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Effect of bi addition on physical properties of $Ge_{12}Se_{88-x}Bi_x$ glassy semiconductors

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ABSTRACT

Reversible switching phenomenon in certain types of chalcogenide glasses 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 $Ge_{12}Se_{88-x}Bi_x$ (x=3, 6, 9, 12, 15, 18, 21 at. %) glassy alloys. It has been found that almost all the parameters, studied here, vary linearly with the increase in Bi content, thus making this suitable for phase change optical recording.

Keywords: Chalcogenide Glasses**,** Average Coordination Number, mean bond energy; Cohesive Energy.

INTRODUCTION

Chalcogenide glasses have drawn prodigious attention because of their potential use in photoresist, microelectronic, optoelectronic, holographic applications and especially their ability to transmit light in the mid to far-infrared region [1-5]. Impurity effects in chalcogenide glasses may have importance in fabricating glassy semiconductors. The infrared transparency of chalcogenide glasses allows their use in optical fibers for transmission of light generated by CO and CO_2 lasers operating in infrared region and such fibers are applied towards high-precision tools in surgery, industrial cutting and welding etc. The investigation of composition dependence of various properties of chalcogenide glasses has been increased in recent years. The physical properties of chalcogenide glasses (high refractive index, low phonon energy, high nonlinearity) also make them ideal for incorporation into lasers and other active devices. Chalcogenide glasses are very interesting materials for reversible phase change optical recording devices. Some chalcogenide materials experience thermally driven amorphous crystalline phase changes, enabling the encoding of binary information on thin films of chalcogenides, forming the basis of rewritable optical discs and non-volatile memory devices. Chalcogenide glasses are the most promising materials for a wider range of wavelengths, near and mid-infrared.

The compositional dependence studies on glassy alloys were reported for Ge-Se based alloys [6–10]. Ge atoms act as bond modifiers thus they strengthen the average bond by cross-linking the Se chain structure, thereby enhancing the properties like glass transition temperature and resistivity. Ge-Se system is a widely studied system and glass formation in this system occurs predominantly in alloys enriched with Se and containing 0-25 at % of Ge. In the present work, we have incorporated Bismuth in the Ge-Se alloy for the compositions belonging to $Ge_{12}Se_{88-x}$ Bi_x (x=3, 6, 9, 12, 15, 18, 21 at. %). The addition of third element used to create compositional and configurational disorder in the material with respect to the binary alloys [11]. It has been established that physical properties in this

system are highly composition dependent [12]. 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 60-90 at % Se, with rest being Ge. Therefore we find it a suitable system for investigation of the variation of certain physical properties. The variation of properties has been discussed on the basis of their compositions in the present paper for $Ge_{12}Se_{88-x}Bi_x$ alloys.

THEORETICAL STUDIES AND DISCUSSION

Bonding Constraints & Average Coordination Number

It may be valuable to consider the transitions in the light of the constraint – counting argument originally proposed by J. C. Phillips for amorphous covalent materials [13]. According to Phillips, the tendency of glass formation would be maximum when the number of degrees of freedom exactly equals the number of constraints.

The average coordination number (Z) was calculated using standard method [14] for the composition $Ge_{12}Se_{88-x}Bi_x$, Z 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 [15,16]. Fig 1 shows values of Z increase with increase in concentration of Bi from 3 to 21 using the calculated values of average coordination number for $Ge_{12}Se_{88-x}Bi_x$ system.

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 $Ge_{12}Se_{88-x}Bi_x$ system, the parameter R is given by

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

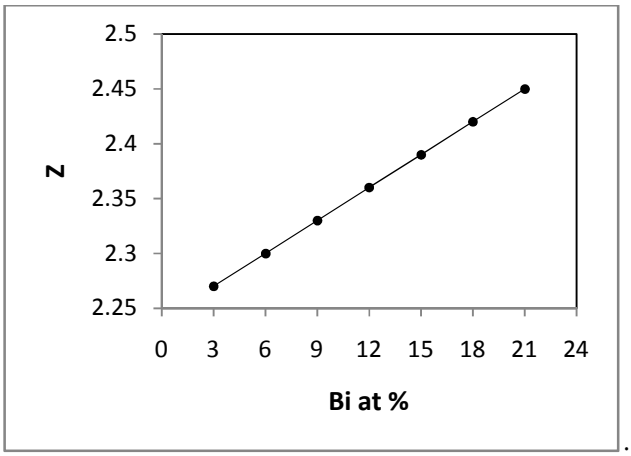

Fig. 1: Variation of Average Coordination Number with Bismuth at. %

where x, y, z are atomic frictions of Ge, Se and Bi respectively. The threshold at R=1 (the point of existence of only heteropolar bonds) marks the minimum selenium content at which a chemically ordered network is possible without metal–metal bond formation. For R>1, the system is chalcogen rich and for R<1, the system is chalcogen poor. From Fig. 2, 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 states.

