

## A Study on Physical Parameters of Pb-Se-Te-Bi System for Optical Memory Devices

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**Abstract** – The Chalcogenide glasses, in last couple of decades, have got a lot of attention because of their promising potential in studies of phase change optical storage media as well as due to interesting structural, physical, electrical, optical and thermal parameters. However, there is a general trend of using some amorphous materials instead of even very carefully prepared crystalline materials, in much needed investigation of such useful chalcogenide based materials. In the present study, the impact of bismuth (Bi) concentration variation on some important physical properties of  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  ( $x=2, 4, 6, 8, 10, 12, 14, 16$  at. %) glassy alloys has been investigated theoretically. Almost all the parameters, studied here, have been found to vary linearly with increase in Bi concentration, thus making this suitable for phase change optical recording and find applications in rewritable optical recording storage media.

**Keywords:** Chalcogenide Glasses, Average Coordination Number, Lone pair, Mean Bond Energy, Glass Transition Temperature

### I. INTRODUCTION

Chalcogenide glasses have received a great deal of attention in last few decades because of their interesting electrical, optical, structural, physical and thermal properties. As a result these material works as new advanced and replaceable technology materials. They shows various applications such as rectifier, infrared optical fibres, photo induced properties for optical storage and optical imagine. Other interesting applications are as photoresistors, solar cells, optoelectronic devices, lasers and thermoelectric devices. More recently, as infrared emitters and solar control coatings, high efficiency fiber amplifiers, thermoelectric and photovoltaic devices have drawn a lot of attention amongst researchers [1-3]. Recently, many researchers reported different nano-chalcogenides as their applications in nano-electronic devices, nano-memory devices etc. and studied their various properties. These glasses exhibit several particular phenomena which are applicable for devices as memory image storage and electrical switching. Chalcogenide materials can be reversibly switched between the amorphous and crystalline state and find applications in rewritable optical recording and in electrically programmable non-volatile memories. This was revolutionized by S. R. Ovshinsky in 1968, with the discovery of a new memory phenomenon in chalcogenide film materials. This phase-change memory effect was named as the “Ovonic memory”. The first version of the phase-change optical disk product was shipped in 1990 from Matsushita/Panasonic [4].

The Selenium based amorphous chalcogenides alloys are more preferred because of its unique property of reversible transformation, which makes these alloys useful for optical memory devices point of view. But there are some disadvantages associated with pure selenium alloy such as short life time and poor sensitivity. These disadvantages can be removed by adding some other materials like Ge, Te, In, Pb, Sb, Bi, etc. The addition of Tellurium improves its corrosion resistance and optical sensitivity. The elements such as Selenium and Tellurium have chain-like bonding which helps these compounds to transform to the amorphous state easily. The two types of bonding forces, one is covalent bonding and the other is weak van der Waals force which appears in chain-chain bindings. These bonding forces are considered to be related for easy amorphizing characteristics of chalcogenide materials. The crystalline structures of the chalcogenide materials belong to hexagonal or monoclinic systems. The former forms a spiral chain bonding structure and the later often forms a ring bonding structure with eight corners. Addition of the other elements to form higher order ternary and quaternary alloys generate bridges between chains or transform them into network structures [5, 6].

In the present work, a quaternary alloy  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  comprising of Se-Te based alloy have been taken. Here, the atomic % of Te and Pb was fixed at 10 atomic %, and then studied the variation in the various important parameters by

varying the concentration of Bismuth from 2-16 atomic %. By varying the Bismuth concentration, it creates compositional and configurational disorder in the material with respect to the ternary alloys [7]. In this paper we are concerned with the theoretical prediction of some parameters related to composition, viz. average coordination number, Lone pair, mean bond energy, glass transition temperature etc. for  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  ( $x=2, 4, 6, 8, 10, 12, 14, 16$  at. %) alloys.

## II. METHODOLOGY

### *Bonding Constraints & Average Coordination Number*

Earlier the two models, Random Covalent Network model (RCNM) and the Chemically Ordered network model (CONM) described the distribution of the three bonds namely A–B, A–A, B–B in binary alloy system. J C Phillips proposed a dynamic model for network glasses, based entirely on topological consideration. According to him, the glass formation tendency is optimized mechanically when the degrees of freedom ( $N_d$ ) for the atoms in the glassy network equals the number of constraints ( $N_{con}$ ) in the network at a critical average coordination number  $\langle r \rangle$  [8].

