Journal of Research in Chemistry

E-ISSN: 2709-9423
P-ISSN: 2709-9415
JRC 2024; 5(1): 40-44

www.chemistryjournal.net
Received: 12-12-2023
Accepted: 19-01-2024

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Chalcogen rich glassy alloys of $Se_{70}Ge_{30-x}In_x$ (x = 0, 5, 10, 15, 20)

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Abstract
$Se_{70}Ge_{30-x}In_x$ (x = 0, 5, 10, 15, 20) glassy alloys have been studied to determine physical parameters such as average co-ordination number, number of constraints, heat of atomization, density, molar volume etc. Band gap has been calculated and correlated with average single bond energy (Hs/m). It was observed that band gap and heat of atomization decreases with increase in Indium concentration. The value of R parameter was found to be greater than one which shows that material is strongly chalcogen rich and it decreases with increase in indium content. The glass transition temperature (Tg) and Electronegativity were calculated by Lankhorst and Pauling scale approach.

Keywords: Bandgap, Average co-ordination number, Electronegativity, Glass transition temperature

1. Introduction
On the basis of various physical properties, covalently bonded chalcogenide glasses have been classified into two main categories: Ge type, which includes tetrahedral coordinated substances, such as a-Ge, a-Si and III – IV compounds. Se type, which includes the chalcogen elements (Se, Te, S) and their multi-component alloys. The Ge-Se glasses have been widely studied due to their wide composition range [1-3].
Ge-Se based glasses usually increase the chemical durability and broaden the IR region. The addition of third element in tetrahedral structure of Ge-Se glasses makes interesting materials because of new attractive and promising properties [4-8]. Chemical ordering in glassy Se-Ge-In alloys has been studied by Rabinal *et al.* [9]. Saiter *et al.* [10] determined the coordination number of indium in $Se_{1-x-y}Ge_xIn_y$ glasses. Thermoelectric power in glassy $Se_{80-x}Ge_{20}In_x$ alloys was studied by Khan *et al.* [11]. In the present work the $Se_{70}Ge_{30-x}In_x$ (x = 0, 5, 10, 15, 20) alloys were studied.

2. Experimental details
Glassy alloys of $Se_{70}Ge_{30-x}In_x$ (x=0, 5, 10, 15, 20) were prepared by well-known quenching technique. The exact proportions of (99.999%) of purity of Se, Ge and in elements, in accordance with their atomic %, were weighed using an electronic balance (LIBROR, AEG-120) with least count of 10^{-4} gm. The mixture of Se, Ge, In, were sealed in quartz ampoule at base pressure of 10^{-5} Torr then ampoule were heated in a furnace for about 10 - 12 hours. During heating ampoules were frequently shaken by rotating the ampoules to ensure the homogeneity of the melt. Quenching was done in ice cooled water. Material was taken out from ampoules and grinded to fine powder in mortar and pestle. Flow chart of material preparation by quenching technique is given below.

