

## Effect of decrease in chalcogen content on some physical parameters of $\text{Ge}_{14}\text{Bi}_x\text{Se}_{76-x}\text{Te}_{10}$ Glasses due to variation in Bi content

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### ABSTRACT

Currently, 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. A study on effect of decrease in chalcogen content due to variation in Bismuth content on some physical parameters viz. average coordination number, number of constraints, cross-linking density, molecular weight, fraction of floppy modes, Lone-pair electron, mean bond energy, glass transition temperature etc., has been summarized in the present article for  $\text{Ge}_{14}\text{Bi}_x\text{Se}_{76-x}\text{Te}_{10}$  ( $x=1.5, 4.5, 7.5, 10.5, 13.5, 16.5, 19.5, 22.5$ ) glassy alloys. To study the glass transition temperature and mean bond energy, Tichy-Ticha approach has been considered. A smooth variation has been found in almost all the parameters, studied here.

**Keywords:** Chalcogenide Glasses; Average Coordination Number; Lone-pair electron; mean bond energy.

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### INTRODUCTION

It has now more or less established that the chalcogenide glasses are very interesting materials for reversible phase change optical recording devices [1-4]. Ever since the reversible switching phenomenon in certain types of chalcogenide glasses was initially reported [5], a lot of attention has been given to improvement and characterization of the properties of chalcogenide glasses, in particular, the materials exhibiting the switching characteristics. The phase change can be reversibly switched between the crystalline and amorphous states, thus finding applications in very useful rewritable optical recording [6, 7]. The selenium exhibits the unique property of reversible phase transformation and also applications like photocells, xerography, memory switching etc. Due to these properties, it becomes attractive, but it is also true that pure selenium has disadvantage like short life time and low photo sensitivity. To overcome these shortcomings of Se, some impurity atoms like Ge, In, Bi, Te, Ga, Sb, Ag, etc. can be used to make alloys with Se, which may not only enhance sensitivity, crystallization temperature but also reduce ageing effects [8, 9].

The Ge-Se system is a widely studied system. The studies on Ge-Se based glassy alloys, by varying compositions, have been reported by several investigators for Ge-Se, Ge-Se-Te, Ge-Se-In, Ge-Se-Bi Ge-Se-As, Ge-Se-Sb, Ge-Se-Ag, [10-16]. Ge atoms strengthen the average bond by cross-linking the Se chain structure as they act as bond modifiers, thereby, enhancing the properties like glass transition temperature and resistivity [17]. The glass formation in Ge-Se system occurs predominantly in alloys enriched with Se and containing 0-25 at % of Ge. Addition of more elements like Bi and Te 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 [18].

## MATERIALS AND METHODS

In the present work, we have incorporated Bismuth and a fixed atomic percentage of Te at the cost of Se content in the Ge-Se alloy for the compositions belonging to  $\text{Ge}_{14}\text{Bi}_x\text{Se}_{76-x}\text{Te}_{10}$  ( $x=1.5, 4.5, 7.5, 10.5, 13.5, 16.5, 19.5, 22.5$ ). It has been established that physical properties in Ge-Se alloy system are highly compositional dependent [19]. The variation of properties has been discussed on the basis of their compositions by increasing Bi content and hence by reducing Se content continuously. The present paper is concerned with the theoretical aspect of the physical parameters related to composition, viz. coordination number, number of constraints, cross-linking density, fraction of floppy modes, molecular weight, lone-pair electron, mean bond energy and glass transition temperature for  $\text{Ge}_{14}\text{Bi}_x\text{Se}_{76-x}\text{Te}_{10}$  alloys.

## RESULTS AND DISCUSSION

### Average Coordination Number & Bonding Constraints

As per the theory given by J. C. Phillips, 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 for amorphous covalent materials [20]. Phillips, in his theory, 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 referred to as “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 maximize when the number of degrees of freedom exactly equals the number of constraints.

