Influence of Bi Concentration on Major Physical Parameters of $Ge_{14}Bi_xSe_{76-x}Te_{10}$ Based Chalcogenide Glasses

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Abstract –*The investigation of some useful properties of chalcogenide glasses with respect to composition has been increased in recent years for characterization and improvement of the properties of chalcogenide glasses and the materials exhibiting particularly the switching phenomenon ever since reversible switching phenomenon in certain types of chalcogenide glasses was first reported. In the present article, the influence of varying the bismuth content on the physical parameters has been studied theoretically for Ge_{14} Bi_x Se_{76-x} Te_{10} (x = 1.5, 4.5, 7.5, 10.5, 13.5, 16.5, 19.5, 22.5 at. %) based chalcogenide glasses. The variation in glass transition temperature has been studied using two approaches, namely the Tichy – Ticha approach and Lankhorst approaches. The smooth variation of almost all parameters, studied here, indicates the suitability of this combination for phase change optical recording and finds valuable applications in rewritable optical recording.*

Keyword – Chalcogenide Glasses, Glass Transition, Heat of Atomization, Mean Bond Energy.

I. INTRODUCTION

During the last couple of decades, chalcogenide glasses generate an important class of amorphous solids because of their technological importance and potential use in optical memory switching, optoelectronic, microelectronic, holographic applications and especially their ability to transmit light in infrared region. One of the recent applications of chalcogenide alloys is in rewritable optical data recording i.e. phase change recording. The phase change recording technology is based on reversible phase transition between amorphous state and crystalline state. Normally, the primary material for phase change recording are based on Ge–Se, Ge–Te , Sb–Te etc. alloys [1, 2], but search for better material combinations still continues due to the ever demanding need for increased storage capacity and data recording rates.

There exist various kinds of amorphous chalcogenides. These may be elemental, binary, ternary or even quaternary. Recently, the attention is extended over Ge-Se system as possible candidates for this type of application. The glass formation in Ge-Se based system occurs predominantly in alloys enriched with Se and containing Ge less 25 at% than. Ternary chalcogenide glasses have been broadly studied in recent past. Both, the Covalent Random Network model (CRNM) and the Chemically Ordered Network model (CONM), satisfy the general 8–N rule under the distribution of bond types in a covalent network with multi elements. Bi–Bi, Bi–Se, and Bi–Te bonds can be formed from Bi–rich glasses, so Se–rich glasses must have Bi–Se, Bi–S, and Se–Se bonds while S-rich glasses Bi–Se, Bi–S, and S–S bonds. In the present work, first a fixed amount of Tellurium (Te) has been incorporated in the Ge-Se alloy to convert it in to a chalcogen rich ternary composition. Then addition of Bismuth (Bi) fourth element is supposed to create compositional and configurational disorder in the material with respect to the ternary alloys converting it into quaternary alloys. It has been established that physical parameters in this system are highly composition dependent [3, 4].

Recently, various researchers have synchronized ternary selenide glasses based on Ge-Se system with addition of Te and have considered basic optical and physical parameters in various glass compositions. As it is well known fact that normally the binary material system has poor stability, which may even be improved by doping other elements such as Bi, Pb, Sb, Ga, As etc. The structural studies of Ge–Se–Te alloys doped by Bi with systematic compositional variation can be advantageous for gaining important insight in the structure property relationship for these compounds.

In the present work, we have incorporated Bi as well as fixed amount of Te with the Ge-Se alloy for the compositions belonging to Ge_{14} Bi_xSe_{76-x} Te_{10} (x = 1.5, 4.5, 7.5, 10.5, 13.5, 16.5, 19.5, 22.5 at. %). The addition of these elements creates a compositional and configurationally

disorder in the material with respect to the binary Ge–Se alloys. It has been established that physical parameters in this present system are highly composition dependent [5, 6]. We find it a suitable system for investigation of the variation of certain physical parameters as glass formation region extends to about 24 at. % of Bi. The variation of properties has been discussed with this present work on the basis of their compositions. This article is concerned with the theoretical prediction of some physical parameters related to composition, viz. average coordination number, mean bond energy, average heat of atomization, glass transition temperature, cohesive energy etc. for Ge_{14} Bi_xSe_{76-x} Te_{10} alloys.