Further Thorpe and his coworkers extended this model to explain the elastic behavior of covalent glasses in terms of the average number of constraints in the system. Phillips–Thorpe approach is based on comparing the number of atomic degrees of freedom with the number of inter-atomic force field constraints. If degrees of freedom are found to be greater than number of constraints, the network is ‘floppy’. But if the number of constraints becomes greater than degrees of freedom then the network becomes over constrained, stressed-rigid structure will percolate throughout the entire network. On the basis of equating the total number of inter-atomic force-field constraints per atom,  $N_c$ , to the number of degrees of freedom per atom,  $N_d$ , a structural phase transition at  $\langle r \rangle = 2.4$  was predicted. At this  $\langle r \rangle$  value, a percolation threshold exists at which the network changes from a floppy-type to a rigid-type and possesses mechanically optimized structures [9, 10].

Later Tanaka gave another structural phase transition at  $\langle r \rangle = 2.67$ . At this threshold, two-dimensional (2D) layer structures are fully evolved. He proposed that for  $\langle r \rangle > 2.67$ , there is a structural transition to three-dimensional (3D) networks due to the increase in the number of cross-linked sites [11]. The average coordination number,  $\langle r \rangle$  for the composition  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  was calculated using standard method [12] is given by

$$\langle r \rangle = \frac{aCN_{Pb} + bCN_{Se} + cCN_{Te} + dCN_{Bi}}{a + b + c + d}$$

where a, b, c and d are the at.% of Pb, Se, Te and Bi respectively and  $CN_{Pb}(4)$ ,  $CN_{Se}(2)$ ,  $CN_{Te}(2)$ ,  $CN_{Bi}(3)$  are their respective coordination number [13].

The glassy network are influenced by mechanical constraints ( $N_c$ ) associated with the atomic bonding and an average coordination number  $\langle r \rangle$  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) [8].

The number of Lagrangian bond-stretching constraints per atom is

$$N_\alpha = \langle r \rangle / 2$$

and, of bond-bending constraints is

$$N_\beta = 2\langle r \rangle - 3$$

The total number of constraints is given by

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

In case if all  $\alpha$  and  $\beta$  constraints are intact and no dangling ends exist in the network, equation implies that the optimum mean coordination number is 2.424 which are known as the rigidity percolation threshold. So this leads to the fact that over-coordinated or under-coordinated structures are not conducive to glass formation and, leads to crystallization on cooling.

According of M. F. Thorpe in 1983, the number of floppy modes per atom,  $f$ , is rather accurately described by the mean-field constraint count according to the relation [14]

$$F = 3 - N_c$$

This led to the realization that a glass network becomes spontaneously rigid when  $f \rightarrow 0$ , defining a floppy to rigid phase transition [15]. The fraction of floppy modes available in a network is given by

$$f = 2 - \frac{5\langle r \rangle}{6}$$

The cross-linking density (X) is equal to the average coordination number of cross linked chain less the coordination number of initial chain [16].

$$X = N_c - 2$$

### *Role of Lone Pair Electrons in glass forming ability & Deviation from the stoichiometry of composition*

Pauling predicted that [17], large number of lone-pair electrons favours glass formation. It is because the strain energy of the system and structures found to be decreasing with an increase in the number of lone-pair electrons. The numbers of lone-pair electrons are calculated by using the relation

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

where L is the number of lone-pair electrons, V is the valance electrons and  $\langle r \rangle$  is the average coordination number. Zhenhua [18] proposed a simple criterion that for a binary system the number of lone-pair electrons must be greater than 2.6 while for the ternary system it must be greater than 1.0.

The parameter R, also play an important role in the analysis of the results in the glassy system. The deviation from stoichiometry is determined by the parameter R. It is expressed by the ratio of covalent bond possibilities of chalcogen atoms to that of non-chalcogen atoms. For the present  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  system, the parameter R can be calculated by [19]

$$R = \frac{bCN_{Se} + cCN_{Te}}{aCN_{Pb} + dCN_{Bi}}$$

where a, b, c and d are the at.% of Pb, Se, Te and Bi respectively. Depending on R values, the chalcogenide systems can be organized into three different categories. If the value of  $R = 1$ , the system reaches the stoichiometric composition as only hetero polar bonds are present. For  $R > 1$  then the system is chalcogen-rich. This is due to the presence of hetero-polar bonds and chalcogen-chalcogen bonds. For  $R < 1$ , the system is chalcogen-poor as there are only hetero-polar bonds and metal-metal bonds present.

