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**THE GLASS-TRANSITION TEMPERATURE AND
BOTH THE TOPOLOGICAL AND CHEMICAL
THRESHOLDS IN CHALCOGENIDE GLASSES**

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The problem of the glass-transition temperature (T_g) is discussed using the idea of the topological and chemical threshold in chalcogenide glasses. Within a simple covalent bond approach it is shown that the short range bonding arrangement mainly determines the T_g values in chalcogenide glasses. Good correlation between T_g and the overall mean bond energy $\langle\langle E \rangle\rangle$, of a covalent network of a glass was found for 186 binary and ternary chalcogenide glasses. This correlation satisfies the Arrhenius relation for viscosity, where the apparent activation energy of viscosity is empirically related to the overall mean bond energy.

1. Introduction

In 1979 Phillips introduced the constraint theory of glass formation¹. The theory predicts the existence of a topological threshold in a continuous covalent network system at a critical chemical composition corresponding to the mean coordination number $\langle\langle CN \rangle\rangle$ of a pseudoatom: $\langle\langle CN \rangle\rangle = 2.4$. In 1988 Tanaka²

showed that composition dependences of various properties for chalcogenide glassy alloys exhibit characteristic extremes at $\langle \text{CN} \rangle = 2.67$. On the basis of topological consideration he supposed that these features can be connected to formation of stable layered structures which are maximally stabilized at a critical chemical composition corresponding to $\langle \text{CN} \rangle = 2.67$. Hence there are two topological thresholds. The first one at $\langle \text{CN} \rangle = 2.4$ (Phillips-Thorpe threshold^{1,3-5} - PTT) and the second one at $\langle \text{CN} \rangle = 2.67$ (Tanaka's threshold² - TT). The implicit assumption of these thresholds is that a covalent network (or rather a continuous covalent network in the case of PTT and a network composed by layer-like entities in the case of TT) is approximated by a network formed by pseudoatoms connected by some average bonds. These thresholds are seen as extremal points in the dependences of e.g. following physical properties versus $\langle \text{CN} \rangle$: (i) the glass-forming ability in $\text{Ge}_x\text{Se}_{1-x}$ system¹, (ii) the mean atomic volume, see e.g. Ref.², (iii) the elastic constant, see e.g. Ref.⁶, (iv) the thermal expansion, see e.g. Ref.⁷, (v) the glass-transition temperature⁸, (vi) the magnitude of photoinduced gap changes in amorphous chalcogenides, see e.g. Refs.^{9,10}. At the same time there exists some evidence indicating possible coexistence of the effects which have topological origin and the effects which have their origin in chemical ordering, see e.g. Refs.^{6,11}. Chemical ordering means formation of a chemical compound in e.g. A_xB_{1-x} glassy system, i.e. the chemical ordering is reached at such a composition of a given alloy (or of a given family of a system) where the maximum value of some average bond energy is reached or the system, from chemical point of view, reaches the most stable state. The corresponding chemical composition is called the chemical threshold (CHT). There is no doubt that in As-S, Se systems an interference between PTT and CHT exists and in Ge-S, Se glasses the interference between TT and CHT exists as well since in As-S, Se systems the chemical compounds $\text{As}_2(\text{S}, \text{Se})_3$ are formed exactly at $\langle \text{CN} \rangle = 2.4$, and in Ge-S, Se systems the chemical compounds $\text{Ge}(\text{S}, \text{Se})_2$ are formed exactly at $\langle \text{CN} \rangle = 2.67$, see Fig. 1. Among the properties discussed in connection with PTT and TT, the glass-transition temperature was also examined. As the glass-transition temperature (T_g) is one of the most important parameters of any glass and since the problem of interference of PTT, TT and CHT is a serious problem, the examination of the compositional trends of the glass-transition temperature and its relation to topology of the network on the one side and to the bonding arrangement on the other side is of considerable importance.

It is aim of this paper to summarize some recent results concerning the problem of compositional trend in T_g of chalcogenide glasses in connection to possible existence of PTT, TT and CHT. The paper is organized as follows. In Part 2 we briefly recapitulate basic information concerning PTT and TT. In Part 3 a simple way based on elemental bond statistic is shown which clearly identifies CHT. Finally in Part 4, following results of Part 3, the simple covalent bond approach is introduced for an estimation of T_g in chalcogenide glasses. A short summary is given in Part 5, while references are summarized in Part 6.

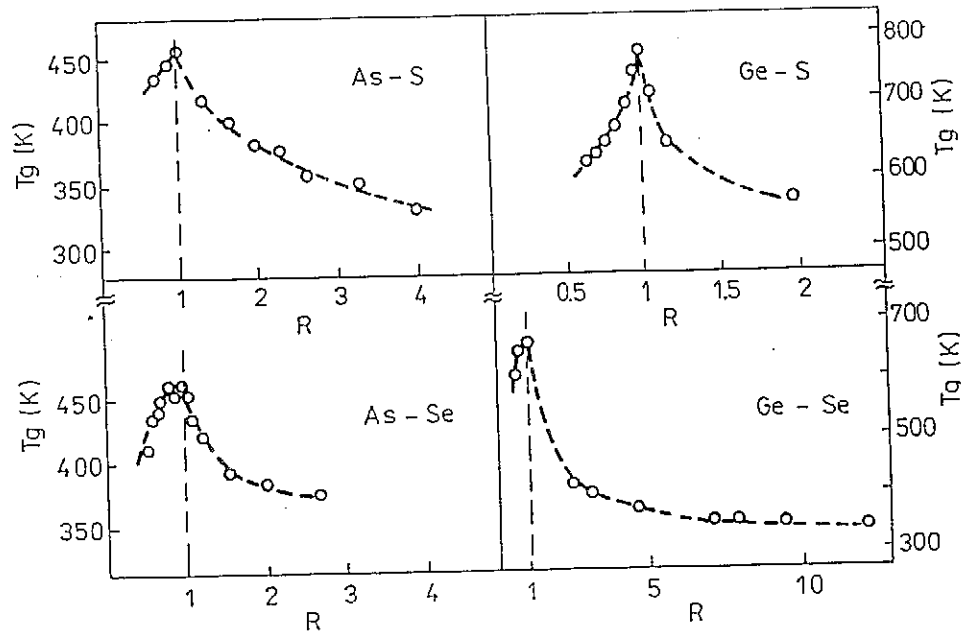


Fig. 1 $T_g(R)$ dependences for As-S, Ge-S, As-Se and Ge-Se glasses. The chemical threshold $R = 1$ is marked by vertical dashed line. For data, see Refs. in Table I

2. Phillips-Thorpe Threshold (PTT) and Tanaka's Threshold (TT)

2.1 Phillips-Thorpe Threshold

The basic idea of Phillips¹ is to relate a number of mechanical degrees of freedom of an atom, denoted by N_d , to the number of constraints imposed on it by the forces from other atoms. It is assumed that only short range order bonding interactions are involved and the number of mechanical constraints (N_c) will be some function of $\langle CN \rangle$. N_c is calculated assuming that small displacements of atoms are controlled by forces expressed by the potential

$$V = \frac{1}{2} \sum_{i,j} \alpha_{ij} (\Delta r_{ij})^2 + \frac{1}{2} \sum_{i,j,k} \beta_{ijk} (\Delta \theta_{ijk})^2 \quad (1)$$

where Δr_{ij} is the change in length of the i - j bond. The corresponding forces are α -forces. $\Delta \theta_{ijk}$ is the change in angle between the bond i - j and j - k . $\Delta \theta_{ijk}$ is controlled by β -forces. Phillips¹ supposed that a critical equilibrium in glassy networks must persist when the number of atomic constraints (N_c) exhaust the available degrees of freedom

$$N_c = N_d \quad (2)$$

The number of constraints per atom as a function of coordination number is

$$N_c = \frac{\langle \text{CN} \rangle}{2} + \langle \text{CN} \rangle \frac{\langle \text{CN} \rangle - 1}{2} = \frac{\langle \text{CN} \rangle^2}{2} \quad (3)$$

