# Effect of Bi content on the physical parameters of Ge<sub>18</sub>Bi<sub>x</sub>Se<sub>82-x</sub> chalcogenide glasses

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**Abstract:** For Ge-Se-Bi glassy chalcogenides, the influence of increasing Bi content on physical properties such as ionicity and covalent character of some combinations, number of constraints, average coordination number (CN), average heat of atomization (H<sub>s</sub>), cross-linking density (X), the stoichiometry of the compositions (R), lone-pair electrons (L), glass transition temperature (T<sub>g</sub>), and so on has been theoretically investigated. In this work, we examined the addition of Bi content in Ge<sub>18</sub>Bi<sub>x</sub>Se<sub>82-x</sub> glassy alloys for (x: 0.5, 2, 4, 6, and 8 at. %) and correlated the physical parameters to theoretical predictions. Cross-linking of chains, average coordination number (CN), mean bond energy, glass transition temperature, and values of N<sub>c</sub> and X all rise as the concentration of Bi increases from 0.5 to 8%, whereas average heat of atomization (H<sub>s</sub>) drops. The current system is consistent with prior studies, which found that a system with a substantial number of lone-pair electrons is a stable state.

Keywords: Chalcogenide Glasses, Glass Transition, Coordination Number, Lone Pair, Average Heat of Atomization.

#### **1** Introduction

The CHG can be elemental semiconductors (S, Se, Te, and so on), binary semiconductors (Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>), or multicomponent combinations (Ge-Se-In, Ge-Se-Bi, etc.). Multicomponent alloys have a three-dimensional network, whereas elemental or binary chalcogenides have a chain or layered structure with several orders ranging locally in onedimensional and two-dimensional. It is generally known that chalcogenide materials satisfy Mott's "8-N bonding rule" [1]. Thermally induced amorphous to crystalline phase changes occur in some chalcogenide materials, allowing binary data to be encoded on thin films of CHG and constituting the basis of rewritable optical and non-volatile memory systems [2]. The phase transition can be switched between amorphous and crystalline states reversibly, making it useful for rewritable optical recording [3-5]. Selenium has the unique ability of reversible phase transition and is used in rectifiers, photocells, and memory switching. However, it has limitations such as photo resistivity and a short lifetime. Adding another element to selenium, such as Bi, Ge, Sb, or as, enhances its corrosion resistance [6], as well as its sensitivity, crystallization temperature, and ageing effects [7]. The Ge atom behaves as a bond modifier, improving properties such as glass transition temperature and bond energy by cross-linking the Se-chain structure [8]. The addition of Bi improves

chemical strength while also widening the IR transparency range. It has been reported [9] that adding Bi atoms to CHG causes a noticeable change in conduction, switching from ptype to n-type. Due to their unique features, CHGs are regarded as promising materials for a variety of applications in several fields of science. The layered or chain structure of elemental or binary chalcogenides has substantial order extending locally in one-dimensional and two-dimensional, but multi-component alloys have a three-dimensional network. Internal stress, hardness, and water resistance are all improved mechanical properties of CHG. Physical features such as high refractive index, low phonon energy, high non-linearity, and so on are also present in these materials. Because of its strong optical nonlinearity and high interaction length, CHG fiber is one of the most attractive choices for use as a nonlinear optical medium. Lenses, windows, fibers, laser fiber amplifiers, and nonlinear components are all made with this glass [10]. Because of their wide transmission window of 2-12 m, CHG can be used as optical fibers. Memory devices, optical fibers, reversible phase change, and optical recording materials are only a few of the uses for these materials [11-12]. The lack of structural rigidity in chalcogenides allows them to be used in a wider range of applications. In the present work, we selected Ge<sub>18</sub>Bi<sub>x</sub>Se<sub>82-x</sub> (x: 0.5, 2, 4, 6, and 8 at. %) glasses to study the effect of compositional variation on their physical parameters. By varying Bi content in all

compositions, we investigated physical properties such as CN, number of constraints, cross-linking density, lone-pair electrons, glass transition temperature, and Hs to determine the importance of the  $Ge_{18}Bi_xSe_{82-x}glass$  system for optical recording devices.

