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Theoretical Predictions of Physical Parameters in Glassy $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$ Alloys

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ABSTRACT

Recently the growing interest in the investigation of the physical properties of chalcogenide glasses stems from the actual and potential technological applications of these materials in solid state devices. The physical parameters viz. average coordination number, number of constraints, cross-linking density, molecular weight, Lone-pair electron, mean bond energy, glass transition temperature etc., with the variation in Germanium content have been studied theoretically in the present article for $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$ ($x = 3, 6, 9, 12, 15, 18$ at. %) glassy alloys. Here the well established Tichy-Ticha approach has been used to study the mean bond energy and glass transition temperature.

Keywords: Chalcogenide Glasses; Average Coordination Number; Lone pair electron; mean bond energy.

INTRODUCTION

The chalcogenide glasses are recently studied by a number of researchers as they are very interesting materials for reversible phase change optical recording devices [1-3]. Ever since the reversible switching phenomenon in certain types of chalcogenide glasses was first reported [4], a lot of attention has been given to characterization and improvement of the properties of chalcogenide glasses in particular the materials exhibiting the switching phenomenon. It is well known that the phase change can be reversibly switched between the amorphous and crystalline state and find applications in rewritable optical recording [5, 6, 7].

As it is well known that amorphous solids possess no long-range order, and not many established techniques capable of identifying non-periodic configurations have been available, physics on amorphous materials is far behind that of the crystalline materials. However, compositional studies seem to be vitally important for amorphous materials. The investigation of composition dependence of various properties of chalcogenide glasses has been increased during last decade. The consideration of glassy characters using topological concepts may give fruitful ideas similar to those obtained through the unified understanding of crystalline properties based on periodic lattices.

As selenium exhibits the unique property of reversible phase transformation and also applications like photocells, xerography, memory switching etc., it seems attractive, but pure selenium has disadvantage like short life time and low photo sensitivity. To overcome this problem, some impurity atoms like Ge, Te, Bi, Ga, In, Sb, Ag etc. can be used to make alloys with Se, which may enhance sensitivity, crystallization temperature and reduce ageing effects

[8, 9, 10]. The compositional dependence studies on glassy alloys were reported for Ge-Se, Se-Te, Ge-Se-In, Ge-Se-Bi, Ge-Se-Sb, Ge-Se-As, Ge-Se-Ag, [11-18]. Addition of third element like Ge to Se-Te 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. 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 [19, 20].

In the present work, we have incorporated Ge in the Se-Te alloy for the compositions belonging to $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$ ($x = 3, 6, 9, 12, 15, 18$ 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 [21, 22]. The variation of properties has been discussed on the basis of their compositions. The present paper is concerned with the theoretical predictions of the physical parameters related to composition, viz. coordination number, constraints, cross-linking density, molecular weight, lone-pair electron, mean bond energy and glass transition temperature etc. for $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$ glassy alloys.

THEORETICAL STUDIES AND DISCUSSION

Average Coordination Number & Bonding Constraints

Phillips gave the mechanical-constraint counting algorithms to explain glass forming tendencies. 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 [23].

For the composition $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$, the average coordination number (Z) was calculated by using the standard method [24]

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

where a , b and c are the at. % of Ge, Se and Te respectively and N_{Ge} , N_{Se} , N_{Te} are their respective coordination number [24]. The calculated values of average coordination number for $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$ ($x=3$ to 18 at. %) system are listed in table 1. It is clear from fig 1 that values of Z increase from 2.06 to 2.36 with increase in concentration of Ge from 3 to 18 at. %.

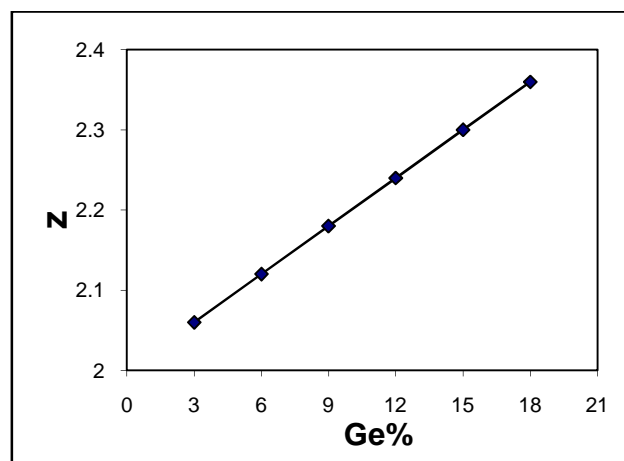


Fig. 1: Variation of Average Coordination Number with Ge at. %

The glassy network are influenced by mechanical constraints (N_c) associated with the atomic bonding and an average coordination number Z which is also related to N_c . There are two types of near-neighbor bonding forces in covalent solids; bond-stretching (α - forces) and bond-bending (β - forces) [25].

