

Physical Evaluation and Topology of $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ Glassy Alloys

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Abstract—Chalcogenides are compounds formed predominately from one or more of the chalcogen elements; S, Se and Te. Over the past few years the significance of chalcogenide glasses has been increased and find new life in a wide range of photonic devices. Several of these glasses are easily formed by melt-quenching over a large range of compositions making them suitable model systems for the investigation of the composition dependence of their properties. This paper reported the impact of Ge content on the physical parameters of $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ ($2 \leq x \leq 14$) system. It has been found that average heat of atomization, glass transition temperature and mean bond energy increases with Ge content. An attempt has been made to explain the varying trend of various parameters with increasing Ge content.

1. INTRODUCTION

Chalcogenide glasses are based on the chalcogen elements e.g Sulphur, Selenium and Tellurium. These glasses can be formed by the addition of other elements such as Ge, As, Sb, Ga, Bi, Pb etc. Chalcogenide glasses can be doped by rare earth elements, such as Er, Nd, Pr etc and hence wide applications of active optical devices have been proposed [1]. Chalcogenide halide glasses additionally contain halogen elements and include TeX (X is a halogen) glasses [2]. Chalcogenide glasses can be regarded as 'soft semiconductor', soft because its atomic structure is flexible and viscous (due to chalcogen atoms having two fold coordination and semiconductor because it possess a band gap energy (~2eV) characteristics of semiconductor materials (1-3eV). The glass forming ability of chalcogens or pseudo-chalcogens combinations has been known for several decades but compare to oxide glasses, especially silicates, this class is just emerging from their infancy [3]. Chalcogenide glasses are generally less robust, more weakly bonded materials than oxide glasses. Structurally glass has moderate atomic connectivity, which is not as rigid as in oxide glasses and not as flexible as in organic polymers. Regarding semiconductors properties, such as electronic mobility, chalcogenide glass appear to possess intermediate properties between crystalline materials and polymers [4]. Thomos et al. studied the composition dependence of thermal properties on the Ge-Se-

Bi system [5]. It also exhibit an interesting property of reversible phase change transformation. This is very useful in optical memory devices. But in the pure state Se has disadvantages of low sensitivity and short life time. This problem can be overcome by alloying Se with some impurity atom. It has been pointed that addition of Te to Se improves the corrosion resistance [6] and lengths the crystallization of amorphous Se [7]. Therefore Se-Te based films are thought to be one of the most promising media which make use of phase change between an amorphous and crystalline state. Amorphous Se binary alloys with Te, due to their electrophotographic applications such as photo receptors in photocopying and laser printing, have been widely studied in both vacuume deposited amorphous film and vitreous bulk form in the past as reported and reviewed by number of authors [8-16]. Hanmei et al. [17] has pointed out that reduction in the band gap on the Te is attributed to lesser energy of Se-Te bonds as compare to Se-Se bonds. Kasap et al. [18] have studied Se-Te alloy with addition of phosphorus as an impurity and studied thermal and mechanical properties. The properties of chalcogenide semiconductors are usually affected by the addition of a third element. The addition of a third element creates compositional and configurational disorder in the material with respect to the binary alloys. Here we choose Ge as an additive to the Se-Te binary alloy because it produces stability and does change the optical properties of chalcogenide glassy semiconductors [19]. Ge also serves to increase the chemical and thermal durability of the glass. Ge-doped glasses have become an attractive material for fundamental research of their structure and properties [20-25]. In the present work, we have modified the composition by varying Ge content in the Ge-Se-Te glasses for a compositions belonging to $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ ($2 \leq x \leq 14$). Physical properties in this system are highly composition dependent [26, 27]. The properties of Se-Te system varies with the change in Ge content. This paper reports the theoretical prediction of some physical parameters related to composition, like coordination number (Z), average heat of atomization (H_s), mean bond

energy and the glass transition temperature (T_g) etc. for $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ glassy alloys.