Hence for $N_d = 3$ we obtain $\langle \text{CN} \rangle = 2.45$, which means that for chemical composition with $\langle \text{CN} \rangle = 2.45$ the system reaches mechanical stability. One can refine this approach assuming that e.g. in binary system A_xB_{1-x} it is valid

$$N_c(A_xB_{1-x}) = xN_c(\text{CN}(A)) + (1-x)N_c(\text{CN}(B)) \quad (4)$$

For a classical case of $\text{Ge}_x\text{Se}_{1-x}$ system this means

$$N_c(\text{Ge}_x\text{Se}_{1-x}) = \frac{x(\text{CN}(\text{Ge}))^2}{2} + \frac{(1-x)(\text{CN}(\text{Se}))^2}{2} = 6x + 2 \quad (5)$$

$$(\text{CN}(\text{Ge}) = 4; \text{CN}(\text{Se}) = 2)$$

Since $N_d = N_c$, we obtain: $3 = 6x + 2$, hence $x = 0.16$ and $\langle \text{CN} \rangle = 2.33$. ($\langle \text{CN} \rangle(\text{Ge}_x\text{Se}_{1-x}) = 2x + 2$).

In the paper by Dohler et al.¹² it was, however, shown that Eq. (3) is correct for $\text{CN}(A, B) \leq 2$. For higher values of CN it has to be modified in the following way

$$N_c(\text{CN}, N_d) = \frac{\text{CN}}{2} + \frac{1}{2}\text{CN}(\text{CN} - 1) \quad (6)$$

for $\text{CN} \leq N_d - 1$. For $\text{CN} = N_d - 1$ Eq. (3) has to be modified in the following way

$$N_c(\text{CN}, N_d) = \frac{\text{CN}}{2} + \frac{1}{2}(N_d - 1)(2\text{CN} - N_d) \quad (7)$$

Using condition $N_c = N_d$ (if $N_d = 3$ is taken) we obtain

$$\text{CN} = (2N_d)^{1/2} = 2.45; \text{ for } \text{CN} \leq N_d - 1 = 2 \quad (8)$$

$$\text{CN} = \frac{N_d(N_d + 1)}{2N_d - 1} = 2.4; \text{ for } \text{CN} \geq N_d - 1 = 2 \quad (9)$$

Replacing CN by $\langle \text{CN} \rangle$ for $\text{Ge}_x\text{Se}_{1-x}$ system we have $\langle \text{CN} \rangle = 2.4$ $x = 0.2$ i.e. close to Phillips' value of critical CN and critical x values in $\text{Ge}_x\text{Se}_{1-x}$ system. For readers' convenience, in Fig. 2 the glass-forming difficulty is plotted to illustrate that really close to $x = 0.2$ ($\langle \text{CN} \rangle = 2.4$) the maximum in glass-forming ability is observed. Alternatively, if we have

$$N_c(\text{Ge}_x\text{Se}_{1-x}; N_d = 3) = xN_c(\text{Ge}) + (1-x)N_c(\text{Se}) \quad (10)$$

we obtain from Eq. (7): $N_c(\text{Ge}) = 7$ and from Eq. (6): $N_c(\text{Se}) = 2$ and hence: $N_c(\text{Ge}_x\text{Se}_{1-x}; N_d = 3) = 2 + 5x$ and using the condition: $N_d = N_c$ we have:

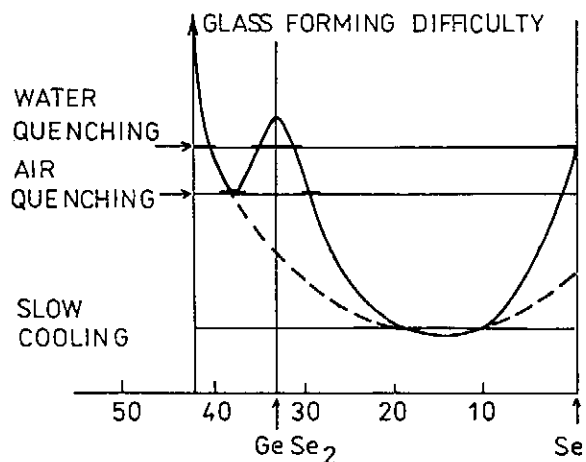


Fig. 2 The difficulty of glass formation as function of x in $\text{Ge}_x\text{Se}_{1-x}$ system, see Ref.¹

$5x = 1$, hence $x = 0.2$ and $\langle \text{CN} \rangle = 2.4$. Finally, we note, as Thorpe³ showed, that fraction of zero-frequency modes (f), i.e. modes which involve displacements costing no energy, relates to the mean coordination number by equation

$$f = \frac{12 - 5\langle \text{CN} \rangle}{6} \quad (11)$$

Canceling the degrees of freedom by the constraints means $f = 0$ and hence from Eq. (11) we obtain $\langle \text{CN} \rangle = 2.4$. Hence the critical mean coordination number divides relevant system into three parts. For $\langle \text{CN} \rangle < 2.4$ the system is floppy, underconstrained or it has mechanical behaviour like a polymeric glass. The floppy regions can be viewed as a continuum (sea) where some rigid areas (islands) are isolated. For $\langle \text{CN} \rangle = 2.4$ the system is mechanically stable ($N_c = N_d$), the rigid regions (islands) start to be nearly connected (as their volume increases), and $\langle \text{CN} \rangle = 2.4$ is a percolation threshold. For $\langle \text{CN} \rangle > 2.4$ the system is rigid, the floppy regions start to be isolated lakes and the rigid structure percolates.

2.2 Tanaka's Threshold

As summarised by Tanaka² the atomic volume (V_a), the bulk modulus (B), and the magnitude of the reversible photodarkening (ΔE) in Ge-As-S, Se glassy system indicate a drastic change in the vicinity of $\langle \text{CN} \rangle = 2.67$ when these properties are plotted versus $\langle \text{CN} \rangle$, see Fig. 3. Tanaka supposed that the constraint for a pseudoatom included in a planar cluster extending in e.g. $x-y$ plane can be expressed as

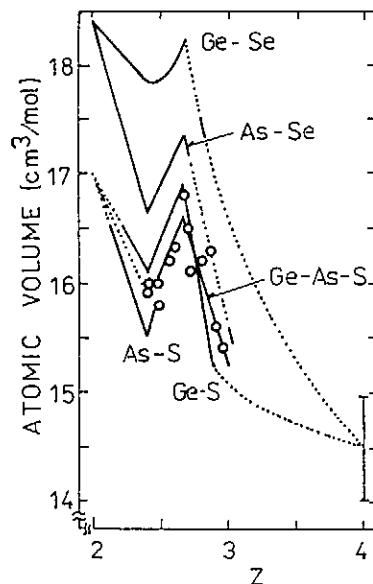


Fig. 3 The atomic volumes for various chalcogenide glasses as a function of coordination number (here denoted by Z), see Ref.²

$$N_d(\langle CN \rangle) = \frac{\langle CN \rangle}{2} + (\langle CN \rangle - 1) \quad (12)$$

The second term, the angular term, is calculated as excess of $\langle CN \rangle$ variables in θ (θ is bond angle) over a rotation freedom in the z axis. As a planar medium configuration is assumed (see Fig. 4) the number of angular constraints is reduced to: $\langle CN \rangle - 1$. Hence the constraint balancing condition $N_d = N_c$ gives $\langle CN \rangle = 2.67$, which means that a two-dimensional glass (or a glass composed of layer-like two dimensional entities) appears to be fixed stably in a three-dimensional space at a chemical composition where $\langle CN \rangle = 2.67$. At least two serious possibilities² could connect TT and PTT. Thorpe³ demonstrated that while a simple rigidity-percolation analysis predicts the elastic transition at $\langle CN \rangle = 2.4$, the existence of ring structures consisting of atoms fewer than six is effective to increase a threshold. Since layer structures represent some kind of a network composed of small rings, a shift of PTT to higher values of $\langle CN \rangle$ could be achieved. Gilroy and Philips¹³ found that TT at $\langle CN \rangle = 2.67$ follows immediately from PTT if e.g. in Ge_xSe_{1-x} system the bond bending constraint for Se atom is neglected. Hence the total number of constraints for a pseudoatom is given by equation

$$N_c = 2x + (1 - x) 5x \quad (13)$$

where the first two terms represent stretching constraint for Ge and Se atoms, while the last term denotes only bending constraint for Ge atom. Hence the constraint balancing condition gives $\langle CN \rangle = 2.67$ in this case.

