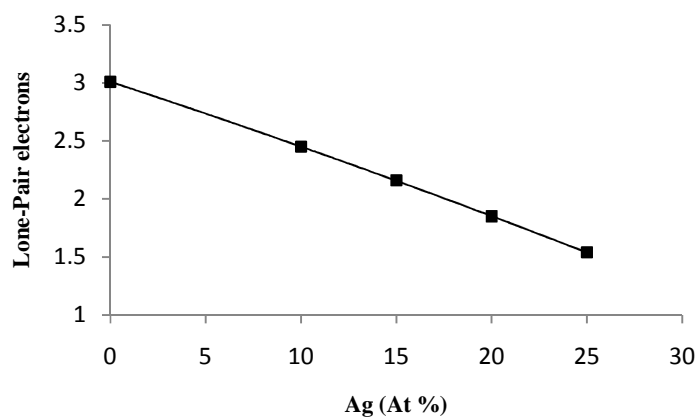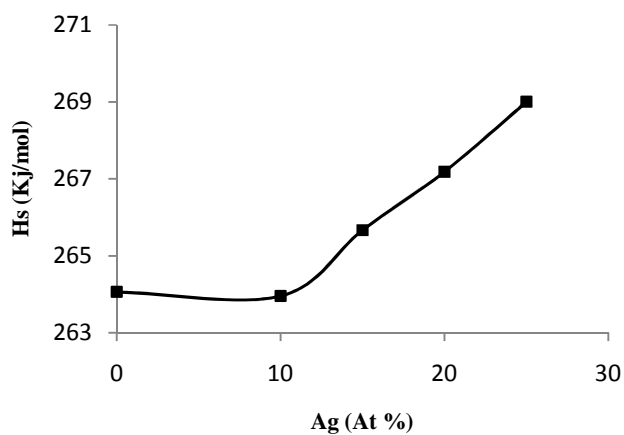
$$A = \text{\C}\Delta Eg/k \qquad (6)$$

Where $\text{\C} = \delta (Z-2)$ and K = Boltzmann constant, δ an independent constant(0.55). Fig(8) shows the variation of A with % of composition. The value of A is listed in table-(2).Fig. - (5) Represent the dependence of A on the composition.

Table-(1) Values of <r> and L for the system $(Ge_{0.25}Se_{0.75})_{100-x}Ag_x$

Composition(x)	<r>	L
X = 0	2.5	3.01
X = 10	2.62	2.45
X = 15	2.7	2.16
X = 20	2.78	1.85
X = 25	2.86	1.54

Table-(2) Values of Hs , ΔEg and A for the system $(Ge_{0.25}Se_{0.75})_{100-x}Ag_x$

Composition(x)	Hs(kj/mol)	ΔEg(eV)	$A \times 10^4$(/kel)
X = 0	264.06	2.73	1.416
X = 10	263.956	2.726	1.598
X = 15	265.666	2.737	1.664
X = 20	267.183	2.747	1.707
X = 25	269	2.757	1.717

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Fig. 1. Coordination no.<r> versus Ag content (at %)

Fig. 2. Lone-pair electrons (L) versus Ag content (at %)
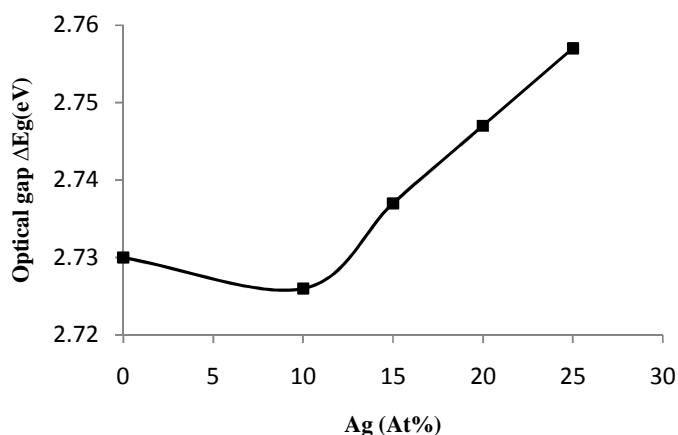