#### Mean Bond Energy & Glass Transition Temperature

As predicted by the Tichy and Ticha [20, 21], the value of glass transition temperature should not only be related to connectedness of the network which is related to  $\langle r \rangle$ , 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  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  system is given by

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

where  $E_c$  and  $E_{rm}$  are overall contribution towards bond energy arising from strong heteropolar bonds and contribution arising from weaker bonds that remains after the strong bonds have been maximized respectively. For  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  system, where  $(a+b+c+d) = 1$ ,  $E_c$  and  $E_{rm}$  are given by

$$E_c = 4aE_{Pb-Se} + 2cE_{Te-Se} + 3dE_{Te-Bi}$$

and

$$E_{rm} = \left[ \frac{2b - 4a - 2c - 3d}{\langle r \rangle} \right] E_{Se-Se}$$

Tichy and Ticha also gave an interesting correlation of mean bond energy with glass transition temperature  $T_g$ . This correlation is given by the relation

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

where the  $\langle E \rangle$  is the mean bond energy.

### III. RESULTS AND DISCUSSION

It is clear from fig. 1 that the value of average coordination number is found to be increasing from 2.22 to 2.36 with increase in concentration of Bi from 2 to 16 at.%. The increase in  $\langle r \rangle$  attribute to the fact that there is increase in

degree of cross-linking density, network rigidity and strength between the atoms. In  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  alloy system for all combination from 2 to 16 at. % for increasing Bi the  $\langle r \rangle$  is less than 2.4. So this investigated alloy is floppy type and approaching towards  $\langle r \rangle = 2.4$ . This indicates that the tendency of glass formation is increasing from 2 to 16 at. %. The value of  $N_c$  which directly depends on  $\langle r \rangle$  is also found to be increasing as shown in fig. 1. The calculated values of cross linking density (X) are shown in fig. 1. It is clear the fig. 1 that value X increase with increase in Bi concentration for 2 to 16 at. %. It is clear from fig. 2 that the values of f decrease with increase in Bi concentration. This indicates that investigated system becomes more and more rigid, which corresponds to a strong tendency for making glasses.

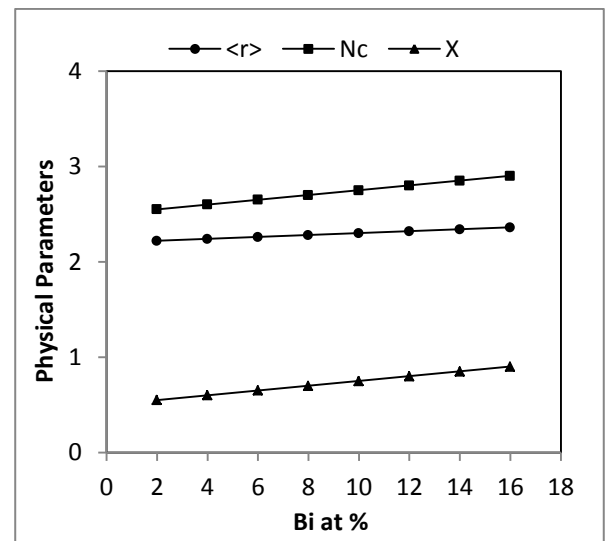


Fig. 1: Variation of Average Coordination Number  $\langle r \rangle$ ,  $N_c$ , X with Bismuth concentration

We have observed that for the  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  glassy system, with the increase in the Bi concentration, the number of lone-pair electrons goes on decreasing. This may be found because of interaction between Bi ion and lone-pair of electrons of bridging Se atom. Here the values of lone-pair of are found to be decreasing from 3.56 to 3.28 with the increase in Bi concentration from 2 to 16 at. % as depicted in fig. 3. The value of lone pair is always greater than 1.0. Any glassy system with large number of lone-pair electrons constitutes a stable state. Chalcogenides with lone-pair electrons are also characterized by flexibility. The flexibility of bonds causes these atoms to readily form amorphous network. It will favour the glass formation.

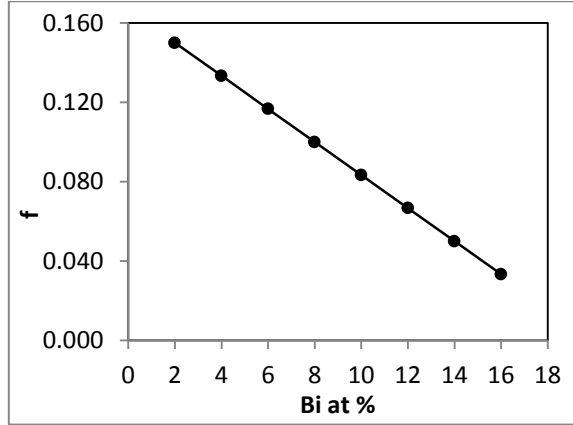


Fig. 2: Variation of f with Bismuth concentration

From fig. 3, it is clear that in  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  system the value of R is chalcogen rich and turning towards less chalcogen rich with the increase in concentration of Bismuth in the system. This decrease is due to the fact that with increase in Bi concentration the number of the non-chalcogen atoms increases and the chalcogen Se atom decreases. As the material is well within the range of being chalcogen rich, so having high energy lone pair electrons leads to qualitative different electronic densities of state.