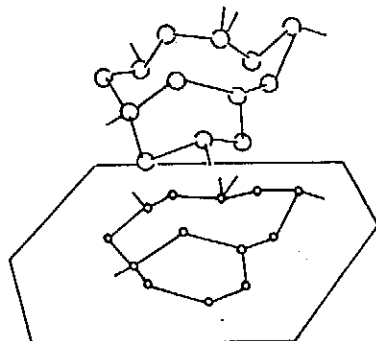


Fig. 4 A structural model for glassy Ge-As-S(Se) and the projected lattice onto a segmental plane²

3. The Chemical Threshold in Chalcogenide Glasses

In recent years a series of papers appeared¹⁴⁻¹⁸ devoted to the problem of possible coexistence (or influence) of topological thresholds with chemical ordering effects in multicomponent glasses. In Refs¹⁴⁻¹⁶ from an analysis of T_g versus $\langle CN \rangle$ and V versus $\langle CN \rangle$ (where V is the mean atomic volume) it is concluded that in $Ge_xSb_ySe_z$, $Ge_xGa_ySe_z$ and $Ge_xIn_ySe_z$ systems chemical ordering effects (chemical thresholds) are seen as some extremal points for various families of a given system at various $\langle CN \rangle$ (including $\langle CN \rangle \approx 2.4, 2.7$). In Ref.¹⁷ mainly chalcogen-rich compositions were examined (hence Tanaka's threshold could not be seriously examined) in Ge-Se, Ge-Sb-Se, Ge-Sb-Se-Te and Ge-Sb-As-Se-Te systems. It was found¹⁷ that only $V(\langle CN \rangle)$ dependences displayed a distinct extreme at $\langle CN \rangle \approx 2.4$ (Phillips-Thorpe threshold). However, no evidence for this threshold was seen in microhardness, Poisson ratio and T_g versus $\langle CN \rangle$. The local extremes were seen at lines joining stoichiometric compounds. Consequently, it is concluded¹⁷ that chemically ordered covalent network dominates atomic arrangement at the tie lines. In Ref.¹⁸ the optical gap (E_{02}) and thermal diffusivity (α) of some Ge-Sb-Se glasses were examined as function of $\langle CN \rangle$. The extremes were found at $\langle CN \rangle \approx 2.6$ for both $E_{02}(\langle CN \rangle)$ and $\alpha(\langle CN \rangle)$ dependences. According to Ref.¹⁸ the occurrence of the threshold at $\langle CN \rangle = 2.6$ for the Ge-Sb-Se glasses studied shows that the chemical ordering effect is not a possible reason for the E_{02} and α behaviour. Consequently, it is supposed¹⁸ that Tanaka's threshold is observed at $\langle CN \rangle = 2.6$. The slight shift in the threshold value ($\langle CN \rangle = 2.67$ for Tanaka's threshold) may be due to ionic character in the bonds due to the presence of the heavier element antimony as

a constituent in these glasses¹⁸. This conclusion contradicts recent results^{14,16}. As there are some uncertainties in the clear displaying of the influence of possible chemical threshold or chemical ordering effects on some properties of chalcogenide glasses, we introduce some data in such coordinates which unambiguously manifest possible existence of a chemical threshold. Instead of plotting the data in property versus $\langle \text{CN} \rangle$ coordinates we use a plot property versus R , where quantity R expresses the ratio of the covalent bonding possibilities of a chalcogen atom to covalent bonding possibilities of non-chalcogen atoms. Hence at $R = 1$ only heteropolar bonds exist and, consequently, this point unambiguously indicates stoichiometric composition or the chemical threshold.

3.2 The Data Selection

For comparative reasons we will examine T_g and V data recently used for study of $T_g(\langle \text{CN} \rangle)$ and $V(\langle \text{CN} \rangle)$ dependences. Table I summarizes glassy systems and properties examined together with corresponding references. The data are taken from different sources hence some fluctuations especially in T_g values could exist since different techniques of glasses preparation, measurement and determination of T_g can play some role. However, these differences cannot significantly influence the overall trends in T_g versus chemical composition or $\langle \text{CN} \rangle$ dependences.

Table I The systems and properties examined. The corresponding references are summarized in the last column

System	Property	Reference
As - S	T_g	19
As - Se	T_g	19, 20
Ge - S	T_g	21
Ge - Se	T_g	19
Ge - As - Se	T_g^* ; V	19 (Tab. 86); Tab. 85)
Ge - Sb - Se	T_g , V ; E_{02}	14, 18
Ge - Ga - Se	T_g , V	16
Ge - In - Se	T_g , V	15

* The temperature corresponding to the viscosity $\sim 10^{13}$ poise is taken as T_g

3.3 Results and Discussion

It is well known that in binary V-VI (As-S, Se) and IV-VI (Ge-S, Se) glassy systems the chemical threshold is seen at stoichiometric $\text{As}_2(\text{S, Se})_3$ and $\text{Ge}(\text{S, Se})_2$ compositions, i.e. at compositions where only heteropolar bonds exist. For reader's convenience in Fig. 1 for As-S, As-Se, Ge-S, and Ge-Se systems the T_g is plotted versus quantity R defined by Eq. (12)

$$R = x(\text{VI}) \frac{\text{CN}(\text{VI})}{1 - x(\text{VI})} \text{CN}(\text{V}; \text{IV}) \quad (12)$$

where $x(\text{VI})$ is atomic fraction of chalcogen, $\text{CN}(\text{VI}, \text{V}, \text{IV})$ is the coordination number of the chalcogen ($\text{CN}(\text{S, Se}) = 2$), arsenic ($\text{CN}(\text{As}) = 3$) or germanium ($\text{CN}(\text{Ge}) = 4$) atom. The threshold at $R = 1$ (the point of the existence of only heteropolar bonds) is evident. For $R > 1$ the system is chalcogen rich, for $R < 1$ the system is chalcogen poor. We suppose that similarly in multicomponent glasses the chemical threshold should be seen at $R = 1$. The quantity R for $\text{Ge}_x(\text{As, Sb})_y\text{Se}_z$ system is given by Eq. (13)

$$R = \frac{2z}{4x + 3y} \quad (13)$$

where $\text{CN}(\text{Sb}) = 3$ is assumed. For $\text{Ge}_x(\text{Ga, In})_y\text{Se}_z$ systems it can be assumed that $\text{CN}(\text{Ga, In}) = 4$ (Refs^{15,16,21}). Since the electronic configuration of Ga, In atoms is s^2p^1 , it is reasonable to assume that the fourfold coordination of Ga and In atoms is due to the dative bond with p lone pair of Se atom. It means that a part of Se atoms can be threefold coordinated. Hence for $\text{Ge}_x(\text{Ga, In})_y\text{Se}_z$ systems the quantity R is given by Eq. (14)

$$R = \frac{2z + y}{4(x + y)} \quad (14)$$

The mean coordination number in this case is

$$\langle \text{CN} \rangle = 4x + 4y + 3y + 2(z - y) = 4x + 5y + 2z \quad (15)$$

which agrees with $\langle \text{CN} \rangle = 8 - 4x + 3y - 6z$, ($x + y + z = 1$) calculated on the basis of the formal valence shell model²². In Figs 5 - 7 the $T_g(R)$ dependences are shown for Ge-Sb-Se, Ge-Ga-Se, Ge-In-Se and Ge-As-Se systems. For all families except for Ge-As-Se the chemical threshold at $R = 1$ is evident. To compare the changes of the mean atomic volume as a function of R , we plotted the quantity C (compactness) versus R in Figs 8 - 10. The compactness was recently used (see e.g. Refs^{23,24}) in connection with discussion of photostructural changes in noncrystalline chalcogenides. It is defined by Eq. (16)