Fig. 3. Variation of Hs(Kj/mol) with Ag content (at %)

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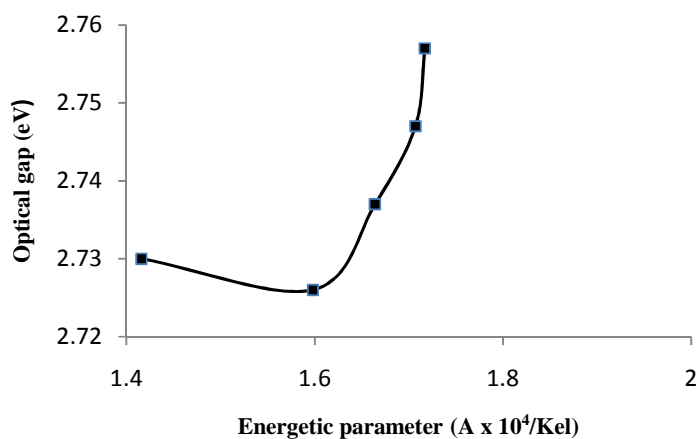**Fig. 4. Variation of Optical gap ΔEg with Ag content (at %)**

Fig. 5. Variation of Energetic parameter (A) with Optical gap ΔEg

CONCLUSION

It is seen that the average coordination no., Optical gap, average heat of atomization and the energetic parameter increases with increasing the silver(Ag) content whereas lone-pair of electrons decrease with increasinf Ag content. According to optical gap with composition approach of B.Angell the energetic parameter is proportional to the optical gap and increases with increasing Ag content.

REFERENCES

[1] M.Mitkova, Wang Yu,P.Boolchand, *Phys.Rev.Lett.* **1999,** 83, 3848
[2] T.Kawaguchi, S.Maruno. *J.Appl.Phys.* **1995**, 77, 628.
[3] S.R.Ovshinsky,*J.Non-Cryst.Solids*, **1992**, 141,200.
[4] A.Zakery, S.R.Elliott, *J.Non-Cryst.Solids*, **2003**1, 330.
[5]T.Wanger, M.Frumar, S.O.Kasap, *J.Optoele. and Adv.Mat.* **2001,** 3, 227.
[6] M.Sola, H.Roststerin, J.Bazan, *J.Solid State electro chem.* **2002**, 6, 279.

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[7] K.Wakamura, *Solid State Ionics*, **2002**, 73, 149.

[8] X-Zhang, H.Ma, J.Lucas, *J.Optoele. and Adv.Mat*. **2003**, 5, 327.

[9] B.Owens, *J. of Power sources*, **2000**, 2, 90.

[10] N.Mehta, D.Sharma, A.Kumar, *Physica B***, 2007,** 39, 108.

[11] R.S.Kundu, K.L.Bhatia, Nawal Kishor, *Physica B,* **1996**,74, 317.

[12] M.T.Dessouky, A.M.Abousehly, *Phil.Mag*. **2008**, 88, 1099.

[13] B.H.Sharmila, J.T.Devraju, S.Ahokan, *J.Non-Cryst.Solids*,**2002**, 303, 372.

[14] J.C.Phillips, *J.Non-Cryst.Solids*, **1997**, 34, 153.

[15] Liang Zhenhua, *J.Non-Cryst.Solids*, **1991**, 127, 298.

[16] L.Pauling, J.Phys. Chem. **1954**, 58, 662.

[17] C.Beniot, P.Aigrainand, M.BalKanski"*Selected constants Relative to Semiconducters*",
Pergamon Press, New York, **1961**.

[18] A.H.Ammar, A.M.Farid, S.S.Fouad, *Physica B*, **2001**, 307,pp- 64-71.

[19] Saurabh Tiwari,Ashish Saxena,Dinesh Saxena, *Internation J. of Phys. And Appl*.**2010**, 2, 1,
pp. 23-29.

[20] B.Angell, J.Amer, *Ceramic Soiety*, **1968**, 51, 117.