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A Study of Some Physical Parameters of $Ge_xSb_{32-x}Te_{68}$ Glassy Semiconductor

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ABSTRACT

The effect of compositional variations on various properties of chalcogenide glasses has been increased in recent years. The effect on the physical properties viz. average coordination number, lone-pair electron Average heat of atomization, mean bond energy, glass transition temperature, etc., with the variation in Ge content has been studied theoretically in the present work for $Ge_xSb_{32-x}Te_{68}$ (x = 3, 6, 9, 12, 15, 18, 21 at. %) glassy semiconductor. The glass transition temperature and mean bond energy have been calculated by using the Tichy-Ticha approach. Almost all the parameters, studied here, except the lone-pair electron L and parameter R, were found to increase with the increase in Ge content, thus making this suitable for phase change optical recording.

Keywords: Chalcogenide Glasses; Average Coordination Number; Average heat of atomization; mean bond energy; Glass Transition Temperature.

INTRODUCTION

For the past couple of decades, chalcogenide glasses have attracted vast interest due to their extensive uses in photo resist, optoelectronics, microelectronics, holographic applications [1-4]. The major advantage of these materials is that these can transmit across a wide range of infrared electromagnetic spectrum [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. More recently, amorphous chalcogenide switching has been applied quite successfully to DVD technology where the quest for discovery of better-suited materials continues. The switching grants researches with an active area of technology as well as fundamental study [6].The bond constraint theory and rigidity theory provide a powerful framework for understanding the structure and physical properties of amorphous materials. Applications of these theories to switching in amorphous chalcogenide materials leads to developing the best composition suited for switching applications [7]. The long researches into amorphous semiconductors have now borne technologies fruit in the development of phase change memory devices that exploit rapidly crystallizing chalcogenide alloy materials in programmable memory devices [8].

The compositional dependence studies on glassy alloys were reported for various combinations like Bi-Se, Ge-Se, Ge-Se-Ag, Bi-Se-Te, Ge-Se-Te, Ge-Se-Pb, Ge-Se-Sb, Ge-Se-Ga, Ge-Se-As etc. [9 – 15]. Through a number of amorphous chalcogenide alloys are reported in the literature, amorphous Ge-Sb-Te glass has received particular attention [16, 17]. Ge atoms act as bond modifiers thus they strengthen the average bond by cross-linking the Te chain structure, thereby enhancing the properties like glass transition temperature and resistivity. Moreover, as these

materials show a continuous change of their various properties with change in their chemical composition, it is possible to investigate the correlation of the features observed in the property-composition dependence with the structural arrangement in the glass [18 – 22].

In Ge-Sb-Te system, bond energies for Sb-Sb and Sb-Te suggest that the Sb-Te bonds account for most of the backscattering signal from Sb atoms. The shorter Sb-Te distance can be attributed to an electrostatic bond between Sb and a positively charged three fold coordinated Te atom. The homopolar Ge bond data suggest that virtually all Ge atoms are bonded to one Ge atom and three Sb atoms are then interspersed evenly throughout the structure with three Te neighbours in Sb_2Te_3 arrangements. The molecular structure of Ge-Sb-Te glasses then includes three local bonding arrangements, viz: (a) Sb_2Te_3 (b) Ge_2Te_3 and (c) threefold coordinated Te atoms, the nearest neighbours of which are Sb and Ge [23].

In the present work, we have modified the composition by varying Ge content in the Ge-Sb-Te glasses for a compositions belonging to $Ge_xSb_{32-x}Te_{68}$ (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 [24, 25]. The Ge-Sb-Te glass system is of special interest as it forms glasses over a wide domain of compositions. The variation of properties has been discussed on the basis of their compositions. The present paper is concerned with the theoretical prediction of some physical parameters related to composition, viz. coordination number, average heat of atomization, mean bond energy and the glass transition temperature etc. for $Ge_xSb_{32-x}Te_{68}$ glassy alloys.

THEORETICAL STUDIES AND DISCUSSION

Bonding Constraints & Average Coordination Number

The mechanical-constraint counting algorithms to explain glass forming tendencies was first given by Phillips [4]. The well known Phillips–Thorpe approach [4, 5] is based on comparing the number of atomic degrees of freedom with the number of inter-atomic force field constraints. The bond constraint theory maintains the balance between stressed and floppy materials in terms of arrange number of constraints per atom in the inter-atomic force field space and the number of degree of freedom in real space. According to Phillips, the tendency of glass formation would be maximum when the number of degrees of freedom exactly equals the number of constraints. Materials characterized by this coordinate are so called ‘good glass formers’. Local configurations play a major role in the application of bond constraint theory.

