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Evaluation of Physical Parameters for $Ge_{10}Se_{90-x}Bi_x$ Chalcogenide Glasses

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ABSTRACT

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. In the present work, the effect on the physical properties with the variation in bismuth content has been studied theoretically for $Ge_{10}Se_{90-x}Bi_x$ *(x = 4, 8, 12, 16, 20, 24, 28 at. %) glassy alloys. Almost all the parameters, studied here, have been found to vary linearly increase in Bi content, thus making this suitable for phase change optical recording and find applications in rewritable optical recording.*

Keywords: Chalcogenide Glasses; Average Coordination Number; Lone-Pair Electrons; Cohesive Energy.

INTRODUCTION

Chalcogenide glasses form an important class of materials among amorphous semiconductors and have attracted much attention in recent past. One of the main reasons for this is the technological importance of these materials. They find potential applications in optical memory cores, switching devices, photovoltaic solar cells, infrared sensors, xerography, photoresist, optoelectronic, microelectronic, holographic applications etc. One of the recent applications of chalcogenide alloys, containing at least one of the chalcogen elements like S, Se or Te, is in rewritable optical data recording i.e. phase change recording. This technology is based on reversible phase transition between crystalline and amorphous state. Recently, a lot of attention is extended over Ge-Se system as possible candidates for above applications [1-6]. Ge–Se system is now a widely studied system and glass formation in this system occurs predominantly in alloys enriched with Se and containing 0–25 at% of Ge. The addition of third element used to create compositional and configurational disorder in the material with respect to the binary alloys. Chalcogenide glasses in Ge–Se system are used as switching, memory elements and optoelectronic devices and are interesting material for infrared optics too. It has been established that physical properties in this system are highly composition dependent [7 – 10].

A number of glassy alloys for Ge-Se, Ge-Se-Ag, Ge-Se-Te, Ge-Se-Sb, Ge-Se-In, Ge-Se-Pb, Ge-Se-As, Ge-Se-Ga have been reported on the basis of compositional dependence [11-15]. It is well known that 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. The chalcogenide glasses can exhibit carrier-type reversal when the concentration of charged additives exceeds that of valence-alternation pairs. Several researchers have studied the effect of Bi on the optical and electrical properties of chalcogenide materials. Addition of third element like Bi 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 [16-19].

In the present work, we have incorporated Bismuth in the Ge-Se alloy for the compositions belonging to $Ge_{10}Se_{90-x}Bi_x$(x = 4, 8, 12, 16, 20, 24, 28 at. %). It has been established that physical properties in this system are highly composition dependent [20, 21]. The Ge-Se-Bi glass system is of special interest as it forms glasses over a wide domain of compositions. The glass formation region in the ternary Ge-Se-Bi system extends to about 20 at % Bi and about 60-80 at % Se, with rest being Ge. It has been suggested that the system is suitable for investigation of the variation of certain physical properties. The variation of properties has been discussed on the basis of their compositions. The present work is concerned with the theoretical prediction of some physical parameters related to composition, viz. coordination number, molecular weight, lone pair electron, average heat of atomization, cohesive energy etc. for $Ge_{10}Se_{90-x}Bi_x$ alloys.

THEORETICAL STUDIES AND DISCUSSION

Bonding Constraints & Average Coordination Number

To explain glass forming tendencies, J C Phillips gave the mechanical-constraint counting algorithms [22]. According to the theory given by him, strongest covalent forces between nearest neighbours serve as Lagrangian (mechanical) constraints defining the elements of local structure (building blocks). The 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 calculated using standard method [23] for the composition $Ge_{10}Se_{90-x}Bi_{x,}$ and is given by

$$Z = \frac{xN_{Ge} + yN_{Se} + zN_{Bi}}{x + y + z}$$

where x, y and z are the at. % of Ge, Se and Bi respectively and $N_{Ge}(4)$, $N_{Se}(2)$, $N_{Bi}(3)$ are their respective coordination number [24, 25].

Fig. 1 shows values of Z increase from 2.24 to 2.48 with increase in concentration of Bi from 4 to 28 using the calculated values of average coordination number for $Ge_{10}Se_{90-x}Bi_x$ (x = 4, 8, 12, 16, 20, 24, 28 at. %) system. Fig.2 shows the variation of molecular weight M with Bi content which shows increase with increase in Bi content at. % from 4 to 28.

According to 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

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

It is clear from fig. 3 that the system becomes more and more rigid, which corresponds to a strong tendency for making glass, as values of f becomes more and more negative on increasing the Bi content.