2. EXPERIMENTAL WORK

2.1 Preparation of Bulk Samples

Bulk samples of $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ ($2 \leq x \leq 14$) were prepared by conventional melt quenching technique. The ampoule cleaning involves the following methods: soap solution, aqua regia (1 part of HNO_3 + 3 parts of HCl) cleaning, acetone cleaning, ultrasonic cleaning and finally these ampoules were flushed with de-ionized water and dried in oven at 100°C for 2-3 hrs. High purity (99.99%) elements with appropriate atomic percentage were weighed using electronic balance with model no. CITIZEN SCALE (CX220). These weighed materials were sealed in a quartz ampoule (length ~ 10 cm and internal diameter ~ 6mm), in a vacuum of ~ 10^{-4} mbar. The ampoules were kept in a vertical furnace and the temperature was raised to 800°C slowly ($3\text{-}4^\circ\text{C}/\text{min}$) for 48 hours. The ampoules were inverted in order to ensure homogenous mixing of the constituent elements. Finally ampoules were rapidly quenched in ice cold water and the material was separated from the quartz ampoules by dissolving the ampoules into a solution of $\text{HF}+\text{H}_2\text{O}_2$. The ingot of the material thus obtained will be characterized by using different experimental techniques.

2.2 Preparation of Thin Films

Thin films of chalcogenide glasses are very useful in terms of their application in memory storage devices like phase change optical recording. Thin films were prepared by different methods like vacuum evaporation, electron beam evaporation, flash evaporation, RF sputtering, Ion Beam evaporation, chemical vapor deposition and plasma enhanced chemical vapor deposition etc. In the present work, thin films of $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ ($2 \leq x \leq 14$) were prepared by thermal evaporation technique using HIND HIVAC (Model no: 12A4D).

3. THEORETICAL STUDIES AND DISCUSSION

3.1 Bonding Constraints (C_t) & Average Coordination Number (Z)

The mechanical-constraint counting algorithms to explain glass forming tendencies was first given by Phillips–Thorpe approach [28, 29] which is based on comparing the number of atomic degrees of freedom with the number of inter-atomic force field constraints. The bond constraint theory keep 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. Phillips explained that, 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 [30] is given by

$$Z = \frac{aN_{\text{Se}} + bN_{\text{Te}} + cN_{\text{Ge}}}{a+b+c}$$

Where a, b and c are the atomic wt. % of Se, Te and Ge respectively and the coordination number of Se, Te and Ge are N_{Se} (2), N_{Te} (2), N_{Ge} (4) resp. [31, 32]. Fig. 1 shows values of Z , increases from 2.00 to 2.28 with increase in varying content of Ge from 2 to 14 atomic wt. % using the calculated values of average coordination number for $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ ($2 \leq x \leq 14$) system.

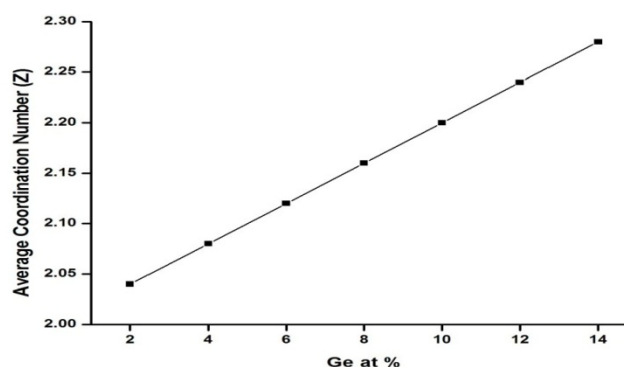


Fig. 1: Variation of Average Coordination number with Ge content.

The glassy network are influenced by mechanical constraints (C) associated with the atomic bonding and an average coordination number Z which is also related to C . There are two types of near-neighbor bonding forces in covalent solids; bond-stretching (x - forces) and bond-bending (y - forces) [28].

The number of Lagrangian bond-stretching constraints per atom is.

$$C_x = Z/2$$

And, of bond-bending constraints is:

$$C_y = 2Z - 3$$

Total numbers of constraints are:

$$C_t = C_x + C_y$$

The values of C_t along with Z for $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ are given in table 1.

Cross-linking density Y is equal to average coordination number of cross linked chain less the coordination number of the initial chain [33]

$$Y = C_t - 2$$

The value of cross linking density (Y) is given in Table 1.

