

RESEARCH ARTICLE

THEORETICALLY PREDICTED DEVIATION IN PHYSICAL PROPERTIES OF GE-BI-S CHALCOGENIDE ALLOYS WITH COMPOSITIONAL VARIATIONS

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Abstract

Chalcogenide glasses (ChGs) semiconductors have several useful properties, especially in their technical applications. The present work explains the compositional dependence of many physical properties of $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ ($x = 0, 10, 20, 30, 35$ and 45 at. %). Increasing Ge content reduces the fraction of floppy modes, the lone pair electrons, the stoichiometric deviation, and the heat of atomization, while the average coordination number ($\langle r \rangle$), constraints, density, and molar volume increased, indicating the alloys have moved from floppy to rigid mode. The average overall bond energy, electronegativity difference, band gap energy, and glass transition temperature were estimated by analyzing the bond energies and its distribution based on the bond ordered network model (CONM). It has been found that all these parameters increase with $\text{Ge} \leq 30$ at. % and decrease with the further increase of Ge content. This behavior can be explained in terms of the network chemical percolation threshold proposed by Tanaka. This threshold represents a topological phase transition from a two-dimensional structure at $r < 2.67$ to a three-dimensional structure at $r \geq 2.67$. The incorporation of Ge into the glassy Bi-S system yields interesting physical properties such as threshold and phase transition, confirming this composition's suitability for optical storage media.

Keywords: Chalcogenide alloys, Average coordination number, Constraints, The overall mean bond, Band gap energy.

1. Introduction

Chalcogenide glasses (ChGs) semiconductors have a variety of useful properties, particularly in their technological applications in IR lasers [1,2], photoreceptor waveguides for IR evanescent wave sensors, cousto-optic devices, and phase change memory, among other things [3-6]. The study of ternary alloys of Ge-Bi-S is of particular interest because of their applications as IR optical elements, antireflection layers, gratings, fibers, polarizers, and optical waveguides [7], optical recording medium for hologram storage with an unusual pattern [8], nonlinear optics, optoelectronics, and high-contrast photolithography owing to their ultra broad luminescence band [9, 10].

In covalent chalcogenide glasses, it has been argued that some transitions exist. According to the constraints theory proposed by Phillips and Thorpe [11, 12], the value $\langle r \rangle = 2.4$ is known as the rigidity percolation threshold (RPT). At $\langle r \rangle = 2.4$, the structure becomes rigid, and stable glasses can be prepared, where at $\langle r \rangle$

lower than 2.4, the structure is floppy. Above this value, the structure is over constrained, and glass formation becomes difficult. Tanaka [13, 14], proposed that the interactions in chalcogenide glasses extend to medium-range scales and are not confined to short-range scales as originally proposed by Phillips and Thorpe [11,12] and the composition dependence of various properties of chalcogenide alloys exhibit characteristic signatures at the average coordination $\langle r \rangle = 2.67$.

The Ge-Bi-S is a prototypical chalcogenide system due to their technological applications. A change in the composition of Ge-Bi-S chalcogenide glasses is accompanied by a significant change in their structural and physical properties [15-21]. The experimental studies of binary $\text{Ge}_x\text{S}(\text{Se})_{1-x}$ [22-25] and ternary of $\text{Ge}_x\text{Bi}(\text{As,Sb})_y\text{S}(\text{Se})_{1-x-y}$ [22-28] revealed that the chemical threshold occurred at the point pointed out by Tanaka, when $\langle r \rangle = 2.67$. Additionally, the measurements of the $\text{Ge}_{20}\text{Bi}_{16}\text{S}_{64}$ glass using X-ray photoelectron spectroscopy (XPS) were reported, as well as the

compositional dependence of the mean atomic volume and packing density of these glasses [29, 30].

To continue these investigations, we report and discuss the compositional dependence of the physical properties of ternary $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$, ($x=0, 10, 20, 30, 35$ and 45 at %) chalcogenide alloys in this paper. An attempt is made to pinpoint the chemical threshold in previously published experimental data. The scarcity of literature on a theoretical prediction of various physical properties of these compositions makes this work particularly interesting.

2. Theoretical analysis and Discussion

2.1. Average coordination number and constraints

The average coordination number $\langle r \rangle$ according to Ioffe and Regel is defined as the average atom's coordination

with its nearest neighbors of the constituents [31]. For the system is calculated using this expression [32]

$$\langle r \rangle = \frac{xN^{\text{Ge}} + yN^{\text{Bi}} + zN^{\text{S}}}{x + y + z} \quad (1)$$

where $x, y,$ and z are the atomic percentage of Ge, Bi and S, respectively, $N^{\text{Ge}}, N^{\text{Bi}}$ and N^{S} represent their respective coordination numbers that are given in **Table 1**. The values of average coordination numbers for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys ($x=0, 10, 20, 30, 35$ and 45 at. %) are calculated and listed in **Table 2**. The obtained values are situated in the range (2.05-2.95) as shown in **Fig. 1**.

