

## Effect of composition and coordination number on some fundamental parameters in the Ge-Se glass

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Chalcogenide glasses of  $\text{Ge}_x\text{Se}_{100-x}$  ( $x=10, 15, 20, 25$  and  $30$  at.%) glasses were prepared by vacuum melting. An empirical relation between the glass transition temperature ( $T_g$ ) and  $\langle r \rangle$  is proposed by applying the Gibbs-Di Marzio equation for the  $T_g$  of a cross-linked polymer as a function of cross-linked density. We found a good agreement with the experimental result of  $T_g$  for  $\text{Ge}_x\text{Se}_{100-x}$  glasses. Several parameters such as mean atomic volume density, compactness, and free volume percentage which are more sensitive to the structure network changes were calculated. Their variation is discussed in connection with the proposed structural model. The variation of the molar volume and  $T_g$  with  $\langle r \rangle$  indicates the coexistence of topological and chemical ordering effects. With the structural modification, the number of lone-pair decreases, and the covalent coupling of the structural network increases with increasing Ge content, due to the increases in the cross-linked between Ge and Se bridge.

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### 1. Introduction

The glass transition mechanism is complex and the relationship between glass transition temperature ( $T_g$ ) and structural properties of glasses is still lacking [1]. Such relationships can be found in particular systems, especially when  $T_g$  is measured under standard conditions, for example at a fixed heating rate and when the structure of the glass system is simplified. However, few proposals were derived to understand that relation, for example, Kauzman has proposed the two-third rule, starting that  $T_g$  scales with the melting temperature [2]. As well, Tanaka deduced an empirical relationship between  $T_g$  and the average coordination number per atom ( $\langle r \rangle$ ):  $\ln(T_g) \approx 1.6 \times \langle r \rangle + 2.3$  [3]. This relation is valid for different glass-forming systems including chalcogenide glasses systems. Moreover, Varshney et al. have used the Gibbs-Di Marzio relation which is based on purely thermodynamical considerations in order to describe the  $T_g$  trends in multi-component chalcogenide glasses [4]. Nevertheless, all these descriptions become more and more complicated if one starts to vary the compositions of glass-forming material. Typical examples are the chalcogenide glasses (e.g. As-Se) or binary glasses involving a network former, (e.g. Ge-Se). Some simple rules for predicting  $T_g$  under the standard condition as a function of the composition and the nature of the atoms involved are existed [4]. One of these relations Tankas relation [5], however, there is still no general formulation of  $T_g$  versus the composition which could give the precise shape and explain with a mathematical model why maxima in  $T_g$  can occur in  $\text{Ge}_x\text{Se}_{100-x}$  glasses at  $x=33$  [6].

For many structural glasses, at least at low concentrations of the modifier,  $T_g$  increases as even small amounts of modifiers are added. In most cases, the function  $T_g(x)$  is quasilinear only for small modifier concentrations (small values of  $x$ ) and in some cases displays a maximum at some value of  $x$ , after which their derivative ( $dT_g/dx$ ) changes and becomes negative. Phillips proposed an elegant explanation of this phenomenon for the  $\text{Ge}_x\text{Se}_{100-x}$  alloy, based on the evaluation of the average number of constraints per structural unit [7].

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Zachariassen [8], found that there is a transition occurs in a small temperature range between 30 and 40 K around the average value denotes the value of  $T_g$ . It is known that the process is not a regular second-order phase transition in the thermodynamical sense [9,10]. The most important elementary process of agglomeration, which is the creation of a new bond (S or Se Bridge) between two clusters, can be analyzed in the case of binary glasses. The modifier transforms the glass former atoms in a well-defined manner (which may change the glass structure when the concentration of the modifier increases). The amount of the modifier can change the coordination number of the elementary basic structure unit of the glass former (e.g four- three- two - one - and zero-fold tetrahedral) in IV-VI-based glasses [11]. The  $\text{Ge}_x\text{Se}_{100-x}$  glass was chosen because it is one of the simplest covalent network glasses for which there is a lot of experimental data [4,12-13] although most of the relationships between  $T_g$  and structural or physical properties are empirical [14].

