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## Effect of compositional dependence on Physical Properties of $\text{Ge}_{22}\text{Se}_{78-x}\text{In}_x$ Glass System

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### ABSTRACT

*In the present work, the effect on the physical properties viz. average coordination number, number of constraints, cross-linking density, molecular weight, fraction of floppy modes, mean bond energy, glass transition temperature etc., with the variation in Indium content has been studied theoretically for  $\text{Ge}_{22}\text{Se}_{78-x}\text{In}_x$  ( $x=3,6,9,12,15,18,21$ at.%) glassy alloys. The glass transition temperature and mean bond energy are calculated by using the Tichy-Ticha approach. It has been found that almost all the parameters, studied here, except mean bond energy  $\langle E \rangle$  and glass transition temperature  $T_g$ , were increased with the increase in In content.*

**Keywords:** Chalcogenide Glasses, Average Coordination Number; Glass Transition; mean bond energy.

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### INTRODUCTION

Chalcogenide glasses are very interesting materials for reversible phase change optical recording devices [1-4]. Since reversible switching phenomenon in certain types of chalcogenide glasses was first reported [5], a lot of attention has been given to characterization and improvement of the properties of chalcogenide glasses in general and the materials exhibiting the switching phenomenon in particular. The phase change can be reversibly switched between the amorphous and crystalline state and find applications in rewritable optical recording [6-8].

The investigation of composition dependence of various properties of chalcogenide glasses has been increased in recent years. As selenium exhibits the unique property of reversible phase transformation and also applications like photocells, xerography, memory switching etc., it seems attractive, but pure selenium has disadvantage like short life time and low photo sensitivity. To overcome this problem, some impurity atoms like Ge, In, Bi, Te, Sb, Ag, etc. can be used to make alloys with Se, which may enhance sensitivity, crystallization temperature and reduce ageing effects [9].

The compositional dependence studies on glassy alloys were reported for Ge-Se, Ge-Se-Pb, Ge-Se-Ga, Ge-Se-As, Ge-Se-Ag, Ge-Se-Te, Ge-Se-Sb, Ge-Se-Bi [10-17]. Ge atoms act as bond modifiers thus they strengthen the average bond by cross-linking the Se chain structure, thereby enhancing the properties like glass transition temperature and resistivity [18]. Ge-Se system is a widely studied system and glass formation in this system occurs predominantly in alloys enriched with Se and containing 0-25 at % of Ge. Several researchers have studied the effect of In on the optical and electrical properties of chalcogenide materials. Addition of third element like In to Ge-Se expands the

glass forming region and also creates compositional and configurational disorder in the system as well as induce large effect on their structural, physical, optical, electronic and thermal properties [19-21].

In the present work, we have incorporated Indium in the Ge-Se alloy for the compositions belonging to  $\text{Ge}_{22}\text{Se}_{78-x}\text{In}_x$  ( $x=3, 6, 9, 12, 15, 18, 21$  at. %). The addition of third element used to create compositional and configurational disorder in the material with respect to the binary alloys [11]. It has been established that physical properties in this system are highly composition dependent [22, 23]. The Ge-Se-In glass system is of special interest as it forms glasses over a wide domain of compositions. The glass formation region in the ternary Ge-Se-In system extends to about 20 at % In and about 60-90 at % Se, with rest being Ge [24]. Therefore we find it a suitable system for investigation of the variation of certain physical properties. The variation of properties has been discussed on the basis of their compositions. The present paper is concerned with the theoretical prediction of the physical parameters related to composition, viz. coordination number, constraints, cross-linking density, fraction of floppy modes, molecular weight, mean bond energy and the glass transition temperature for  $\text{Ge}_{22}\text{Se}_{78-x}\text{In}_x$  alloys.