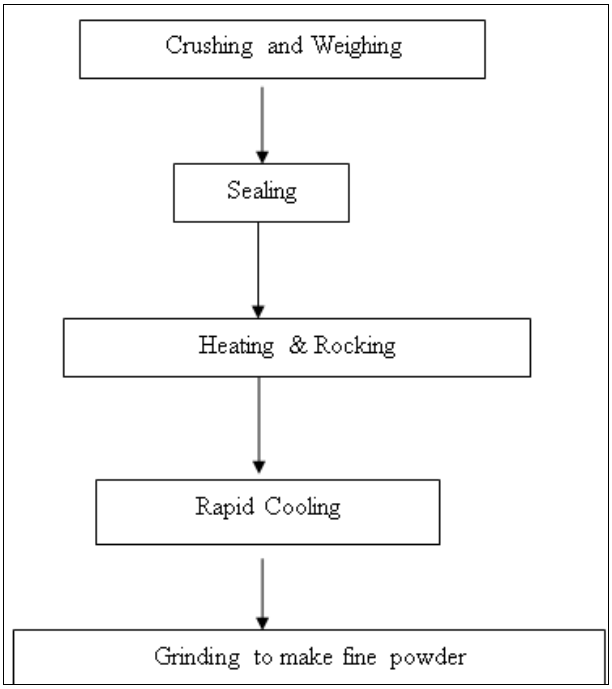

Chart 1: Flow chart of material preparation by quenching technique

3. Results and discussion

3.1 Average Coordination Number and Constraints

For the glassy system $Se_{70}Ge_{30-x}In_x$ (x = 0, 5, 10, 15, 20) average co-ordination number can be calculated by the following relation [12] which signifies the cross linking in a covalent bonded glassy system.

$$m = \frac{\alpha N(Se) + \beta N(Ge) + \gamma N(In)}{\alpha + \beta + \gamma}$$

where α, β, γ are the atomic percentages and N(Se), N(Ge), N(In) are the co-ordination numbers of Se, Ge, In which is 2, 4 and 3, respectively. The total number of constraints, are given as

$N_t = N_{bs} + N_{bb}$

Where N_{bs} is the number of bond stretching constraints and N_{bb} is the number of bond bending constraints. The values of N_{bs}, N_{bb} can be determined as

$N_{bs} = \frac{m}{2}$ and $N_{bb} = 2m - 3$

The effective average co-ordination number can be calculated by using the formula [13].

$$m_{eff} = \frac{2(N_t + 3)}{5}$$

Thorpe estimated the number of constraints by using the Maxwell counting [14], since there are m bonds, each of them is shared with two atoms. In each atom there are 2m-3 bond bending constraints that come from angular forces. Floppy modes with respect to degree of freedom is

$$f = 2 - \frac{5m}{6}$$

The value of *f* becomes zero when value of average co-ordination number (m) approaches the critical value of 2.4.

1. When m < 2.4 then network is polymeric glass in which rigid regions are isolated.
2. As m increases, the network goes through the transition at $m = m_c = 2.4$, at this the rigidity percolates and the glass transform to rigid structure. The m_c value is called rigidity percolation or mechanical threshold.
3. Network with m > 2.4 are amorphous solids.
4. The calculated values of average co-ordination number m, N_t, N_{bs}, N_{bb} are given in Table-1. It was inferred that average co-ordinate number decreases as Indium content increases. A graph of average co-ordination number (m) versus Indium % in case of $Se_{70}Ge_{30-x}In_x$ glassy alloy was plotted (Fig.1)

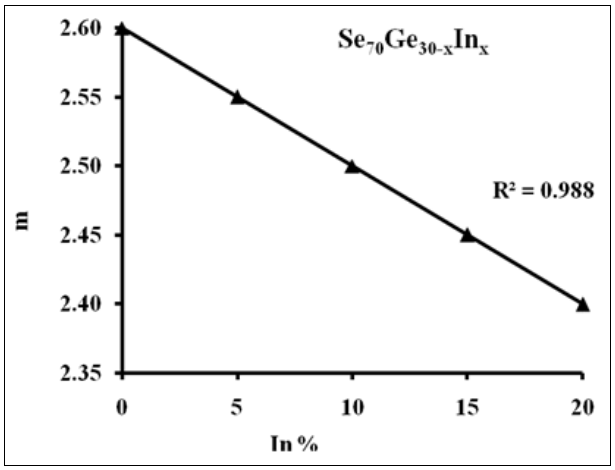

Fig 1: A plot of average co-ordination number (m) versus % of Indium in case of $Se_{70}Ge_{30-x}In_x$ glassy alloy

3.2 Deviation from stoichiometry of composition

Parameter R indicates the deviation of the glassy system from stoichiometry and is expressed as the ratio of covalent bonding possibilities of chalcogen atom to the non-chalcogen atoms [15]. For $Se_{70}Ge_{30-x}In_x$ glassy alloys parameter R is given as

$$R = \frac{\alpha N(Se) + \beta N(Ge)}{\gamma N(In)}$$

Where α, β, γ are the atomic percentages of Se, Te and In, respectively.