For the composition  $\text{Ge}_{14}\text{Bi}_x\text{Se}_{76-x}\text{Te}_{10}$  the average coordination number ( $Z$ ) was calculated by using the standard method [21]

$$Z = \frac{wCN_{Ge} + xCN_{Bi} + yCN_{Se} + zCN_{Te}}{w + x + y + z}$$

where  $w, x, y$  and  $z$  are the atomic % of Ge, Bi, Se and Te respectively and  $CN_{Ge}, CN_{Bi}, CN_{Se}, CN_{Te}$  are their respective coordination number [22]. It is clear from fig 1 that values of  $Z$  increase from 2.30 to 2.51 with increase in concentration of Bi from 1.5 to 22.5 at %.

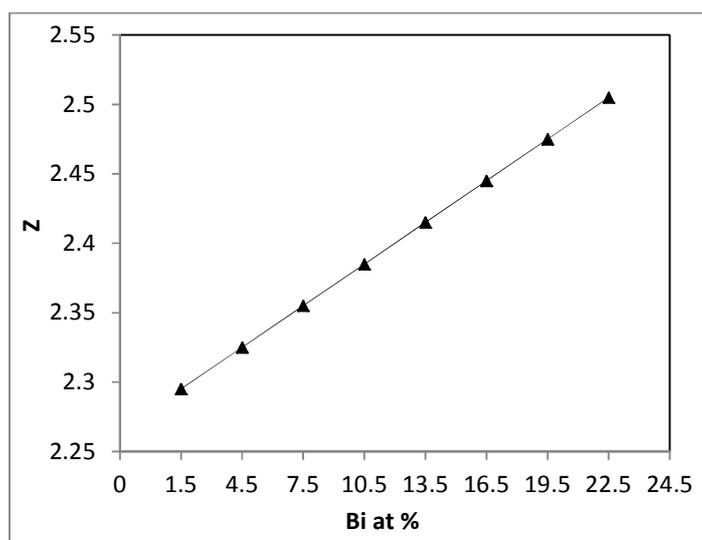


Fig. 1: Variation of Average Coordination Number with Bismuth at. %

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-neighbour bonding forces in covalent solids; bond-stretching ( $\alpha$ - forces) and bond-bending ( $\beta$ - forces) [23].

The number of Lagrangian bond-stretching constraints per atom is given by

$$N_\alpha = Z / 2$$

and, of bond-bending constraints is given by

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

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

The total number of constraints is given by

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

The variation of  $N_c$  along with  $Z$  for  $\text{Ge}_{14}\text{Bi}_x\text{Se}_{76-x}\text{Te}_{10}$  are illustrated in fig. 2. It depicts the variation of  $N_c$  with Bi at %. Here the values of  $N_c$  are found to be increasing from 2.74 to 3.26 with increase in Bi 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.  $N_c = N_d$ .

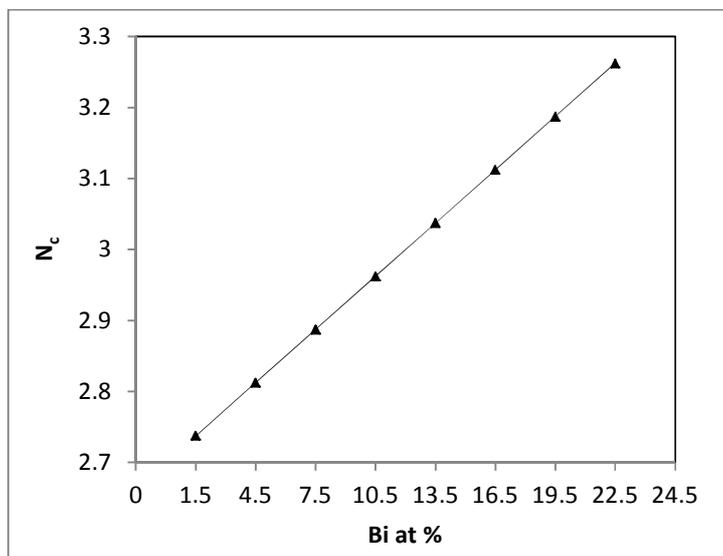


Fig. 2: Variation of number of constraints with Bi at. %

The cross-linking density( $X$ ) is equal to the average coordination number of cross linked chain less the coordination number of initial chain [24].

$$X = N_c - 2$$

The variation of cross linking density ( $X$ ) and molecular weight ( $M$ ) are shown fig. 3 and fig. 4 respectively. It is clear from fig. 3 and fig. 4 respectively that the values of cross linking density  $X$  and molecular weight  $M$  increases with increase in Bi content.