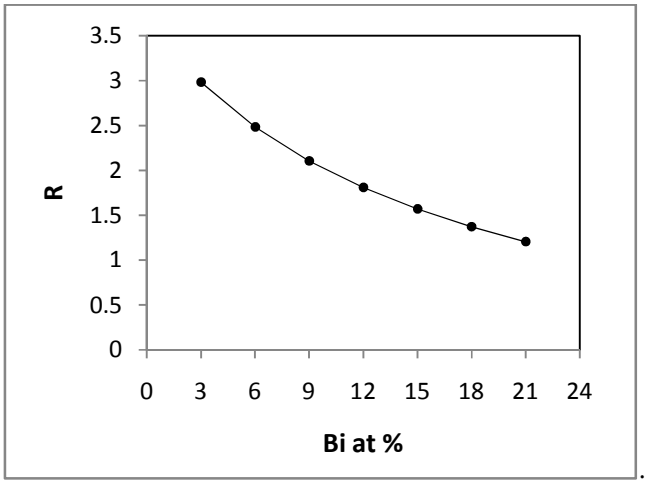

Fig. 2: Variation of parameter R with Bi content

Lone pair electrons and glass forming ability

The view point proposed by Pauling [17], increasing in the number of lone-pair electrons decreases the strain energy in a system and structures with large numbers of lone–pair electrons favors glass formation. The number of lone–pair of electrons is calculated using the relation [18]

$L = V - Z$

where L is the number of lone pair electrons, V is the valance electron and Z is the average coordination number. It is clear from the variation of lone-pair electrons that with the increase of Bi content, the number of lone–pair electrons decreases continuously in $Ge_{12}Se_{88-x}Bi_x$ system. A simple criterion was proposed by Zhenhua for a binary system and ternary system i.e. for a binary system the number of lone-pair electrons must be larger than 2.6 and for ternary system it must be larger than 1. The variation in values of lone-pair electrons for $Ge_{12}Se_{88-x}Bi_x$ system concludes that the present system under study is exhibiting good glass forming ability (Fig. 3).

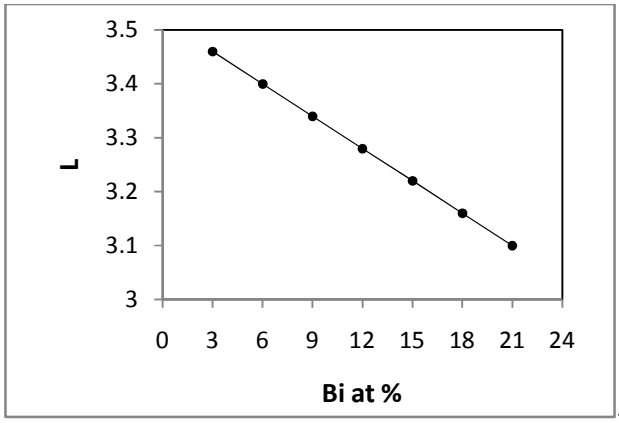

Fig. 3: Variation of Lone pair electrons with Bi content

Mean Bond Energy And Glass Transition Temperature

There are many properties of chalcogenide glasses which are related to overall mean bond energy <E>. According to Tichy and Ticha [19], the value of glass transition temperature should not only be related to connectedness of the network which is related to Z, but should also be related to the quality of connections, i.e., the mean bond energy between the atoms of the network. The overall mean bond energy for the $Ge_{12}Se_{88-x}Bi_x$ 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 $Ge_x Se_y Bi_z$ system, where (x + y + z) = 1, in selenium rich systems (R>1) where there are heteropolar bonds and chalcogen-chalcogen bonds

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

and

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

It is clear from Fig. 4 that <E> increases with increase in concentration of Bi from 3 to 21 at. % i.e. selenium rich region.