R = 1 indicates heteropolar bonds, R > 1 signifies that the system is chalcogen rich while R < 1 indicates chalcogen poor material. The values of R listed in Table-1 indicated that material is chalcogen rich.

3.3 Average heat of atomization and band gap

According to Pauling [16], the heat of atomization Hs (A-B) of a binary semiconductor formed from atom A and B at certain temperature and presence is a sum of heats of formation ΔH and average of heats of atomization Hs (A) and Hs (B) that correspond to the average non-polar energies of the two atoms, is given by the relation [17].

$$H_s = \Delta H + \frac{H_s(A) + H_s(B)}{2}$$

Where ΔH in the above relation is proportional to the square of the difference between the electro negativities of two atoms involved,

$$\Delta H \ \alpha \ (\chi_A - \chi_B)^2$$

in case of ternary and higher order semiconductor materials, the average heat of atomization H_s is defined as

$$H_s = \frac{\alpha H_s(Se) + \beta H_s(Ge) + \gamma H_s(In)}{\alpha + \beta + \gamma}$$

Where, H_s (Se), H_s (Ge), H_s (In) are the heat of atomization of Se, Ge and In, respectively.

Fig.2-3 shows plots of average heat of atomization Hs and average single bond energy (Hs/m) versus % of Indium. Fig. 4 shows variation of average single bond energy with average coordination number.

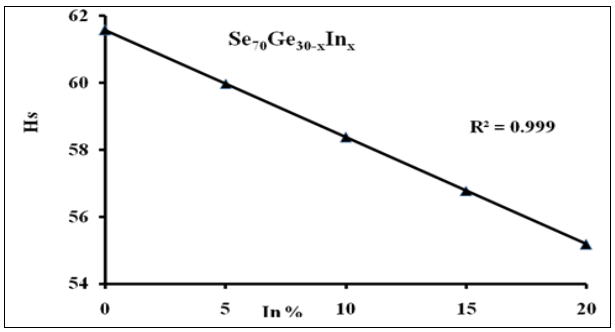

Fig 2: Plot of average heat of atomization Hs versus % of Indium in case of $Se_{70}Ge_{30-x}In_x$ glassy alloy.