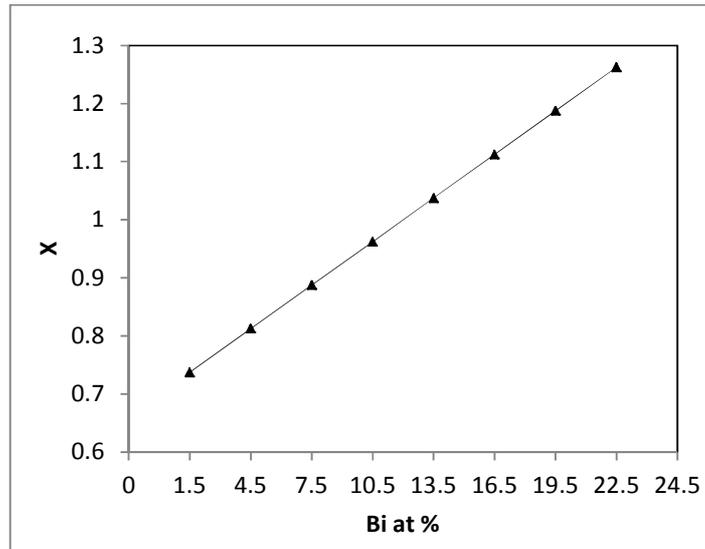


Fig. 3: Variation of cross-linking density with Bi content

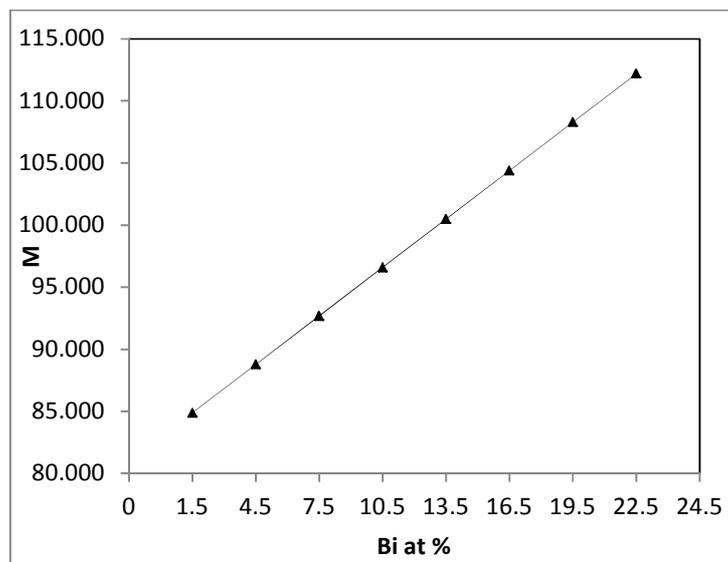


Fig. 4: Variation of Molecular weight with Bi content

According to M. F. Thorpe [26], 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

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

This led to the realization that a glass network will become spontaneously rigid when  $f \rightarrow 0$ , defining a *floppy to rigid phase transition* [26].

The values of fraction of floppy modes ( $f$ ) become more and more negative (0.0875 to -0.0875) with increase in Bi content from 1.5 to 22.5 at. %, as depicted in fig. 5. This shows that the system becomes more and more rigid, which corresponds to a strong tendency for making glass.