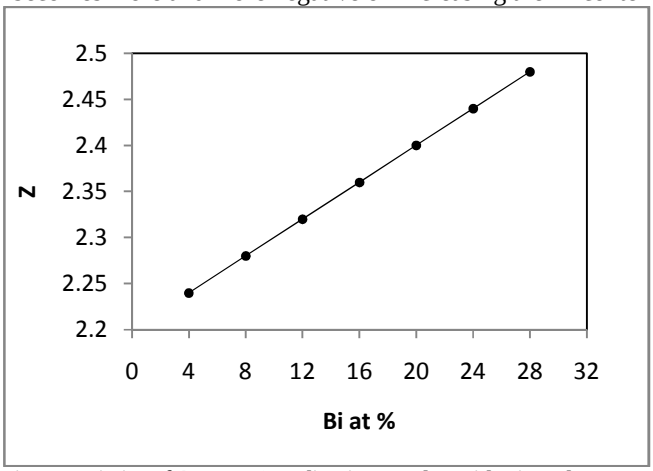

Fig. 1: Variation of Average Coordination Number with Bismuth content

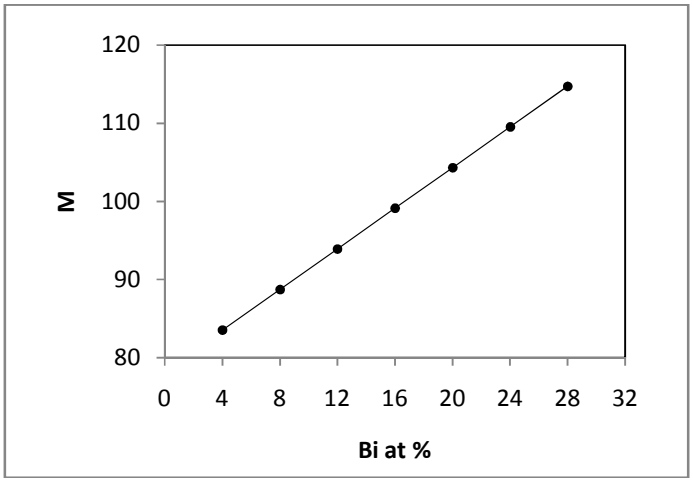

Fig. 2: Variation of Molecular weight with Bi content

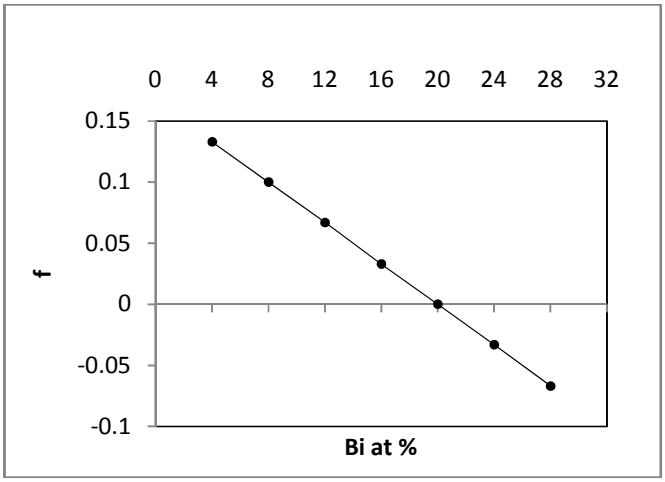

Fig. 3: Variation of fraction of floppy modes with Bi content

Role of Lone Pair Electrons

According to Pauling [27], an increase in the number of lone-pair electrons decreases the strain energy in the system and structures with large number of lone-pair electrons favours glass formation. The numbers of lone-pair electrons are calculated by using the relation [28]

$$L = V - Z$$

where L is the number of lone-pair electrons, V is the valance electrons and Z is the average coordination number. It is observed that for the glassy system $Ge_{10}Se_{90-x}Bi_x$, that on increasing the Bi content, the number of lone-pair electrons goes on decreasing. This may be due to the interaction between Bi ion and lone-pair of electrons of bridging Se atom.

Zhenhua [28] proposed a simple criterion for a binary system and a ternary system, i.e., for a binary system the number of lone-pair electrons must be greater than 2.6 while for a ternary system it must be greater than 1.0. In our system $Ge_{10}Se_{90-x}Bi_x$, the values of lone-pair of electrons are found to be greater than 1.0 and it is decreasing from 3.52 to 3.04 with the increase in Bi content from 4 to 28 at % as depicted in fig 4. So this explains the fact that the present system under investigation can be obtained in amorphous glassy state. A system with large number of lone-pair electrons constitutes a stable state. Chalcogenides with lone-pair electrons are also characterized by flexibility [29]. This flexibility of bonds causes these atoms to readily form amorphous network, either alone or with a variety of other atomic constituents.