II. THEORETICAL STUDIES

2.1 Electro-negativity

Several definitions of electro-negativity have been proposed by different investigators. According to Pauling, electro-negativity is the power of an atom or molecule to attract electron to it. Electro-negativity of a composition may be defined as the geometric mean of all the constituents forming a compound.

2.2 Bonding Constraints & Average Coordination Number

To consider the transitions in the light of the constraint – counting argument originally proposed by J. C. Phillips for amorphous covalent materials is very useful in the current scope of work [7]. To explain glass forming tendencies, Phillips suggested the mechanical-constraint counting algorithms. 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 average coordination number (Z) is given by calculating using standard method [8] for the composition Ge_{14} Bi_xSe_{76-x} Te_{10} as

$$Z = \frac{\alpha N_{Ge} + \beta N_{Se} + \gamma N_{Bi} + \delta N_{Te}}{\alpha + \beta + \gamma + \delta}$$

where α, β, γ and δ are the at. % of Ge, Se, Bi and Te respectively and $N_{Ge}(4)$, $N_{Se}(2)$, $N_{Bi}(3)$ and $N_{Te}(2)$ are their respective coordination number [9].

2.3 Deviation from the Stoichiometry of Composition

The parameter R that determines the deviation from stoichiometry is expressed by the ratio of content bond possibilities of chalcogen atoms to that of non-chalcogen atoms. For the present Ge_{14} Bi_xSe_{76-x} Te_{10} system, the parameter R is given by [10]

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

where α, β, γ and δ are atomic frictions of Ge, Se, Bi 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.

2.4 Mean Bond Energy

There are several properties of chalcogenide glasses, related to overall mean bond energy <E>. According to Tichy and Ticha [11, 12], the value of glass transition temperature should not only be related to connectedness of the network which is related to average coordination number, but should also be related to the quality of connections, i.e., the mean bond energy between the atoms of the network. The overall mean bond energy for the Ge_{14} Bi_xSe_{76-x} Te_{10} system is given by

$$< E >= E_c + E_{rm}$$

where E_c is overall contribution towards bond energy arising from strong heteropolar bonds and E_{rm} is contribution arising from weaker bonds that remains after the strong bonds have been maximized. For $Ge_\alpha Se_\beta Bi_\gamma Te_\delta$ system, where (α + β + γ + δ) = 1, in selenium rich systems (R>1) where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E_c = 4\alpha E_{Ge-Se} + 3\gamma E_{Bi-Se} + 2\delta E_{Se-Te}$$

and

$$E_{rm} = \left[\frac{2\beta - 4\alpha - 3\gamma - 2\delta}{Z}\right] E_{Se-Se}$$

denotes the average homopolar bonding energy.

2.5 Average Heat of Atomization

In case of ternary and higher order semiconductor materials, the average heat of atomization H_s, as proposed by Pauling, for the compounds like $Ge_\alpha Se_\beta Bi_\gamma Te_\delta$ is being considered as a direct measure of the cohesive energy and thus average bond strength, as [13, 14]

$$H_s = \frac{\alpha H_s^{Ge} + \beta H_s^{Se} + \gamma H_s^{Bi} + \delta H_s^{Te}}{\alpha + \beta + \gamma + \delta}$$

The average heat of atomization for the present composition [Ge_{14} Bi_xSe_{76-x} Te_{10}] is calculated by using the relations for H_s.

2.6 Glass Transition Temperature

To calculate the glass transition temperature, we used two famous approaches, namely the Tichy – Ticha approach and Lankhorst approaches.

An impressive correlation of mean bond energy with glass transition temperature T_g was illustrated by Tichy and Ticha [11, 12] by the relation

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

where T_g is in Kelvin and <E> is in eV/atom

According to Lankhorst approach, glass transition temperature is related to heat of atomization by an empirical relation given by [13]

$$T_g = 3.44H_s - 480$$

where T_g is in Kelvin and H_s is in KJ/mol.