The average coordination number (Z) was calculated using standard method [26] for the composition $Ge_xSb_{32-x}Te_{68}$, Z is given by

$$Z = \frac{xN_{Ge} + yN_{Sb} + zN_{Te}}{x + y + z}$$

where x, y and z are the at. % of Ge, Sb and Te respectively and $N_{Ge}(4)$, $N_{Sb}(3)$, $N_{Te}(2)$ are their respective coordination number [27, 28]. Fig. 1 shows values of Z increase from 2.35 to 2.53 with increase in concentration of Ge from 3 to 21 at. % using the calculated values of average coordination number for $Ge_xSb_{32-x}Te_{68}$ (x = 3, 6, 9, 12, 15, 18, 21 at. %) system.

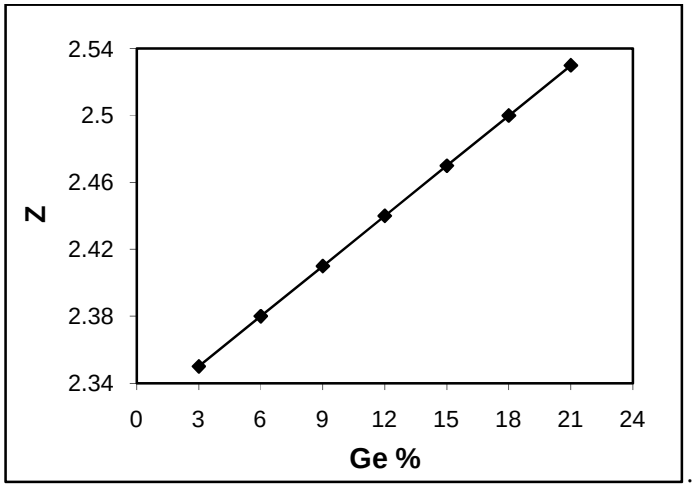

Fig. 1: Variation of Average Coordination Number with Ge at. %

Table 1

Ge	Sb	Te	Z	L	R	Hs	<E>	Tg
3	29	68	2.35	3.30	1.374	51.77	1.72	256
6	26	68	2.38	3.24	1.333	52.23	1.75	266
9	23	68	2.41	3.18	1.295	52.68	1.78	275
12	20	68	2.44	3.12	1.259	53.13	1.81	284
15	17	68	2.47	3.06	1.225	53.58	1.85	294
18	14	68	2.5	3.00	1.193	54.04	1.88	304
21	11	68	2.53	2.94	1.162	54.49	1.91	315

Lone Pair Electrons & Glass Forming Ability

As per the view point proposed by Pauling [29, 30], an increase 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. If L is the number of lone pair electrons, V is the valance electron and Z is the average coordination number, the number of lone–pair of electrons is calculated using the relation [31]

$$L = V - Z$$

The results of Lone-pair electron for $Ge_xSb_{32-x}Te_{68}$ system are tabulated in table 1.Variation of lone-pair electron with Ge content are shown in fig. 2. It is clear from the variation of lone-pair electrons that with the increase of Ge content, the number of lone–pair electrons decreases continuously in $Ge_xSb_{32-x}Te_{68}$ system. This behaviour is caused by the interaction between the Ge ion and lone-pair electrons of bridging Te atom. The role of lone-pair electrons in the glass formation decreases by this interaction. 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. This is clear from the table 1, that the values of lone-pair electrons for $Ge_xSb_{32-x}Te_{68}$ system decreases from 3.30 to 2.94 with increase in concentration of Ge from 3 to 21 at. %. From this it may be concluded that the present system under study is exhibiting good glass forming ability.