## THEORETICAL STUDIES AND DISCUSSION

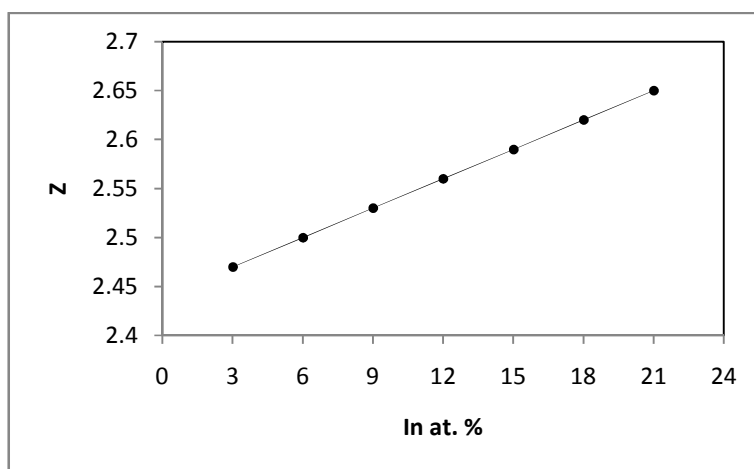
### Bonding Constraints & Average Coordination Number

It may be valuable to consider the transitions between  $z = 2.4$  and  $2.67$  in the light of the constraint – counting argument originally proposed by J. C. Phillips for amorphous covalent materials [25]. Phillips gave the mechanical-constraint counting algorithms to explain glass forming tendencies. The strongest covalent forces between nearest neighbours serve as Lagrangian (mechanical) constraints defining the elements of local structure (building blocks). Constraints associated with the weaker forces of more distant neighbours must be intrinsically broken leading to the absence of long-range order. The well known Phillips–Thorpe approach is based on comparing the number of atomic degrees of freedom with the number of inter-atomic force field constraints. If the number of degrees of freedom is greater than the number of constraints, the network is “floppy”; conversely, if the network becomes over-constrained, stressed-rigid structures will percolate throughout the entire network. According to Phillips, the tendency of glass formation would be maximum when the number of degrees of freedom exactly equals the number of constraints.

The average coordination number ( $Z$ ) was calculated using standard method [26] for the composition  $\text{Ge}_{22}\text{Se}_{78-x}\text{In}_x$ ,  $Z$  is given by

$$Z = \frac{xN_{\text{Ge}} + yN_{\text{Se}} + zN_{\text{In}}}{x + y + z}$$

where  $x$ ,  $y$  and  $z$  are the at. % of Ge, Se and In respectively and  $N_{\text{Ge}}(4)$ ,  $N_{\text{Se}}(2)$ ,  $N_{\text{In}}(3)$  are their respective coordination number [27, 28]. The calculated values of average coordination number for  $\text{Ge}_{22}\text{Se}_{78-x}\text{In}_x$  ( $x=3, 6, 9, 12, 15, 18, 21$  at. %) system are listed in table 1. It is clear from fig 1 that values of  $Z$  increase from 2.47 to 2.65 with increase in concentration of In from 3 to 21.



**Fig. 1: Variation of Average Coordination Number with Indium at. %**

The glassy network are influenced by mechanical constraints ( $N_c$ ) associated with the atomic bonding and an average coordination number  $Z$  which is also related to  $N_c$ . There are two types of near-neighbor bonding forces in covalent solids; bond-stretching ( $\alpha$ - forces) and bond-bending ( $\beta$ - forces) [29].

The number of Lagrangian bond-stretching constraints per atom is

$$N_\alpha = Z/2$$

And, of bond-bending constraints is

$$N_\beta = 2Z - 3$$

For the case when all  $\alpha$  and  $\beta$  constraints are intact and no dangling ends exist in the network, equation implies that the optimum mean coordination number is 2.40 which is known as the rigidity percolation threshold. Highly over-coordinated or under-coordinated structures are not conducive to glass formation and, upon cooling, lead to crystalline solids. In 1983, M. F. Thorpe [30] pointed out that the number of floppy modes per atom,  $f$ , is rather accurately described by the mean-field constraint count according to the relation,