2.7 Cohesive Energy and Theoretical Energy Band Gap

The cohesive energy measures the average bond strength of the glass system. By using a chemical bond approach (CBA) method, the bond energies may be assumed to be additive. The cohesive energy for Ge_{14} Bi_xSe_{76-x} Te_{10} (x = 1.5, 4.5, 7.5, 10.5, 13.5, 16.5, 19.5, 22.5 at. %) systems are calculated by summing the bond energies over all bonds expected in the system by using the relation [15]

$$CE = \sum C_i D_i$$

where C_i and D_i are the number of expected chemical bonds and energy of each bond respectively. The variation in the values of theoretical band gap (E_g) with composition can be described by the following relation [15].

$E_g = lE_g(Ge) + mE_g(Se) + nE_g(Bi) + pE_g(Te)$ where l, m, n and p are the volume fractions and E_g(Ge), E_g(Se), E_g(Bi) and E_g(Te) are the optical gaps of elements Ge, Se, Bi and Te respectively.

III. RESULTS AND DISCUSSIONS

It is well known that the elements with more than 90% covalent character are more promising for smooth glass formation. The chemical bonding related atomic parameters such as electro negativity and ionicity provides a mean for classify and understand many basic properties of materials. The electro-negativity is found to decrease from 2.421 to 2.310 with increase in concentration of Bi from 1.5 to 22.5 at % as illustrated in fig. 1.

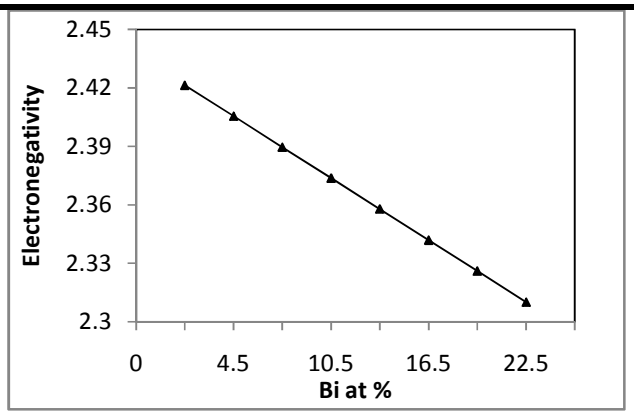

Fig. 1 Variation of electro negativity with Bi content

The values of average coordination number (Z) increase from 2.295 to 2.505 with increase in concentration of Bi from 1.5 to 22.5 at % using the calculated values of average coordination number for Ge_{14} Bi_xSe_{76-x} Te_{10} (x = 1.5, 4.5, 7.5, 10.5, 13.5, 16.5, 19.5, 22.5 at. %) system. This variation of Z with Bi content is depicted in fig. 2.

From fig. 3, it is clear that present system [Ge_{14} Bi_xSe_{76-x} Te_{10}] is more or less chalcogen rich and turning towards chalcogen poor with the increase in content of Bismuth in the system simultaneously decrease in Se content. As the alloys are chalcogen rich and so having the high energy lone pair electrons leads to qualitative different electronic densities of state. The valence band is then non bonding and does not significantly contribute to the cohesive energy. 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.