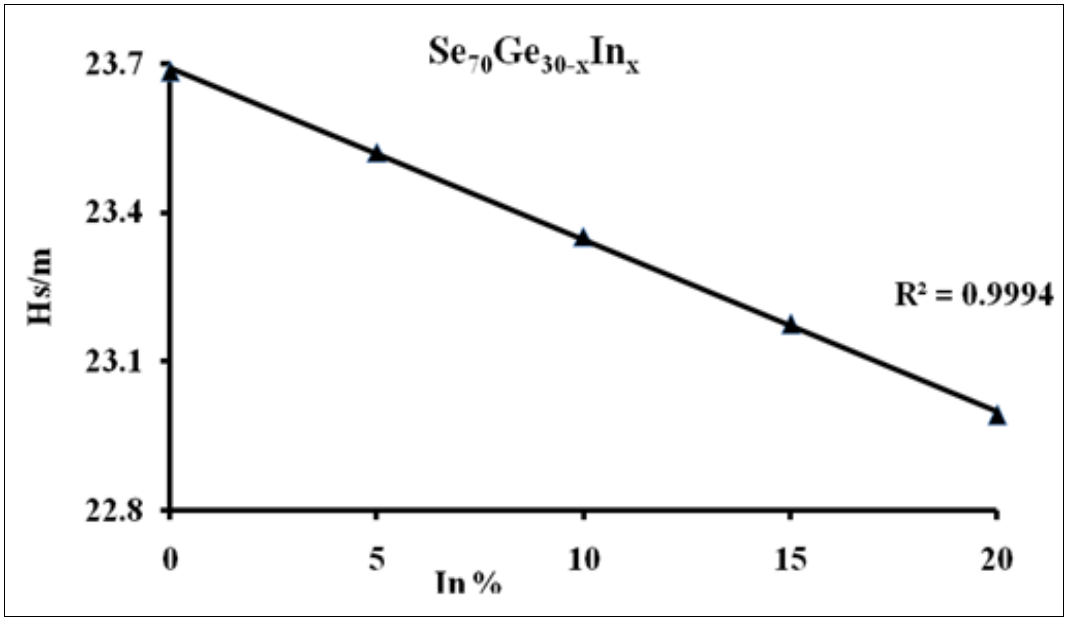

Fig 3: Plot of average single bond energy (Hs/m) versus % of Indium in case of $Se_{70}Ge_{30-x}In_x$ glassy alloy.

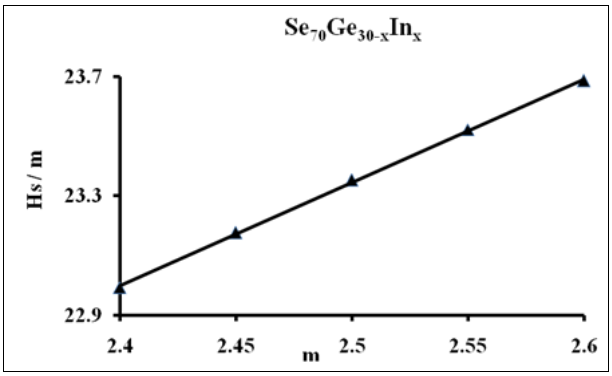

Fig 4: Plot of average single bond energy Hs/m versus average co-ordination number (m) in case of $Se_{70}Ge_{30-x}In_x$ glassy alloy.

The band gap values may be correlated to the bond strength of the system. Average single bond energy (Hs/m) specifies the bond strength. Band gap values have been calculated using Shimakawa's relation [18].

$$E_g(Se_\alpha - Ge_\beta - In_\gamma) = \alpha E_g(Se) + \beta E_g(Ge) + \gamma E_g(In)$$

Where α, β, γ are the volume fractions and Eg(Se), Eg(Ge) and Eg(In) are the energy gaps of Se, Ge and In, respectively. The variation of band gap (Eg) with Indium % is shown in Fig. 5 and the values of E_g are given in Table-2.

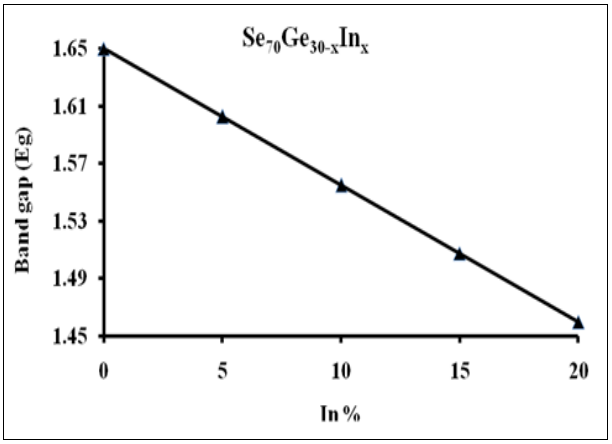

Fig 5: Plot of composition dependence of band gap in $Se_{70}Ge_{30-x}In_x$ alloys.

3.4 Density, Molar Volume, Molecular weight, packing density

The density (ρ) for $Se_{70}Ge_{30-x}In_x$ glass system was calculated using the relation [19].

$$\rho = (\sum_i \frac{m_i}{d_i})^{-1}$$

Where m_i is the fraction of mass and d_i is the density of i^{th} structural unit. As the structural modifications take place, higher density Indium atoms replace low density atoms. Thus, the density of the system increases for each composition with increase in % of In (Table 2).