One of the main purposes of this study is to investigate the effect of  $\langle r \rangle$  on some of the basic properties such as density, molar volume, compactness, and  $T_g$ . A semi-quantitative attempt was made to correlate the properties with the values of the cross-linking density  $X$  and the network connectivity  $kX$ . In addition, the Gibbs-Di Marzio model was applied to determine the structural variation such as the cross-linking density and the network connectivity using experimental data of  $T_g$ . Moreover, the value of the system-dependent relation constant B for the Ge-Se glasses was determined.

## 2. Experimental techniques

High purity (~99.999 %) Ge and Se (purchased from Aldrich) inappropriate preparations were weighted according to their atomic percentages (at.%) inserted into a quartz glass ampoule (1.2 cm diameter). The contents samples are 15 g in total were sealed at a pressure of  $10^{-4}$  Torr, and heated in a rotating furnace at around 1300 K for 24 h. The melt was quenched in ice water at 273 K to obtain the Ge-Se glass with different compositions of  $\text{Ge}_x\text{Se}_{100-x}$  ( $x=10, 15, 20, 25, \text{ and } 30$ ).

The thermal behavior was investigated using a Du Pont 1090 differential thermal analysis. The temperature calibration of the instrument was performed using the well know melting temperature of high purity Indium supplied with the instrument with a temperature accuracy of around  $\pm 0.1$  K.

The crystallization thermograms were recorded under a uniform heating rate ( $\beta$ ) ranging from 3.5 to 40 K/min. Typically 20 mg of sample in powdered form (particle size less than 54  $\mu\text{m}$ ) was scanned over a temperature range from 300 to ~650 K. The values of  $T_g$  were determined with accuracy  $\pm 0.1$  K using the microprocessor of the thermal analyzer.

## 3. Results and discussions

### 3.1. Glass transition temperature analysis

A chalcogenide glass system can be thought of as a network chain in which cross-linking units are added. A model that describes the relationship of  $T_g$  to increased cross-linking was developed by Di-Marzio [15]. They developed a theory based on equilibrium principles and assumed that the glass transition is a second-order phase transition that relates to the increase of  $T_g$ , at the growing presence of these cross-linking agents. Their theory successfully explained the  $T_g$  data in polymers [16-17]. Di-Marzio [18] later adopted this theory for glass transition versus chain stiffness to take into account the effect of cross-linking upon the  $T_g$ . The  $T_g$  of the cross-linked glass versus cross-linking density  $X$  could be expressed by the Gibbs-Di Marzio equation:

$$T_g = \frac{T_0}{(1-kX)} \quad (1)$$

Here  $T_0$  is the glass transition temperature of the non-cross-linked parent chain, and  $k$

presents the fraction of repeat units that are connected to more than two other units. Several properties, such as  $T_g$ , density, molar volume, and free volume have indeed been found to depend upon  $\langle r \rangle$ . In addition, modified the Gibbs-Di Marzio equation and expressed  $T_g$  in terms of the  $\langle r \rangle$ , which is widely used for the description of network glasses [4]. They redefined, for multi-component chalcogenide glasses,  $X$  as being equal to the  $\langle r \rangle$  of the cross-linked chain minus the coordination number of the initial chain (Se), *i.e.*:

$$X = \langle r \rangle - 2 \quad (2)$$

The Gibbs-Di Marzio equation may then be rewritten in terms of  $\langle r \rangle$  as:

$$T_g = \frac{T_0}{1 - B\{\langle r \rangle - 2\}} \quad (3)$$

We noticed that the constant  $k$  in Eq. (1) has been changed to a new constant  $B$  in Eq. (3), where  $B$  is only a system-dependent constant, related eventually to the bond interchange (which is responsible for the system-dependent structural relaxation). It is to be recognized that  $0 < B(\langle r \rangle - 2) < 1$ . It was found that the constant  $B$  was calculated from the  $T_g$  estimations and it was found a lie between 0.55 and 0.75, depending on the considered system and the involved atom [4].