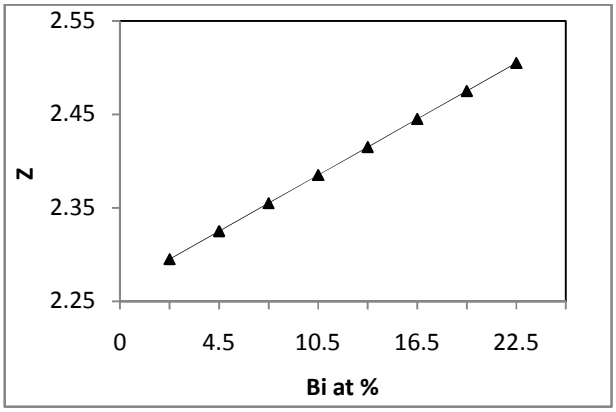

Fig. 2: Variation of Average Coordination Number with Bi content

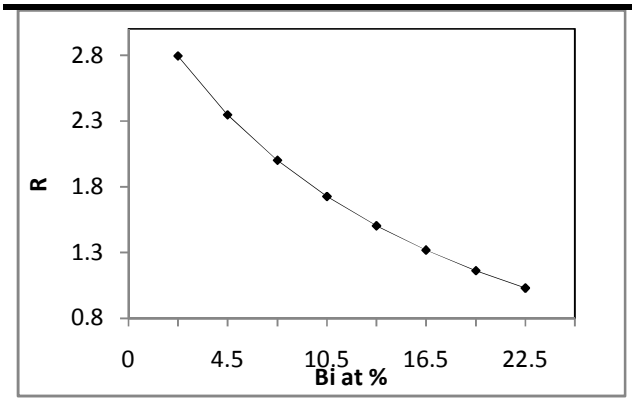

Fig. 3: Variation of parameter R with Bi content

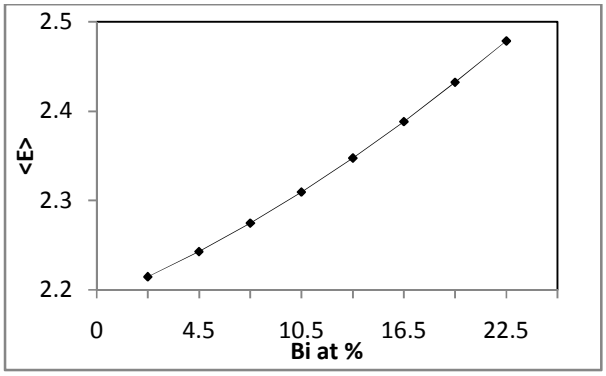

Fig. 4: Variation of overall mean bond energy with Bi content

It is clear from fig. 4 that the overall mean bond energy <E> increases from 2.215 to 2.479 with increase in concentration of Bi from 1.5 to 22.5 at % i.e. selenium rich region.

A graphical representation of average heat of atomization per single bond H_s for Ge_{14} Bi_xSe_{76-x} Te_{10} with the variation in Bi content is depicted in fig. 5. Average single bond energy H_s which is a measure of cohesive energy for Ge_{14} Bi_xSe_{76-x} Te_{10} (x = 1.5, 4.5, 7.5, 10.5, 13.5, 16.5, 19.5, 22.5 at. %) system decreases from 244.65 to 240.47 with increase in Bi from 1.5 to 22.5 at %.

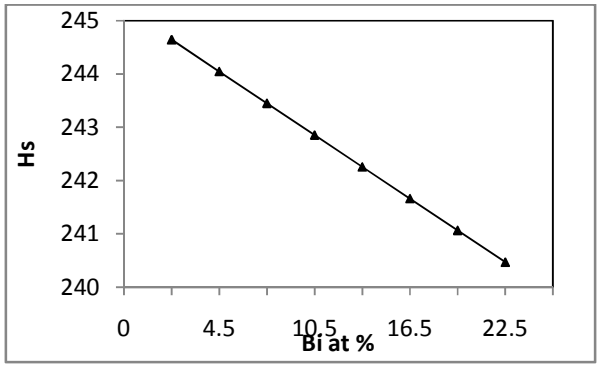

Fig. 5: Variation of average heat of atomization per single bond H_s with Bi content

As mentioned above, the glass transition temperature T_g has been calculated using two well known approaches viz.: Tichy - Ticha approach as well as Lankhorst approach. The variations of T_g with Bi content using both the relations separately are shown in fig. 6. In case of Tichy-Ticha relation, a rise in glass transition temperature from 408.84 to 491.04 with increasing the content of Bi due to rise in overall mean bond energy of the glassy system is depicted from the fig 6, while it is found to be decreasing from 361.58 to 347.205 when calculated using Lankhorst relation. It is clear from the fig. 4 & 5 that in the present combination, the overall mean bond energy <E> is increasing i.e., Se rich state, while the average heat of atomization per single bond H_s is decreasing with increase in concentration of Bi from 1.5 to 22.5 at %. This is because of the fact that the concentration of chalcogen (Se) is decreasing with the increase in concentration of Bi, and also the heat of atomization for Se is quite low as compared to Ge, which in turn results in decreasing the value of average heat of atomization per single bond H_s and hence the value of glass transition temperature T_g using Lankhorst relation.