Table 1: Some physical properties of constituent elements

Property\Element	Ge	Bi	S
Atomic number	32	83	16
Atomic weight (a.m.u)	72.64	208.98	32.065
Density (g/cm ³)	5.32	9.79	2.07
Atomic radius (pm)	125	160	100
Coordination number N_x	4	3	2
Valence electron, V	4	5	6
Melting point (K)	1211.4	544.7	388.4
Bond energy, EA-A (Kcal/mol)	37.6	25	50.9
Heat of atomization, H_s (Kcal/mol)	372	209.6	277
Electronegativity, χ	2.01	1.9	2.58
Band gap energy, E_g^{the} (eV)	0.95	0.2275	2.10

Table 2: Values of average coordination number $\langle r \rangle$, bond bending constraints N_α , bond stretching constraints N_β , total no. of constraints N_{cons} , valence electrons V, lone pair electron L_p , deviation from the stoichiometry R, fraction of floppy modes f and average heat of atomization H_s for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys

x at. %	$\langle r \rangle$	N_α	N_β	N_{cons}	V	$L_p = V - \langle r \rangle$	R	f	H_s (eV/atom)
0	2.05	1.025	1.1	2.125	5.95	3.9	12.7	2.9100	11.8
10	2.25	1.125	1.5	2.625	5.75	3.5	3.09	0.1250	12.2
20	2.45	1.225	1.9	3.125	5.55	3.1	1.57	-0.0417	12.6
30	2.65	1.325	2.3	3.625	5.35	2.7	0.96	-0.2083	13
35	2.75	1.375	2.5	3.875	5.25	2.5	0.77	-0.2916	13.2
45	2.95	1.475	2.9	4.375	5.05	2.1	0.51	-0.4580	13.6

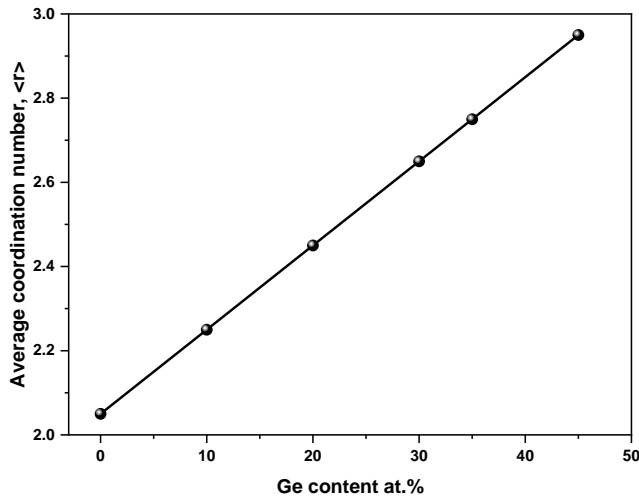


Fig. 1: Variation of average coordination number $\langle r \rangle$ as function of Ge content for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys ($x=0,10, 20, 30,35$ and 45 at. %)

For more understanding of this behavior for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys, the constraints theory proposed by Phillips and Thorpe was applied [11]. In a covalently bonded glassy network two types of constraints should be considered: bond-stretching (N_α) and bond-bending (N_β) [33]. Given the average coordination number of the network $\langle r \rangle$, both N_α and (N_β) can be easily calculated from $\langle N \rangle$: $N_\alpha = \langle r \rangle / 2$ and $(N_\beta) = 2\langle r \rangle - 3$. Thus the total number of constraints N_{con} can be expressed as [34]:

$$N_{con} = \left[\frac{5}{2} \langle r \rangle - 3 \right] \quad (2)$$

According to the constraints theory, the value $\langle r \rangle = 2.4$ is known as the rigidity percolation threshold (RPT). At $\langle r \rangle = 2.4$, the number of constraints N_{con} acting on the network are balanced by the degree of freedom N_d available for the atoms in the network, the structure becomes just rigid, and stable glasses can be prepared. In a glass with $\langle r \rangle$ lower than 2.4, the structure is floppy. Above this value, the structure is over constrained, and glass formation becomes difficult. In contrast, Tanaka introduced a different concept related to interactions in chalcogenide glasses that extends to the medium range scale rather than the short-range scale originally proposed by Phillips and Thorpe [11]. It is shown that composition dependence of various properties of chalcogenide alloys exhibit characteristic signatures at the average coordination $\langle r \rangle = 2.67$ and on the basis of topological consideration, the signatures can be connected to the formation of stable layer structures. The calculated values of N_{con} of $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ system are listed in **Table 2**. It is noted that the N_{con} increases with increasing Ge content and that an amorphous to crystalline transformation occurs at $\langle r \rangle \geq 2.65$, which corresponds to $x \geq 30$ at.% as evidenced later by the experimental data, which is consistent with Tanaka's proposal.

2.2. Fraction of floppy modes

The uncoordinated networks having finite fraction of zero frequency normal vibration modes termed as floppy modes in absence of weak long range forces [35]. The fraction f of zero frequency modes is given by

$$f = 2 - \frac{5}{6} \langle r \rangle \quad (3)$$

The values of f are calculated for varying composition of Ge and listed in **Table 2**. As Ge content is increased in the systems, the fraction of floppy modes goes from positive to more and more negative indicating an increase in the rigidity of the system [36].

2.3. Lone pair electrons

Zhenhua [37] introduced a simple criterion for computing the ability of a chalcogenide system to retain its vitreous state; the criterion contains the number of lone-pair electrons which is necessary for obtaining the system in its vitreous state. For a binary system the number of lone-pair electrons must be larger than 2.6 and for a ternary system it must be larger than 1. For a large number of lone-pair electrons the strain energy in a system decreases and thus structure with large numbers of lone-pair electrons favor glass formation. The number of lone pair electrons in a chalcogenide glass system can be calculated by using the relation [38]:

$$L_p = V - \langle r \rangle \quad (4)$$

where V is the valence electrons which equal to unshared lone-pair electrons and is generalized as:

$$V = \frac{xV^{Ge} + yV^{Bi} + zV^S}{x + y + z} \quad (5)$$

where x , y , and z are the atomic percentage of Ge, Bi and S, respectively, V^{Ge} , V^{Bi} and V^S represent their respective valence electrons that given in **Table 1**. The values of the average valence of the electron and lone-pair electrons of $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys are listed in **Table 2**.

