

Study of Average Coordination Number Using Topological Concept in Ge-In-Se Glasses

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ABSTRACT

The growing interest in the investigation of the properties of chalcogenide glasses stems from the actual and potential technological applications of these materials in solid state devices. Moreover, several of these glasses are easily formed by melt-quenching over a large range of compositions making them suitable model systems for the investigation of the composition dependence of their properties. In this paper, we reported the results from measurement of the glass composition $Ge_{22}In_xSe_{78-x}$ ($x=2, 4, 6, 8, 10$), the dependence of glass transition temperature T_g , atomic percentage of Se and atomic density with variation in average coordination number (Z) on the basis of topological considerations.

Keywords: Chalcogenide Glasses, Coordination Number; Glass Transition; Atomic Density.

INTRODUCTION

To grasp the structure of disordered solids has been one of the longstanding problems in condensed-matter physics [1]. For crystalline materials, Understanding the relationships between microscopic structures and macroscopic properties has been a subject in solid-state physics. As it is well known that amorphous solids possess no long-range order, and not many established techniques capable of identifying nonperiodic 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. On the basis of the amorphous structure of covalent glasses, building elements may be classified into two components; one is normal bonding structure consisting of covalent bonds of densities on orders of 10^{22} - 10^{23} cm^{-3} , which can be specified by chemical and topological natures, and the other one is defects, e.g., impurities, valence-alternation pairs, dangling and wrong bonds, i.e., the homopolar bonds in stoichiometric alloys [2,3]. The density of defective bonds is, in general, less than 10^{-2} of that for the covalent bonds, and therefore structural behaviours are determined mostly by the normal configurations. Further, these are primarily responsible for such electronic properties as the band-gap energy. Thus, 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.

The coordination number is preserved in covalent glasses, obeying the so-called 8 - N rule, where N is the valency of an atom. The rule suggests that the numbers of nearest-neighbor atoms for Se, In, and Ge are 2, 3, and 4, respectively. The average coordination number Z of covalent bonds is a good measure representing characters of atomic units [4,5,6]. If a sample has a composition of $Ge_xIn_ySe_{1-x-y}$, then

$$Z = 4x + 3y + 2(1 - x - y) \quad (1)$$

It should be kept in mind that an implicit assumption made on using the average coordination number is indiscriminate in species of valence bonds. The chemical property is obscured, and instead, the topological nature will emerge.

Topological considerations

It may be valuable to consider the transitions at $Z = 2.4$ and 2.67 in light of the constraint-counting argument originally proposed by Phillips for amorphous covalent materials [5,7,8]. Taking the short-range structure into account, according to Phillips' constraints theory, in the glasses having the highest stability, the number of topological constraints N_{co} , evaluated for an atom is equal to the number of the flexibility, namely the spatial dimension $N_d = 3$:

$$N_{co} = N_d \quad (2)$$

For a material having the coordination number of Z , $N_{co}(Z)$ can be expressed as a sum of radial and angular valence-force constraints: [5, 9-11]

$$N_{co}(Z) = Z/2 + (2Z - 3), \quad (3)$$

where 2 in the angular term corresponds to the two freedoms θ and ϕ in a polar-coordinate representation (r , θ and ϕ) of an atom bonded to another atom located at the origin, and 3 can be related to the system rotation around x , y , and z axes. Combining the eqs. (2) and (3), we obtain $Z = 2.4$, i.e., the coordination number of the most stable glass is 2.4. The same conclusions are also drawn by percolative arguments and counting the number of zero frequency modes [11-14]. However, this is a surprising result as it is not material specific and there are no adjustable parameters involved in calculations [5, 15].

Later extending the Phillips's prediction, Tanaka expressed the constraint for an atom included in a planar cluster extending in two dimensional glass structure [5, 9-11].

$$N_{co}(Z) = 3 = Z/2 + (Z - 1) \quad (4)$$

where the angular term is calculated as excess degrees of Z variables in θ over a rotation freedom around the z axis. The number of the angular constraints is reduced to $(Z - 1)$ because of the presumption of the planar medium-range configurations. If the cluster is laid in a three-dimensional space, each atom must have three independent freedoms for stable existence. The expression in eqn (4) gives $Z = 2.67$, i.e., a two-dimensional glass may be fixed stably in a three-dimensional space, if the coordination number is 2.67.

