Effect of Compositional Variations on Physical Properties of Ge-Se-In Glassy Semiconductors

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ABSTRACT

The effect on the physical properties viz. average coordination number, number of constraints, cross-linking density, lone-pair electrons, mean bond energy, glass transition temperature etc., with the variation in Indium content has been studied theoretically for Ge-Se-In glassy semiconductors. In the present work, we have taken three different compositions belonging to Ge-Se-In system viz: Ge20Se80-xInx, Ge22Se78-xInx, Ge24Se76-xInx (x = 3, 6, 9, 12, 15, 18, 21 at. %) and studied with theoretical prediction of the physical parameters related to these compositions. The present system is found to be in accordance with the earlier researches according to which system with large number of lone-pair electrons constitutes a stable state. Here, the glass transition temperature and mean bond energy are calculated by using the Tichy-Ticha approach.

Keywords: Chalcogenide glasses, Coordination number, Lone-pair electrons, Glass transition, Mean bond energy.

I. INTRODUCTION

In the present era of modern technology, chalcogenide glasses have attracted much interest due to their potential use in photoresist, microelectronic, optoelectronic applications and especially their ability to transmit light in the mid to far infrared region [1-5]. The physical properties of chalcogenides (high refractive index, low phonon energy, high non linearity) also make them ideal candidate for incorporation into lasers and other active devices. Some of the chalcogenide materials experience thermally driven amorphous to crystalline phase changes, hence enabling the encoding of binary information on thin films of chalcogenide glasses and forming the basis of rewritable optical and non-volatile memory devices. The phase change can be reversibly switched between amorphous and crystalline state and find applications in rewritable optical recording [6-8].

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 Ge-Se-In glassy semiconductors. 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 investigating the temperature requirement for a particular technological application [25]. Here in the present paper, we have taken three different compositions belonging to Ge-Se-In system viz: Ge$_{20}$Se$_{80-x}$In$_x$, Ge$_{22}$Se$_{78-x}$In$_x$, Ge$_{24}$Se$_{76-x}$In$_x$ (x = 3, 6, 9, 12, 15, 18, 21 at %) and studied with the theoretical prediction of the physical related to composition, viz. coordination number, constraints, cross-linking density, fraction of floppy modes, lone-pair electrons, mean bond energy and the glass transition temperature for Ge-Se-In system.

II. THEORETICAL STUDIES AND DISCUSSION

2.1 Bonding Constraints and Average Coordination Number

Initially Phillips proposed the idea of studying the properties of network glasses in terms of the average coordination number [26,27] and then it was well supported by Thorpe [28]. Phillips–Thorpe approach is based on comparing the number of atomic degrees of freedom with the number of inter-atomic force field constraints. On the basis of equating the total number of interatomic force-field constraints per atom, $N_c$, to the number of degrees of freedom per atom, $N_d$, a structural phase transition at $Z = 2.4$ was predicted [26-28]. At this $Z$ value, a percolation threshold exists at which the network changes from a floppy-type to a rigid-type and possesses mechanically optimized structures. Subsequently, Tanaka [29] predicted that medium range order has to be considered in the constraint balancing condition ($N_c = N_d$), since some network glasses such as Ge-As-Se possess a layered structure. Under these conditions, he predicted another structural phase transition at $Z = 2.67$. At this threshold, two-dimensional (2D) layer structures are fully evolved. For $Z > 2.67$, there is a structural transition to three-dimensional (3D) networks due to the increase in the number of cross-linked sites. These topological transitions have been observed in many glass systems.

The interpretation of the features observed in the property-composition dependence for chalcogenide glasses has focused on the chemically ordered covalent network (COCN) model. In this model, heteropolar bonds are favoured at all compositions, and the structure is assumed to be composed of 3-D cross-linked structural units of the stable chemical compounds of the system with excess, if any, of the elements dispersed among these units. As a result of the chemical ordering or the chemical thresholds of the system are observed in the compositional dependence of the properties of the chalcogenide glasses [30,31].