Fig. 2 shows the variation of lone pair electrons L_p and valence electrons V with Ge content. It is clear that the lone pair electrons L_p and valence electrons V are decreases continuously with the increase in Ge content. This result is caused by the interaction between the Ge and the lone-pair electrons of a bridging S atom. The interaction decreases the role of lone-pair electrons in the

glass formation. The minimum value of lone pair of electrons in the present study is 2.1 leading to conclude that the system under study is a good glass former.

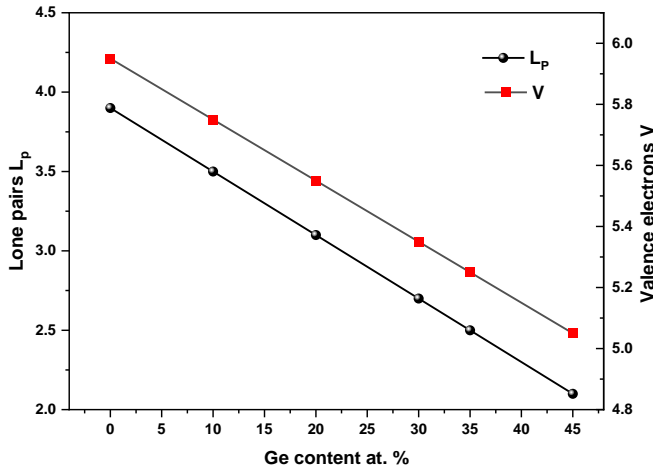


Fig. 2: Variation of lone pair electrons and valence electrons as function of Ge content for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys ($x=0,10,20,30,35$ and 45 at. %).

2.4. Deviation from the stoichiometry of composition

The deviation of stoichiometry R is expressed by the ratio of covalent bonding possibilities of chalcogen atom to that of nonchalcogen atom. Values of R were found to be larger than unity for such glasses, which indicate chalcogen-rich materials and less than unity for the glass which shows chalcogen-poor materials. Thus, for $\text{Ge}_x\text{Bi}_y\text{S}_z$, ($x+y+z=1$) glassy system, the values of R was calculated using the following known relation [39]:

$$R = \frac{zN^S}{xN^{Ge} + yN^{Bi}} \quad (6)$$

The values of R listed in **Table 2**, indicated that the $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys chalcogen-rich materials for $x < 30$ at.% and chalcogen-poor materials for $x \geq 30$ at. %.

2.5. The average heat of atomization

According to Pauling [40] the heat of atomization $H_S(A-B)$ at standard temperature and pressure of a binary semiconductor formed from atoms A and B is the sum of the heat of formation ΔH and the average of the atomization H_S^A and H_S^B that corresponds to the average non-polar bond energy of the two atoms [41]:

$$H_S(A-B) = \Delta H + \frac{1}{2}(H_S^A + H_S^B) \quad (7)$$

The first term in Eq. (7) is proportional to the square of the difference χ_A and χ_B of the two atoms. $\Delta H \propto (\chi_A - \chi_B)^2$. In order to extend this idea to ternary and higher-order semiconductor compounds, the

average heat of atomization of H_S is defined for a compound $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ as a direct measure of the cohesive energy and thus of the average bond strength as [42, 43]:

$$H_S = \frac{xH_S^{Ge} + 5H_S^{Bi} + (95-x)H_S^S}{x+y+z} \quad (8)$$

In the few materials for which it is known, the amount of heat of formation ΔH is about 10% of the heat of atomization and is therefore neglected. Hence in ternary compounds H_S as give by Eq.(8) is applicable. The results of H_S for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ glasses using the values of H_S for Ge, Bi and S elements [44,45], which given in **Table 1** are listed in **Table 4**. The result reveals that the addition of Ge leads to a change in the considered properties. The increase of Ge content leads to the increase of H_S and $\langle r \rangle$ values.

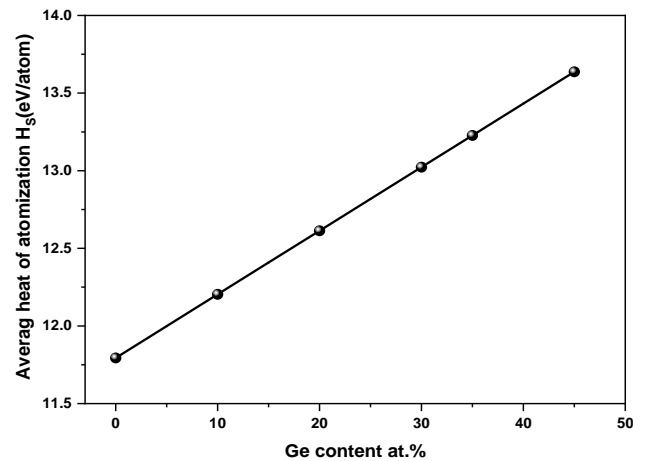


Fig. 3: Variation of average heat of atomization as function of Ge content for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys ($x=0,10,20,30,35$ and 45 at. %).