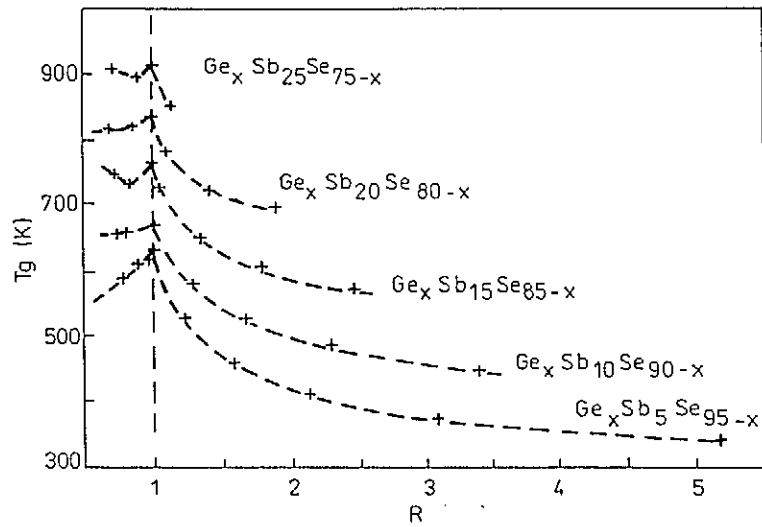


Fig. 5 $T_g(R)$ dependences for Ge-Sb-Se glasses. For reader's convenience the T_g values are shifted as follows: $T_g(\text{Sb} = k * 5) = T_g(\text{Sb} = 5) + 100(k - 1)$, [K]; $k = 1, 2, 3, 4, 5$. The chemical threshold $R = 1$ is marked by vertical dashed line. For data, see Refs in Table I

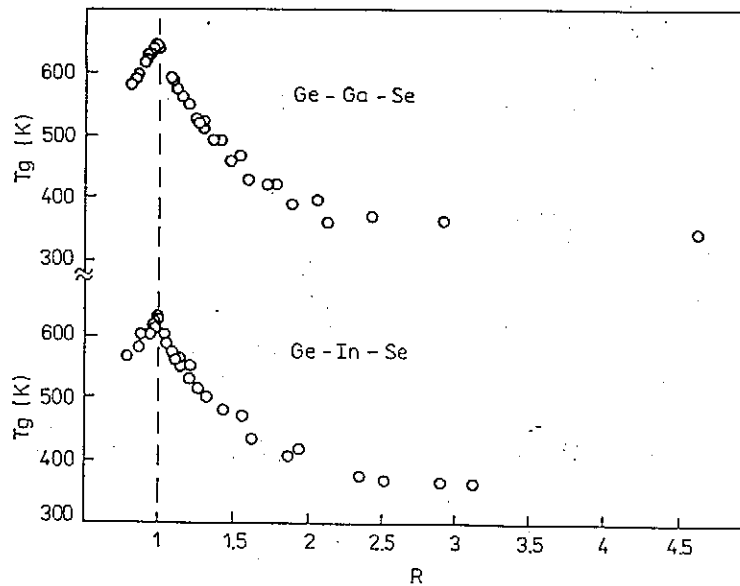


Fig. 6 $T_g(R)$ dependences for Ge-Ga-Se and Ge-In-Se glasses. The chemical threshold $R = 1$ is marked by vertical dashed line. For data, see Refs in Table I

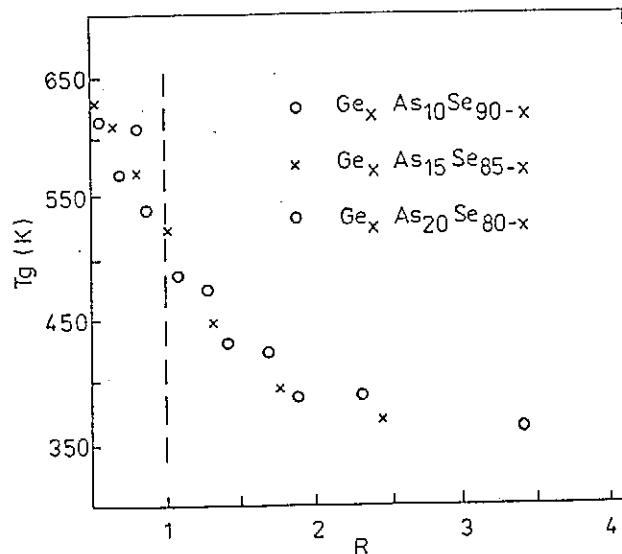


Fig. 7 $T_g(R)$ dependences for Ge-As-Se glasses. The chemical threshold $R = 1$ is marked by vertical dashed line. For data, see Refs in Table I

$$C = \frac{\sum_i \frac{x_i A_i}{\rho_i} - \sum_i \frac{x_i A_i}{\rho}}{\sum_i \frac{x_i A_i}{\rho}} \quad (16)$$

where x_i , A_i , ρ_i , and ρ stand for atomic fraction ($\sum_i x_i = 1$), atomic weight, atomic density of i -th element, and the density of a given glass, respectively. Hence C reflects normalized change of the mean atomic volume due to chemical interaction of the elements forming the network of a given solid. For families of Ge-Sb-Se system and for $\text{Ge}_x(\text{Ga}, \text{In})_y\text{Se}_z$ glasses the threshold is seen at $R = 1$ (Figs 8, 9). We note that only by overlooking those Ge-Sb-Se glasses with $R \approx 1$ the $V(\langle \text{CN} \rangle)$ dependence shows a threshold at $\langle \text{CN} \rangle \sim 2.7$ (Ref.¹⁴). In upper part of Fig. 9 the $C(\langle \text{CN} \rangle)$ dependence indicates the absence of Tanaka's threshold at $\langle \text{CN} \rangle \sim 2.7$. However, it is correct to say that for $\text{CN}(\text{Ga}, \text{In}) = 3$ the threshold shifts in $C(\langle \text{CN} \rangle)$ coordinates to the vicinity of $\langle \text{CN} \rangle \sim 2.7$. In this case, however, the chemical threshold in $T_g(R)$ and $C(R)$ plot remains for $R = 1$ since