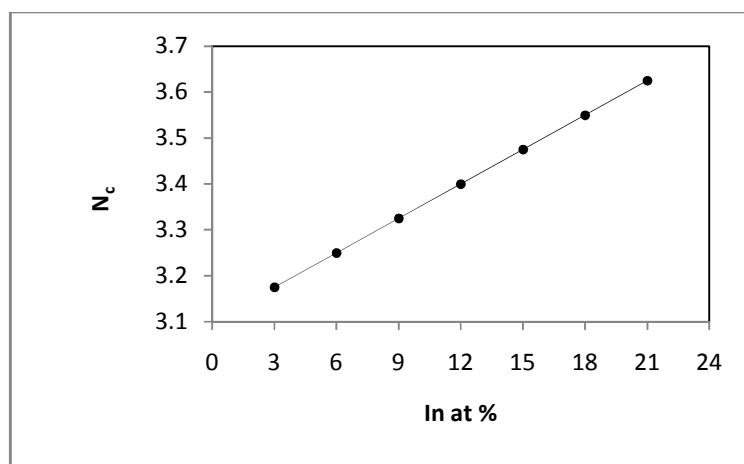
$$F = 3 - N_c \quad (2)$$

This led to the realization that a glass network will become spontaneously rigid when  $f \rightarrow 0$ , defining a *floppy to rigid phase transition* [31].

The total number of constraints is given by

$$N_c = N_\alpha + N_\beta$$

The values of  $N_c$  along with  $Z$  for  $\text{Ge}_{22}\text{Se}_{78-x}\text{In}_x$  are given in table 1. Fig. 2 depicts the variation of  $N_c$  with In at %. Here  $N_c$  increase from 3.175 to 3.625 with increase in In at.%, which shows in our composition that the number of constraints  $N_c$  acting on the network are balanced by the number of degrees of freedom  $N$  available from the atoms in the network. This means that network is isostatically rigid, no stress is present i.e.  $N_c = N_d$ .

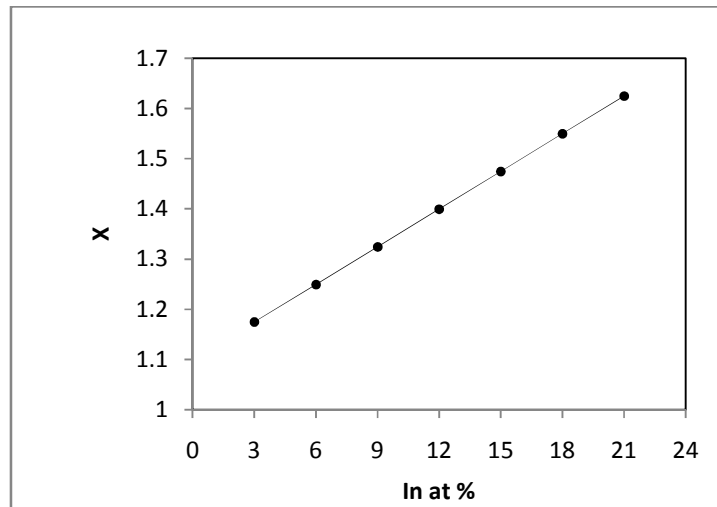


**Fig. 2: Variation of number of constraints with In at. %**

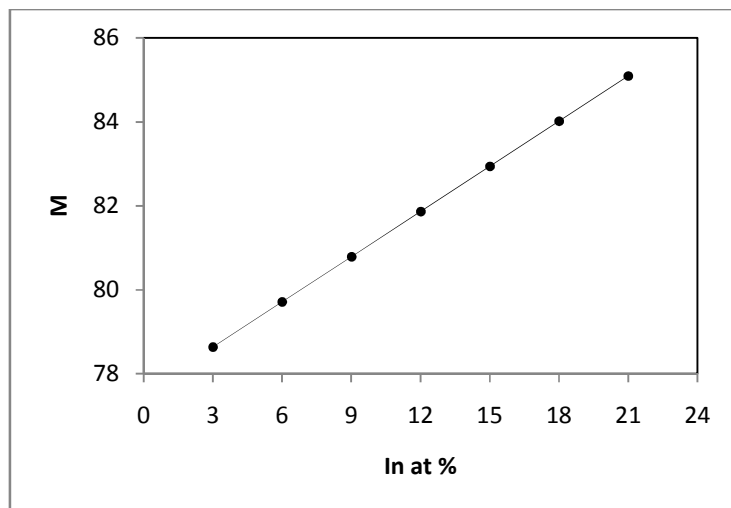
The cross-linking density( $X$ ) is equal to the average coordination number of cross linked chain less the coordination number of initial chain [32].

$$X = N_c - 2$$

The values of cross linking density ( $X$ ) and molecular weight ( $M$ ) are shown in table 1. From fig. 3 it is clear that the value  $X$  increase with increase in In content. Fig.4 shows the variation of  $M$  with In content.