2.6. Bond energy, cohesive energy and electronegativity

The possible bonds in Ge-Bi-S system are Ge-S, Ge-Bi, Bi-S, Ge-Ge, Bi-Bi and S-S. The chemical order network model (CONM) [46] suggests that heteropolar bonds are favored over homopolar bonds and they are formed in the sequence of their decreasing bond energy. The bond energy of heteropolar bonds is determined by the method suggested by using the bond energy of homopolar bonds and the electronegativity of the atoms involved [47]. The bond energies E_{A-B} for heteronuclear bonds have been calculated by using the following relation:

$$E_{A-B} = [E_{A-A} \cdot E_{B-B}]^{\frac{1}{2}} + 30(\chi_A - \chi_B)^2 \quad (9)$$

where E_{A-A} and E_{B-B} are the homopolar bond energies of atoms A and B, respectively, and χ_A and χ_B are their respective electronegativities. Homopolar bond energies and electronegativities used to calculate heteropolar energies are tabulated in **Table 1** [48]. The heteropolar bonds formed in $Ge_xBi_5S_{95-x}$ system E_{Ge-S} , E_{Ge-Bi} and E_{Bi-S} , and their energies are in Kcal/mole, are 53.49, 31.022, and 49.54 respectively. Cohesive energy is the stabilization energy of an infinitely large cluster of material per atom and also reflects the average bond strength. Cohesive energy for the investigated samples has been calculated with the help of Chemical bond approach method [49]. According to CBA the bonds are formed in the sequence of decreasing bond energy until the available valence of atoms is satisfied and the bond energies are assumed to be additive. Therefore, the

cohesive energy was calculated by summing the bond energies over all bonds expected in the material as the following:

$$CE = \sum_i \frac{C_i E_i}{100} \quad (10)$$

where C_i and E_i represent the number of expected chemical bonds and its energy, respectively. The values of cohesive energy along with the chemical bond distribution for $Ge_xBi_5S_{95-x}$ alloys are tabulated in

Table 3 and replotted in **Fig. 4**. It can be observed that the C.E increases with increase in Ge content. The increase in C.E and band gap of the system is attributed to the increase in average bond energy of the system because of the formation of Ge–S bond on the expense of Bi–S and S–S bonds. A similar trend of increase in CE with an increase in Ge content is observed for other chalcogenide glasses [50].

Table 3: Values of cohesive energy CE, electronegativity χ , distribution of chemical bonds and theoretical band gap energy $E_g^{the.}$ for $Ge_xBi_5S_{95-x}$ glassy alloys

x at. %	Distribution of Chemical bonds (CONM)						χ	$\Delta\chi$	E_g^E (eV)	E_g^B (eV)	CE (eV/atom)
	P_{Ge-S}	P_{Bi-S}	P_{S-S}	P_{Bi-Bi}	P_{Ge-Bi}	P_{Ge-Ge}					
0		0.1463	0.8537				2.54	0.0995	0.779	0.871	2.258
10	0.3556	0.1333	0.5111				2.48	0.2933	1.429	1.52	2.524
20	0.6531	0.1224	0.2245				2.41	0.4555	1.74	1.94	2.789
30	0.9057	0.0755		0.0188			2.36	0.5676	1.87	2.187	3.01
35	0.8727				0.1091	0.0182	2.33	0.5094	1.74	2.024	3.031
45	0.6780				0.1017	0.2203	2.27	0.4107	1.46	1.699	3.057

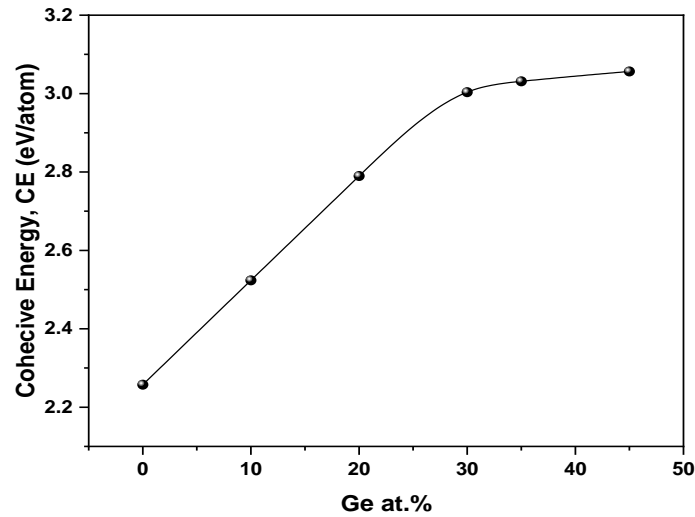


Fig. 4: Cohesive energy, CE as function of Ge content for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys ($x=0, 10, 20, 30, 35$ and 45 at. %).

The electronegativity of the system has been calculated from Sanderson's principle. According to this principle, the electronegativity of an alloy is the geometric mean of the electronegativities of the isolated atoms [51]

$$\chi \approx \left(\prod_{i=1}^p \chi_i \right)^{\frac{1}{p}} \quad (11)$$

If the molecule contains P atoms (same and/or different) and χ_i , where ($i=1, 2, 3, \dots, p$) denote their isolated atom electronegativities listed in **Table 1**. The value of χ for all the composition is tabulated in

Table 3. It has been observed that the χ increases with increase in Ge content due to the large electronegativity of Ge (2.01) as compared to Bi (1.9).

Since the glass network is viewed as one giant macromolecule, we can calculate its total electronegativity to estimate the degree of ionicity or covalency of the entire compound. In fact, ionicity or electronegativity is very important for estimating how much electrons move and how much chemical bonds are stretched and/or bent. This concept was first introduced by Pauling [40] for individual chemical bonds in molecules, and was also used by Philips [52] for crystal structures. The overall electronegativity difference $\Delta\chi$ can be estimated from the electronegativity difference between heteropolar bonds weighted by the fraction of each bond present as follows:

$$\Delta\chi = P_{A-B}|\chi_A - \chi_B| + P_{B-C}|\chi_B - \chi_C| + P_{A-C}|\chi_A - \chi_C| \quad (12)$$

where χ_A , χ_B and χ_C are the electronegativity of A, B and C elements, respectively. The obtained values of the $\Delta\chi$ are given in

Table 3.

