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Effect on physical properties of $Ge_{20}Se_{80-x}Ga_x$ glass system with compositional variations

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ABSTRACT

The effect on the physical properties viz. average coordination number, number of constraints, cross-linking density, molecular weight, fraction of floppy modes, Lone-pair electron, mean bond energy, glass transition temperature etc., with the variation in Gallium content has been studied theoretically in the present article for $Ge_{20}Se_{80-x}Ga_x$ (x=2 to 16 at. %) *glassy alloys. Tichy-Ticha approach has been used to study the glass transition temperature and mean bond energy. It has been found that almost all the parameters, studied here, except molecular weight, fraction of floppy modes, Lone-pair electron and* the parameter R *were increased with the increase in Ga content.*

Keywords: Chalcogenide Glasses; Average Coordination Number; Glass Forming Ability; mean bond energy.

INTRODUCTION

During the recent past, the chalcogenide glasses are studied by a number of researchers as they are very interesting materials for reversible phase change optical recording devices [1-4]. Ever since the reversible switching phenomenon in certain types of chalcogenide glasses was first reported [5], 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 [6, 7].

The investigation of composition dependence of various properties of chalcogenide glasses has been increased during last decade. 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, In, Bi, Te, Ga, Sb, Ag, etc. can be used to make alloys with Se, which may enhance sensitivity, crystallization temperature and reduce ageing effects [8, 9].

The compositional dependence studies on glassy alloys were reported for Ge-Se, Ge-Se-Te, Ge-Se-In, Ge-Se-Bi Ge-Se-As, Ge-Se-Sb, Ge-Se-Ag, [10-16]. 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 [17, 18]. 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. Addition of third element like Ga 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 [19].

In the present work, we have incorporated Gallium in the Ge-Se alloy for the compositions belonging to $Ge_{20}Se_{80-x}Ga_x$ (x=2, 4, 6, 8, 10, 12, 14, 16 at. %). The addition of third element used to create compositional and configurational disorder in the material with respect to the binary alloys [12]. It has been established that physical properties in this system are highly composition dependent [20, 21]. The variation of properties has been discussed on the basis of their compositions. The present paper is concerned with the theoretical prediction of the physical parameters related to composition, viz. coordination number, constraints, cross-linking density, fraction of floppy modes, molecular weight, lone-pair electron, mean bond energy and the glass transition temperature for $Ge_{20}Se_{80-x}Ga_x$ alloys.

THEORETICAL STUDIES AND DISCUSSION

Average Coordination Number & Bonding Constraints

According to J. C. Phillips it may be valuable to consider the transitions between z = 2.4 and 2.67 in the light of the constraint – counting argument originally proposed for amorphous covalent materials [22]. 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. The well known Phillips–Thorpe approach is based on comparing the number of atomic degrees of freedom with the number of inter-atomic force field constraints. If the number of degrees of freedom is greater than the number of constraints, the network is “floppy”; conversely, if the network becomes over-constrained, stressed-rigid structures will percolate throughout the entire network. According to Phillips, the tendency of glass formation would be maximum when the number of degrees of freedom exactly equals the number of constraints.

For the composition $Ge_{20}Se_{80-x}Ga_x$, the average coordination number (Z) was calculated by using the standard method [23]

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

where a, b and c are the at. % of Ge, Se and Ga respectively and N_{Ge}, N_{Se}, N_{Ga} are their respective coordination number [24]. The calculated values of average coordination number for $Ge_{20}Se_{80-x}Ga_x$ (x=2 to 16 at. %) system are listed in table 1. It is clear from fig 1 that values of Z increase from 2.42 to 2.56 with increase in concentration of Ga from 2 to 16.