The average coordination number ($Z$) is calculated using standard method [32] for the three composition of Ge-Se-In system, $Z$ is given by

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

where $x$, $y$, and $z$ are the at. % of Ge, Se and In respectively and $N_{Ge}(4)$, $N_{Se}(2)$, $N_{In}(3)$ are their respective coordination number [33,34]. The calculated values of average coordination number for Ge$_{20}$Se$_{80-x}$In$_x$, Ge$_{22}$Se$_{78-x}$In$_x$, Ge$_{24}$Se$_{76-x}$In$_x$ (x = 3, 6, 9, 12, 15, 18, 21 at %) systems are listed in Table 1. It is clear from Figure 1 that values of Z increase with increase in concentration of In from 3 to 21 which as well as increase in Ge content from 20 to 24 in Ge-Se-In system.

![Figure 1: Variation of Average Coordination Number with Indium at. % (a- Ge$_{20}$Se$_{80-x}$In$_x$, b- Ge$_{22}$Se$_{78-x}$In$_x$, c- Ge$_{24}$Se$_{76-x}$In$_x$)](image)

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-neighbour bonding forces in covalent solids; bond-stretching ($\alpha$- forces) and bond-bending ($\beta$- forces) [26].

The number of Lagrangian bond-stretching constraints per atom is

$$N_\alpha = Z/2$$

And, of bond-bending constraints is

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

So the total number of constraints is given by

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

The values of $N_c$ along with $Z$ for all the three compositions of Ge-Se-In system are given in Table 1. Fig. 2 depicts the variation of $N_c$ with In at %. Here $N_c$ increases with increase in In at.% for all the three compositions, 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 $N_d$ available from the atoms in the network. This means that network is isostastically rigid, no stress is present i.e. $N_c = N_d$. 

![Image](image)
The cross-linking density \( X \) is equal to the average coordination number of cross linked chain less the coordination number of initial chain \[35\].

\[
X = N_c - 2
\]

The values of cross linking density \( X \) for all the three compositions are shown in Table 1. From Figure 3 it is clear that the value \( X \) increases with increase in In content as well as increase in Ge content from 20 to 24.

According to Thorpe [28], 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 \( f \) for Ge-Se-In system are listed in Table 1. It has been observed from the Table and Figure 4 that the value of \( f \) becomes more and more negative with increase in In content from 3 to 21 at. % as well as increase in Ge content from 20 to 24. This shows that the system becomes more and more rigid, which corresponds to a strong tendency for making glass \[36\].

### 2.2 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 Ge-Se-In system, the parameter \( R \) is given by \[37,38\]

\[
R = \frac{yCN(Se)}{xCN(Ge) + zCN(In)}
\]

where \( x, y, z \) are atomic frictions of Ge, Se and In respectively.
Other parameters, such as parameter R, also play an important role in the analysis of the results. Depending on R values, the chalcogenide systems can be organized into three different categories [39]:

(a) For R = 1, the system reaches the stoichiometric composition since only hetero-polar bonds are present.

(b) For R > 1, the system is chalcogen-rich. There are hetero-polar bonds and chalcogen–chalcogen bonds present.

(c) For R < 1, the system is chalcogen-poor. There are only hetero-polar bonds and metal–metal bonds present.

The values of R are mentioned in Table 2. From Figure 5, it is clear that our system is more or less chalcogen rich up to x = 12 at. % for almost all the three compositions but on further increase in the Indium content beyond x = 12 at. %, the values of R goes on decreasing further and all the systems are heading towards chalcogen poor. 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.

Table 2

<table>
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<tr>
<th>Ge&lt;sub&gt;20&lt;/sub&gt;Se&lt;sub&gt;80-x&lt;/sub&gt;In&lt;sub&gt;x&lt;/sub&gt;</th>
<th>T&lt;sub&gt;g&lt;/sub&gt;</th>
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<th>T&lt;sub&gt;g&lt;/sub&gt;</th>
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2.3 Role of Lone Pair Electrons and Glass Forming Ability

According to Pauling [40], an increase in the number of lone-pair electrons decreases the strain energy in the system and structures with large number of lone-pair electrons favours glass formation. The numbers of lone-pair electrons are calculated by using the relation [41]

\[ L = V - Z \]

where L is the number of lone-pair electrons, V is the valance electrons and Z is the average coordination number. It is observed that for the glassy system Ge-Se-In, that on increasing the In content, the number of lone-pair electrons goes on decreasing. This may be due to the interaction between In ion and lone-pair of electrons of bridging Se atom.