Let us now denote the coordination number of the modifier atom by  $m'$  (such as a Ge atom in  $\text{Ge}_x\text{Se}_{100-x}$  systems) while the non-modifier atom by  $m$  (such as a Se atom). Then the relation between  $T_g$  and the modifier concentration,  $m'$  and  $m$ , in a poorly modifier system is given by [3]:

$$\left(\frac{dT}{dx}\right)_{x=0} = \frac{T_0}{\text{Ln}(m'/m)} \quad (4)$$

The value of  $T_g$  in binary glass increases with the addition of a modifier, that increases the  $\langle r \rangle$  for  $m' > m$  and decreases with the addition of a modifier that decreases  $\langle r \rangle$  for  $m' < m$ .

The value of  $\langle r \rangle$  is given by:

$$\langle r \rangle = m(100 - x) + m'x \quad (5)$$

Sreeram [4] started the investigation of multi-component chalcogenide systems from pure vitreous Se, hence  $m=2$ . Kerner gives the analytical expression of the constant  $B$  involving only the coordination number  $m'$  and  $m$  related to Eq. (4) with the modified Gibbs-Di Marzio equation as follows [14]:

$$\frac{1}{B} = (m' - m)\text{Ln}\left(\frac{m'}{m}\right) \quad (6)$$

The value of  $B$  can now be computed for binary systems if the coordination number of atoms is known. According to Eq. (6) and since  $m'$  and  $m$  are the coordination numbers of Ge and Se respectively, the value of  $B$  is equal to 0.72. Table (1) represents the values of  $\langle r \rangle$  and experimental value of  $T_g$  ( $T_{g\text{exp}}$ ) in comparison with the theoretical values of  $T_g$  ( $T_{g\text{th}}$ ) which determine from the Gibbs-Di Marzio equation. Fig. 1a shows a satisfactory agreement between the experimental and the theoretical values of  $T_g$  for the  $\text{Ge}_x\text{Se}_{100-x}$  system. This figure proves that Gibbs-Di Marzio's equation of  $T_g$  agrees well with our  $\text{Ge}_x\text{Se}_{100-x}$  system results. We applied the Gibbs-Di Marzio equation to calculate the network connectivity  $kX$  by using our experimental values of the glass transition.

Table 1. Values of the average coordination number  $\langle r \rangle$ , the theoretical ( $T_{g\text{th}}$ ) and experimental ( $T_{g\text{exp}}$ ) glass transition temperature, density ( $\rho$ ), molar volume ( $V_m$ ), compactness ( $\delta$ ), FVP, refractive index ( $n_0$ ), and the calculated network connectivity ( $kX$ ) for the  $\text{Ge}_x\text{Se}_{100-x}$  glass.

composition	$\langle r \rangle$	$T_{g\text{exp}}$	$T_{g\text{th}}$	$\rho$ (g/cm <sup>3</sup> )	$V_m$ (cm <sup>3</sup> /mol)	$\delta$	FVP	$n_0$	$kX$
<b>Ge<sub>10</sub>Se<sub>90</sub></b>	2.2	369	361.5	4.328	18.097	-0.287	10.82	3.03	0.144
<b>Ge<sub>15</sub>Se<sub>85</sub></b>	2.3	395	384.3	4.341	17.937	-0.278	10.79	3.04	0.216

<b>Ge<sub>20</sub>Se<sub>80</sub></b>	2.4	443	407.2	4.361	17.815	-0.274	10.76	3.09	0.288
<b>Ge<sub>25</sub>Se<sub>75</sub></b>	2.5	510	430	4.331	17.869	-0.286	12.00	3.8	0.36
<b>Ge<sub>30</sub>Se<sub>70</sub></b>	2.6	580	425.5	4.291	17.96	-0.302	13.23	3.92	0.432