The number of Lagrangian bond-stretching constraints per atom is

And, of bond-bending constraints is

$$N_{\alpha} = Z / 2$$

The total number of constraints is given by

$$N_{\beta} = 2Z - 3$$

$$N_c = N_{\alpha} + N_{\beta}$$

The values of N_c for $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$ are given in table 1. Here N_c increase from 2.15 to 2.90 with increase in Ge at. %.

The cross-linking density(X) is equal to the average coordination number of cross linked chain less the coordination number of initial chain [26].

$$X = N_c - 2$$

The values of cross linking density (X) and molecular weight (M) are shown in table 1. From fig. 2 it is clear that the value X increases from 0.15 to 0.90 with increase in Ge content from 3 to 18 at. %. The variation of M with Ge content is given in fig. 3, which shows that M is decreasing with the increase in Ge content from 3 to 18 at. %.

Lone pair electrons and glass forming ability

Pauling proposed that 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 favours glass formation [27]. The number of lone-pair of electrons is calculated using the relation [28]

$$L = V - Z$$

where L is the number of lone pair electrons, V is the valance electron and Z is the average coordination number. The results of Lone-pair electron for $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$ system are tabulated in table 1. Variation of lone-pair electrons with Ge content are shown in fig. 4.

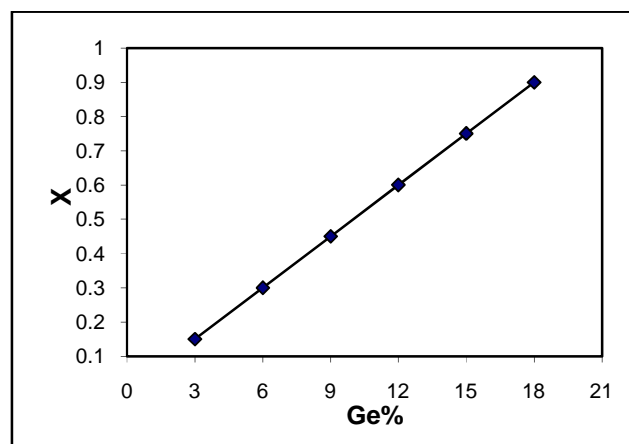


Fig. 2: Variation of cross-linking density X with Ge content

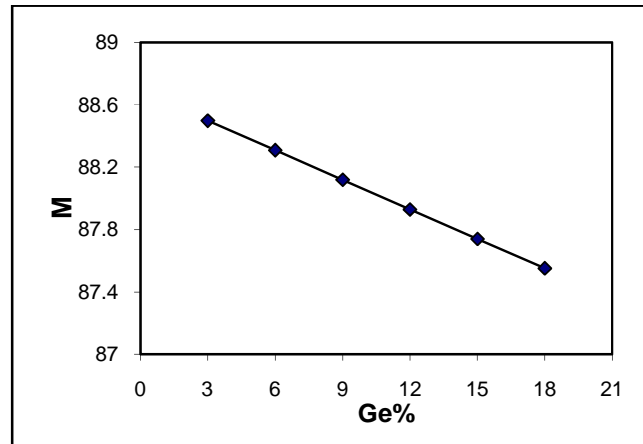


Fig. 3: Variation of Molecular weight M with Ge content

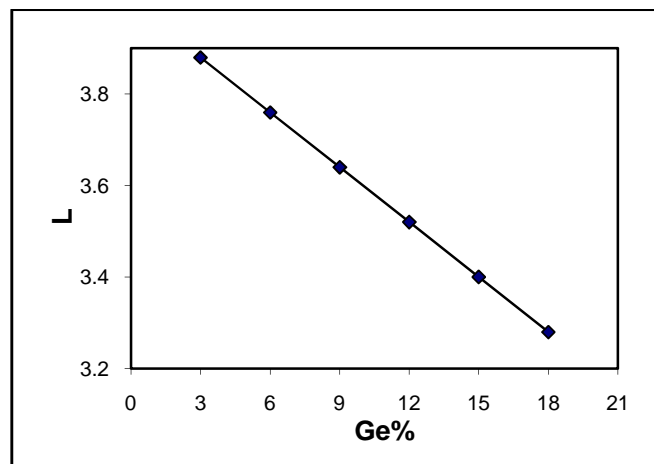


Fig. 4: Variation of Lone-pair electrons with Ge content

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 $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$ system. This behaviour is caused by the interaction between the Ge ion and lone-pair electrons of bridging Se atom. The role of lone-pair electrons in the glass formation decreases by this interaction. A simple criterion was proposed by Zhenhua [28] 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 $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$ system varies between 3.28 and 3.88, concludes that the present system, under study, is exhibiting good glass forming ability.