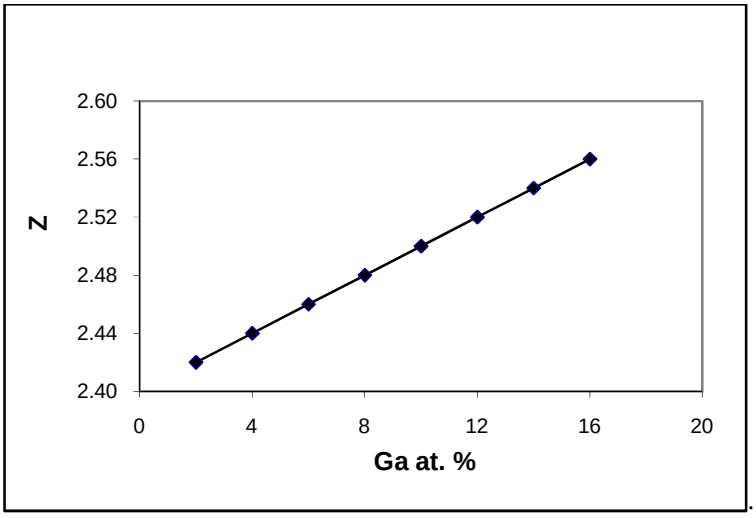

Fig. 1: Variation of Average Coordination Number with Gallium at. %

The glassy network are influenced by mechanical constraints (N_{con}) associated with the atomic bonding and an average coordination number Z which is also related to N_{con}. 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

$$N_\alpha = Z / 2$$

And, of bond-bending constraints is

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

For the case when all α and β constraints are intact and no dangling ends exist in the network, equation implies that the optimum mean coordination number is 2.40 which is known as the regiditty percolation threshold. Highly over-coordinated or under-coordinated structures are not conducive to glass formation and, upon cooling, lead to crystalline solids. M. F. Thorpe [26] pointed out that the number of floppy modes per atom, f, is rather accurately described by the mean-field constraint count according to the relation,

$$F = 3 - N_{con} \quad (2)$$

This led to the realization that a glass network will become spontaneously rigid when $f \rightarrow 0$, defining a *floppy* to *rigid phase transition* [27].

The total number of constraints is given by

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

The values of N_{con} along with Z for $Ge_{20}Se_{80-x}Ga_x$ are given in table 1. Fig. 2 depicts the variation of N_{con} with Ga at %. Here N_{con} increase from 3.05 to 3.40 with increase in Ga at.%, which shows in our composition that the number of constraints N_{con} acting on the network are balanced by the number of degrees of freedom N available from the atoms in the network. This means that network is isostastically rigid, no stress is present i.e. $N_{con} = N_d$.

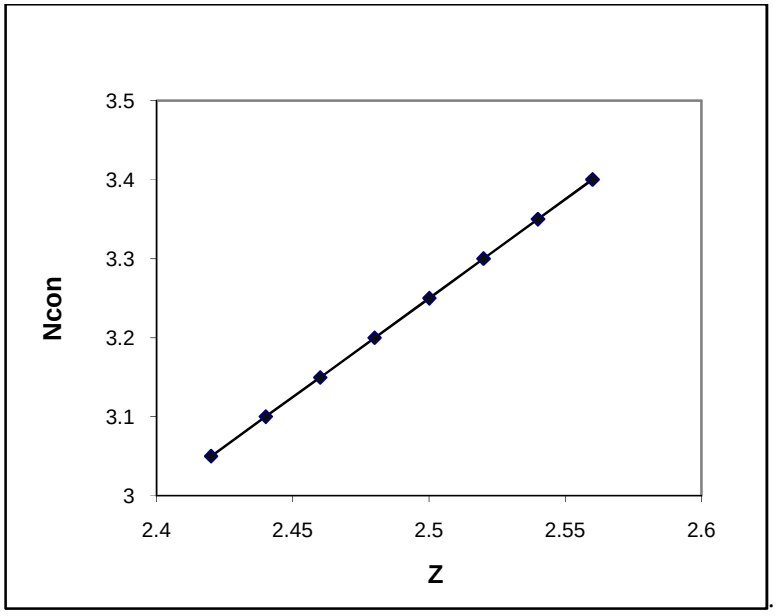

Fig. 2: Variation of number of constraints with Ga at. %

The cross-linking density(X) is equal to the average coordination number of cross linked chain less the coordination number of initial chain [28].

$$X = N_c - 2$$

The values of cross linking density (X) and molecular weight (M) are shown in table 1. From fig. 3 it is clear that the value X increase with increase in Ga content. Fig.4 shows the variation of M with Ga content.

