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Atomic Density versus Average Coordination Number in Ge–In–Se Glasses

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The variation of the atomic density ρ with the average coordination number Z for glasses belonging to the $\text{Ge}_x\text{In}_6\text{Se}_{94-x}$ and $\text{Ge}_x\text{In}_{12}\text{Se}_{88-x}$ families of the Ge–In–Se system is investigated. The ρ – Z dependence displays broad maxima at Z values of 2.42 and 2.58 for families with 6 and 12 at% In, respectively. These maxima are ascribed to changes from a floppy to a rigid type network and from a two-dimensional layered structure to a three-dimensional network, respectively. The minima exhibited in the ρ – Z dependence at $Z = 2.63$ for the In_6 family and at $Z = 2.71$ for the In_{12} family, corresponding to the tie-line compositions, are attributed to chemical ordering effects.

1. Introduction

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 [1]. These applications include memory and threshold switching, xerography, inorganic photoresists and IR detection and transmission. 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. Such studies on mechanical [2], optical [3], thermal [4], electrical [5], physico-chemical [6, 7] and electronic [8] properties were recently reported.

In this paper the dependence of atomic density on composition is reported and discussed in light of the ordered bond network model and topological models.

2. Experimental

Twenty three different compositions of the Ge–In–Se system were prepared by the conventional melt-quenching technique. The high purity (5N) constituent elements were sealed under a vacuum of $\approx 10^{-3}$ Pa into cylindrical quartz tubes. The tubes were then transferred to a furnace and heated to a temperature of 450 °C for 24 h. The temperature of the furnace was then raised to 850 °C and held at this temperature for another 48 h. During the melting process the containers were frequently agitated in order to intermix the constituents and thus ensuring the homogenization of the melt. The glasses were obtained by quenching the containers to 0 °C in an ice–water mixture.

The ambient macroscopic density measurements were performed by the Archimedes method. The samples used for density measurements were carefully chosen free from

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cracks and cleaned in methanol to remove surface contaminations. The details of the measurements have been reported in an earlier publication [9]. The accuracy of the density measurement, and consequently of ϱ , was estimated to be less than $\pm 1\%$. The atomic density was calculated from the formula

$$\varrho = \varrho_0 N_A / \sum_i c_i A_i, \quad (1)$$

where ϱ_0 , N_A , c_i and A_i are the measured density, Avogadro's number, atomic concentration and atomic weight of the i -th component, respectively.

3. Results and Discussion

The average coordination number Z for the glass composition $\text{Ge}_x\text{In}_y\text{Se}_{100-x-y}$ is calculated using the relation [10]

$$Z = [xN_c(\text{Ge}) + yN_c(\text{In}) + (100 - x - y)N_c(\text{Se})]/100, \quad (2)$$

where $N_c(\text{Ge})$, $N_c(\text{In})$ and $N_c(\text{Se})$ are the average coordination numbers of Ge, In and Se, respectively, and x , y , and $(100 - x - y)$ are their respective atomic concentrations in the glassy alloy. Average coordination numbers of four for Ge and two for Se, obeying the so-called "8 - N " rule [11], were adopted. An average coordination number of three for In, a value that was recently obtained by us [12] 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 2.22 to 2.74 and from 2.28 to 2.8 in glasses with 6 and 12 at% In, respectively.

The variation of ϱ with Z (Fig. 1) for glasses with 6 at% In shows a broad maximum at $Z = 2.42$, corresponding to the composition $\text{Ge}_{18}\text{In}_6\text{Se}_{76}$. This maximum is understood using the notion of rigidity percolation in covalent glasses which was initially