2.7. The overall mean bond energy

According to Tichy and Ticha [39], the value of glass transition temperature should not be only 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. Since the difference in the bond energies of heteronuclear and homonuclear bonds is substantial, so chemically ordered network are expected where the number of heteronuclear bonds is maximized i.e. they are more favorably formed than homonuclear bonds. Based on this assumption the overall mean bond energy $\langle E \rangle$ is given by [53]:

$$\langle E \rangle = E_c + E_m \quad (13)$$

where E_c is the mean bond energy of average cross-linking per atoms i.e., the overall contribution towards bond energy arising from strong heteronuclear bonds [54] such that:

$$E_c = P_{rich} E_{hb}, R > 1 \text{ (chalcogen - rich)} \\ \text{or} \\ E_c = P_{poor} E_{hb}, R < 1 \text{ (chalcogen - poor)} \quad (14)$$

where P_{rich} and P_{poor} are the degrees of cross-linking per atoms for chalcogen-rich case and the chalcogen-poor one, respectively given by:

$$P_{rich} = (xN^{Ge} + yN^{Bi}) / (x + y + z) \quad (15)$$

$$P_{poor} = (xN^S) / (x + y + z)$$

The average heteronuclear bond energy E_{hb} is given by:

$$E_{hb} = \frac{xN^{Ge}E_{Ge-S} + yN^{Bi}E_{Bi-S}}{xN^{Ge} + yN^{Bi}} \quad (16)$$

where E_{Ge-S} and E_{Bi-S} are the heteropolar bond energies of Ge-S and Bi-S heteropolar bonds, respectively. The second term in Eq. (13) E_{rm} is the average bond energy per atom of the remaining matrix i.e. the contribution arising from weaker bonds that remain after the strong bonds have been maximized [55], which is defined as

$$E_{rm} = \frac{2[0.5\langle r \rangle - P_{rich}]E_{S-S}}{\langle r \rangle}, R > 1 \quad (17)$$

$$E_{rm} = \frac{2[0.5\langle r \rangle - P_{poor}]E_{\langle \rangle}}{\langle r \rangle}, R < 1$$

where E_{S-S} is the homopolar bond energy of S-S bonds (given in Table 1) and $E_{\langle \rangle}$ is the average bond energy of a 'metal-metal' bond in the chalcogen-poor region and given as:

$$E_{\langle \rangle} = (E_{Ge-Ge} + E_{Bi-Bi} + E_{Ge-Bi}) / 3 \quad (18)$$

The values of P_{rich} , P_{poor} , E_c , E_{rm} and $\langle E \rangle$ of $Ge_xBi_5S_{95-x}$ alloys are given in Table 4 and plotted in Fig. 5. It shows overall mean bond energy $\langle E \rangle$ as a function of composition, increases with increases Ge contents in region of $0 \leq x \leq 30$, and shows maximum at the chemical threshold, $\langle r \rangle \approx 2.67$ (at $x=30$ at. %) according to Tanaka proposal, then decreases with further increases Ge content. This behavior in $\langle E \rangle$ can be interpreted according to the chemical approaches which interpreted that to the energy of bonds occurred in the system. When the Ge content is increased by $x < 30$, the strong heteropolar bonds Ge-S are increased at the expense of the weak homopolar bonds S-S, leading to a reduction in system's internal energy that means an increase in $\langle E \rangle$. The Ge-Bi bonds (31.049 Kcal/mol) and Ge-Ge (37.6 Kcal/mol) are increased at the expense of the Ge-S bonds (53.49 Kcal/mol) as the Ge content increases by $x \geq 30$ as well as the homopolar bonds S-S (50.89 Kcal/mol) disappear, thereby raising the system's internal energy

and decreasing $\langle E \rangle$. This confirms a deviation in the structural and optical properties at this threshold (at $x=30$ at. %).

Table 4: Values of the parameters, R , P_r , P_p , E_{hb} , E_c , E_{rm} , $\langle E \rangle$, and H_g of $Ge_xBi_5S_{95-x}$ glassy alloys

x at. %	P_r, P_p	E_{hb} (eV/atom)	E_c (eV/atom)	E_{rm} (eV/atom)	$\langle E \rangle$ (eV/atom)
0	0.15	2.152	0.323	1.8875	2.19
10	0.55	2.277	1.252	1.13	2.36
20	0.95	2.297	2.182	0.496	2.66
30	1.3	2.30	2.9962	0.0256	3
35	1.2	2.31	2.7686	0.1725	2.91
45	1	2.311	2.311	0.437	2.725

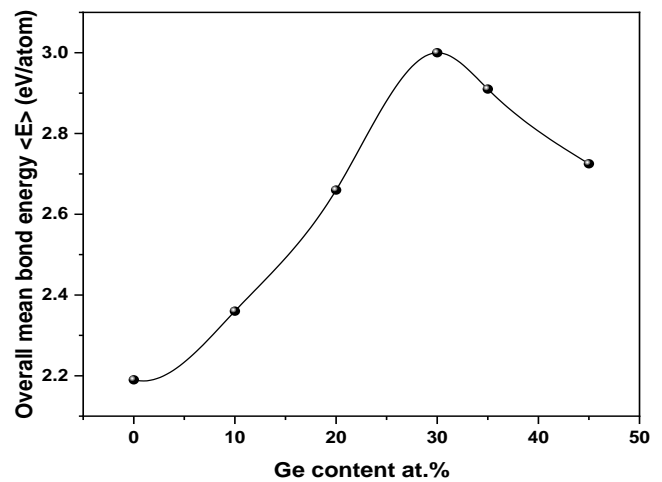


Fig. 5: Variation of overall mean bond energy as function of Ge content for $Ge_xBi_5S_{95-x}$ alloys ($x=0, 10, 20, 30, 35$ and 45 at. %).