**Lone pair electrons and glass forming ability**

According to Pauling [27], increasing in the number of lone-pair electrons decreases the strain energy in a system and structures with large numbers of lone-pair electrons favors glass formation. The number of lone-pair of electrons is calculated using the relation [28]

$$L = V - Z$$

where L is the number of lone pair electrons, V is the valance electron and Z is the average coordination number. The results of Lone-pair electron for Ge<sub>14</sub>Bi<sub>x</sub>Se<sub>76-x</sub>Te<sub>10</sub> system with Bi content is illustrated in fig.6.

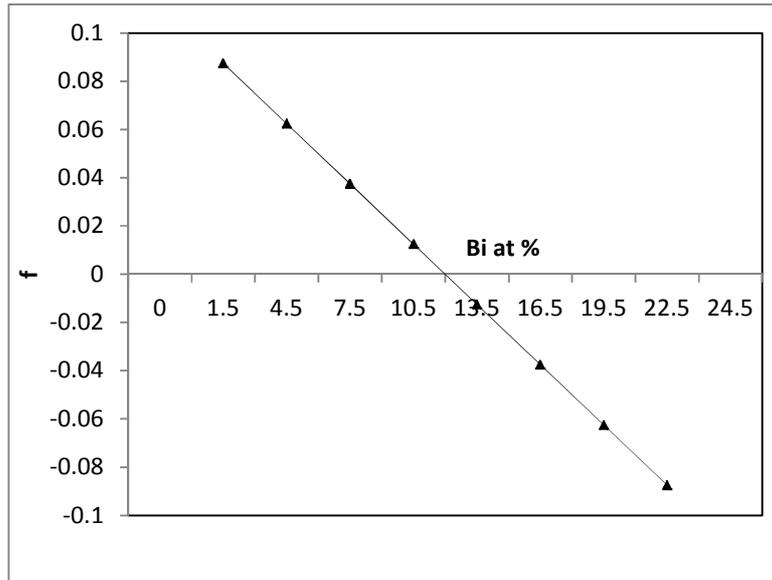


Fig. 5: Variation of fraction of floppy modes with Bi content

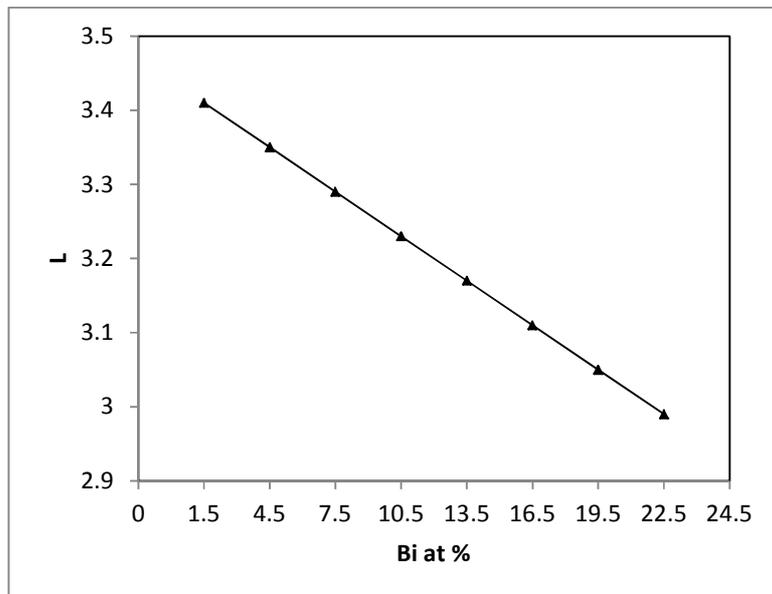


Fig. 6: Variation of Lone-pair electrons with Bi content

It is clear from fig. 6 that with the increase of Bi content, the number of lone-pair electrons decreases continuously in  $\text{Ge}_{14}\text{Bi}_x\text{Se}_{76-x}\text{Te}_{10}$  system. This behaviour is caused by the interaction between the Bi ion and lone-pair electrons of bridging Se atom. The role of lone-pair electrons in the glass formation decreases by this interaction. A simple criterion was proposed by Zhenhua, for a binary system the number of lone-pair electrons must be larger than 2.6 and for ternary system it must be larger than 1. The values of lone-pair electrons for  $\text{Ge}_{14}\text{Bi}_x\text{Se}_{76-x}\text{Te}_{10}$  system were found to decrease from 3.41 to 2.99, from which it may be concluded that the present system under study is exhibiting good glass forming ability.