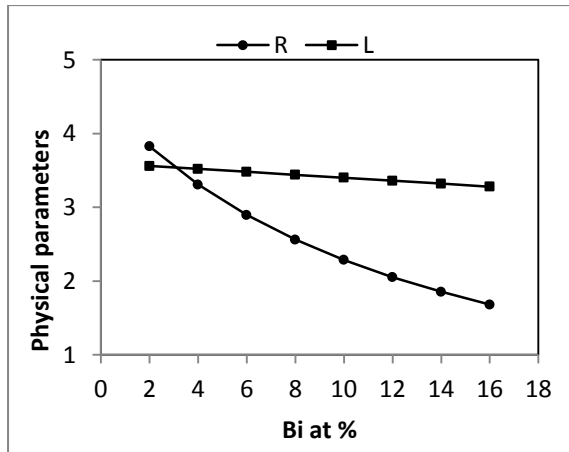


Fig. 3: Variation of parameter R & L with Bismuth concentration

It is clear from fig. 4 that  $\langle E \rangle$  increases from 1.810 to 1.956 with increase in concentration of Bi from 2 to 16 at. %. This increase may be predicted because system investigated here is Se rich. The variation of  $T_g$  with Bi concentration is shown in fig. 5, which is clearly depicting the rise in glass transition temperature from 283.12 K to 328.29K with increasing the concentration of Bi due to rise in mean bond energy of the glassy system.

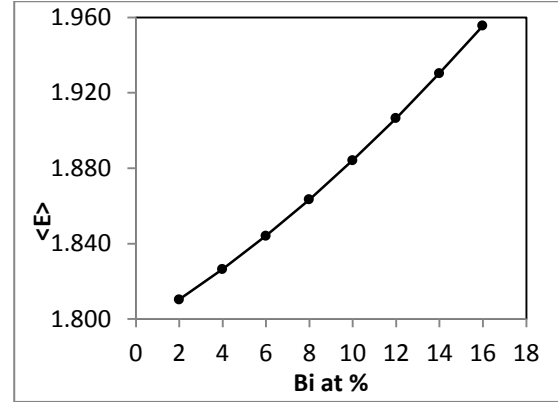


Fig. 4: Variation of parameter  $\langle E \rangle$  with Bismuth concentration

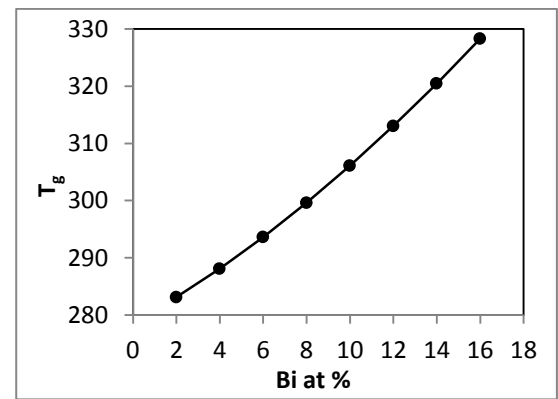


Fig. 5: Variation of parameter  $T_g$  with Bismuth concentration

#### IV. CONCLUSIONS

Here, in the present article, the influence of Bismuth concentration on some important physical parameters of Pb-Se-Te based glassy alloys has been investigated. The addition of Bi to Pb-Se-Te based glassy alloys leads to change in the physical properties. It has also been shown in the present article that Bi atom leads to the cross linking of chains and in turn slightly increases the average coordination number of the system. Various physical parameters viz. average coordination number, lone-pair electrons, mean bond energy, glass transition temperature have been calculated theoretically for  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  ( $x=2, 4, 6, 8, 10, 12, 14, 16$  at. %) alloys. The values of parameter R shows that our system is sufficiently chalcogen rich for all the samples with Bi concentration ranging from 2 to 16 at. %. The parameter R in our system makes it an ideal example of chalcogen rich materials. The present system consisting of  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  ( $x=2, 4, 6, 8, 10, 12, 14, 16$  at. %) glassy alloys is in accordance with the earlier researches according to which system with large number of lone-pair electrons constitutes a stable state. It is clear from various figures depicted above that almost all the parameters vary linearly with the increase in concentration of Bi ranging from 2 to 16 at. % in  $Pb_{10}Se_{80-x}Te_{10}Bi_x$  glassy system and subsequently

making this present system suitable considerably for phase change optical recording and find applications in rewritable optical recording.

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