2.8. Glass transition temperature

The glass transition temperature, T_g^{the} measurements are important to determine whether glasses could withstand the service temperature requirement for a particular application such as memory switching, inorganic photo resists, IR transmission and detection through lenses e.g. [28,56]. The path followed by the glass transition temperature, T_g^{the} measurements of the studied compositions can be traced with the knowledge of well-known values of $\langle r \rangle$ or $\langle E \rangle$ according to the proposal of several scientists:

Tanaka gives a simple empirical relationship between glass transition temperature T_g^{the} and mean coordination number $\langle r \rangle$ for glasses composed of covalent molecules held together by vander Waals forces [57]:

$$T_g^{the} = \exp(1.6\langle r \rangle - 2.3) \quad (19)$$

- i) Gibbs and Di Marzio have developed a second-order phase transition model and obtained an empirical relationship (GDM equation) between the transition temperature and the density of cross-linking agents inserted inside a system of molecular chains [56, 58]:

$$T_g^{Th} = \frac{T_o}{1 - 0.75(\langle r \rangle - 2)} \quad (20)$$

where $T_o=245$ K is the glass transition temperature of sulfur element in pure case.

The GDM empirical equation for the glass transition temperature T_g^{the} was modified in order to describe the T_g^{the} trends in chalcogenides as following [28]:

$$T_g^{the} = \frac{T_o}{1 - 0.7(\langle r \rangle - 2)} \quad (21)$$

where $T_o=245$ K is the glass transition temperature of sulfur element in pure case. This equation which we will denote by VGDM equation.

- ii) Micoulaut *et al.* performed theoretical calculations of T_g^{the} , which can be obtained using the following stochastic method [59]:

$$\left. \begin{aligned} T_g^{the} &= \frac{T_o}{1 - \beta(\langle r \rangle - 2)} \\ \beta &= 0.55, \text{ for } \langle r \rangle < 2.4 \\ \beta &= 0.72, \text{ for } \langle r \rangle \geq 2.4 \end{aligned} \right\} \quad (22)$$

- iii) On the otherwise, Tichy and Ticha calculate the T_g^{the} based on chemical bond approaches (CBA) and $\langle E \rangle$ values as follows [27,39]:

$$T_g^{the} = 311(\langle E \rangle - 0.9) \quad (23)$$

The values of T_g^{the} of $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ compositions based on by the theoretical methods mentioned are calculated and given in **Table 5**. As observed in **Fig. 6**, all results confirm that the glass transition energy increases continuously with increasing Ge content, whereas the only result calculated by the Tichy method shows an increase in transition energy as the Ge content reaches a certain level $x \leq 30$ at. % (chemical threshold) followed by a sudden decrease at $x > 30$ at. %, this attributed to the behavior in the $\langle E \rangle$ values. A similar relationship between the glass transition temperature and the overall bond energy for other chalcogenide material has been reported earlier [60].

Table 5: Values of the T_g^{the} for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ glassy alloys according to different theoretical models

x at. %	Theoretical Glass transition temperature T_g^{the} (K)				
	Tanaka	GDM	VGDM	Micoulaut	Tichy
0	265.07	254.54	253.88	251.92	402.12
10	365.03	301.53	296.96	284.05	454.99
20	502.70	369.81	357.66	362.42	546.42
30	692.29	478.04	449.54	460.52	652.47
35	812.40	560	515.78	532.60	627.59
45	1118.78	852.17	731.34	775.31	567.57

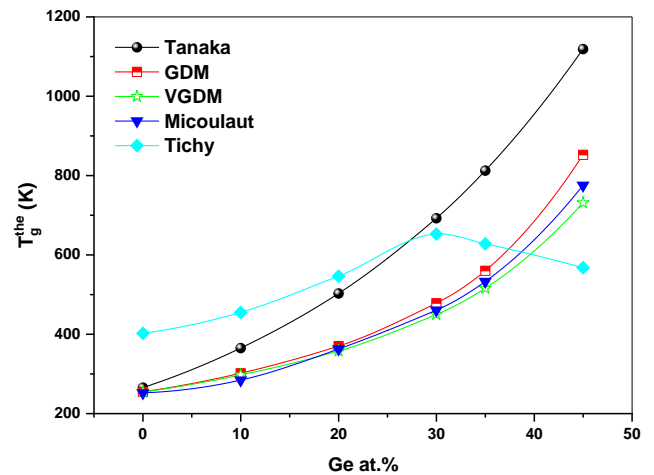


Fig. 6: Variation of theoretical glass transition temperature T_g^{the} as function of Ge content for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys ($x=0,10,20,30,35$ and 45 at. %).