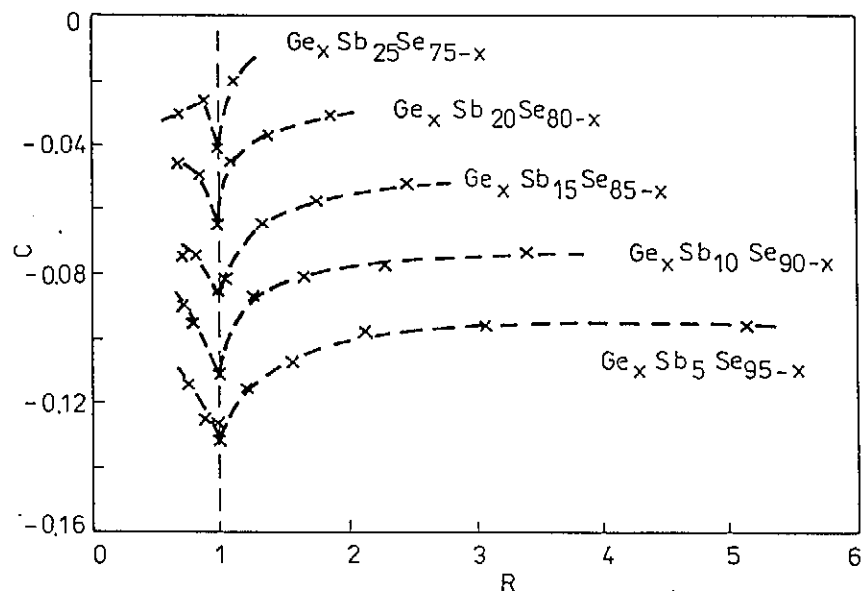


Fig. 8 $C(R)$ dependence for Ge-Sb-Se glasses. For reader's convenience the C values are shifted as follows: $C(\text{Sb} = K + 5) = C(\text{Sb} = 5) + 0.01(k - 1)$; $k = 1, 2, 3, 4, 5$. The chemical threshold $R = 1$ is marked by vertical dashed line. For data, see Ref. in Table I

$$\frac{2z+y}{4(x+y)} = 1 = \frac{2z}{4x+3y}$$

$$\frac{2z+y}{4(x+y)} > 1 \Rightarrow \frac{2z}{4x+3y} > 1 \quad (17)$$

$$\frac{2z+y}{4(x+y)} < 1 \Rightarrow \frac{2z}{4x+3y} < 1$$

Of interest is the fact that in Ge-As-Se system where no tendency of the appearance of chemical threshold is seen in $T_g(R)$ coordinates (Fig. 7) the Tanaka's threshold at $\langle \text{CN} \rangle \approx 2.7$ seems to be evident in $C(\langle \text{CN} \rangle)$ coordinates much better than it is seen in $V(\langle \text{CN} \rangle)$ coordinates (see Fig. 3a Ref.¹⁴). We note that in $C(R)$ coordinates (not shown here) the considerable scatter of C values in the vicinity of $R \approx 1$ makes it impossible to identify any threshold. Finally, in Fig. 11 optical gaps (E_{02}) taken from Ref.¹⁸ for two Ge-Sb-Se families are plotted versus R . Here a clear chemical threshold for the $\text{Ge}_x\text{Sb}_{10}\text{Se}_{90-x}$ family can be seen. For the $\text{Ge}_x\text{Sb}_5\text{Se}_{95-x}$ family with the chemical threshold ($R \approx 1$) at $x = 29.16$ observed extreme lies at $\langle \text{CN} \rangle$ in the region: $2.6 < \langle \text{CN} \rangle < 2.65$ (Ref.¹⁸) it is, however, region $0.96 < R < 1.08$. Hence we suppose that the extremal points in $E_{02}(\langle \text{CN} \rangle)$ and $\alpha(\langle \text{CN} \rangle)$ dependences found in Ref.¹⁸ in

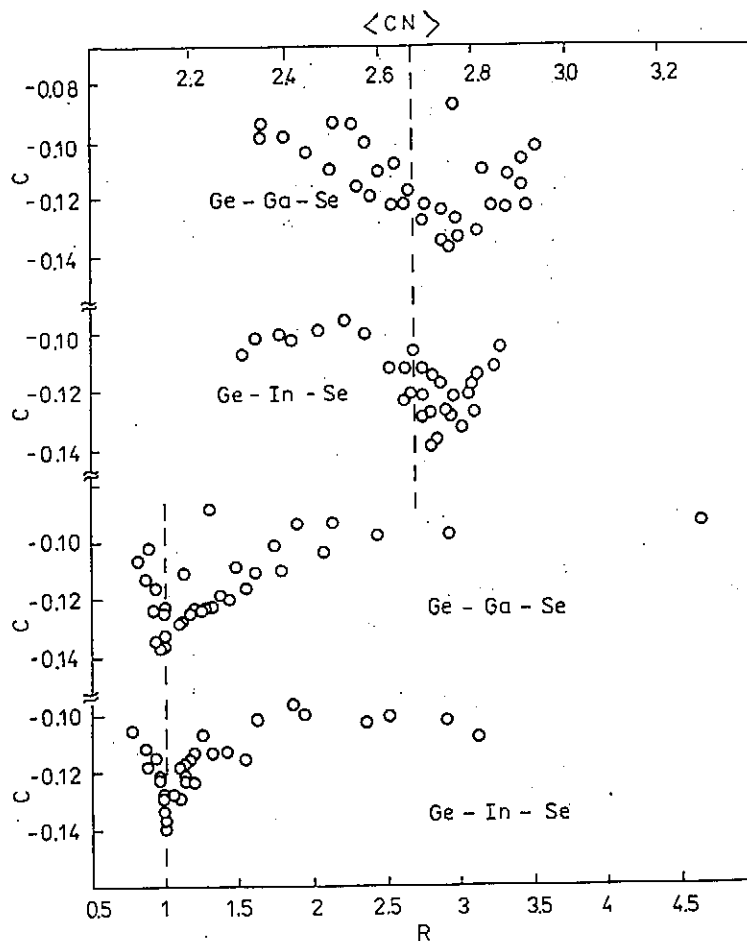


Fig. 9 Upper part $\sim C(\langle CN \rangle)$ dependences for Ge-Ga-Se and Ge-In-Se glasses. Dashed vertical line indicates Tanak's threshold ($\langle CN \rangle \approx 2.7$). Here $\langle CN \rangle$ is calculated from Eq. (15). Lower part - $C(R)$ dependences for Ge-Ga-Se and Ge-In-Se glasses. The chemical threshold $R = 1$ is marked by dashed vertical line. For data, see Refs in Table I

Ge-Sb-Se glasses around $\langle CN \rangle \sim 2.6$ could also be due to the chemical threshold.

We briefly summarize:

- (i) From our $T_g(R)$ and $C(R)$ diagrams of examined glasses it is evident that it is a chemical threshold (i.e. the chemical composition where only heteropolar bonds exist) where the extremal values of T_g and C are observed in a given system or family of the systems.
- (ii) The exception from this finding seems to be T_g and C values for

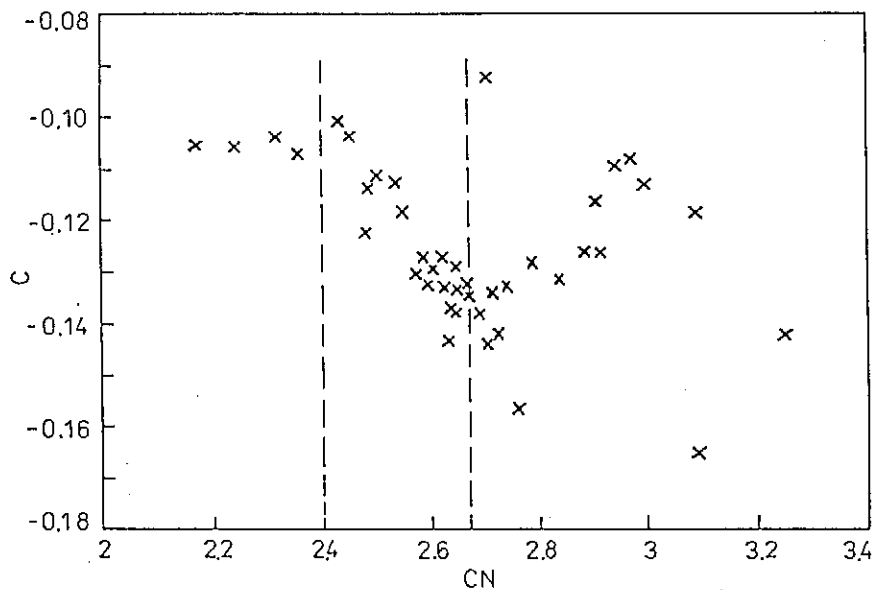


Fig. 10 $C(\langle CN \rangle)$ dependence for Ge-As-Se glasses. Dashed vertical lines indicate Phillips-Thorpe threshold ($\langle CN \rangle = 2.4$) and Tanaka's threshold ($\langle CN \rangle = 2.7$). For data, see Ref. in Table I

Ge-As-Se system where no clear indication of the chemical threshold is observed. Consequently, in this system Tanaka's threshold at $\langle CN \rangle \sim 2.7$ in $C(\langle CN \rangle)$ coordinates is well documented. The reason for such behaviour is not clear at present.