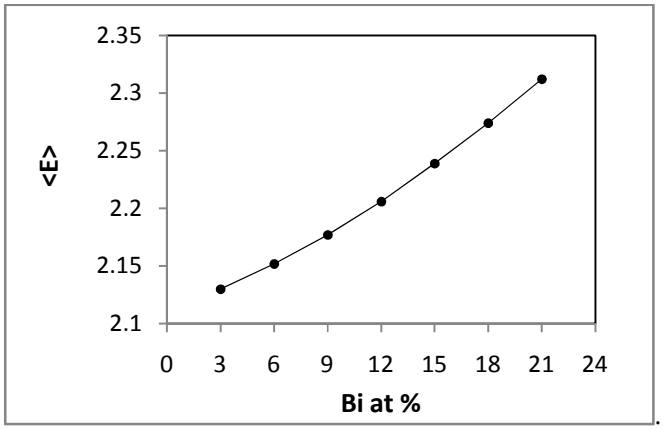

Fig. 4: Variation of overall mean bond energy with Bi content

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

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

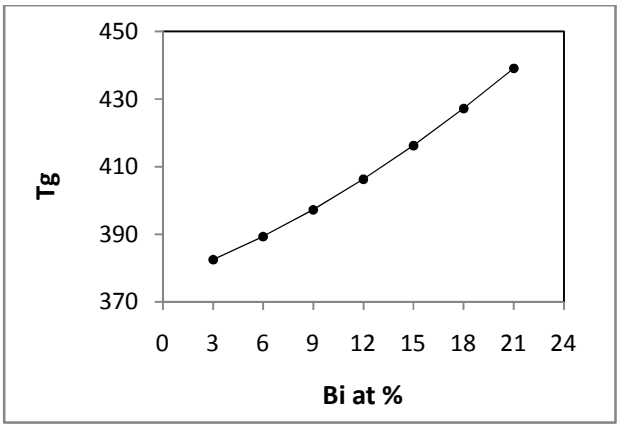

Fig. 5: Variation of glass transition temperature T_g with Bi content

The variation of T_g with Bi content is shown in Fig. 5, which is clearly depicting the rise in glass transition temperature with increasing the content of Bi due to rise in mean bond energy of the glassy system.

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 [20]

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

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 3 to 21 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.

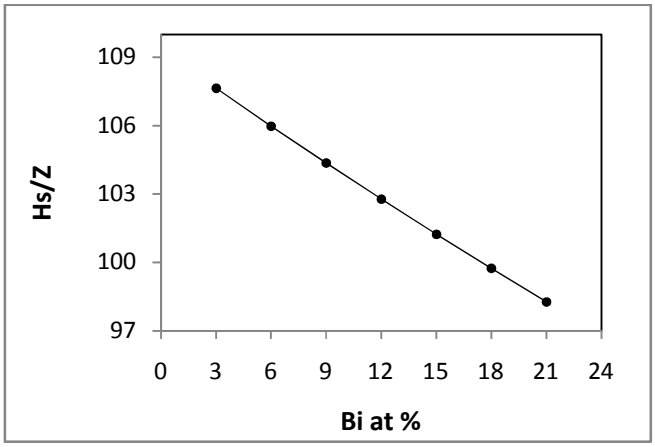

Fig 6 : Variation of average heat of atomization with Bi content

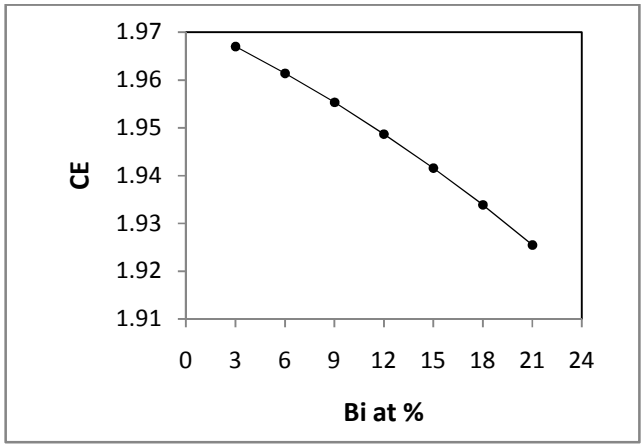

Fig. 7: Variation of cohesive energy with Bi content

Cohesive Energy

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 [21]. 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 3 to 21 at % for all the this composition.

CONCLUSION

The addition of Bi to Ge-Se glassy alloys leads to change in the physical properties. As it is clear from various figures given above that almost all the parameters vary linearly with the increase in content of Bi. 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. It has been observed that Bi atom leads to the cross linking of chains and increases the average coordination number of the system. It has been concluded from various figures that values of almost all the parameters vary with increase in concentration of Bi from 3 to 21 at. % in $Ge_{12}Se_{88-x}Bi_x$. The values of parameter R show that our system is an ideal example of chalcogen rich materials. The results here clearly depict the rise in overall mean bond energy and glass transition temperature with increasing the content of Bi from 3 to 21 at.%, making this system for memory devices applications.

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