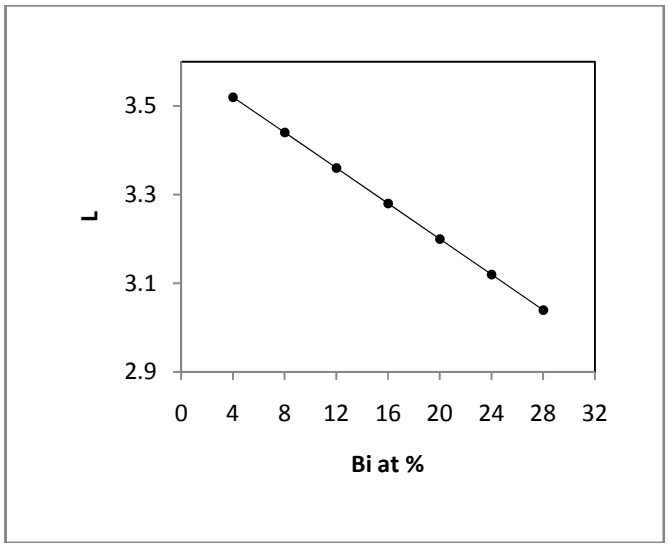

Fig. 4: Variation of Lone-pair electrons with Bi content

Deviation from the stoichiometery 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 $Ge_{10}Se_{90-x}Bi_x$ system, the parameter R is given by [30]

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

where x, y, z are atomic frictions of Ge, Se and Bi respectively.

Other parameters, such as parameter R, also play an important role in the analysis of the results. Depending on R values, the chalcogenide systems can be organized into three different categories [31].

(a) For R = 1, the system reaches the stoichiometric composition since only hetero polar bonds are present.
(b) For R > 1, the system is chalcogen-rich. There are hetero-polar bonds and chalcogen–chalcogen bonds pre-sent.
(c) For R < 1, the system is chalcogen-poor. There are only hetero-polar bonds and metal–metal bonds present.

From fig. 5, it is clear that our system is more or less chalcogen rich and turning towards chalcogen poor with the increase in content of Bismuth in the system. As the material is 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.

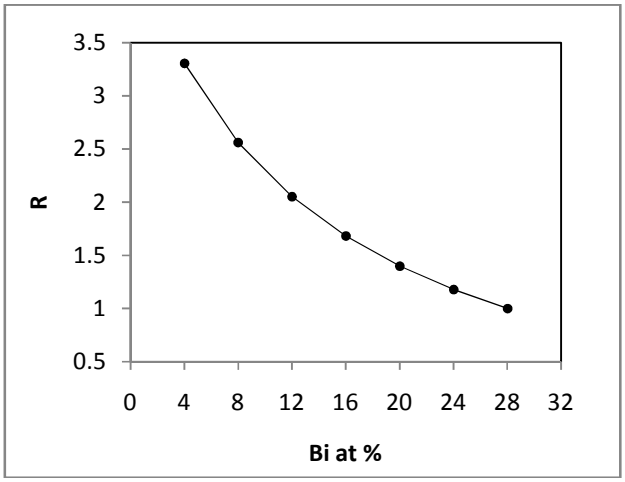

Fig. 5: Variation of parameter R with Bi content

Average Heat of Atomization

In case of ternary and higher order semiconductor materials, the average heat of atomization H_s is defined for a compound $A_a B_b C_c$ is considered as a direct measure of the cohesive energy and thus average bond strength, as [32]

$$H_s = \frac{aH_s^A + bH_s^B + cH_s^C}{a+b+c}$$

where a, b, c are the ratios of A(Ge), B(Se), and C(Bi) respectively. The values of average heat of atomization of Ge-Se-Bi ternary system is calculated by using this relation and the values of heat of atomization in the units of KJ/mol, i.e., 376.6, 227, 207.1 for Ge, Se and Bi respectively. Average single bond energy H_s/Z which is a measure of cohesive energy, decreases with increase in Bi content from 4 to 28 at % for all the this composition, resulting in increase of optical band gap. A graphical representation of average heat of atomization per single bond H_s/Z with the variation in Bi content is given in Fig. 6.