Table 1

x	Z	C _x	C _y	C _t	Y
2	2.04	1.02	1.08	2.1	0.1
4	2.08	1.04	1.16	2.2	0.2
6	2.12	1.06	1.24	2.3	0.3
8	2.16	1.08	1.32	2.4	0.4
10	2.20	1.10	1.40	2.5	0.5
12	2.24	1.12	1.48	2.6	0.6
14	2.28	1.14	1.56	2.7	0.7

Lone Pair Electrons and Glass Forming Ability

According to Pauling, 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 [34, 35]. If L , V , and Z are the number of lone pair electrons, valence electrons and average coordination number respectively then the lone-pair of electrons is calculated by using the relation [36]:

$$L = V - Z$$

The results of Lone-pair electron for $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ system are tabulated in table 1. Variation of lone-pair electron with Ge content are shown in fig. 2. It clears that with the increase of Ge content, the number of lone-pair electrons, decreases continuously in this 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.

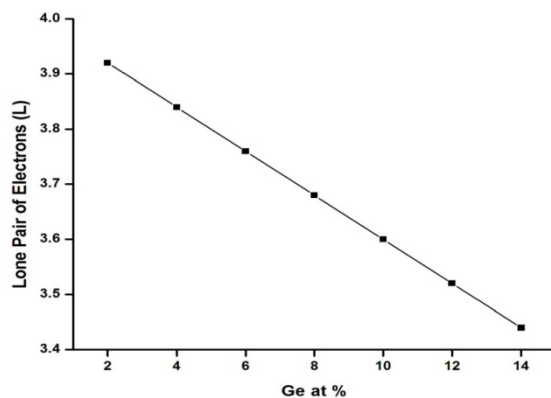


Fig. 2: Variation of Lone Pair of electron with Ge content.

For a binary system the number of lone-pair electrons must be greater than 2.6 and for ternary system it must be greater than 1. This criterion was proposed by Zhenhua. This is clear from the table 2, that the values of lone-pair electrons for $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ system decreases from 4.00 to 3.44 with increase in concentration of Ge from 2 to 14 at. %. From this it may be concluded that the present system under study is exhibiting good glass forming ability.

3.2 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 $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ system, the parameter R is given by [37]:

$$R = \frac{xN_{\text{Se}} + yN_{\text{Te}}}{zN_{\text{Ge}}}$$

Where x , y , z are atomic wt. % of Se, Te and Ge respectively. The values of R are given in table 2. The parameter R also plays an important role in the analysis of the results. Depending on R values, the chalcogenide systems can be organized into three different categories: For $R = 1$, the system reaches the stoichiometric composition, since only hetero polar bonds are present. For $R > 1$, the system is chalcogen-rich. There are hetero-polar bonds and chalcogen-chalcogen bonds present.

For $R < 1$, the system is chalcogen-poor. There are only hetero-polar bonds and metal-metal bonds present. The values of R are found to decrease from 24.50 to 3.070 for our compositions with increase in concentration of Ge from 2 to 14 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.

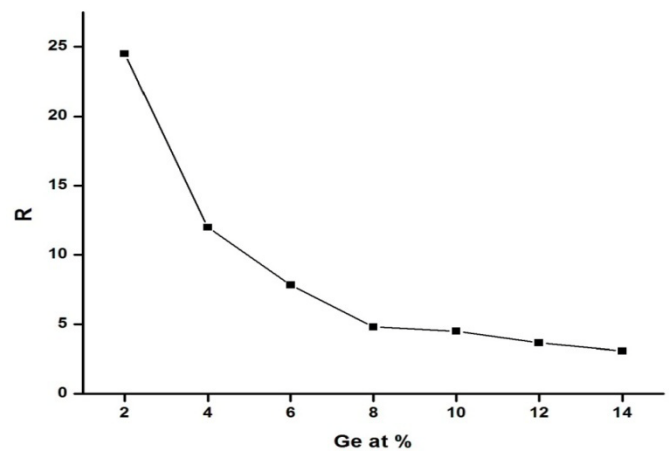


Fig. 3: Variation of Parameter R with Ge content.

Table 2

x	Z	V	L	R
2	2.04	5.96	3.92	24.5
4	2.08	5.92	3.84	12.00
6	2.12	5.88	3.76	7.833
8	2.16	5.84	3.68	4.812
10	2.20	5.80	3.60	4.500
12	2.24	5.76	3.52	3.660
14	2.28	5.72	3.44	3.070

3.3 Average Heat of Atomization

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 [34, 35]

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

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

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

In few materials, the amount of heat of formation ΔH is about 10% of the heat of atomization and may therefore be neglected. So H_s is given by:

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

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

$$H_s = \frac{xH_s^A + yH_s^B + zH_s^C}{x + y + z}$$

Where x, y, z are the ratios of A (Se), B (Te), and C (Ge) respectively. From the table 3, it is clear that average heat of atomization (H_s), increases from 221 to 239 KJmol^{-1} with increase in Ge content from 2 to 14 at %. The graphical representation of average heat of atomization H_s with the variation in Ge content is shown in fig. 4.