Zhenhua [41] proposed a simple criterion for a binary system and a ternary system, i.e., for a binary system the number of lone-pair electrons must be greater than 2.6 while for a ternary system it must be greater than 1.0. In our system Ge-Se-In system, the values of lone-pair of electrons are found to be greater than 1.0 and it is decreasing with the increase in In content for all the three combinations of Ge-Se-In system from 3 to 21 at. %, as depicted in Figure 6. So this explains the fact

Figure 5: Variation of Parameter R with In Content (a-Ge<sub>20</sub>Se<sub>80-x</sub>In<sub>x</sub>, b-Ge<sub>22</sub>Se<sub>78-x</sub>In<sub>x</sub>, c-Ge<sub>24</sub>Se<sub>76-x</sub>In<sub>x</sub>)

Figure 6: Variation of Lone-pair Electrons with In Content (a-Ge<sub>20</sub>Se<sub>80-x</sub>In<sub>x</sub>, b-Ge<sub>22</sub>Se<sub>78-x</sub>In<sub>x</sub>, c-Ge<sub>24</sub>Se<sub>76-x</sub>In<sub>x</sub>)
that the present system under investigation can be obtained in an amorphous glassy state. A system with large number of lone-pair electrons constitutes a stable state. Chalcogenides with lone-pair electrons are also characterized by flexibility [42]. This flexibility of bonds causes these atoms to readily form amorphous network, either alone or with a variety of other atomic constituents.

2.4 Mean Bond Energy and Glass Transition Temperature

There are many properties of chalcogenide glasses which are related to overall mean bond energy \(<E>\). According to Tichy and Ticha [37,38], 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 Ge-Se-In glass system is given by

\[
<E> = E_c + E_{rm}
\]

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 Ge\(_x\) Se\(_y\) In\(_z\) system, where \((x + y + z) = 1\), in selenium rich systems \((R > 1)\) where there are heteropolar bonds and chalcogen-chalcogen bonds

\[
E_c = 4xE_{Ge-Se} + 3zE_{Se-In}
\]

and

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

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

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

and

\[
E_{rm} = \frac{4x + 3z - 2y}{Z}E_{<<}
\]

where

\[
E_{<<} = \frac{1}{3[E_{Ge-Ge} + E_{In-In} + E_{Se-Se}]}\]

denotes the average homopolar bonding energy. The values of \(E_c\), \(E_{rm}\), and \(<E>\) are given in Table 2. As it is clear from Figure 7 that \(<E>\) increases with increase in concentration of In from 3 to 12 at. % for almost all the three compositions but on further increase in the Indium content beyond \(x = 12\) at. %, the values of \(T_g\) goes on decreasing further. This decrease in the values of \(T_g\) is due to fall in the values of parameter \(R\) and then subsequent decrease in the values of mean bond energy of the glassy system.

III. Conclusion

The addition of In to Ge-Se glassy alloys leads to change in the physical properties. It has been concluded from various figures and tables given above that values of \(Z\), \(X\), and \(N_c\) increase with increase in Ge content from 20 to 24 in Ge-Se-In system. The values of parameter \(R\) shows that our system is more or less chalcogen rich up to \(x =12\) at. %, the values of \(R\) goes on decreasing further and all the systems are heading towards chalcogen poor region. This decrease is 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 [37,38] by the relation

\[
T_g = 311[<E> - 0.9]
\]

The values of \(T_g\) corresponding to \(<E>\) is mentioned in Table 2 and the variation of \(T_g\) with In content is shown in Figure 8, which is clearly depicting the rise in glass transition temperature with increasing the content of In from 3 to 12 at. % for almost all the three compositions...
but on further increase in the Indium content beyond $x = 12$ at. 
%, the values of $T_g$ goes on decreasing further. This decrease in 
the values of glass transition temperature is due to fall in 
the values of parameter R and then subsequent decrease in the 
values of mean bond energy of the glassy system.