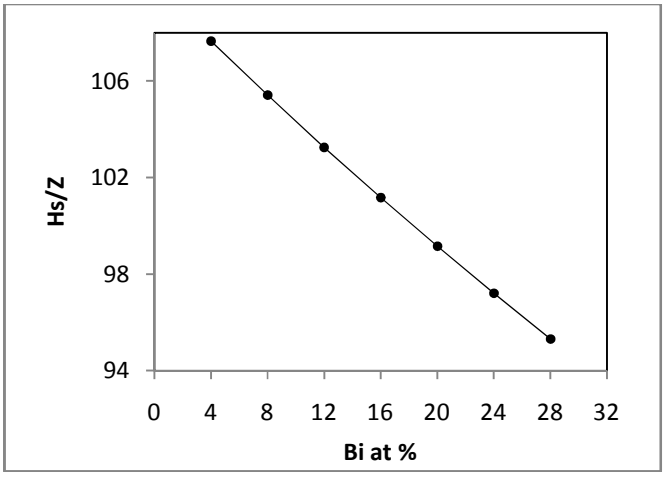

Fig. 6 : Variation of average heat of atomization with Bi content

Cohesive Energy & Band Gap

Cohesive energy measures the average bond strength of the system. By using the chemical bond approach (CBA) method, the bond energies are assumed to be additive. The cohesive energy for investigated samples has been

calculated [33]. The cohesive energy for the Ge-Se-Bi system are calculated by summing the bond energies over all bonds expected in the system by using the relation:

$$CE = \sum C_i D_i$$

where C_i and D_i are the number of expected chemical bonds and energy of each bond respectively. The variation of cohesive energy with Bi content is shown in Fig. 7 which indicates a decrease in cohesive energy with increase in Bi content from 4 to 28 at % for all the this composition.

It has been observed that the variation in the values of theoretical band gap (Eg) with composition can be described by the following relation [34]

$$Eg(ABC) = aEg(A) + bEg(B) + cEg(C)$$

where a, b, and c are the volume fractions and Eg(A), Eg(B) and Eg(C) are the optical gaps of elements A(Ge), B(Se), and C(Bi) respectively. The values of theoretical band gap (Eg) decreases with the increase in the Bi content from 4 to 28 at % [Fig. 8].

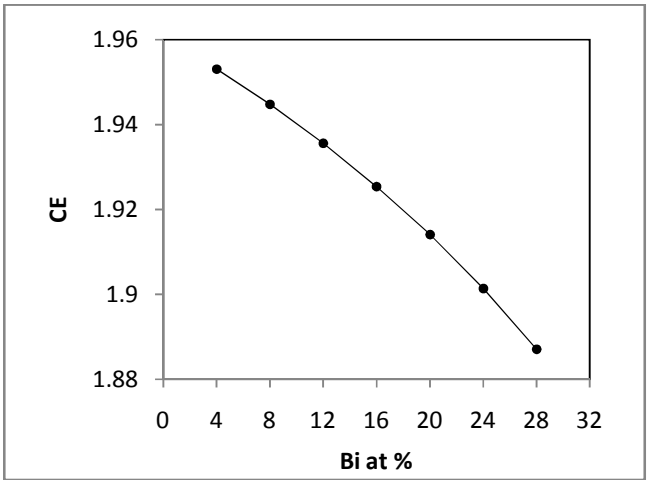

Fig. 7 : Variation of cohesive energy with Bi content

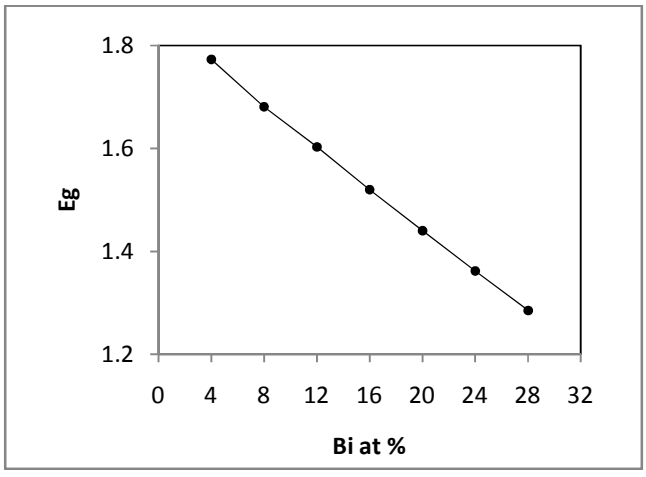

Fig.8: Variation of theoretical band gap with Bi content

CONCLUSION

The influence of Bi content on physical and optical parameters of Ge-Se glassy alloys has been investigated here. The addition of Bi to Ge-Se glassy alloys leads to change in the physical properties. It has been observed that Bi atom leads to the cross linking of chains and increases the average coordination number of the system. The values of parameter R show that our system is an ideal example of chalcogen rich materials. As it is clear from various figures given above that almost all the parameters vary linearly with the increase in content of Bi from 4 to 28 at. % in $Ge_{10}Se_{90-x}Bi_x$.

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