Table 3

x	H_s (KJmol^{-1})	$\langle E \rangle$ (eV)	T_g
2	221	1.99	338.99
4	224	2.17	394.97
6	227	2.35	450.95
8	230	2.54	510.04
10	233	2.73	569.13
12	236	2.92	628.22
14	239	3.12	690.42

3.4 Mean Bond Energy ($\langle E \rangle$) & Glass Transition Temperature (T_g)

There are many properties of chalcogenide glasses which are related to overall mean bond energy $\langle E \rangle$. According to Tichy and Ticha [38, 39], the value of glass transition temperature should not only be related to connectedness of the network which is related to Z, should also be related to the quality of connections, that is the mean bond energy between ($\langle E \rangle$) the atoms of the network. The overall mean bond energy for the $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ system is given by

$$\langle E \rangle = E_c + E_{rm}$$

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 $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ system, where $(x + y + z) = 1$, in selenium rich systems ($R > 1$) where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E_c = zN_{Ge}E_{Ge-Se} + yN_{Te}E_{Se-Te} + zN_{Ge}E_{Ge-Te}$$

$$E_{rm} = \frac{[xN_{Se} - yN_{Te} - zN_{Ge}]}{r} E_{Se-Se}$$

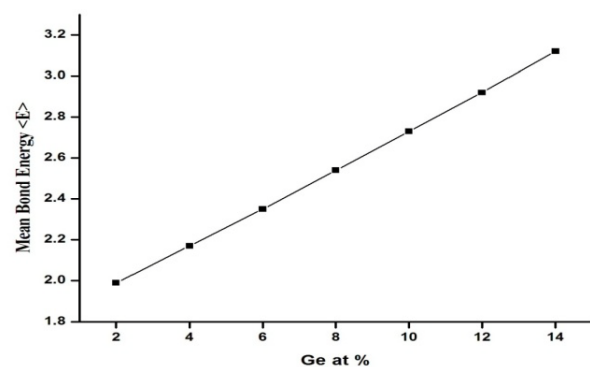


Fig. 5: Variation of Mean Bond Energy with Ge content.

It is clear from fig. 5 that $\langle E \rangle$ increases from 1.99 to 3.12 with increase in concentration of Ge from 2 to 14 at. %. That is the selenium rich region. An impressive correlation of mean bond energy with glass transition temperature T_g was illustrated by Tichy and Ticha by the relation [38, 39]

$$T_g = 311[\langle E \rangle - 0.9]$$

The variation of T_g with Ge content is shown in fig. 6, which shows that there is the rise in glass transition temperature with the increase in Ge content due to rise in mean bond energy of the glassy system.

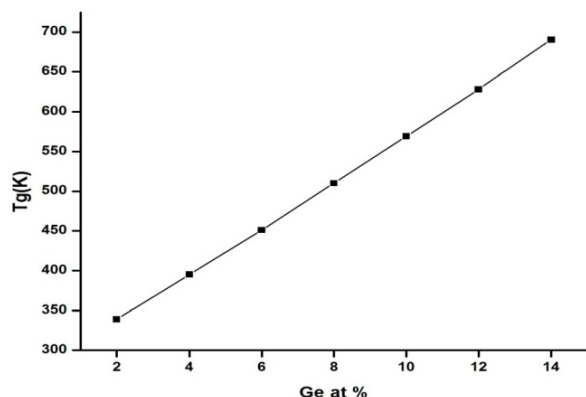


Fig. 6: Variation of Glass Transition with Ge content.

4. CONCLUSIONS

It is concluded that the variation in Ge content in Ge-Se-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 L and R, increase with the increase in content of Ge in $\text{Se}_{70-x}\text{Te}_{30}\text{Ge}_x$ system. It has been found that average heat of atomization H_g , increases with increase in Ge content. It is also found that mean bond energy $\langle E \rangle$ is proportional to glass transition temperature (T_g) and both increases with the increase in Ge content.

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