4. Covalent Bond Approach to the Glass-transition Temperature of Chalcogenide Glasses

4.1 Introduction

The glass-transition temperature (T_g) or the softening temperature (T_s) is one of the most important parameters for characterization of glassy state. Considerable attention has been devoted to the explanation of the origin of T_g and to the correlation of T_g with the other physical or chemical properties of glasses. In chalcogenide glasses these correlations are mostly based on the explicit or implicit assumption that to reach T_g (or T_s , or the onset of fluidity) one must overcome the cohesive forces responsible for solid behaviour of a glass. One should at least partly destroy a network of a given glassy matrix in such a way that entities of the network are macroscopically movable at $T \sim T_g$. Consequently, T_g is related to the rigidity of the network which is usually

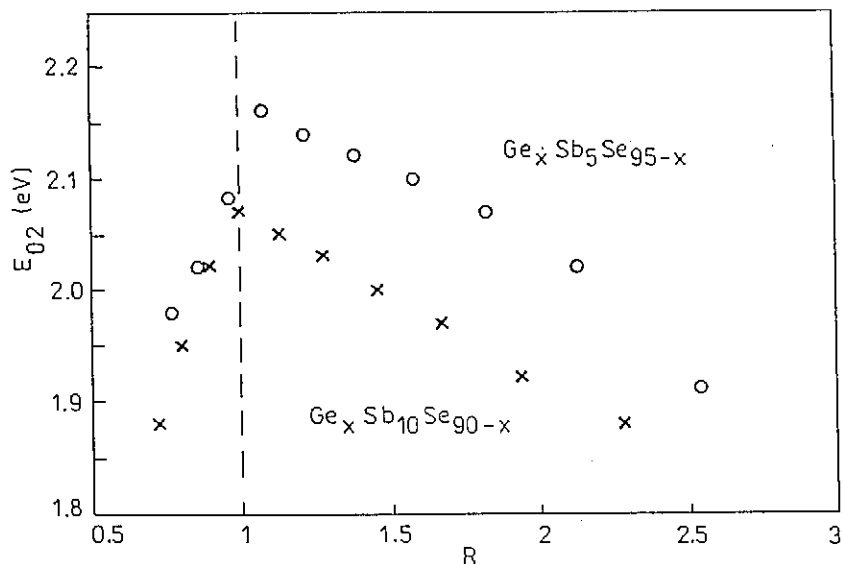


Fig. 11 $E_{02}(R)$ dependence for some Ge-Sb-Se glasses. The chemical threshold $R = 1$ is marked by dashed vertical line. For data, see Ref. in Table I

associated with the mean coordination number ($\langle CN \rangle$) and/or it is related to some typical bond energy or cohesive energy between atoms or entities of a glass. It was shown e.g. by Dembovskii²⁵ that for certain chalcogenide glasses $T_g \sim 433\langle CN \rangle$, where $\langle CN \rangle = \sum x_i CN_i$, x_i is atomic fraction of the i -th component of a glass and CN_i is coordination number of i -th atom. Another relation has been reported by De Neufville and Rockstad²⁶ for correlation between the optical gap (E_g), T_g and $\langle CN \rangle$. This correlation is based on the Vogel-Fulcher relation for viscosity

$$\mu^{-1} = \mu_0^{-1} \exp\left(-\frac{A}{T - T_0}\right) \quad (18)$$

It is assumed that T_g can be taken as a measure of the onset of diffusion motion and thus it corresponds to a fixed value of viscosity ($\mu(T_g) \sim 10^{13}$ poise). In such case T_g can be related to $\langle CN \rangle$ which reflects a number of bonds/atom (i.e. it reflects the connectedness of a network) and to E_g , a measure of average bond energy. Hence Eq. (18) takes the form

$$T_g = T_0 + \frac{\delta(\langle CN \rangle - 2)E_g}{32.2K_B} \quad (19)$$

where $32.2 = \ln(\mu(T_g)/\mu(T_0))$. The quantities T_0 and δ are the system parameters for given class of glasses²⁶. Sarrach et al.²⁷ showed that for

Ge-Se-Te glasses the compositional dependence of T_g can be understood according to models which deal with the local covalent bond configurations. In fact it was found²⁷ that the compositional dependence of T_g can be related to degree of polymerization and to the optical gap. Both of these, together, provide a measure of the dissociation energy of the nearest covalent bond in the system²⁷. In selenide glasses, actually in Se rich glasses, Se_n chains determine T_g and the modifications with addition of impurities are responsible for a change in T_g according to Berkes²⁸. Hence it is assumed that the average bond coordination in the system is directly related to T_g so that

$$T_g = \frac{T_g(\text{Se})}{2} \langle \text{CN} \rangle \quad (20)$$

For As-Se and Ge-Se systems the transform which gives the fraction $\text{As}_2\text{Se}_{3/2}(x')$ or $\text{GeSe}_{4/2}(x')$ in terms of As(x) or Ge(x) ($x' = x/(1 - 3x/2)$) for $\text{As}_x\text{Se}_{1-x}$ system and $x' = x/(1 - 2x)$ for $\text{Ge}_x\text{Se}_{1-x}$ system should be used for calculation of $\langle \text{CN} \rangle$ (Ref.²⁸). Linke²⁹ assumed that the mean atomization enthalpy ($\langle H_a \rangle$) reflects the cohesive forces which must be overcome to reach T_g and consequently T_g should relate to $\langle H_a \rangle$. For certain classes of glasses Linke found $T_g \sim \langle H_a \rangle$ (Ref.²⁹). Tanaka³⁰, assuming Arrhenius relation for viscosity

$$\mu = \mu_0 \exp\left(\frac{E}{K_B T}\right); \quad \mu(T_g) \sim 10^{13} \text{ poise}, \quad \mu_0 \sim 10^0 - 10^{-5} \text{ poise} \quad (21)$$

derived the relation

$$\ln(T_g) = 1.6 \langle \text{CN} \rangle + 2.3 \quad (22)$$

In this derivation it is assumed that the activation energy of viscosity (E) is given by the equation

$$E = E_0 n^{(\text{CN})-1} \quad (23)$$

where $E_0 \sim 0.18$ eV is a typical cohesive energy of van der Waals bonding and the term $n^{(\text{CN})-1}$ ($n \sim 5$) gives the number of atoms belonging to an atomic unit. Further it was assumed that fluidity is warranted e.g. by slipping movements³¹ of distorted layers. It means that the van der Waals cohesive force should be overcome to reach the softening of a glass. However, for chalcogenide glasses with homopolar bonds of the type As-As; Ge-Ge Tanaka supposed³⁰ that nearly compositionally invariant T_g reflects a fact that for homopolar bond energy E_h could be valid: $E_h \leq E_0 n^{(\text{CN})-1}$ and consequently the softening of the glass could be due to the breaking of these bonds. We note that T_g values in As-Se-Te glasses satisfy this assumption ($T_g \sim E_h$) (Ref.³²). In a recent paper by Sreeram, Swiler and Varshneya³³ the modified Gibbs-DiMarzio

equation in the form

$$T_g = \frac{T_o}{1 - \beta(\langle \text{CN} \rangle - 2)} \quad (24)$$

has been successfully used for calculation of T_g values of some Ge-Sb-Se, Ge-Sb-Se-Te and Ge-As-Sb-Se-Te glasses. The term $(\langle \text{CN} \rangle - 2)$ in Eq. (24) stresses the role of crosslinking, T_o is T_g of the noncrosslinked parent chain and β is a system parameter. If the glass-transition temperature is related to network rigidity (here the influence of a defect states created by broken bonds, VAPS and IVAPS as well as kinetic phenomena are neglected) than T_g should be related not only to the connectedness of the network (which is reflected in $\langle \text{CN} \rangle$) but it should also be related to the quality of connections, i.e. to some bond energy between atoms of the network (in the case of covalent network) or to some interaction energy between entities (in the case of a molecular solid). Actually, only DeNeufville and Rockstad²⁶, Sarrach et al.²⁷ and Tanaka³⁰ took into consideration both the connectedness (related to $\langle \text{CN} \rangle$) and some energy (related to E_g , see Eq. (19) or related to E_o , see Eq. (23)).