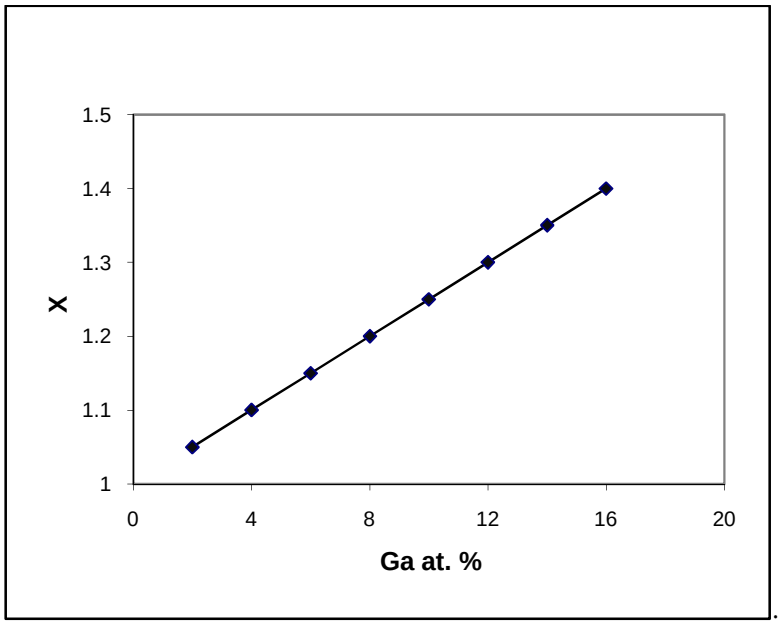

Fig. 3: Variation of cross-linking density with Ga content

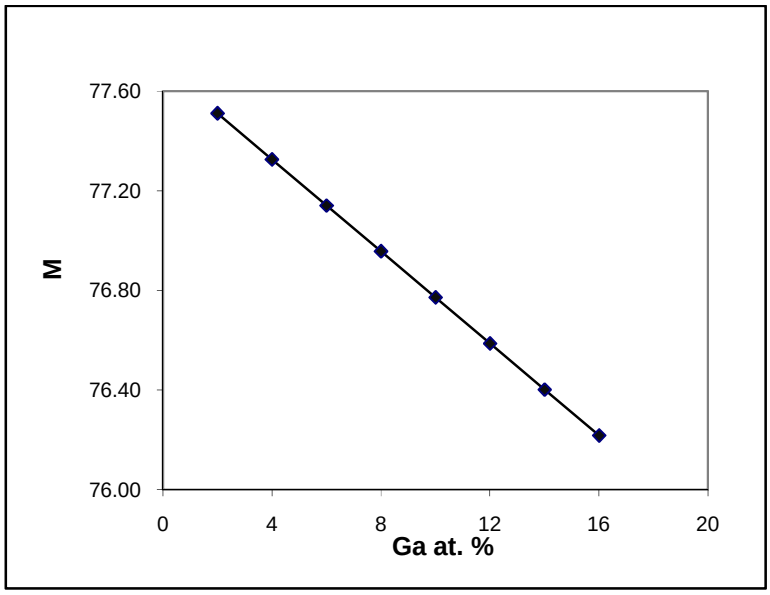

Fig. 4: Variation of Molecular weight with Ga content

According to Thorpe, 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

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

The values of f are listed in table 1. It has been observed from the table and fig. 5 that the value of f becomes more and more negative (-0.017 to -0.133) with increase in Ga content from 2 to 16 at. %. This shows that the system becomes more and more rigid, which corresponds to a strong tendency for making glass [29].