**Fig. 3: Variation of cross-linking density with In content**



**Fig. 4: Variation of Molecular weight with In content**

According to Thorpe, the uncoordinated network having finite fraction of zero frequency normal vibrations modes termed as floppy modes in absence of weak long range forces. The fraction of floppy modes available in a network is given by

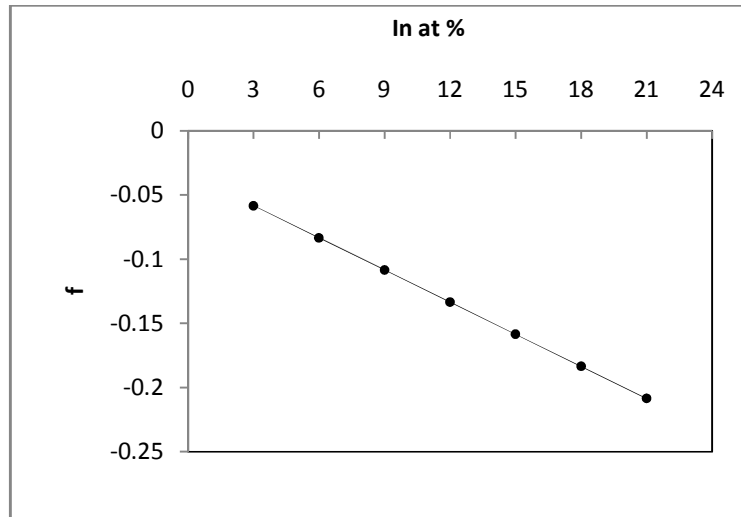
$$f = 2 - \frac{5Z}{6}$$

The values of  $f$  are listed in table 1. It has been observed from the table and fig. 5 that the value of  $f$  becomes more and more negative (-0.0583 to -0.2083) with increase in In content from 3 to 21 at. %. This shows that the system becomes more and more rigid, which corresponds to a strong tendency for making glass [33].

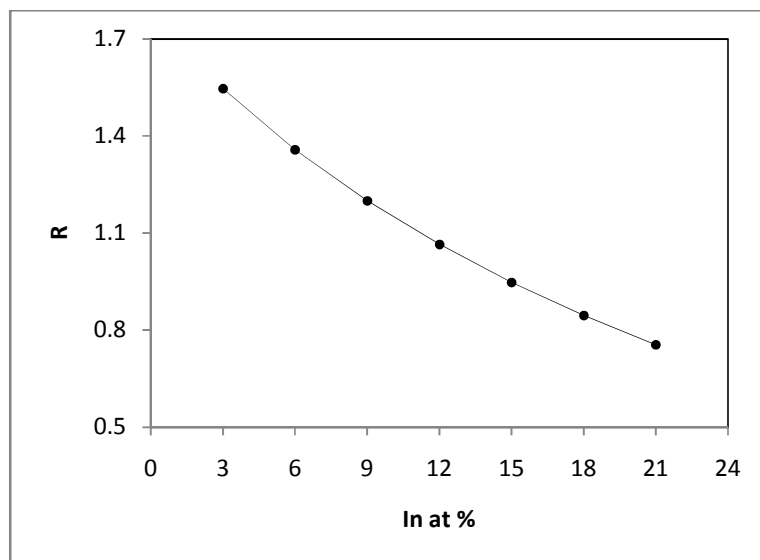
#### **Deviation from the stoichiometry of composition**