MATERIALS AND METHODS

For the preparation of Ge-In-Se glasses, high purity elements (99.999 %) in appropriate atomic percentage were weighed in to quartz ampoules. The ampoules, sealed under high vacuum conditions (10^{-5} Torr) were suspended in a vertical furnace at 900°C for 24 hours, shaken vigorously for homogeneous mixing. The temperature was raised at a rate of 3 to 4 K/min. The melt was rapidly quenched in ice-water mixture. The quenched samples were removed from the ampoule by dissolving the ampoule in a mixture of $\text{HF} + \text{H}_2\text{O}_2$ for about 20 hours. The samples were then kept at room temperature in dark for about one month for attainment of thermodynamic equilibrium as stressed by Abkowitz in chalcogenide glasses [16]. Amorphous nature of the samples was ensured by the absence of any sharp peaks in the X-ray diffractograms. The prepared solid solution in powder form has been used for thermal analysis using the Differential Thermal Analysis (DTA). This material was first sealed in a standard aluminium pan and the calorimetric thermo grams of various compositions of the samples were obtained with DTA calorimeter in the temperature range $50\text{--}700^\circ\text{C}$ at various heating rates ($10\text{--}20\text{ K min}^{-1}$). Calorimetric measurements were made under non-isothermal conditions to study glass transition temperature T_g .

RESULTS AND DISCUSSION

Thorpe also interpreted Transition from an under constrained to an over constrained network [10,11] in terms of percolation of rigidity in an inhomogeneous medium containing both rigid and floppy regions. Anomalous features in many physical properties have been reported around $Z = 2.4$ to $Z = 2.67$ in several systems. The ternary glass

system Ge-In-Se has got one of the largest glass forming regions among chalcogenide glasses. Therefore, it is particularly well suited to test the validity of the above concepts. Germanium, Indium and selenium are elements of groups IV, V, and VI respectively. This brings about the covalent character of the interaction between their atoms and results in a broad glass-forming region. In the three component Ge-In-Se system, selenium will react with germanium and produce structural units of $\text{GeSe}_{4/2}$. When germanium is introduced into indium selenides, gradual composition changes takes place in the system forming $\text{GeSe}_{4/2}$ and $\text{InSe}_{3/2}$ structural units. Also, formation of complex structural units like $\text{Ge}_{4/2}\text{In}_2\text{Se}_{4/2}$ occurs. Approximate thermo chemical calculations indicate that in the three component Ge-In-Se system, there can be several sections with different contents of structural units and consequently, with different physical and chemical properties. There can be sections in which the structure is determined mainly by bonds of the selenium type [17].

The composition dependence of many physical properties of Ge-In-Se system of glasses show anomalous variations at $Z = 2.4$ and at $Z = 2.67$. Elastic constants of Ge-In-Se glasses show a threshold behaviour at $Z = 2.4$ [3], but the data do not match with a previous report [15]. The persistent infrared spectral hole burning studies of the effect of network topology on low temperature relaxation in Ge-In-Se system of glasses do not show any indication of a rigidity transition or any other unusual features at $Z = 2.4$ [18]. On the other hand, the composition dependence of optical band gap and thermal diffusivity show threshold maxima at $Z = 2.67$ [19].

The average coordination number Z for the glass composition $\text{Ge}_{22}\text{In}_x\text{Se}_{78-x}$ is calculated using the relation

$$Z = [22\text{Nc}(\text{Ge}) + x\text{Nc}(\text{In}) + (78 - x)\text{Nc}(\text{Se})] / 100 \quad (5)$$

where $\text{Nc}(\text{Ge})$, $\text{Nc}(\text{In})$ and $\text{Nc}(\text{Se})$ are the average coordination numbers of Ge, In and Se, respectively. Average coordination numbers of four for Ge, three for In and two for Se, obeying the so-called $(8 - N)$ rule [20], were adopted. An average coordination number of three for In, a value that was recently obtained by earlier workers [21] from extended X-ray absorption fine structure (EXAFS) measurements on Ge-In-Se glasses was used in the calculation of Z . The compositions prepared covered a range of Z values from 2.48 to 2.64 with a decrease in Se concentration from 76 to 68 [Fig. 1]. The variation of glass transition temperature T_g with Z is shown in fig. 2. The graph indicates the increase in T_g with increase in Z but decreasing Se at %.