#### Deviation from the stoichiometry of composition

To determine the deviation from stoichiometry, the parameter 'R' has been calculated. The R parameter is expressed by the ratio of content bond possibilities of chalcogen atoms to that of non-chalcogen atoms. For  $\text{Ge}_{14}\text{Bi}_x\text{Se}_{76-x}\text{Te}_{10}$  system, the parameter R is given by [29, 30]

$$R = \frac{yCN(\text{Se}) + zCN(\text{Te})}{wCN(\text{Ge}) + xCN(\text{Bi})}$$

where w, x, y and z are atomic fractions of Ge, Bi, Se and Te respectively. 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. 7, it is observed that the present system is chalcogen rich, but turning towards chalcogen poor with the increase in content of bismuth 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.

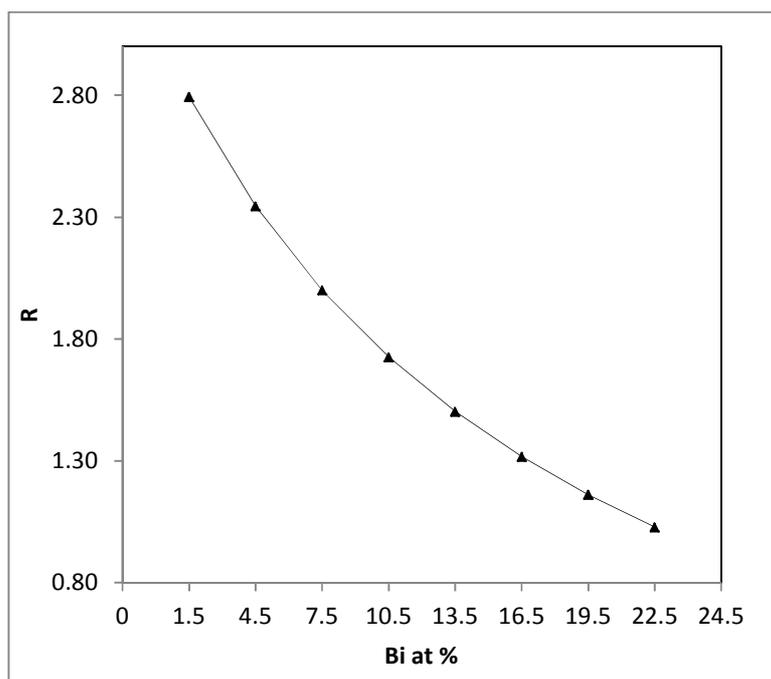


Fig. 7: Variation of parameter R with Bi content

#### Mean Bond Energy and Glass Transition Temperature

There are various properties of chalcogenide glasses which may be related to overall mean bond energy  $\langle E \rangle$ . According to Tichy and Ticha, 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  $\text{Ge}_{14}\text{Bi}_x\text{Se}_{76-x}\text{Te}_{10}$  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  $Ge_w Bi_x Se_y Te_z$  system, where  $(w + x + y + z) = 1$ , in selenium rich systems ( $R > 1$ ) where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E_c = 4wE_{Ge-Se} + 3xE_{Bi-Se} + 2zE_{Se-Te}$$

and

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

denotes the average homopolar bonding energy.  $\langle E \rangle$  has been found to increase with increase in concentration of Bi from 1.5 to 22.5 at. % as depicted in fig. 8.