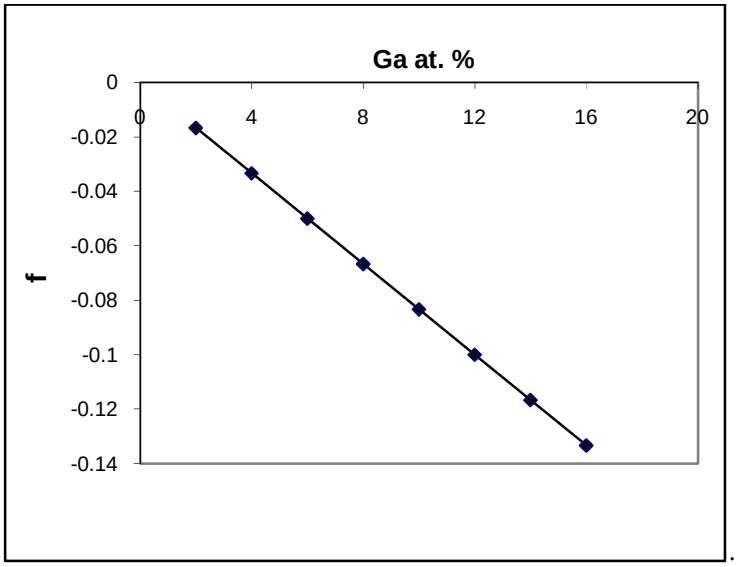

Fig. 5: Variation of fraction of floppy modes with Ga content

Lone pair electrons and glass forming ability

The view point proposed by Pauling [30], 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 [31]

$$L = V - Z$$

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 $Ge_{20}Se_{80-x}Ga_x$ system are tabulated in table 1.Variation of lone-pair electrons with Ga content is shown in fig.6.

It is clear from the variation of lone-pair electrons that with the increase of Ga content, the number of lone–pair electrons decreases continuously in $Ge_{20}Se_{80-x}Ga_x$ system. This behaviour is caused by the interaction between the Ga 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 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 $Ge_{20}Se_{80-x}Ga_x$ system varies from 2.56 to 3.12, concludes that the present system under study is exhibiting good glass forming ability.

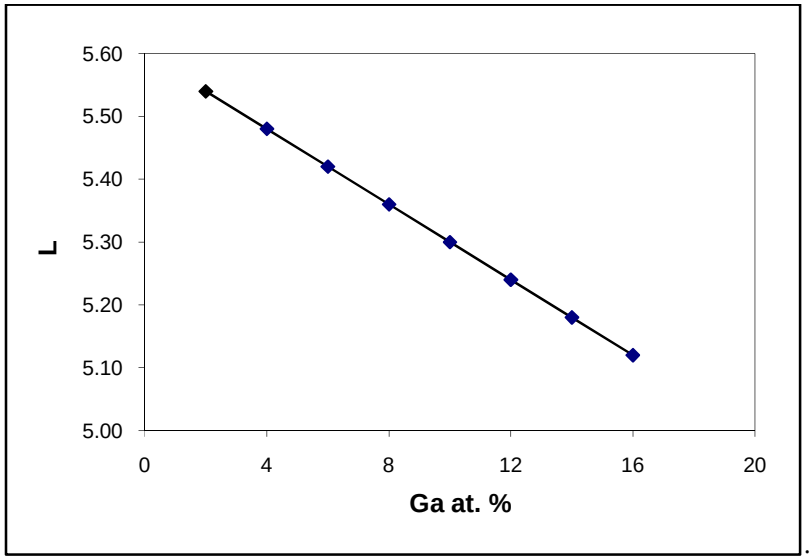

Fig. 6: Variation of Lone-pair electrons with Ga content

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 $Ge_{20}Se_{80-x}Ga_x$ system, the parameter R is given by [32, 33]