2.9. Theoretical optical band gap

Neffati et al. [61] proposed a theoretical estimate of E_g^{the} using two approaches that exhibit good agreement with experimental data for most of the ternary or quaternary compounds via a correction given by the introduction of the overall electronegativity difference of the compound as follows:

$$\left. \begin{aligned} E_g^E &= \sqrt{3.72 \Delta \chi [\alpha E_g(A) + \beta E_g(B) + \gamma E_g(C)]} \\ E_g^B &= \sqrt{3.72 \Delta \chi [P_{A-B} E_g(AB) + P_{B-C} E_g(BC) + P_{A-C} E_g(AC)]} \end{aligned} \right\} \quad (24)$$

where $E_g(A)$, $E_g(B)$ and $E_g(C)$ are the band gaps energies of the individual elements listed in **Table 1** [61, 62] and α , β and γ their volume fractions. While P_{A-B} , P_{B-C} and P_{A-C} are the portions of the (A-B), (B-C) and (A-C) heteropolar bonds (listed in

Table 3). $E_{g(AB)}$, $E_{g(BC)}$, $E_{g(AC)}$ are the available band gaps for each binary system. The binary compounds expected to occur in Ge-Bi-S system are GeS_2 ($E_{g(\text{GeS})} = 2.35$ eV), GeBi , ($E_{g(\text{GeBi})} = 0.856$ eV) and Bi_2S_3 ($E_{g(\text{BiS})} = 1.76$ eV) [61, 63, 64]. The value of E_g^E and E_g^B of $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys are calculated and listed in

Table 3. Fig. 7 shows that the band gap energy increases with increasing in Ge content for $0 \leq x \leq 30$ at. %, and decreases with further increase in Ge content. Such a behavior was also observed of $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ (for $x > 30$ at. %) [65]. According to Tanaka [66], the compositional dependence of some physical properties such as the density and the band gap energy manifest extrema and/or thresholds also at $\langle r \rangle = 2.67$. He assumes that this is a signature of a topological phase transition from two-dimensional ($\langle r \rangle < 2.67$) to three-dimensional ($\langle r \rangle > 2.67$) structures. Moreover, the band gap energy is a bond-sensitive property [67]. Therefore, the overall trend in $\langle E \rangle$ and band gap seems to be influenced mainly by chemical bond arrangements. Both have the same behavior with increasing Ge content in the studied systems. Also, the electronegativity difference $\Delta\chi$ confirms the behavior of the band gap energy as seen in Fig. 7.

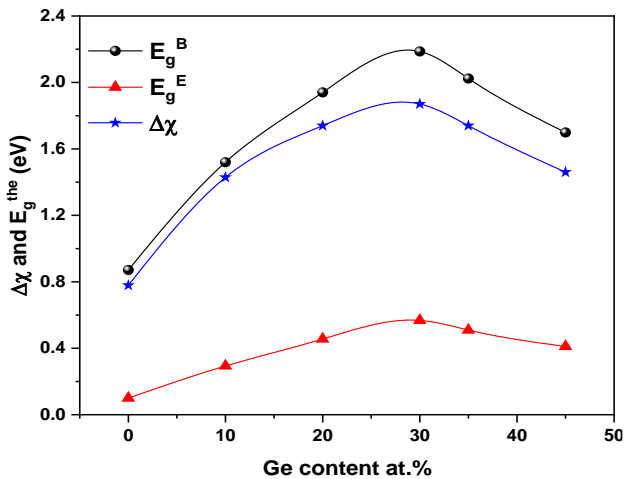


Fig. 7: Variation of the $\Delta\chi$ and E_g^{the} as function of Ge content for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys ($x=0, 10, 20, 30, 35$ and 45 at %).

2.10. Density and molar volume

The density is an important physical parameter and is related to the change in atomic weight, atomic volume of the elements constituting the system [68]. The density is a measure of the rigidity of a system; theoretically was calculated by [69]:

$$d_{\text{cal}} = \left[\sum_i \frac{x_i}{d_i} \right]^{-1} \quad (25)$$

where x_i and d_i are the fraction of weight and density of the i^{th} structural unit. Another parameter that is related to the density d_{cal} namely the molar volume V_m is also calculated using the following equation [70]:

$$V_m = \sum_i \frac{x_i \cdot M_i}{d_{\text{cal}}} \quad (26)$$

where x_i and M_i are the atomic concentration and atomic weight of the i^{th} component, respectively. Calculated d_{cal} , M_i and V_m values of $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys are reported in Table 6. The addition of Ge content to the system improves the density, as seen in Fig. 8. This increase in density may be caused by the replacement of S by Ge with more density and larger size. On the other hand, the Packing density is defined as a ratio of used space to the allocated space and can be calculated using density ($N_A d_{\text{cal}} / M$), where N_A is Avogadro's number and M is molecular weight. The values of packing density are found to decrease with the addition of Ge content up to $x=30$ at. % and then increased with the further increase in Ge content as illustrated in Fig. 9. It may be said that the change in packing density is due to a change in the atomic radius and mass of the bonds formed in the system [71].

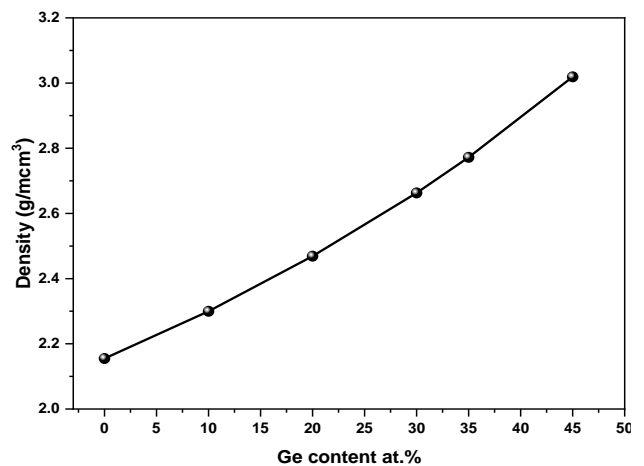


Fig. 8: Variation of density as function of Ge content for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys ($x=0, 10, 20, 30, 35$ and 45 at. %).