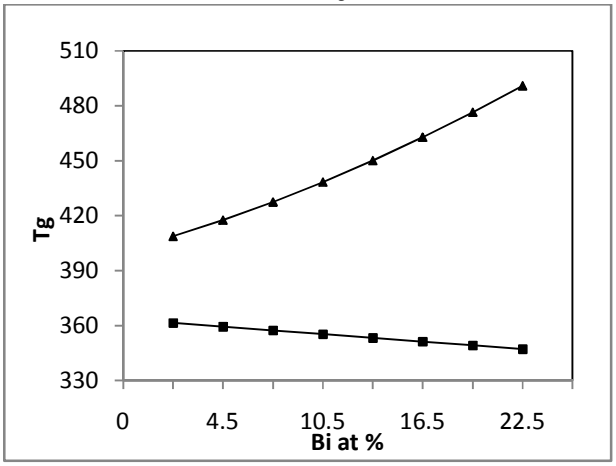

Fig. 6: Variation of glass transition temperature T_g with Bi content
[▲- Tichy Ticha relation, ■-Lankhorst relation]

The variation in cohesive energy for Ge_{14} Bi_xSe_{76-x} Te_{10} system with Bi content is shown in fig. 7 which indicates a decrease in cohesive energy from 1.988 to 1.934 with increase in concentration of Bi from 1.5 to 22.5 at %.

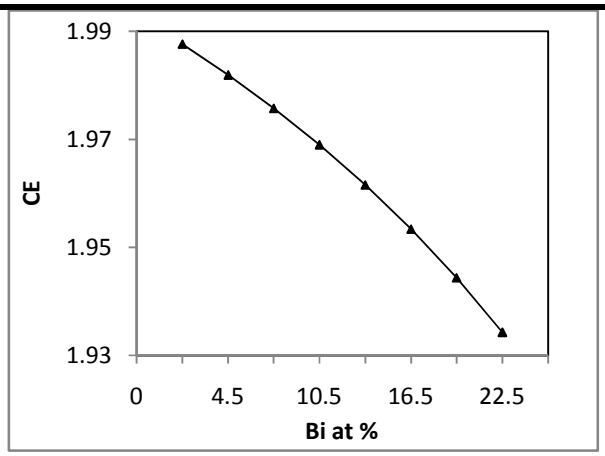

Fig. 7: Variation of cohesive energy with Bi content

The variation of theoretical band gap for $Ge_{14}Bi_xSe_{76-x}Te_{10}$ glasses with change in Bi content is illustrated in fig. 8. The values of theoretical band gap (E_g) for $Ge_{14}Bi_xSe_{76-x}Te_{10}$ decreases from 1.601 to 1.182 with increase in concentration of Bi from 1.5 to 22.5 at %, thus, making this combination useful for optical storage applications.

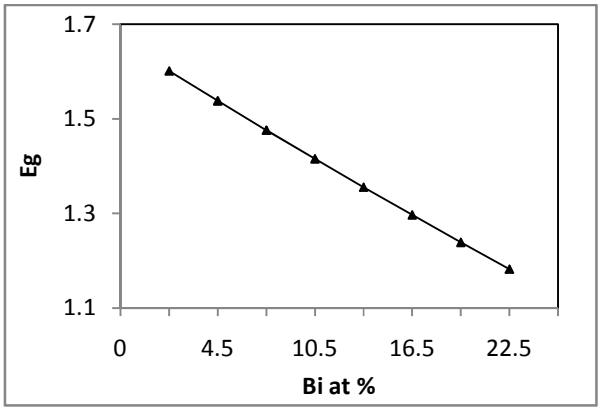

Fig. 8: Variation of Theoretical Energy Band Gap E_g with Bi content

IV. CONCLUSION

In the present work, various physical parameters viz.: average coordination number, mean bond energy, average heat of atomization, glass transition temperature, cohesive energy etc. for $Ge_{14}Bi_xSe_{76-x}Te_{10}$ alloys have been studied and analyzed with the influence of Bi content on physical and optical parameters. The addition of Bi to Ge–Se–Te glassy alloys leads to change from floppy to intermediate or rigid region. In the present work almost all the parameters were found to vary linearly with the increase in content of Bi from 1.5 to 22.5 at %. It has been found that mean bond energy <E> is proportional to glass transition temperature and both increases with the increase in content of Bi. The values of theoretical band gap (E_g) for $Ge_{14}Bi_xSe_{76-x}Te_{10}$ were found to decrease with increase in concentration of Bi from 1.5 to 22.5 at %, thus, making this combination useful for optical storage applications.

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