We correlate the properties of the Ge-Se glass with the values of the cross-linking density  $X$  and the network connectivity  $kX$ . We noticed that the  $X$  increased with increasing the  $\langle r \rangle$ . We applied the modified Gibbs-Di Marzio equation to our system to determine the experimental value of B, so the modified Gibbs-Di Marzio equation for our system can be written by using the experimental value of  $T_o$  and B:

$$T_g = \frac{316}{[1-0.71(\langle r \rangle - 2)]} \quad (7)$$

Fig. 1b shows the relation between  $T_g$  and Ge content. We determine the experimental value of  $(m'/m)$ , the value of  $\ln(m'/m)$  is positive and equal to 0.723 and  $m'/m=2.06$  which is very closed to 4/2. This implies that the energy involved in the creative bond of the type AB atoms is greater than the energy involved in the creative bond of AA-type atoms. The experimental value of the system-dependent constant B which is related eventually to the bond interchange [14] equal to 0.71 and for our system, this value is a good agreement with the value of B [5] which varies between 0.55 and 0.75.

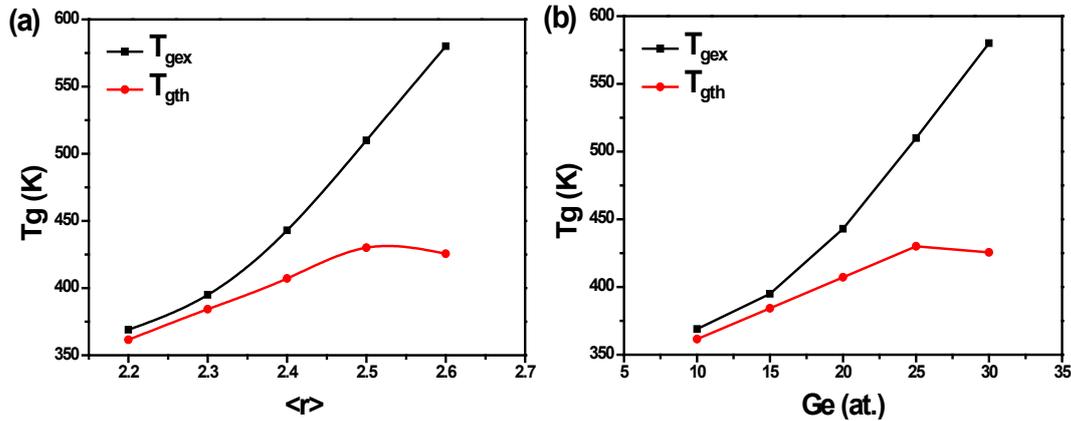


Fig. 1. (a) Comparison between the variations of experimental ( $T_{gex}$ ) and theoretical ( $T_{gth}$ ) glass transitions values versus the average coordination number  $\langle r \rangle$ , (b) the relation between  $T_{gex}$  and  $T_{gth}$  versus the modifier content (Ge).

The observed dependence of  $T_g$  on composition could be predicted qualitatively on the basis of a chemically ordered network model [19-20], in which the formation of hetero-polar bonds are favored over the formation of homo-polar bonds. In this model, the glass structure is assumed to be composed of cross-linked structural units of stable chemical compounds (hetero-polar bonds). Our result indicates that the network connectivity (which defines the average number of bridging per network forming atom) increases with increasing the modifier content. The atoms of the modifier (Ge) produce cross-linking between Ge-Se glass could be attributed to increasing the amount of Se bridging due to the formation of the Ge-Se bond. Ray [20] has shown that the fraction of effective cross-linking sites diminishes with an increasing cross-linking atom. It is reasonable to assume that the transformation temperature of these glasses is closely related to the cross-link density and network connectivity of the amorphous structure since the value of the constant  $k$  should be independent of the composition. The structure change from a two-dimensional (2D) layered structure formed through the branching of the Se chain is fully developed at this composition, creating new stable structural units.