#### **II THEORETICAL STUDIES AND DISCUSSIONS**

#### 1. Ionic Character of Covalent Bond.

It is known that CHGs are made from materials such as Sulphur, Selenium, and Tellurium, which have predominantly covalent bonds. The degree of covalency in the bond of amorphous glass under investigation can be calculated by using the Pauling relationship [13]:

Amount of covalent character =  $e^{-0.25(\chi_A - \chi_B)^2}$ 

where  $\chi_A$  and  $\chi_B$  are the electro negativities of atoms A and B. The ionicity introduces a tendency towards ordering because of the non-directional character. The ionicity of a bond is calculated using the Pauling formula:

Percentage of ionic character = 1 -  $e^{-0.25(\chi_A - \chi_B)^2}$ 

Pauling defined electro negativity as the strength of an atom or molecule to attract electrons to it. The electro negativity of a composition is defined as the geometric mean of all the constituents forming a compound. It has been shown that elements with more than 90% covalent character are more promising for glass formation. In our case, the covalent characters for Ge-Bi, Ge-Se, and Se-Bi bonds are 92.96, 99.99, and 93.22, respectively [14]. This can be interpreted by the fact that the increasing value of bond strength increases the glass forming tendency.

### 2. Bonding Constraints and Average Coordination Number

The bonding schemes (the 8-N rule) in chalcogenide network glasses have been reported to be compatible with the Random Covalent Network RCNM and Chemically Ordered Network Model CONM [15-16]. The CONM has been utilized to better understand the characteristics of CHG property-composition dependence. In CONM, the creation of heteropolar bonds takes precedence over the production of homopolar bonds. As a result, the glass structure can be made up of GeSe<sub>2</sub> and Bi<sub>2</sub>Se<sub>3</sub> cross-linked structural units with an excess of Ge or Se dispersed across the Ge-Se-Bi glass systems. Phillips proposed [17-18] that the properties of network glasses be studied in terms of the average coordination number, which Thorpe [19] confirmed. The coordination number is the average atoms coordinated with its nearest neighbours of the constituents. It is useful in explaining the cross linking and testing the validity of topological concepts [20] The Phillips- Thorpe procedure compares the number of inter-atomic force field limitations to the number of atomic degrees of freedom. A structural phase transition at CN = 2.4 was predicted by comparing the total number of interatomic force-field restrictions per atom, N<sub>c</sub>, to the number of degrees of freedom per atom, N<sub>d</sub> [19]. The network transforms from a floppy to a rigid type at this CN value, with mechanically adjusted structures. Tanaka [21] estimated that when CN = 2.67, another structural phase transition would occur. Twodimensional layer structures have fully formed at this point. There is a structural shift to three-dimensional networks when CN > 2.67. This is due to a rise in the number of sites that are cross-linked. For the Ge<sub>18</sub>Bi<sub>x</sub>Se<sub>82-x</sub> system, the average coordination number (CN) is computed using the conventional approach [22]. The value of CN is given by:

$$CN = \frac{\alpha CN(Ge) + \beta CN(Bi) + \gamma (CN(Se))}{\alpha + \beta + \gamma}$$
(1)

where  $\alpha$ ,  $\beta$  and  $\gamma$  are the at. % of Ge, Bi and Se respectively and CNGe (4), CNBi (3) CNSe (2), are their respective coordination number [23-25]. Figure 1 shows the relationship between CN and Bi content, indicating that CN values rise as Bi concentration rises from 0.5 to 8%. Bond-stretching ( $\alpha$ - forces) and bond-bending ( $\beta$ forces) are two types of near-neighbor bonding forces described in covalent solids [18]. Each atom has the following number of Lagrangian bond-stretching constraints:

$$N_a = \frac{CN}{2} \tag{2}$$

The number of bond-bending constraints is:

$$N_b = 2CN - 3$$
(3)  
The total number of constraints is given by

$$N_{c} = N_{c} + N_{b} \tag{4}$$

The cross-linking density (X) is identified as the average coordination number of a cross-linked chain being fewer than that of the initial chain [25]:

$$X = N_c - 2 \tag{5}$$

According to Thorpe [19], the uncoordinated network has a finite fraction of zero frequency normal vibration modes termed as floppy modes in the absence of weak long-range forces. The fraction of floppy modes in a network is determined by:



**Figure 1**: depicts the effect of bismuth concentration on CN in  $Ge_{18}Bi_xSe_{82-x}$  chalcogenide glasses.

#### 3. Deviation from the Stoichiometry of Composition (R)

This variable is defined as the ratio of chalcogen atoms' covalent bonding possibilities to those of non-chalcogen atoms. The R value for the Ge-Se-Bi system is given by [26-27]:

$$\mathbf{R} = \frac{\gamma CN(Se)}{\alpha CN(Ge) + \beta CN(Bi)}$$
(7)

The chalcogenide systems can be classified into three groups:

(a) Stoichiometric (only heteropolar bonds are present). For R = 1

(b) chalcogen-rich (chalcogen–chalcogen bonds and heteropolar bonds are present). For R > 1

(c) chalcogen-poor (hetero-polar bonds and metalmetal bonds are present). For R < 1Figure 2 shows the changes in R with respect to Bi ratio, illustrating that R reduces with increasing Bi content and that all the compositions are chalcogenide rich.



**Figure 2:** For  $Ge_{18}Bi_xSe_{82-x}$  chalcogenide glasses, parameter R changes with Bi concentration.

For the  $Ge_{18}Bi_xSe_{82-x}$  system, Fig. 3 shows the change of the total number of constraints  $N_c$  and crosslinking density X with Bi (at. %). It is obvious that when the amount of Bi in an alloy increase, both  $N_c$  and X increase. This demonstrates that the amount of constraints applying to the network,  $N_c$ , is balanced by the number of degrees of freedom offered from the atoms,  $N_d$ . The behavior of both the proportion of floppy mode f and the valence electron V with regard to Bi ration is illustrated in Fig. 4, which demonstrates that as the Bi content increases from 0.5 to 8 (at. %), the value of f becomes increasingly negative. This indicates that the system is becoming increasingly rigid, which coincides with a strong desire to produce glass [28]. The valence electrons for the compositions drop as the Bi content increases, as shown in Fig. 4.

#### **4.** Lone Pair Electrons' Role in Glass Formation A lone pair is a pair of valence electrons that do not

participate in forming covalent bonds with the neighbouring atoms. An increase in the number of lone pair electrons produces a decrease in the system's strain energy and the formation of glassy structures, thus according to Pauling [13]. L is computed using the formula

$$\mathbf{L} = \mathbf{V} - \mathbf{Z} \tag{8}$$

where L indicates the number of lone-pair electrons and V indicates the valance electrons. The correlation between lone pair electrons L and Bi content is represented in Figure 5. It can be seen in this diagram that when the Bi concentration in the glassy system  $Ge_{18}Bi_xSe_{82-x}$  rises, L drops. The interaction between the Bi ion and the lone pair of electrons of the bridging Se atom can be regarded as the explanation. According to Zhenhua [29], the number of lone-pair electrons in a binary system must be larger than 2.6, whereas in a ternary system it must be greater than 1.0. As shown in Fig. 5, the values of lone pair electrons in our system,  $Ge_{18}Bi_xSe_{82-x}$ , are greater than 1.0 and decrease as the Bi content increases from 0.5 to 8.0%.



Fig. 3 Variations of total number of constraints  $N_c$  and crosslinking density X with Bi content for  $Ge_{18}Bi_xSe_{82-x}$  chalcogenide glasses.



**Figure 4**: shows variations in the fraction of floppy mode available in a network f and valence electrons V for  $Ge_{18}Bi_xSe_{82-x}$ chalcogenide glasses.

The fact that the  $Ge_{18}Bi_xSe_{82-x}$  system can be formed in an amorphous glassy state is explained by the previous observations. A stable state is a system with a large number of lone-pair electrons. Flexibility is also a feature of chalcogenides containing lone-pair electrons. The atoms create an amorphous network as a result of the flexible bonds, which can occur alone or in combination with a variety of different atomic constituents.



Figure 5: Variation of Lone-pair electrons with Bi content for  $Ge_{18}Bi_xSe_{82-x}$  chalcogenide glasses.