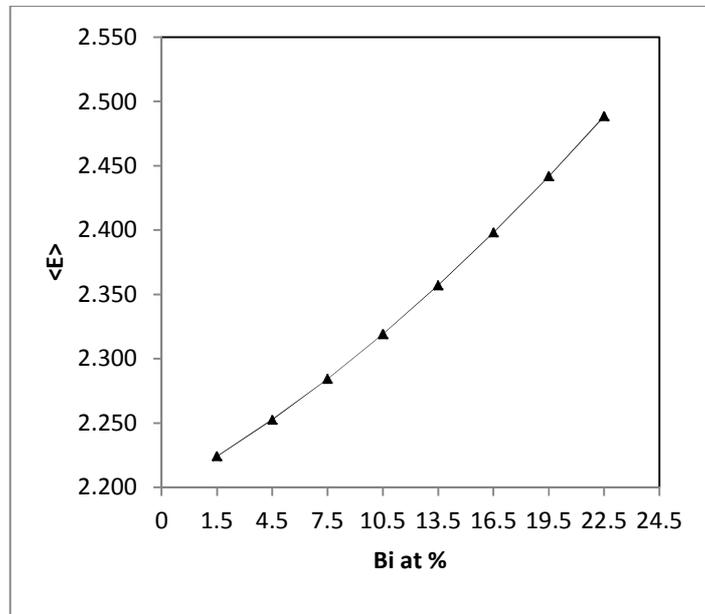


Fig. 8: Variation of overall mean bond energy with Bi content

An impressive correlation of mean bond energy with glass transition temperature  $T_g$  was illustrated by Tichy and Ticha by the relation [29, 30]

$$T_g = 31[\langle E \rangle - 0.9]$$

The variation of  $T_g$  with Bi content is shown in fig. 9, which is clearly depicting the rise in glass transition temperature from 408.84 to 491.04 with increasing the content of Bi from 1.5 to 22.5 at. % due to rise in mean bond energy of the glassy system.

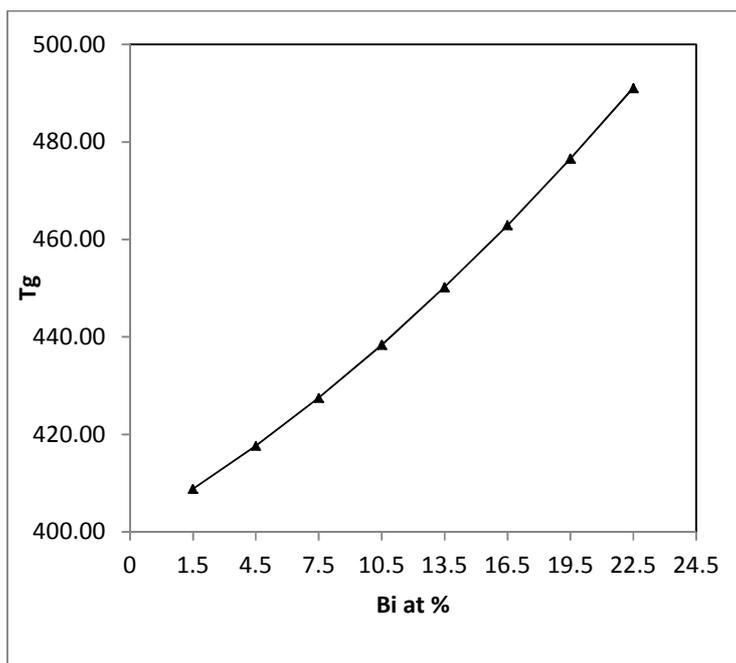


Fig. 9: Variation of glass transition temperature with Bi content

### CONCLUSION

The incorporation of Bi and Te to Ge-Se glassy alloys leads to significant change in the physical properties. By studying various figures given in the text, it is clear that almost all the parameters, mentioned above, except fraction of floppy modes, Lone-pair electron and the parameter R, were found to be increased with the increase in Bi content. The positive values of R confirm the alloys as chalcogen rich up to our extreme limit i.e. up to  $x = 22.5$  at. %. The values of lone-pair electrons show a satisfactorily good glass forming ability of present glass system. The results also show that mean bond energy  $\langle E \rangle$  is proportional to glass transition temperature and both increases with the increase in content of Bi.

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