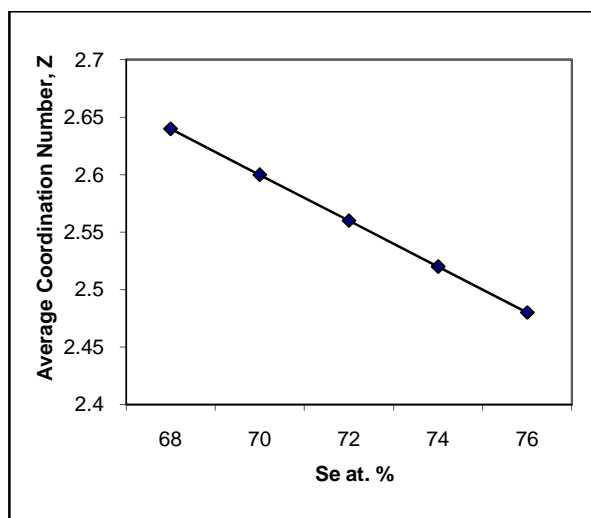


Fig.1 : Variation of Average Coordination Number with Se at. %

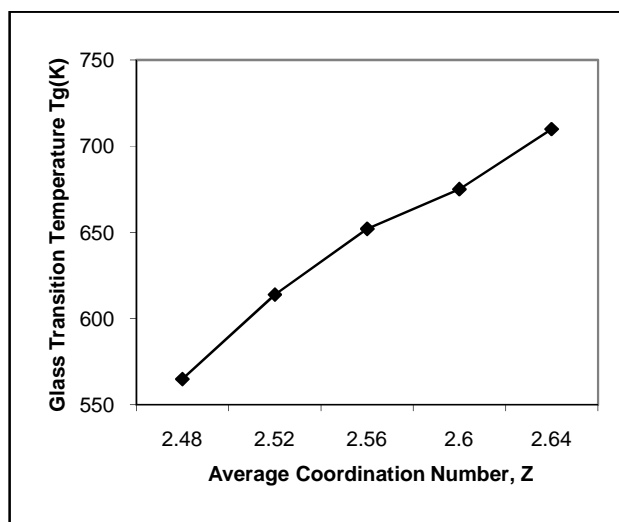


Fig. 2: variation of glass transition temperature T_g with Z

The ambient macroscopic density measurements were performed by the Archimedes method. The samples used for density measurements were carefully chosen free from cracks and cleaned in methanol to remove surface contaminations. The atomic density was calculated from the formula [22]

$$\rho = \rho_0 N_A / \sum c_n A_n \quad (6)$$

where ρ_0 , N_A , c_n and A_n are the measured density, Avogadro's number, atomic concentration and atomic weight of the n^{th} component, respectively.

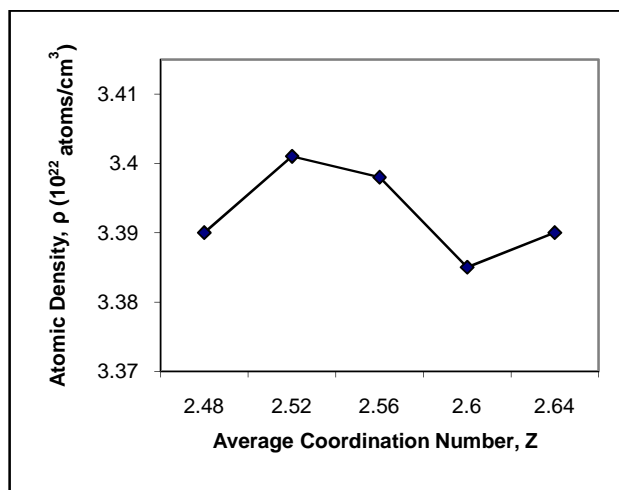


Fig. 3: Variation of atomic density with Z

The variation of ρ with Z for glasses with 72 at% Se is shown in fig. 3. The $\rho - Z$ dependence for glasses with 74 at% Se reveals a broad maximum at $Z = 2.52$ corresponding to the composition with 22 at % Ge. This maximum can be accounted for by using Tanaka's structural transition model [23-25].

CONCLUSION

The dependence of glass transition temperature T_g , atomic percentage of Se and atomic density with variation in average coordination number (Z) on the basis of topological consideration has been found suitable and in accordance with earlier reported works. The anomalies observed in the atomic density-composition dependence and Average Coordination Numbers in glasses of the Ge-In-Se system are found to be consistent with the models of topological transition and the ordered bond network model given by Phillips, Thorpe and Tanaka.

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