The molar volume of the glassy system has been calculated as,

$$V_m = \frac{\sum X_i M_i}{\rho}$$

Where X_i is the atomic fraction of i^{th} element and M_i is the molecular weight of the i^{th} component in the sample. The values of molar volume V_m are given in Table 2. From table it was inferred that molar volume V_m decreases with Indium content. The variation of density and molar volume versus average co-ordination number is shown in Fig.6-7. These figures clearly indicate that density is inversely proportional to volume.

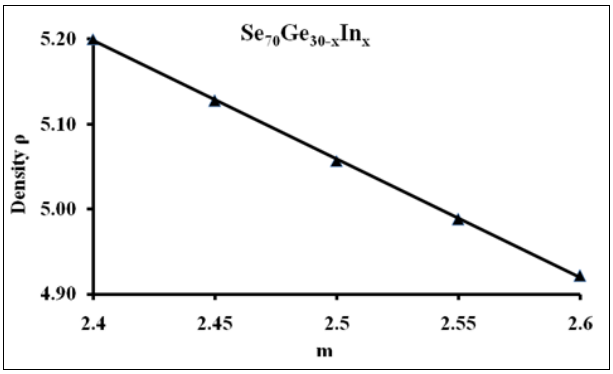

Fig 6: A plot of density versus average co-ordination number in case of $Se_{70}Ge_{30-x}In_x$ glassy alloy

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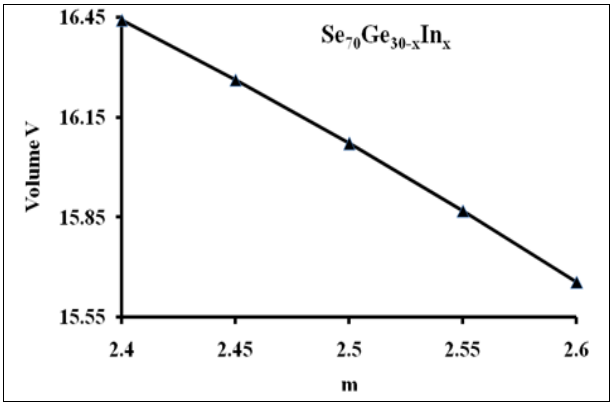

Fig 7: A plot of Volume versus average co-ordination number in case of $Se_{70}Ge_{30-x}In_x$ glassy alloy

The packing density of the system depends upon the mass and atomic radius of then constituting elements and can be calculated using,

$$paking density = \frac{N \times \rho}{M}$$

Where *N* is Avogadro's number, *ρ* is density of the system as calculated above and *M is* the molecular weight. The calculated values in case of $Se_{70}Ge_{30-x}In_x$ given in Table-2, indicates that packing density increases with the addition of Indium.

3.5 Electro-Negativity

Electro negativity differences in alloys were first recognized and qualitatively described by Miedema *et al*. [20]. The difference in electro negativity and electronic density at the boundary of the atomic cell determines the heat of formation of metallic alloy systems. The electron density at the cell boundary is related to the compressibility of the pure metal. The work function of a metal is a measure for its electro negativity. Metals and metallic compounds have low electro negativity differences and low average electro-negativities.

Electro-negativity of composition is simply geometrical mean of all constituents of that particular composition. In the present composition electronegativity have been calculated using Pauling scale method. It has been observed that electronegativity decreases with increases in Indium percentage which is shown in Fig.8.

The numbers of lone pair electrons have been calculated by using the following relation [21].

$$L = V - \langle r \rangle$$

Where L and V are the lone pair electrons and valence electrons, respectively. The number of lone pair electrons obtained by using above equation shows that with the increase in the indium concentration, number of the lone pair electron decreases.