### 3.2. Density, molar volume, and compactness

The densities of glass are governed by both the atomic mass and the structure of the components. If chemical compositions are known, deviations from the ideal behavior provide

information on the structural differences. Systematic determinations of density as a function of chemical composition are therefore important. Assuming that the increase in the volume during the melting of a solid is inherent in the amorphous state (super-cooled liquid), then the structure of amorphous solids should contain free volume.

The mean gram atomic volume ( $V_m$ ) was calculated using the following relation [22].

$$V_m = \sum A_i X_i / \rho \quad (8)$$

where  $A_i$  and  $X_i$  are the atomic weight and atomic fraction of the glass element, respectively, and  $\rho$  is the experimental density of the glass. The free volume percentage (FVP) in the glass was obtained using the relation:

$$FVP = \frac{(V_m - V_c)}{V_m} 100\% \quad (9)$$

The calculation of  $V_c$  for the composition  $\text{Ge}_x\text{Se}_{100-x}$  was performed using the formula:

$$V_c = xV_{(Ge)} + yV_{(Se)} \quad (10)$$

where  $V_{(Ge)}$  and  $V_{(Se)}$  are the atomic volumes of Ge and Se elements. The compactness ( $\delta$ ) is a measure of the normalized change of the mean atomic volume due to the chemical interaction of the elements forming the network of a given solid [23]. Consequently, the mean atomic volume  $V_T$  is more sensitive to the structure network changes. The value of  $\delta$  was calculated using the formula [24-25]:

$$\delta = \frac{(\sum V_i - V_{exp})}{V_{exp}} \quad (11)$$

where  $V_i$  corresponds to the volume of its component in elemental form and  $V_{exp}$  stands for experimentally found density and volume of the whole sample respectively.

Fig. 2 shows the dependence of the change of both the mean-gram atomic volume (the molar volume  $V_m$ ) and the density of the investigated compositions. The density of the investigated glasses was found experimentally, by the Archimedes method. Fig. 3 shows the relation between the FVP and the compactness with the average coordination number. The prominent features observed in these figures are that there is a maximum value of the density and  $\delta$  at  $\langle r \rangle = 2.4$ , while FVP shows a minimum value at  $\langle r \rangle = 2.4$ . Our results can be explained using the chemically ordered network (CON) model [19-20] and the Topological model [26,28]. In the CON mode, atoms bond favorably with atoms of different kinds than with the same kind, thus maximizing the amount of chemical ordering. This is because the maximum number of hetero-polar bonds is formed first. The remaining part of the valence requirement is met by homo-polar bonding at random. Based on this bonding scheme, the structure of Ge-Se glasses can be pictured to be made up of structural units (S.U) of  $\text{GeSe}_4$  tetrahedral in accordance with the 4-2 coordinated network configuration.

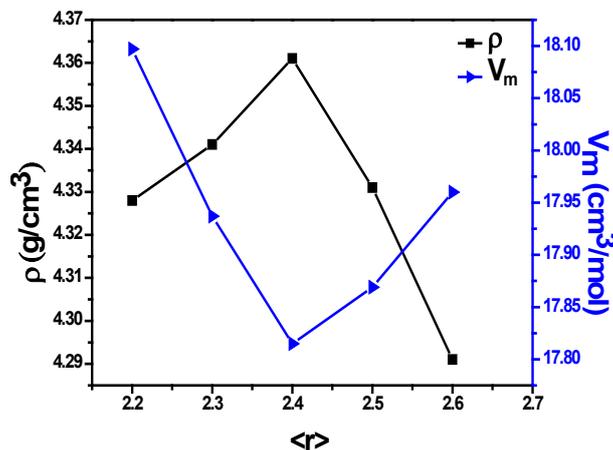


Fig. 2. The variation of the density of the composition ( $\rho$ ), left-hand side, and the molar volume ( $V_m$ ), right-hand side, with the average coordination number  $\langle r \rangle$ .