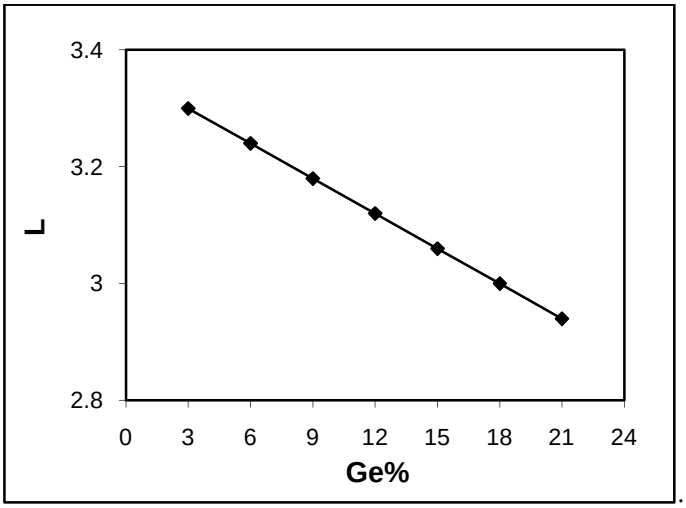

Fig. 2: Variation of Lone-pair electrons with Ge content

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 $Ge_xSb_{32-x}Te_{68}$ system, the parameter R is given by [32]

$$R = \frac{zCN(Te)}{xCN(Ge) + yCN(Sb)}$$

where x, y, z are atomic frictions of Ge, Sb, and Te respectively.

The values of R are mentioned in table 1. 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. The values of R are found to decrease from 1.374 to 1.162 for our compositions with increase in concentration of Ge from 3 to 21 at. %. From fig. 3, it is clear that our system is chalcogen rich and may turn towards chalcogen poor with the increase in content of Ge in the system.

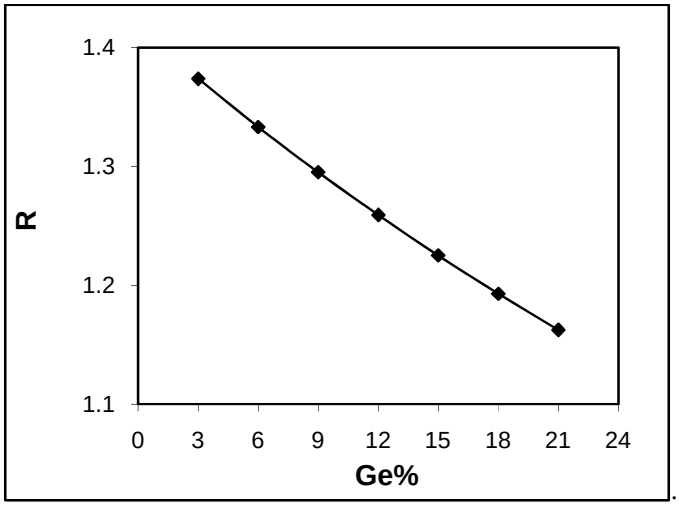

Fig. 3: Variation of parameter R with Ge content

Average Heat of Atomization

As proposed by Pauling [29, 30], the heat of atomization H_s(A-B) at standard temperature and presence of a binary semiconductor formed from atom A and B is a sum of heats of formation ΔH and average of heats of atomization H_s^A and H_s^B that correspond to the average non-polar energies of the two atoms, is given by the relation

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

The term ΔH in the above relation is proportional to the square of the difference between the electro negativities χ_A and χ_B of two atoms involved i.e.

$$\Delta H \alpha (\chi_A - \chi_B)^2$$

In few materials, the amount of heat of formation ΔH is about 10% of the heat of atomization and may therefore be neglected. Hence

$$H_s = \frac{1}{2}(H_s^A + H_s^B)$$

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

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

where a, b, c are the ratios of A(Ge), B(Sb), and C(Te) respectively. From the table 1, it is clear that average heat of atomization H_s, increases from 51.77 to 54.49 with increase in Ge content from 3 to 21 at %, resulting in increase of optical band gap. A graphical representation of average heat of atomization H_s with the variation in Ge content is shown in fig. 4.