The parameter  $R$  that determines the deviation from stoichiometry is expressed by the ratio of content bond possibilities of chalcogen atoms to that of non-chalcogen atoms. For  $\text{Ge}_{22}\text{Se}_{78-x}\text{In}_x$  system, the parameter  $R$  is given by [34, 35]

$$R = \frac{yCN(Se)}{xCN(Ge) + yCN(Bi)}$$



**Fig. 5: Variation of fraction of floppy modes with In content**



**Fig. 6: Variation of parameter R with In content**

where x, y, z are atomic fractions of Ge, Se and In respectively. The values of R are mentioned in table 2. The threshold at R=1 (the point of existence of only heteropolar bonds) marks the minimum selenium content at which a chemically ordered network is possible without metal–metal bond formation. For R>1, the system is chalcogen rich and for R<1, the system is chalcogen poor. From fig. 6, it is clear that our system is more or less chalcogen rich and turning towards chalcogen poor with the increase in content of indium in the system. The major limitation of this approach is that it does not account for molecular interactions, which play a vital role in the relaxation process in the glass transition region.

**Mean Bond Energy And Glass Transition Temperature**

There are many properties of chalcogenide glasses which are related to overall mean bond energy  $\langle E \rangle$ . According to Tichy and Ticha [34, 35], the value of glass transition temperature should not only be related to connectedness of the network which is related to  $Z$ , but should also be related to the quality of connections, i.e., the mean bond energy between the atoms of the network. The overall mean bond energy for the  $\text{Ge}_{22}\text{Se}_{78-x}\text{In}_x$  system is given by

$$\langle E \rangle = E_c + E_{rm}$$

where  $E_c$  is overall contribution towards bond energy arising from strong heteropolar bonds and  $E_{rm}$  is contribution arising from weaker bonds that remains after the strong bonds have been maximized. For  $\text{Ge}_x\text{Se}_y\text{In}_z$  system, where  $(x + y + z) = 1$ , in selenium rich systems ( $R > 1$ ) where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E_c = 4xE_{\text{Ge-Se}} + 3zE_{\text{Se-In}}$$

and

$$E_{rm} = \left[ \frac{2y - 4x - 3z}{Z} \right] E_{\text{Se-Se}}$$

And in selenium poor region ( $R < 1$ )

$$E_c = \frac{2y(4xE_{\text{Ge-Se}} + 3zE_{\text{Se-In}})}{4x + 3z}$$

And

$$E_{rm} = \frac{4x + 3z - 2y}{Z} E_{\diamond}$$

where

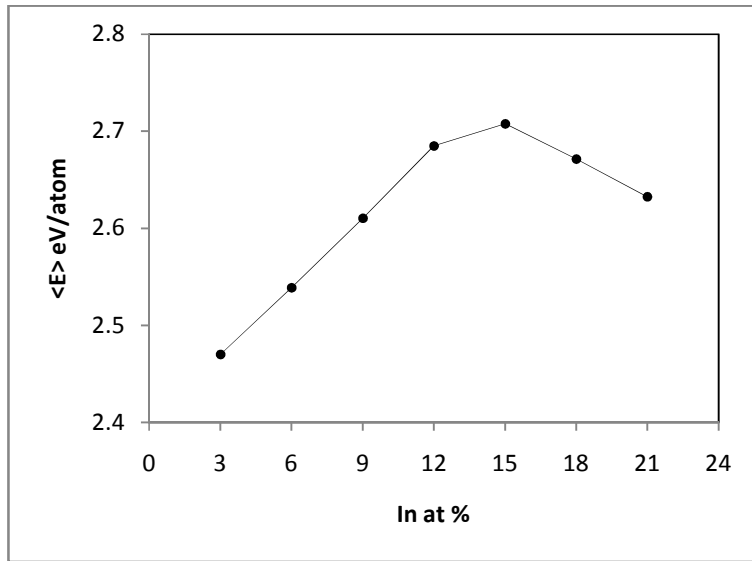
$$E_{\diamond} = \frac{1}{3[E_{\text{Ge-Ge}} + E_{\text{In-In}} + E_{\text{Se-Se}}]}$$

denotes the average homopolar bonding energy. The values of  $E_c$ ,  $E_{rm}$ , and  $\langle E \rangle$  are given in table 2. As it is clear from fig. 7 that  $\langle E \rangle$  increases with increase in concentration of In from 3 to 15 at. % and then decrease due to fall in value of  $R$  i.e. selenium poor region.