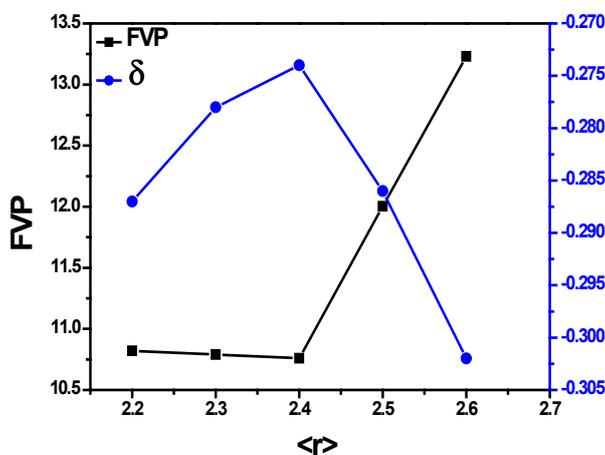


Fig. 3. The relation between the free volume percentage (FVP), left-hand side, and the compactness ( $\delta$ ), right-hand side, versus the average coordination number  $\langle r \rangle$ .

The stoichiometric compositions  $\langle r \rangle = 2.4$  exhibits extreme in properties. The stability of the network with  $\langle r \rangle = 2.4$  where the floppy-to-rigid transition takes place can be associated with atomic arrangements that became more tightly bound and with shorter bond length. The stability of the structure at  $\langle r \rangle = 2.4$  is due to the presence of compact tetrahedral structure units and does not allow bond modifications. This caused a decrease in the mean atomic volume of the network, hence with a maximum in its compactness and a minimum in free volume. From our previous result on the refractive index, we noticed that [29], the value of the refractive index is highly increased for  $\langle r \rangle$  greater than 2.4, Fig. 4. This version can be attributed to the structural rearrangement caused by an increase in materials density as Ge content increased.

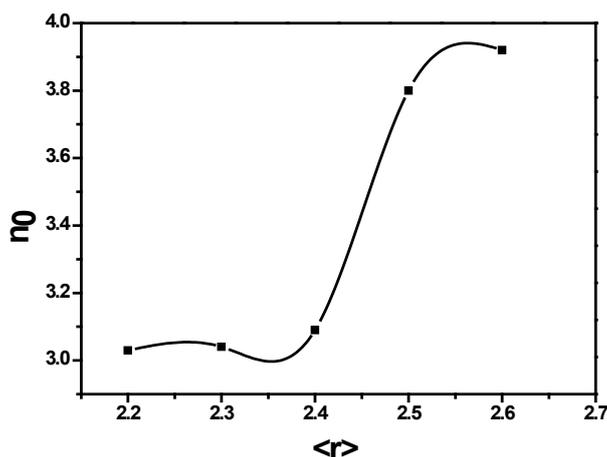


Fig. 4. The variation of refractive index ( $n_0$ ) against the average coordination number  $\langle r \rangle$ .

The observed maximum of the density at  $\langle r \rangle$  equal to 2.4 would imply that the packing of atoms becomes closest if Se-Se bridging bond exists per GeSe 4/2 molecule. However, the introduction of the amount of Ge  $\langle r \rangle$  greater than 2.4 in the Ge-Se system produces further disorder and reduces the network rigidity, thus allowing bond rearrangements, with a further increase of Ge content. The connection of GeSe 4/2 molecules will require more space due to the

possibility of the torsion reduced [30].