## 5. Average Heat of Atomization (Hs) and Cohesive Energy

The average heat of atomization  $(H_s)$  is the energy required to convert one mole of element in its standard state at room temperature to gaseous state. It reflects the relative bond strengths and consequently can interpret the behavior of the semiconductor physical properties that relate to the relative bond strengths, such as the energy gap, electrical and thermal activation energy, conductivity, glass transition temperature, etc.

Pauling [13] postulated that  $H_s$  (A-B) is a sum of heats of formation  $\Delta H$  and an average of heats of atomization  $H_s^A$  and  $H_s^B$  that correspond to the average non-polar energies of the two atoms in the presence of a binary semiconductor produced from atoms A and B.

$$H_s = \Delta H + \frac{1}{2} \left( H_s^A + H_s^B \right) \tag{9}$$

 $\Delta H$  is proportional to the square of the difference between the two atoms' electro negativities,  $\chi_A$  and  $\chi_B$ , as follows:

$$\Delta H \alpha (\chi_A - \chi_B)^-$$
 (10)  
The value of  $\Delta H$  is approximately 10% of the heat of atomization and can thus be ignored. Hence,

$$H_{s} = \frac{1}{2} \left( H_{s}^{A} + H_{s}^{B} \right) \tag{11}$$

 $H_s$  is defined for a compound  $A_a B_b C_c$  as a direct measure of the cohesive energy and, consequently, average bond strength in ternary semiconductor materials, as:

$$H_{s} = \frac{\alpha H_{s}^{A} + \beta H_{s}^{B} + \gamma H_{s}^{C}}{\alpha + \beta + \beta + \gamma}$$
(12)

For Ge, Bi, and Se, the values of  $H_s$  in units of KJ/mol are 376.6, 207.1, and 227, respectively. For  $Ge_{18}Bi_xSe_{82-x}$  CHGs, the average single bond energy Hs/Z, which is a measure of cohesive energy, reduces as the Bi content increases from 0.5 to 8 at. %, as seen in Fig. 6.

#### 6. Mean Bond Energy and Glass Transition Temperature

The glass transition temperature represents the temperature above which an amorphous matrix can attain various structural configurations and below which the matrix is frozen into a structure which can not easily change to another structure. Tg is an important parameter in studying the stability of glassy materials. Furthermore, cohesive forces must be overcome for movement of atoms in glass network. So, Tg must be related to the magnitude of these forces. Therefore, theoretical models are used to determine Tg, which assumes it to be proportional to cohesive forces,  $\langle E \rangle$  and network rigidity. The Tichy and Ticha [30–31] models follow that, for the Ge-Se-Bi glass system, the overall mean bond energy is computed as follows:

$$\langle E \rangle = E_c + E_{rm} \tag{13}$$



Fig. 6 Variation of Hs/Z Average single bond energy with Bi content for  $Ge_{18}Bi_xSe_{82-x}$  chalcogenide glasses.

where  $E_c$  denotes the overall contribution of strong heteropolar bonds to bond energy, and  $E_{rm}$  denotes the contribution of weaker bonds after the strong bonds have been maximized. If R > 1,

$$E_c = 4\alpha E_{Ge-Se} + 3\beta E_{Se-Bi}$$

$$E_{rm} = \frac{2\gamma - 4\alpha - 3\beta}{z} E_{<>} \tag{14}$$

The Tichy and Ticha relation [30–31] can be used to compute the glass transition temperature  $T_{\rm g}$  using the mean bond energy.

$$T_g = 311 \left[ < E > -0.9 \right] \tag{15}$$

The dependence of  $T_g$  on Bi content is shown in Fig. 7 revealing increasing of  $T_g$  with increasing Bi ratio.



**Figure. 7** Glass transition temperature Tg varies with Bi content in  $Ge_{18}Bi_xSe_{82-x}$ chalcogenide glasses by using Tichy and Tichaequation (15).

Another correlation of glass transition temperature  $T_g$  was clarified Lankhorst [4] as follows:

 $T_g = 3.44 \ H_s - 480 \eqno(16)$  Using the former equation, the variations of  $T_g$  with Bi content is depicted in Fig. 8.



**Figure 8**: Glass transition temperature  $T_g$  as a function of Bi at. % for  $Ge_{18}Bi_xSe_{82-x}$  chalcogenide glasses clarified by Lankhorst equation (16).