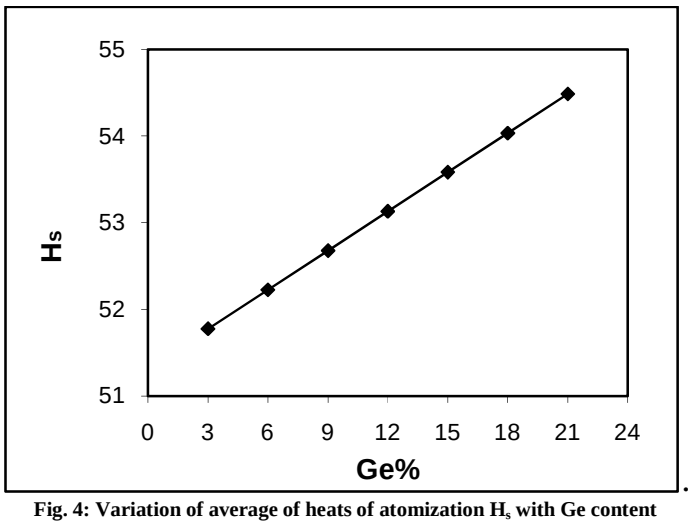

Fig. 4: Variation of average of heats of atomization H_s with Ge content

Mean Bond Energy & Glass Transition Temperature

There are many properties of chalcogenide glasses which are related to overall mean bond energy <E>. According to Tichy and Ticha [33, 34], 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 $Ge_xSb_{32-x}Te_{68}$ 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 $Ge_x Sb_y Te_z$ system, where (x + y + z) = 1, in selenium rich systems (R>1) where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E_c = 4xE_{Ge-Te} + 3zE_{Te-Sb}$$

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

It is clear from fig. 5 that <E> increases from 1.72 to 1.91 with increase in concentration of Ge from 3 to 21 at. %, i.e. in selenium rich region.

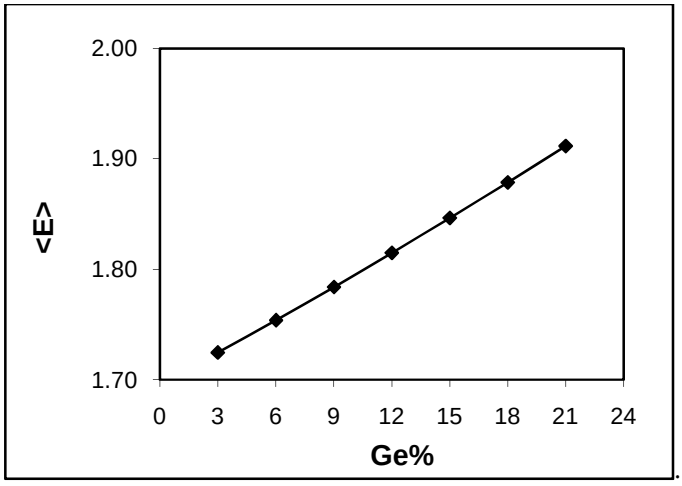

Fig. 5: Variation of overall mean bond energy with Ge content

An impressive correlation of mean bond energy with glass transition temperature T_g was illustrated by Tichy and Ticha by the relation [33, 34]

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

The variation of T_g with Ge content is shown in fig. 6, which is clearly depicting the rise in glass transition temperature with increasing the content of Ge due to rise in mean bond energy of the glassy system.

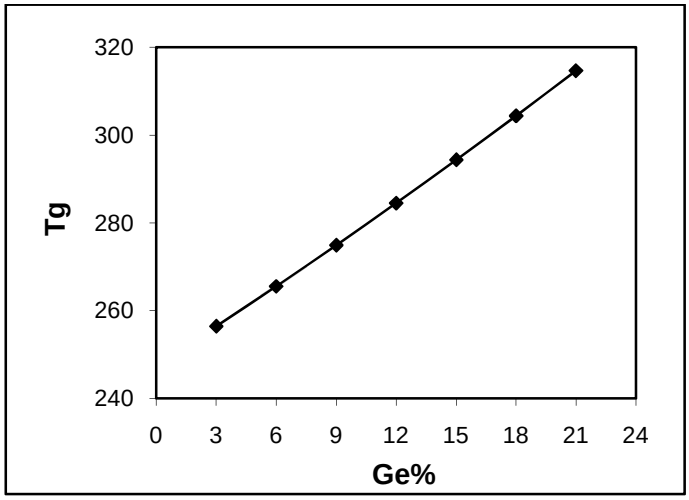

Fig. 6: Variation of glass transition temperature T_g with Ge content

CONCLUSION

It is concluded here that the variation in Ge content in Ge-Sb-Te glassy alloys leads to change in the physical properties. As it is clear from various figures and table given above that almost all the parameters, except the lone pair electron L and parameter R, increase with the increase in content of Ge in $Ge_xSb_{32-x}Te_{68}$ system. It has been found that average heat of atomization H_s, increases with increase in Ge content from 3 to 21 at %, resulting in increase of optical band gap. It is also found that mean bond energy <E> is proportional to glass transition temperature and both increases with the increase in content of Ge.

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