The largest free volume corresponds to Ge-rich glass, which suggests that the free volume and dimensionality of the network may be related to the occurrence and extent of such structural effects. Usually, 3D networks have larger free volumes, larger network connectivity, and smaller compactness compared to layered (2D) or chain (1D) structures, and this condition appears to be valid for our results. We suggest that the Ge-Se system is characterized by a layer structure in which covalent bonding is restricted in two dimensions in the plane of the layer and with Van der Waals forces in the third dimension. The topological model based on the constraints theory has found acceptance in accounting for the features observed in the property-composition data of several chalcogenide glass systems. In this mode, the properties are discussed in terms of the  $\langle r \rangle$ , which is indiscriminate to the species of the valence bond. Taking short-range structure into account and equating the number of operative constraints to the number of degrees of freedom, the Extension of this model to 2D networks considering medium rang ordering indicated [31] the occurrence of a morphological transition to three-dimensional network due to cross-linking at  $\langle r \rangle = 2.4$ . Both short and medium-range orders reflect upon the mean atomic volume of chalcogenide glasses. Therefore these transitions are seen in the  $V_m$  versus  $\langle r \rangle$  plot and marked by occurrences of a minimum in  $V_m$  at  $\langle r \rangle = 2.4$  and the value of  $V$  increase with increasing the value of  $\langle r \rangle$ . The composition with  $\langle r \rangle = 2.4$  exhibits the floppy to rigid transition. Accordingly, it could be confirmed that the validity of the topological model based on the structural dimensionality consideration is a suitable model for discussing the variation of the physical parameters of the  $\text{Ge}_x\text{Se}_{100-x}$  system with its compositions. In particular, the variation of the molar volume and glass transition temperature with  $\langle r \rangle$  for Ge-Se glasses indicates the coexistence of topological and chemical ordering effects [32].

### 3.3. Efficiency and structural modification

The physical basis of structural modification, in general, is determined by changes in (i) the dimensions of the structural units, (ii) their configuration, and (iii) the concentration of units with different configurations, as well as changes in concentration and/or type of defects. The structure difference between the non-crystalline and the crystalline forms can be characterized by the excess entropy of the former. It has been shown by Nemilove [33] that the entropy of the structural disorder of non-crystalline solids consists of two parts. The first one,  $\Delta S_{const}$  does not depend on the condition of specimen preparation, and is a function of the configuration of elementary structural units forming the network of crystalline materials and is given by:

$$\Delta S_{const} = 0.4 \times \frac{2}{3} \times D \quad (12)$$

where D denotes the parameter which characterizes the number of dimensions in which covalently bonded clusters can extend. In glassy Se of  $N_c=2$ , the network dimension is approximately unity. Upon introducing the Ge atom to glassy Se, the one-dimensional molecules are cross-linked and a gradual structure transformation from  $D = 1$  to 2 takes place. Hence, we can evaluate  $\Delta S_{const}$  for our  $\text{Ge}_x\text{Se}_{100-x}$  system as:

$$\Delta S_{const} = 0.4 \times \frac{2}{3} \times 2 = 0.533 \quad (13)$$

The second part  $\Delta S_{var}$  depends on the condition of preparation of the specimen as assumed by Dembovsky [34] and is a function of the average number of lone-pair electrons per atom. Thus, the degree of possible changes in the structure and the properties which we call the structure modification ( $\Delta\varphi$ ) is determined by the ratio:

$$(\Delta\varphi) = \frac{\Delta S_{var}}{\Delta S_{const}} \quad (14)$$

This ratio should increase with increasing the number of lone-pair electrons,  $(N_{os}-N_c)/2$ , and decreasing the covalent coupling of the structural network.  $N_c$  and  $N_{os}$  are the  $\langle r \rangle$  and the

average number of electrons in the outermost shells of the atoms respectively. The covalent coupling of the structural network is determined by the number of covalent bonds per atom ( $N_c/2$ ) and their covalency (with increasing ionicity or metallicity of the bonds). The ionicity of the bonds can be determined by considering the electro-negativity difference of the atoms. It is known that the metal city of the bonds increases with the increase of atomic number in the periodic table, however, it is rather difficult to estimate the metal city in terms of this quantity. The degree of metalization ( $M$ ) is taken to be proportional to the average number of electrons per atom with respect to selenium, as:

$$M = (N_c - N_{c(Se)}) \times 10^{-2} \quad (15)$$

In view of this consideration, it is interesting to investigate  $\Delta\phi$ . The meaning of  $\Delta\phi$  is expressed by the fact that, the possibility of obtaining various structural configurations in glassy increases with an increase in the degree of freedom of the structural units and of the number of lone-pair electrons capable of forming unusual structural units for a given material. The influence of Ge on the number of covalent bonds per atom ( $N_c/2$ ) the degree of metalization  $M$  as well as on the number of lone-pair electrons,  $(N_{os}-N_c)/2$ , are listed in Table 2.