The difference in behavior of  $T_g$  with Bi content is related to the applied model. But, using Tisha model we found good agreement between calculate value and experimental value of  $T_g$ . Where,  $T_g$  found to be 115.8 and 108.4 °C for the calculated and experimental values respectively [32]. So Ticha model is more appropriate than Lankhorst model.

#### 7. CONCLUSION

When the amount of Bi in  $Ge_{18}Bi_xSe_{82-x}$  glassy alloys is increased, the whole category of physical properties changes. For each content of Bi (x: 0.5, 2, 4, 6, and 8 at. %), various physical properties such as average coordination number, lone pair electrons, mean bond energy, glass transition temperature, average heat of atomization, and cohesive energy have been calculated theoretically for Ge<sub>18</sub>Bi<sub>x</sub>Se<sub>82-x</sub>glassy alloys. It has been observed that Bi causes chain cross-linking and raises the system's average coordination number. As can be seen from the figures above, all of the parameters change linearly as the concentration of Bi rises. For every bismuth content, the values of parameter R demonstrate that our system is chalcogen rich. The glassy Ge<sub>18</sub>Bi<sub>x</sub>Se<sub>82-x</sub> system features a significant number of lone-pair electrons, making it a stable state. The results show that increasing the amount of Bi causes a rise in mean bond energy, glass transition temperature, and the parameters Nc and X, as well as a drop in Hs. The values of atomic parameters such as covalent character and ionicity demonstrate that materials for the Ge-Se-Bi glassy chalcogenides have a strong glass forming tendency. When the concentration of Bi is increased from 0.5 to 8%, the system becomes rigid and has a strong tendency to form glass.

#### 8. References

- Mott, N.F.; Davis, E.A.; Electronic Processesin Noncrystalline Materials. Second Edition, Oxford University Press, Oxford 1979.
- Saxena, M.; Gupta, S.; Agarwal, A.; Chawla, S.; A Topological Study on Physical Properties of Ge-Se-Bi Glass System for Phase Change Optical Storage. *MIT Int. J. Elect. and Communication Engg*, 2013, 3(2), 76-82.
- Saxena, M.; Kukreti, A. K.; Gupta, S.; Agarwal, M. K.; Effect of compositional variations on physical properties of Ge-Se-In glassy semiconductors. *MIT Int. J. Elect. & Comm. Engg*, (2013), *3*(1), 29-35.
- Lankhorst, M.H.R; Modelling glass transition temperatures of chalcogenide glasses. Applied to phase-change optical recording materials. J. Non Cryst. Solids, 2002, 297, 210-219.
- Saxena, M.; A crystallization study of amorphous Tex(Bi2Se3)1-x alloys with variation of the Se content. J. Phys. D Appl. Phys., 2005, 38, 460–463.
- López-Alemany, P.L.; Vázquez, J.; Villares, P.; Jiménez-Garay, R.; A Kinetic Analysis on Non-Isothermal Glass-Crystal Transformation in Glassy Semiconductors. Application to the Sb0.16As0.29Se0.55Alloy. Physica Scripta, 2001, 63 (5),409.
- Saxena, M.; Gupta, S.; Effect of Compositional Dependence on Physical Properties of Ge16Se84-xBix

Glass System for Phase Change Optical Recording. MIT Int. J. Elect. & Comm. Engg., 2012, 2(2), 63-67.