In this part we examine the correlation between the glass-transition temperature of 186 chalcogenide glasses and overall bond energy of the covalent glassy network. Following the results of Sreeram et al.³³ and our recent results, see Part 3 of this paper, we assume that since chemical ordering effects seem to be pronounced in T_g versus chemical composition dependences, the covalent bond approach can be taken as an acceptable first approximation for network of chalcogenide glasses.

4.2 Data and Data Selection

In Table II are summarized systems whose T_g data (see Part 3) are taken into consideration, the number of T_g values used, references, bonds and bond energies used for the calculation of the overall mean bond energy. In the data selection two restriction have been made. First we take into consideration T_g values of glasses with chalcogen content equal to or less than 90 at. %. The reason is that in glasses with higher chalcogen content the matrix is composed of entities of parent glass (Se_m, S_n) and those arising from crosslinking. In this case the molecular character of the glassy matrix and its influence on the T_g values cannot perhaps be neglected and covalent bond approach should not be correct. It is in this region where Tanaka's³⁰ approach probably should be taken into consideration. Second there are indications that for glasses in Ge-As-Se system with the content of Se < 55 at. % the radial distribution function³⁴ gives an estimate of $\langle \text{CN} \rangle \sim 3.6 - 3.7$. This indicates that the standard assumption $\text{CN}(\text{Ge}) = 4$, $\text{CN}(\text{As}) = 3$ and $\text{CN}(\text{Se}) = 2$ is not valid. According to Krebs³⁵ this could be due to the low selenium content. In such case in liquid state the network has to break apart because there are not sufficient Se atoms

Table II The systems whose T_g data were used, number of T_g values used, references, chemical bonds and bond energies*

System	No. of T_g values	Ref.	Bond	Bond Energy eV	Bond	Bond energy eV	Bond	Bond energy eV
As-Se	13	19	As-Te	1.41	In-In	1.3	Ge-Sb	1.48
As-S	13(10)	19, 20	As-Se	1.8	Sb-Sb	1.31	Ge-As	1.54
Ge-Se	10	19	Sb-Se	1.86	As-As	1.38	Ge-Ga	1.6
Ge-S	10	31	As-S	2.0	Ga-Ga	1.48		
Ge-As-Se	42	19	In-Se	2.09	Ge-Ge	1.63		
Ge-Sb-Se	32	14, 18	Ge-Se	2.12	Se-Se	1.9		
Ge-Ga-Se	32	16	Ga-Se	2.32	S-S	2.2		
Ge-In-Se	37	15	Ge-S	2.4	Ge-In	1.47		

* Heteropolar bond energies were calculated using Pauling's relation

to form enough Ge-Se-As bridges, the mobility of atoms increases and hence the atoms are forced to higher coordination numbers. For this reason we take into consideration only T_g values of Ge-As-Se glasses with Se > 55 at.%, where we believe: CN(Ge) = 4, CN(As) = 3, CN(Se) = 2.

4.3 Discussion

We assume that to reach T_g one should overcome some energetical barrier. There are probably two contributions to this barrier. The first contribution is accompanied by the breaking of the network in such way that mobile entities are created. The second contribution, most probably a smaller one, is accompanied by some energy necessary to reorient entities to move. We suppose that the first contribution is most important and it is relevant to covalent bond approach. Moreover, we suppose that this contribution is proportional to some overall mean bond energy (\bar{E}) which is a function of the mean coordination number ($\langle \text{CN} \rangle$), kind of bonds, degree of crosslinking and bond energy forming a network. Examined systems (Table I) can be divided into two groups. In the first group (I) the condition CN(Se) = 2 is fulfilled for all the glasses discussed. This is the case of binary systems: $A_x C_{1-x} (\text{As}_x (\text{S}, \text{Se})_{1-x}; \text{Ge}_x (\text{S}, \text{Se})_{1-x})$ and ternary systems $A_x B_y C_z$ where B = As or Sb. Since CN(Ge) = 4, CN(As) = CN(Sb) = 3, CN(Se) = CN(S) = 2, the mean coordination numbers are

$$\begin{aligned} \langle \text{CN} \rangle &= x\text{CN}(\text{A}) + (1-x)\text{CN}(\text{C}) \\ \langle \text{CN} \rangle &= x\text{CN}(\text{A}) + y\text{CN}(\text{B}) + z\text{CN}(\text{C}) \end{aligned} \quad (25)$$

In the second group (II): $\text{A}_x\text{B}_y\text{C}_z = \text{Ge}_x(\text{Ga}, \text{In})_y\text{Se}_z$ the coordination number of B atom is assumed to be four^{16,22}: $\text{CN}(\text{Ga}) = \text{CN}(\text{In}) = 4$, see Part 3.2, part of Se atoms should be threefold coordinated. Hence, the mean coordination number for these glasses is

$$\langle \text{CN} \rangle = x\text{CN}(\text{A}) + y\text{CN}(\text{B}) = 3y + (z-y)\text{CN}(\text{C}) \quad (26)$$

where $3y$ means that there is y threefold coordinated Se atoms and hence there is $(z-y)$ twofold coordinated Se atoms ($\text{CN}(\text{C}) = 2$). We showed (see Part 3) that except for $\text{Ge}_x\text{As}_y\text{S}_z$ in every other system considered (or in the families of $\text{Ge}_x\text{Sb}_y\text{Se}_z$) the quantity R defined by Eq. (27)

$$\begin{aligned} R(\text{I}) &= z \frac{\text{CN}(\text{C})}{x\text{CN}(\text{A}) + y\text{CN}(\text{B})} \\ R(\text{II}) &= \frac{z\text{CN}(\text{C}) - y}{x\text{CN}(\text{A}) + y\text{CN}(\text{B})} \end{aligned}$$

divides a system (or a family of the system) into three parts. For $R = 1$ the system reaches stoichiometric composition since only heteropolar bonds are present. It is a point of the chemical threshold where usually maximal values of T_g are observed. For $R > 1$ the system is chalcogen rich (r). There are heteropolar bonds + chalcogen - chalcogen bonds present. For $R < 1$ the system is chalcogen poor (p). There are only heteropolar bonds + "metal-metal" bonds present. We define the degree of crosslinking/atom (P_r) for $R > 1$ and P_p for $R < 1$

$$\begin{aligned} P_r(\text{I II}) &= \frac{x\text{CN}(\text{A}) + y\text{CN}(\text{B})}{x + y + z} \\ P_p(\text{I}) &= \frac{z\text{CN}(\text{C})}{x + y + z} \\ P_p(\text{II}) &= \frac{z\text{CN}(\text{C}) + y}{x + y + z} \end{aligned} \quad (28)$$

The symbols I, II stand for groups I and II of the glasses discussed. The mean bond energy of an average crosslinking/atom value (\bar{E}_c) is given by

$$\begin{aligned} \bar{E}_c &= P_r E_{h.b.}; \quad R > 1 \\ \bar{E}_c &= P_p E_{h.b.}; \quad R < 1 \end{aligned} \quad (29)$$

where the average heteropolar bond energy is given by Eq.