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 $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$ system, the parameter R is given by [29, 30]

$$R = \frac{bCN(\text{Se}) + cCN(\text{Te})}{aCN(\text{Ge})}$$

where a, b, c are atomic fractions of Ge, Se and Te respectively. The values of R are mentioned in table 1. 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:

- 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

It is clear from the values of R that our system is very much chalcogen rich. 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.

Mean Bond Energy And Glass Transition Temperature

There are many properties of chalcogenide glasses which are related to overall mean bond energy $\langle E \rangle$. Tichy and Ticha [29, 30] reported that 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 $\text{Ge}_x\text{Se}_{80-x}\text{Te}_{20}$ 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 $\text{Ge}_a\text{Se}_b\text{Te}_c$ system, where $(a + b + c) = 1$, in selenium rich systems ($R > 1$) where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E_c = 4aE_{\text{Ge-Se}} + 2cE_{\text{Se-Te}}$$

and

$$E_{rm} = \left[\frac{2b - 4a - 2c}{Z} \right] E_{\text{Se-Se}}$$

denotes the average homopolar bonding energy. The values of E_c , E_{rm} , and $\langle E \rangle$ are given in table 1. It is clear from fig. 5 that $\langle E \rangle$ increases with increase in concentration of Ge from 3 to 18 at. % .

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

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

The values of T_g corresponding to $\langle E \rangle$ is mentioned in table 2 and 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.

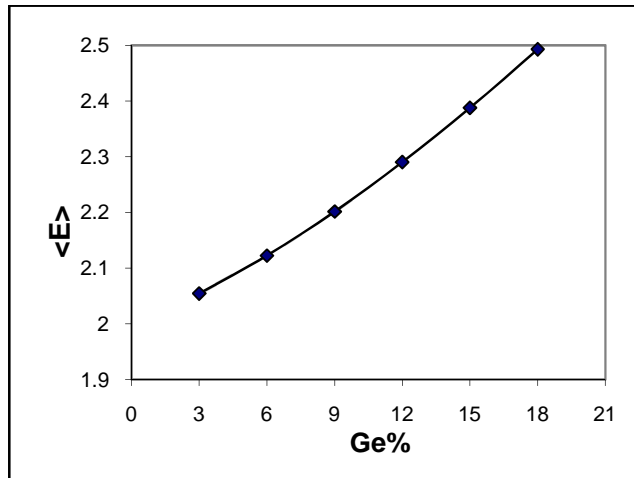


Fig. 5: Variation of overall mean bond energy with Ge content

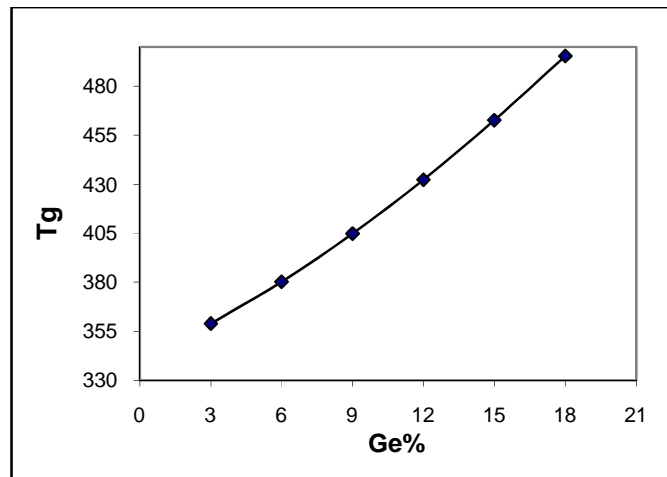


Fig. 6: Variation of glass transition temperature T_g with Ge content

Table 1

Ge a	Se b	Te c	Z	N_c	X	M (g/mol)	L	R	$\langle E \rangle$ eV/atom	T_g (K)
3	77	20	2.06	2.15	0.15	88.50	3.88	16.17	2.054	358.96
6	74	20	2.12	2.3	0.3	88.31	3.76	7.833	2.123	380.28
9	71	20	2.18	2.45	0.45	88.12	3.64	5.056	2.202	404.83
12	68	20	2.24	2.6	0.6	87.93	3.52	3.667	2.290	432.34
15	65	20	2.3	2.75	0.75	87.74	3.40	2.833	2.387	462.60
18	62	20	2.36	2.9	0.9	87.55	3.28	2.278	2.493	495.39

CONCLUSION

The addition of Ge to Se-Te glassy alloys leads to change in the physical properties. As it is clear from various figures and tables given above that almost all the parameters, mentioned above, except molecular weight, Lone-pair electron and the parameter R were increased with the increase in Ge content. The positive values of R confirm the alloys as chalcogen rich. The values of lone-pair electrons show good glass forming ability of present glass system. The results also show that mean bond energy $\langle E \rangle$ is proportional to glass transition temperature and both increases with the increase in content of Ge. The present system is in accordance with the earlier researches according to which system with large number of lone-pair electrons constitutes a stable state.

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