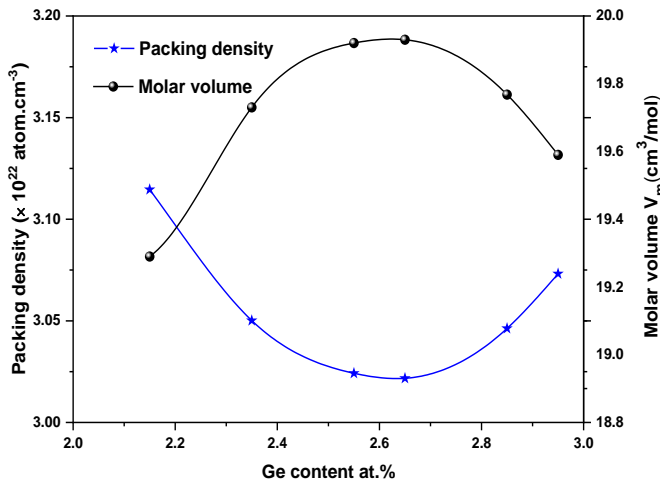


Fig. 9: Variation of packing density and molar volume as function of Ge content for $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$ alloys ($x=0,10,20,30,35$ and 45 at. %).

Table 6: Values of atomic weight M , density d_{cal} , molar volume V_m , and packing density

x at. %	$\langle r \rangle$	M_i (g/mol)	d_{cal} (g/cm ³)	V_m (cm ³ /mol)	Packing density $\times 10^{22}$ (atom.cm ⁻³)
0	2.05	40.91	2.155	18.982	3.172
10	2.25	44.97	2.3	19.54	3.08048
20	2.45	49	2.469	19.855	3.03485
30	2.65	53.08	2.663	19.93	3.02171
35	2.75	55.112	2.772	19.88	3.02942
45	2.95	59.169	3.019	19.59	3.07314

3. Conclusion

The physical properties of the $\text{Ge}_x\text{Bi}_5\text{S}_{95-x}$, ($x=0, 10, 20, 30, 35$ and 45 at %) chalcogenide glasses have been investigated. From the above theoretically analyzed parameters we can conclude that the fraction of floppy modes, the number of lone pair electrons, deviation from the stoichiometry, and the heat of atomization, reduced with the addition of Ge content, while the average coordination number $\langle r \rangle$ and the number of constraints increased, indicating that the alloy changed from a floppy to a rigid mode. A shift near $\langle r \rangle = 2.67$ predicts a percolation threshold at this coordination number corresponding at 30% Ge content. The glass transition temperature T_g^{the} , electronegativity difference $\Delta\chi$, band gap energy E_g^{the} , and average overall bond energy $\langle E \rangle$ changed at that threshold, increasing before and reducing after it was exceeded. This behavior can be attributed to the progressive replacement of the weak homopolar S-S bonds by the stronger heteropolar Ge-S bonds in the $0 \leq \text{Ge} < 30\%$ range, the glass network becomes more and more cross-linked with higher and higher mean bonding energies. As the Ge concentration rises by $x > 30$, the heteropolar bond Ge-S disappears and is replaced by the homopolar and Ge-Bi bonds, which increases the system's internal energy and causes decreases in the T_g^{the} , E_g^{the} and $\langle E \rangle$ making the current system suitable for phase change optical recording.

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مقالة بحثية

التنبؤ نظرياً بالانحراف في الخصائص الفيزيائية لسبائك Ge-Bi-S الشالكوجينية مع التغيرات التركيبية

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المُلخَص

تمتلك أشباه الموصلات المصنوعة من المواد الشالكوجينية الزجاجية (ChGs) العديد من الخصائص المفيدة، لا سيما في تطبيقاتها التقنية. يقدم هذا العمل دراسة لتأثير التركيز المتزايد لعنصر الجرمانيوم على الخواص الفيزيائية لسبائك $(\text{Ge}_x\text{Bi}_5\text{S}_{95-x})$ الشالكوجينية عند ستة نسب

مختلفة للجرمانيوم ($x=0, 10, 20, 30, 35$ and 45 at.). مع زيادة محتوى الجرمانيوم نقصت عدد الأنماط المرنة، وإلكترونات الزوج الوحيد، والانحراف عن التشبع التكافوي، وحرارة الانحلال، بينما زادت كل من متوسط عدد التناسق (r)، والقيود، والكثافة، والحجم المولي، مما يشير إلى أن السبائك قد تحولت من النمط المرن إلى النمط الجاسي. تم حساب متوسط طاقة الرابطة الكلية، و السالبيية الكهربائية، و عرض فجوة الطاقة، ودرجة حرارة الانتقال الزجاجية بتحليل طاقات الرابطة المكونة وتوزيعها بناءً على نموذج الروابط الكيميائية (CONM). وجد أن كل هذه الخواص تزداد قيمتها بزيادة محتوى الجرمانيوم إلى أن يصل تركيزه إلى 30% ثم تتناقص مع زيادة تركيز الجرمانيوم أكبر من 30%. تم تفسير هذا السلوك بناءً على عتبة الترشيح الكيميائي (حد الجساءة) للشبيكة التي اقترحها تاناكا حيث تمثل هذه العتبة انتقالاً طوبولوجياً من الهيكل ثنائي الأبعاد عند $r < 2.67$ إلى الهيكل ثلاثي الأبعاد عند $r \geq 2.67$. نتج عن دمج الجرمانيوم في نظام البزموت-الكبريت الزجاجي خصائص فيزيائية مثيرة للاهتمام مثل انتقال العتبة والتحويلات الطورية، مما يؤكد ملائمة هذا المركبات لوسائط التخزين الضوئية.

الكلمات المفتاحية: السبائك الشالكوجينية، متوسط عدد التناسق، القيود، متوسط طاقة الربط الكلية، فجوة الطاقة.

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