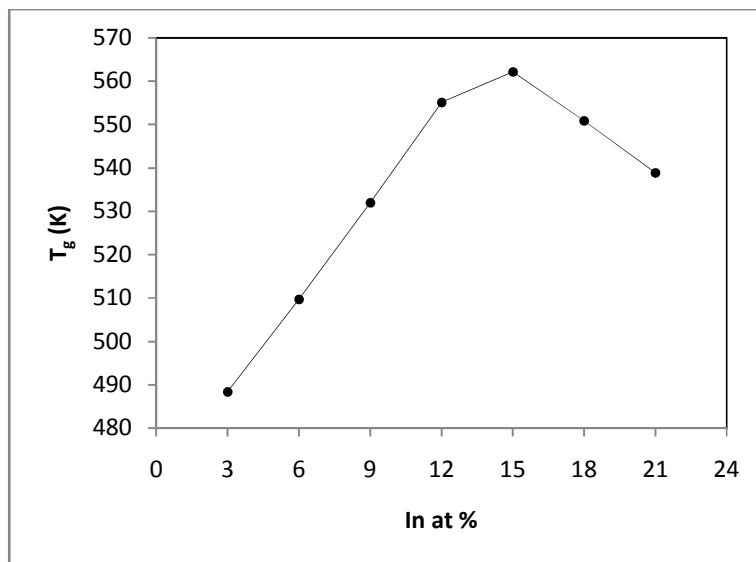
An impressive correlation of mean bond energy with glass transition temperature  $T_g$  was illustrated by Tichy and Ticha [34, 35] by the relation

$$T_g = 311[\langle E \rangle - 0.9]$$

The values of  $T_g$  corresponding to  $\langle E \rangle$  is mentioned in table 2 and the variation of  $T_g$  with In content is shown in fig. 8, which is clearly depicting the rise in glass transition temperature with increasing the content of In up to  $x = 15\%$  due to rise in mean bond energy of the glassy system and then there is a fall in the values of  $T_g$  due to fall in mean bond energy of the glassy system.



**Fig. 7: Variation of overall mean bond energy with In content**



**Fig. 8: Variation of glass transition temperature  $T_g$  with In content**

**Table 1**

Ge	Se	In	Z	$N_c$	X	f	M (g/mol)
22	75	3	2.47	3.175	1.175	-0.0583	78.6387
22	72	6	2.5	3.25	1.25	-0.0833	79.7145
22	69	9	2.53	3.325	1.325	-0.1083	80.7902
22	66	12	2.56	3.4	1.4	-0.1333	81.866
22	63	15	2.59	3.475	1.475	-0.1583	82.9417
22	60	18	2.62	3.55	1.55	-0.1833	84.0174
22	57	21	2.65	3.625	1.625	-0.2083	85.0932

Table 2

x Ge	y Se	z In	R	Ec eV/atom	Erm eV/atom	<E> eV/atom	Tg (K)
22	75	3	1.54639	2.061	0.409259	2.470297	488.3623
22	72	6	1.35849	2.2491	0.28991	2.538994	509.727
22	69	9	1.2	2.4371	0.173391	2.610521	531.972
22	66	12	1.06452	2.6252	0.059603	2.684779	555.0663
22	63	15	0.94737	2.6652	0.043516	2.708674	562.4976
22	60	18	0.84507	2.5363	0.135199	2.671482	550.9309
22	57	21	0.75497	2.4078	0.224806	2.632633	538.8488

## CONCLUSION

The addition of In to Ge-Se glassy alloys leads to change in the physical properties. As it is clear from various figures and tables given above that almost all the parameters, except mean bond energy <E> and glass transition temperature  $T_g$ , increase with the increase in content of In. It has been found that mean bond energy <E> is proportional to glass transition temperature and both increases with the increase in content of In up to  $x = 15\%$  and then decreases due to decrease in the mean bond energy of the glassy system.

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