- Feinleib, J.; de Neufville, J.; Moss, S.C.; Ovshinsky, 2 S.R.; Rapid Reversible Light- Induced Crystallization Of Amorphous Semiconductors, Appl. Phys. Lett., 1971, 18, 254.
- Tiwari, S.; Saxena, A.K.; Saxena, D.; Optical characterization of Ge0.15Se0.85-xAgx (00.20) Glasses. Adv. In Appl. Science Research, 2011, 2(5), 2 77.
- Singh, A.K.; Recent advancement in metal containing multi component chalcogenide glasses. Opto- 2 Electronics Review, 2012, 20(3), 226-238.
- Saxena, M.; Gupta, S.; A consistent approach towards bi doping mechanism in quaternary Ge-Bi-Se-Te chalcogenide glasses. World Research Journal of 25. Engineering and Technology, 2013, 2 (1), 26 – 29.
- 12. Saxena, M.; Effect of age on thermal characterization of Bi-Se-Te glasses. World Research Journal of Engineering and Technology, 2014, 3 (1), 41–44.
- 13. Pauling, L.; The Nature of Chemical Bonds. Cornell University Press, New York, 1960.
- Saxena, M.; Kukreti, A. K.; Gupta, S.; Agarwal, M. K.; Rastogi, N.; Effect of compositional dependence on Physical Properties of Ge22Se78-xInx Glass System. Archives of Applied Science Research, (2012), 4(2), 994.
- 15. Lucovsky, G.; Geils, R.H.; Keezer, R.C.; The Structure of Non-Crystalline Materials. Edited by P.H. Taylor and Francis, London, 1977, 127.
- 16. Lucovsky, G.; de Neufville, J.P.; Galeener, F.L.; Study of the optic modes of Ge0. 30S0.70 glass by infrared and Raman spectroscopy. Physics Review B, 1974, 45, 1591.
- 17. Phillips, J.C.; Topology of covalent non-crystalline solids, 1. Short-range order in chalcogenide alloys and a-Si (Ge). J. Non Cryst. Solids, 1979, 34, 153.
- Phillips, J.C.; Thorpe, M.F.; Constraint Theory, Vector Percolation and Glass Formation. Solid State Comm., 1985, 53, 699-702.
- 19. Thrope, M.F.; Continuous Deformationsin random networks. J. Non Cryst. Solids, 1983, 57, 355-370.
- 20. Fayek, S. A., Maged, A. F., & Balboul, M. R., Optical and electrical properties of vacuum evaporated In

doped Se amorphous thin films. Vacuum, 53(3-4), 1999, 447-450.

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- 21. Tanaka, K.; Structural phase transitions in chalcogenide glass. Phys. Rev. B, 1989, 39, 1270.
- Sharma, P.; Katyal, S.C.; Effect of Tellurium Addition on the Physical Properties of Germanium Selenide Glassy Semiconductors. Physica B: Physics of Condensed Matter, 2008, 403, 3667.
- 23. Saffarini, G.; Atomic Density versus Average Coordination Number in Ge–In–Se Glasses. Phys. Stat. Solidi (b), 1999, 213, 261.
- 24. Sayed, El.; Farag, M.; Sallam, M.M.; Composition dependence of the grain size, activation energy and coordination number in Ge40-xInxSe60 ( $10 \le x \le 40$  at. %) thin films. Egypt J. Solids, 2007, 30(1), 1-11.
  - . Saxena, M.; Gupta, S.; An Influence of Composition on Physical Parameters of Ge-Se-Bi Glassy Chalcogenides. MIT International Journal of Electronics and Communication Engineering, January 2015, 5(1), 14–18.
- 26. Tichy, L.; Ticha, H.; On theChemicalThreshold inChalcogenide Glasses. Mater. Lett., 1994, 21, 313.
- 27. Tichy, L.; Ticha, H.; Covalent bond approach to the glass transition temperature of chalcogenide glasses. J. Non Cryst. Solids, 1995, 189, 141.
- Wakkad, M. M.; Shokr, E.K.; Mohamed, S. H.; Optical and calorimetric studies of Ge-Sb-Se glasses. J. Non Crystalline Solids, 2000, 265(1), 157-166.
- 29. Zhenhua, L.; Chemical bond approach to the chalcogenide glass forming tendency. J. Non-Crystalline Solids, 1991, 127, 298.
- 30. Tichy, L.; Ticha, H.; On theChemicalThreshold inChalcogenide Glasses. Mater. Lett., 1994, 21, 313.
- Tichy, L.; Ticha, H.; Covalent bond approach to the glass transition temperature of chalcogenide glasses. J. Non Cryst. Solids, 1995, 189, 141.
- 32. Hakeem, A. A.; Abd El-Raheem, M. M.; Wakkad, M. M.; Mohamed, H. F.; Ali, H. M.; Mohamed, S. K.; Diab, A. K.; Modeling of thermal studies on melt quenched Ge18Bi4Se78 chalcogenide. *Physica Scripta*, (2021), 96(12), 125727.