REFERENCES

   of Chalcogenide Glasses: A Review”, J Non-crystalline Solids, 
   2003, 330, 1.
2. Manish Saxena and P.K. Bhatnager, “Crystallization Study of 
3. L. Petri, N. Carlie, K. Richardson, et.al., “Effect of the 
   Substitution of S for Se on the Structure of the Glasses in the 
   System Ge0.23Sb0.07S0.70–xSex”, J. Phys. Chem. Solid, 2005 
   66, 1788.
4. Shilpa Gupta, A. Agarwal, Manish Saxena, “Study of 
   Crystallization Kinetics of Some Tex(2Se3)1–x Glassy 
5. S.R. Ovinsky, “Reversible Electrical Switching Phenomena in 
6. P.K. Jain, N. Jain and N.S. Saxena, “Activation Energy of 
   Crystallization and Enthalpy Released of Se0.6In0.4Sb3”, 
7. MHR Lankhorst, “Modelling Glass Transition Temperatures 
   of Chalcogenide Glasses. Applied to Phase-change Optical 
   219.
   Te1−x(Bi3Se4)1−x alloys with variation of the Se content”, J. Phys. 
   Dependence on Physical Properties of Ge1−xSxBi3 Glass 
   System for Phase Change Optical Recording”, MIT Int. J. 
10. P. Sharma, S.C. Katyal, “Far-infrared Transmission and 
    Bonding Arrangement in Ge10Se90-xTex Semiconducting 
11. I. Sharma, S.K. Tripathi, P.B. Barman, “Correlation between 
    the Physical and Optical … of Physical Properties in Se-In 
    Glassy Semiconductors” Physica B: Condensed Matter, 2008, 
    403, 624.
    thermodynamic properties of (Se0.7Te0.3)1–xAgx (0 < x < 4) 
13. G. Saffarini, J. M. Saiter, “Compactness in Relation to the Mean 
    Coordination Number in Glassy Ge8xBi6xS36-x”, Chal. 
    Calorimetric Studies of Ge-Sb-Se Glasses”, J Non Cryst. Solids, 
    Ge0.15Se0.85,Ag, (0<x<0.20) Glasses”, Advances in Appl. 
18. J. Feinleib, J. de Neufville, S.C. Moss and S.R. Ovshinsky, 
    “Rapid Reversible Light-Induced Crystallization of Amorphous 
19. R. Kumar, A. Kumar, V.S. Rangra, “A Study of Physical 
    Properties of Ge-Se-In Glassy Semiconductors”, Optoelec. & 
20. M.S. Kamboj, R. Thangaraj, “Calorimetric Studies of Bulk 
    33.
    Constraints in Ge-In-Se Glasses”, J. Non Cryst. Solids, 1993, 
    162, 294.
22. M. Fadel, “The Effect of the Sb Content on the Physical 
    Properties of Amorphous Se0.75Ge0.25j Thin Films”, Vacuum, 
    1999, 52, 277.
    Additions on the Optical Properties of (As–Sb–Se) thin films”, 
    York, 1981.
    Equation to Describe the Glass Transition”, J. Non-Cryst. 
    Short-range Order in Chalcogenide Alloys and a-Si(Ge)”, J. 
    Percollation and Glass Formation”, Solid State Comm., 1985, 
    53, 699.
28. M.F. Thorpe, “Continuous Deformations in Random Networks”, 
30. P. Trone, M. Bengoussan, A. Brenac, C. Sebenne, “Optical-
    Absorption Edge and Raman Scattering in Ge-Sel-1x Glasses”, 
31. G. Lucovsky, F.L. Galeener, R.C. Keezer, R.H. Geils, H.A. Six, 
    “Structure Interpretation of the Infrared and Raman Spectra 
    of Glasses in the Alloy System Ge1-XSx”, Phys. Rev. B, 1974, 
    10, 5134.
32. P. Sharma, S.C. Katyal, “Effect of Tellurium Addition on the 
    Physical Properties of Germanium Selenide Glassy 
    Semiconductors”, Physica B: Physics of Condensed Matter, 
    2008, 403, 3667.
33. G. Saffarini, “Atomic Density versus Average Coordination 
    Number in Ge–In–Se Glasses”, Phys. Stat. Solidi (b), 1999, 
    213, 261.
34. El. Sayed, M. Farag, M.M. Sallam, “Composition Dependence of the 
    Grain Size, Activation energy and Coordination Number in 
    Ge40,In60 (10 ≤ x ≤ 40 at. %) thin films”, Egypt J. Solids, 
    2007, 30(1), 1-11.
35. Manish Saxena, Atul K Kukreti, Shilpa Gupta, Manuj K 
    Agarwal and Nikhil Rastogi, “Effect of Compositional