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

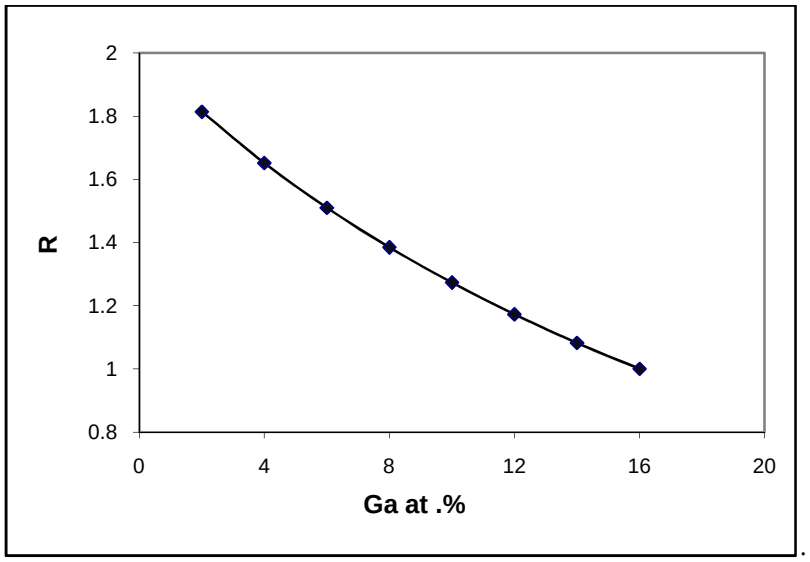

Fig. 7: Variation of parameter R with Ga content

where a, b, c are atomic frictions of Ge, Se and Ga respectively. The values of R are mentioned in table 2. 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. 7, it is clear that our system is chalcogen rich and turning

towards chalcogen poor with the increase in content of gallium in the system (after x = 14 at. %). 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 <E>. According to Tichy and Ticha, 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 $Ge_{20}Se_{80-x}Ga_x$ 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 $Ge_a Se_b Ga_c$ system, where (a + b + c) = 1, in selenium rich systems (R>1) where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E_c = 4aE_{Ge-Se} + 3cE_{Se-Ga}$$

and

$$E_{rm} = \left[\frac{2b - 4a - 3c}{Z}\right] E_{Se-Se}$$

denotes the average homopolar bonding energy. The values of E_c, E_{rm}, and <E> are given in table 2. It is clear from fig. 8 that <E> increases with increase in concentration of Ga from 2 to 16 at. % .