Table 2. Values of parameters used for determining the structure modification ( $\Delta\phi$ ) for the  $Ge_xSe_{100-x}$  system.

composition	$N_c$	$N_c/2$	$N_{os}$	$(N_{os}-N_c)/2$	$M$	$\Delta\phi$
<b>Ge<sub>10</sub>Se<sub>90</sub></b>	2.2	1.1	5.8	1.8	0.002	3.377
<b>Ge<sub>15</sub>Se<sub>85</sub></b>	2.3	1.15	5.7	1.7	0.003	3.189
<b>Ge<sub>20</sub>Se<sub>80</sub></b>	2.4	1.2	5.6	1.6	0.004	3
<b>Ge<sub>25</sub>Se<sub>75</sub></b>	2.5	1.25	5.5	1.5	0.005	2.181
<b>Ge<sub>30</sub>Se<sub>70</sub></b>	2.6	1.3	5.4	1.4	0.006	2.627

One can see from the previously listed results that  $\Delta\phi$  decreases with increasing the Ge concentration, since  $(N_{os}-N_c)/2$  decreases, while  $N_c/2$  as well as  $M$  increases. The assumption mentioned above is confirmed by the chain-crossing model (CCM) proposed by Trance et al. [35] and Phillips's theoretical model [7] of Se with Ge, in which he concluded that the glass formation in the  $Ge_xSe_{100-x}$  is up to  $x=0.33$ . From our previous RDF measurements for the system [36] we also support the above arguments.

#### 4. Conclusion

The theoretical values of  $T_g$  based on the Gibbs-Di Marzio equation well agree with the experimental values for the  $Ge_xSe_{100-x}$  system. The results show that the network connectivity and the cross-link density increase with increasing the Ge content. This attributed to increasing the amount of Ge-Se bond, consequently the structure change from 2D to 3D layered structure and creating new stable structural units GeSe 4/2. A maximum value of the density and compactness is observed at  $\langle r \rangle = 2.4$ , where the free volume percentage has a minimum value. These results explain by the chemically ordered network model, where the stability of the network at  $\langle r \rangle = 2.4$  is attributed to the transition from floppy-to-rigid takes place. This transition associated with atomic arrangements becomes more tightly bound and with shorter bond length, this causes a decrease in the mean atomic volume of the network, hence with a maximum in its compactness and a minimum in free volume. The presence of Ge leads to  $\langle r \rangle$  larger than 2.4 in the Ge-Se system produces further disorder and reduces the network rigidity, thus allowing bond rearrangements. The connection of GeSe 4/2 molecules will require more space due to the possibility of the torsion reduced. We suggest that the Ge-Se system is characterized by a layer structure in which covalent bonding is restricted in 2D in the plane of the layer and with Van der Waals forces in the third dimension. Usually, 3D networks have larger free volumes, larger

network connectivity, and smaller compactness compared to 2D or 1D structures. The variation of the physical parameters of  $\text{Ge}_x\text{Se}_{100-x}$  with  $\langle r \rangle$ , such as the variation of the molar volume and glass transition temperature indicates the coexistence of topological and chemical ordering effects in the Ge-Se structure. The structural modification decreases with increasing the Ge content, as a result of increases in the cross-linked between Ge and Se bridge. The number of lone-pair-electrons decreases, consequently, the covalent coupling of the structural network  $N_c/2$  increases.

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