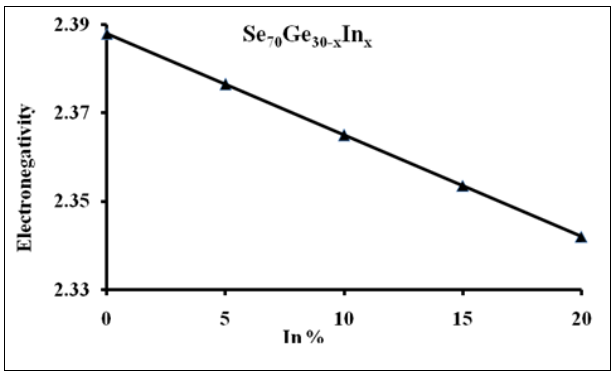

Fig 8: Shows plots of Electro-negativity versus Indium % in case of $Se_{70}Ge_{30-x}In_x$ glassy alloy

3.6 Glass Transition temperature

Lankhorst [22] has introduced a model to estimate the glass transition temperature based on enthalpy of atomization. This method is useful for development of phase change materials for rewritable optical recording. According to this model glass transition temperature is related to heat of atomization by an empirical relation given as

$$T_g = 3.44\ Hs - 480$$

Where T_g is in Kelvin and Hs is in KJ/mol. Heat of atomization or the enthalpy of atomization is the enthalpy

change that is required for total separation of all atoms in a chemical compound such that the compound bonds are broken and component atoms are reduced to individual atoms. The calculated values of glass transition temperature are given in table 2. It is evident from table that glass transition temperature T_g (K) decreases with indium at %.

Table 1: Values of average co-ordination number m, Constrants and parameter R

Sample	Average Co-ordination number (m)	Degree of freedom *(f)*	N_{bs}	N_{bb}	N_t	R
$Se_{70}Ge_{30}$	2.60	0.16	1.30	2.20	3.50	1.55
$Se_{70}Ge_{25}In_5$	2.55	0.10	1.26	2.06	3.32	1.47
$Se_{70}Ge_{20}In_{10}$	2.50	0.08	1.25	2.00	3.25	1.40
$Se_{70}Ge_{15}In_{15}$	2.45	0.04	1.22	1.90	3.12	1.33
$Se_{70}Ge_{10}In_{20}$	2.40	0.0	1.20	1.80	3.00	1.27

Table 2: Calculated values of physical parameters in $Se_{70}Ge_{30-x}In_x$ (x=0, 5, 10, 15, 20) glassy alloy.

Sample	Density ρ(g/cm^3)	Volume (cm^3/mole)	Molecular weight M (g mole)	Packing density (atom/cm^3)	Band gap(eV)	Heat of atomization (kcal/g atom)	Hs/m	T_g (k)
$Se_{70}Ge_{30}$	4.92	15.66	77.05	3.85×10^{22}	1.65	61.58	23.68	405.47
$Se_{70}Ge_{25}In_5$	4.99	15.87	74.01	4.06×10^{22}	1.60	59.98	23.52	382.46
$Se_{70}Ge_{20}In_{10}$	5.06	16.07	70.97	4.30×10^{22}	1.55	58.38	23.35	359.45
$Se_{70}Ge_{15}In_{15}$	5.13	16.26	67.93	4.55×10^{22}	1.50	56.78	23.18	336.45
$Se_{70}Ge_{10}In20$	5.20	16.44	64.90	4.83×10^{22}	1.46	55.18	22.99	313.44

4. Conclusion

The addition of Indium to $Se_{70}Ge_{30}$ glassy alloy leads to change in the physical properties. The average coordination number decreases with increase in Indium concentration which indicates that the number of constraints decreases hence the value of optical band gap will strongly depends upon Hs. It was found that the value of average heat of atomization (Hs) as well as average single bond energy (Hs/m) decreases with the addition of In**.** The value of band gap (Eg), has also been calculated and was found decrease with increase in % of Indium. In the present composition electro-negativity also decreases with indium.

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