$$E_{h.b.} = \frac{x \text{CN(A)}E_{A-C} + y \text{CN(B)}E_{B-C}}{x \text{CN(A)} + y \text{CN(B)}} \quad (30)$$

where E_{A-C} , E_{B-C} are heteropolar bond energies of A-C and B-C heteropolar bonds, see Table II. We define the average bond energy/atom of the "remaining matrix" ($\bar{E}_{r.m.}$)

$$\begin{aligned} \bar{E}_{r.m.} &= 2 \left(\frac{\langle \text{CN} \rangle}{2} - P_r \right) \frac{E_{C-C}}{\langle \text{CN} \rangle}; \quad R > 1 \\ \bar{E}_{r.m.} &= 2 \left(\frac{\langle \text{CN} \rangle}{2} - P_p \right) \frac{E_{<>}}{\langle \text{CN} \rangle}; \quad R < 1 \end{aligned} \quad (31)$$

In Eq. (31) E_{C-C} is the homopolar bond energy of S-S or Se-Se bond, see Table II, and $E_{<>} = (E_{A-A} + E_{B-B} + E_{A-B})/3$ is an average bond energy of a "metal-metal" bond in chalcogen poor region. Finally the overall mean bond energy is given by

$$\langle E \rangle = \bar{E}_C + \bar{E}_{r.m.} \quad (32)$$

For the 186 glasses summarized in Table II we calculated the values of overall mean bond energy ($\langle E \rangle$). The plot of T_g versus $\langle E \rangle$ (actually versus $\langle E \rangle - 0.9$) is shown in Fig. 12. Despite scatter of T_g values a good correlation between T_g and $(\langle E \rangle - 0.9)$ is evident. For most of the data the accuracy is not worse than $\pm 0.1 T_g$. This correlation satisfies the Arrhenius relation for viscosity in the form

$$\mu(T_g) = \mu_0 \exp\left(\frac{E}{K_B T_g}\right) \quad (33)$$

Taking $\mu(T_g) \approx 10^{13}$ poise, $\mu_0 = 10^{-3}$ poise and $E = \langle E \rangle - 0.9$ we obtain: $T_g \approx 314(\langle E \rangle - 0.9)$. The linearization of T_g versus $\langle E \rangle$ data using least square fit gives: $T_g \approx 311(\langle E \rangle - 0.9)$, see full line in Fig. 12. For comparison in Fig. 13 the plot T_g versus $\langle \text{CN} \rangle$ is shown indicating higher scatter in T_g values. We believe that our result can be taken as an acceptable demonstration that mainly the bonding arrangement determines the values of T_g in chalcogenide glasses. This does not mean that intermolecular interaction has no influence on T_g . There are experimental indications (e.g. from pressure experiments, see e.g. Refs^{31,36}) that intermolecular interaction influence T_g . Moreover, it is perhaps this interaction which takes a role in relaxation processes in the glass-transition region. We believe that this interaction enhances the changes of some properties in the vicinity of Tanaka's threshold^{2,38}. However, the overall compositional trend in T_g seems to be influenced mainly by the chemical bond arrangement.

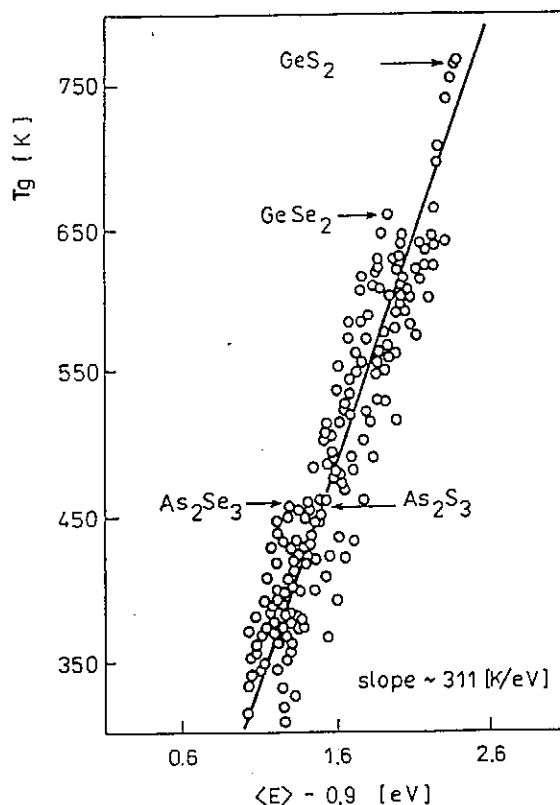


Fig. 12 The variation of T_g with the "overall" mean bond energy ($\langle E \rangle - 0.9$). Full line - least square fit. The slope of full line ~ 311 K/eV. Data sources, see Table II

We briefly summarize:

- (i) For 186 glasses, with T_g ranging from ~ 320 to 760 (K) a good correlation between T_g and $\langle E \rangle$ in the form: $T_g \approx 311(\langle E \rangle - 0.9)$ was observed.
- (ii) This correlation satisfies the Arrhenius relation for viscosity.

5 Summary

In this paper we tried to summarize some recent results concerning the problem of network structure of glasses considered from the point of view of network mechanical stability. Both the Phillips-Thorpe threshold and Tanaka's threshold are relevant to this problem. In real heteronuclear systems, however, most probably not only a network rigidity (i.e. connectedness) but also an actual chemistry (chemical bonding) play a role. It is most probably important when

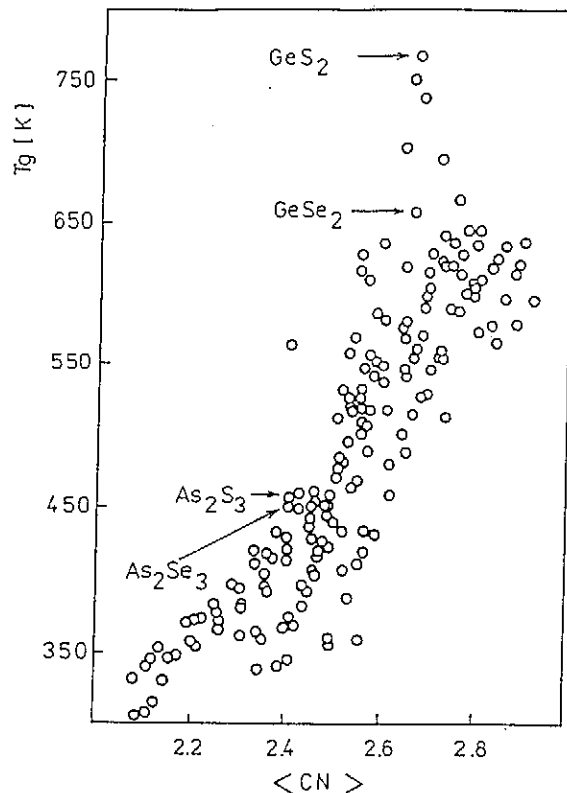


Fig. 13 The variation of T_g with the mean coordination number ($\langle CN \rangle$). Data sources, see Table II

examined properties are related to cohesive forces of a given solid. We defined a chemical threshold, in glassy alloys, corresponding to such chemical composition where only heteropolar bonds exist. We showed that it is this point where extreme values of the glass-transition temperature and compactness (except of Ge-As-S system) in various glass-forming chalcogenide systems are reached. Following this finding and assuming that chalcogenide glasses could be taken as a covalent solids we calculated "overall mean bond energy" ($\langle E \rangle$) related through the Arrhenius relation to the viscosity and thus related to the glass-transition temperature (T_g). For 186 chalcogenide glasses we found good correlation between $\langle E \rangle$ and T_g . This correlation indicates that it is most probably a chemical bond arrangement which determines mainly the glass-transition temperature of chalcogenide glasses.

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