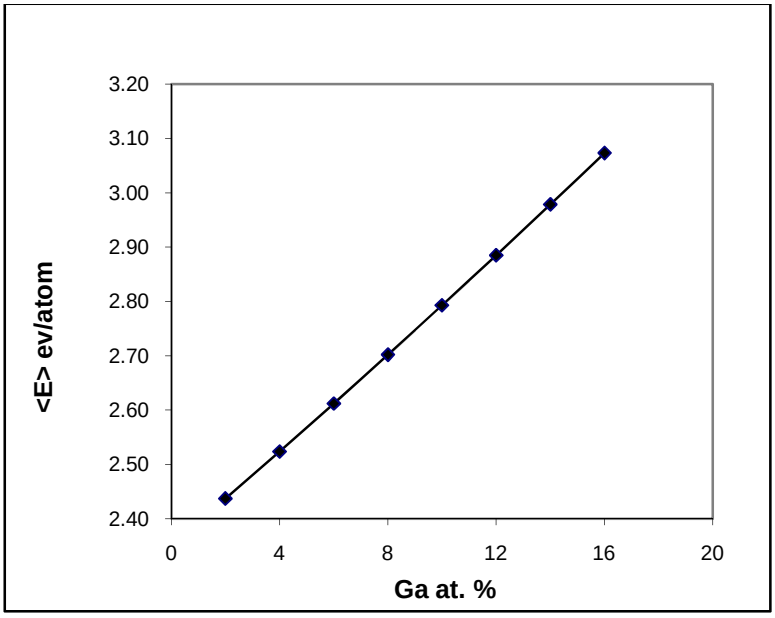

Fig. 8: Variation of overall mean bond energy with Ga content

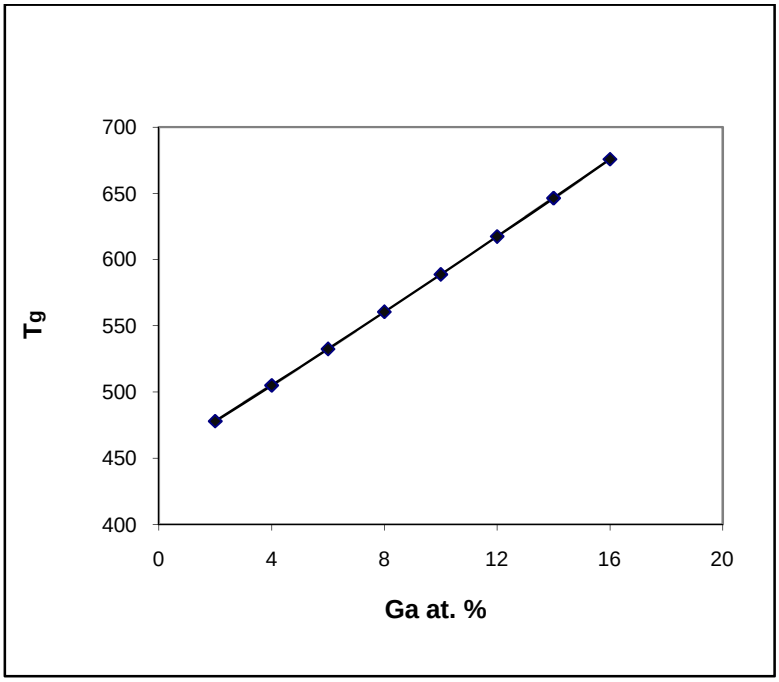

Fig. 9: Variation of glass transition temperature T_g with Ga content

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

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

The values of T_g corresponding to <E> is mentioned in table 2 and the variation of T_g with Ga content is shown in fig. 9, which is clearly depicting the rise in glass transition temperature with increasing the content of Ga due to rise in mean bond energy of the glassy system.

Table 1

Ge	Se	Ga	Z	N_{con}	X	f	M (g/mol)	L
20	78	2	2.42	3.05	1.05	-0.017	77.51	3.12
20	76	4	2.44	3.1	1.1	-0.033	77.33	3.04
20	74	6	2.46	3.15	1.15	-0.050	77.14	2.96
20	72	8	2.48	3.2	1.2	-0.067	76.96	2.88
20	70	10	2.50	3.25	1.25	-0.083	76.77	2.80
20	68	12	2.52	3.3	1.3	-0.100	76.59	2.72
20	66	14	2.54	3.35	1.35	-0.117	76.40	2.64
20	64	16	2.56	3.4	1.4	-0.133	76.22	2.56

Table 2

a Ge	b Se	c Ga	R	E_c eV/atom	E_{rm} eV/atom	<E> eV/atom	T_g (K)
20	78	2	1.81	1.885	0.552	2.437	477.96
20	76	4	1.65	2.055	0.469	2.524	505.02
20	74	6	1.51	2.224	0.388	2.612	532.50
20	72	8	1.38	2.394	0.308	2.702	560.39
20	70	10	1.27	2.564	0.229	2.793	588.68
20	68	12	1.17	2.734	0.151	2.885	617.36
20	66	14	1.08	2.903	0.075	2.978	646.41
20	64	16	1.00	3.073	0.000	3.073	675.84

CONCLUSION

The addition of Ga to Ge-Se 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, fraction of floppy modes, Lone-pair electron and the parameter R were increased with the increase in Ga content. The positive values of R confirm the alloys as chalcogen rich up to x = 16 at. %. The values of lone-pair electrons show god glass forming ability of present glass system. The results also show that mean bond energy <E> is proportional to glass transition temperature and both increases with the increase in content of Ga.

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