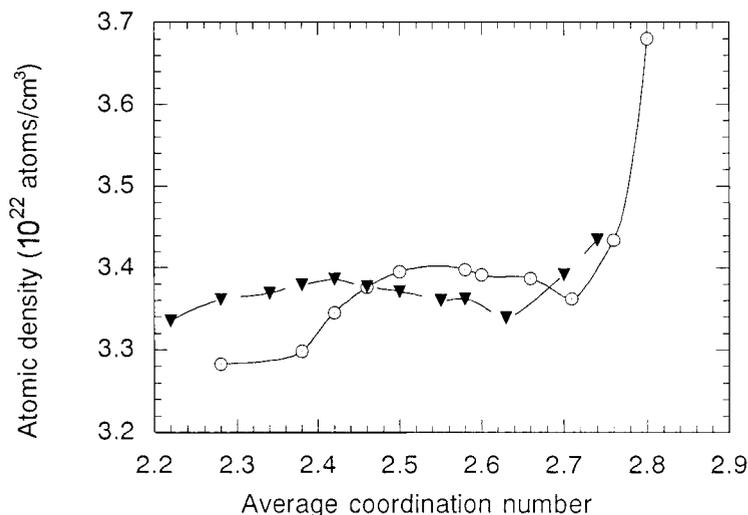


Fig. 1. The variation of atomic density with the average coordination number for compositions with 6 at% (▼) and 12 at% In (○). The lines drawn are a mere connection of the data points to guide the eye

presented by Phillips and subsequently modified by Thorpe [13 to 16]. They developed a mean field theory for the number of zero-frequency modes in a covalent network glass. Taking into account the constraints by bond-stretching and bond-bending forces and equating the number of topological constraints per atom (N_c) to the number of degrees of freedom per atom (N_d), rigidity percolation exists at $Z = 2.4$. Networks with $N_c < N_d$ (polymeric glasses) are referred to as under-cross-linked and contain large floppy regions with a few rigid inclusions while in those with $N_c > N_d$ (amorphous solids), referred to as over-cross-linked, the rigid regions have percolated to form a solid with a few floppy inclusions. The network with $N_c = N_d$, for which $Z = 2.4$, is a percolation threshold at which the transition from a floppy polymeric glass to a rigid amorphous solid takes place and at which the mechanical stability of the network is optimized. The stability of the network with $Z = 2.4$ is associated with atomic arrangements that become more tightly bound and having shorter bond lengths thus resulting in a minimum in the mean atomic volume and consequently in a maximum of ρ of the glass.

The observed threshold in this work at $Z = 2.42$, marking the floppy-to-rigid transition in glasses with 6 at% In, is slightly higher than the theoretical prediction of 2.4. This small systematic shift between the observed rigidity percolation threshold and the predicted one has been reported in amorphous $\text{Ge}_{100-x}\text{Se}_x$ from the results of the steady state photoconductivity [17], Mössbauer site intensity ratio [18], Raman scattering [19], molar volume [20] and X-ray spectroscopic studies [21]. It has also been noted in ternary Ge–As–Se [22] glasses. Therefore, it may be presumed that the observed threshold in real glasses occurs in the slightly over-cross-linked regime.

The ρ – Z dependence for glasses with 12 at% In reveals a broad maximum at $Z = 2.58$ corresponding to the composition with 17 at% Ge. This maximum can be accounted for by using Tanaka's structural transition model [23 to 25]. Tanaka, by including medium range structures (MRS) into the Phillips balance condition ($N_c = N_d$), predicted the presence of a threshold at $Z = 2.67$. At this Z value, two-dimensional (2D) structures are fully evolved and a transition from the 2D structures into 3D networks takes place due to the increase in the number of cross-linked sites. Therefore, the maximum in ρ at $Z = 2.58$, for glasses with 12 at% In, can be attributed to a structural phase transition from 2D structures into 3D networks.

The negative shift in the Z value marking the structural phase transition observed in this work, may be due to the inclusion of 12 at% of the heavy metal In into the covalent Ge–Se network. In this case the possibility of the formation of iono-covalent bonds should be taken into consideration. Under these circumstances, Tanaka's estimate of the balance condition, derived for covalent networks only, is not a valid one. The larger shift in the Z value marking Tanaka's threshold ($\Delta Z = 0.09$) as compared with that corresponding to Phillips' threshold ($\Delta Z = 0.02$) is ascribed to the incorporation, into the Ge–Se network, of a higher amount of In (12 at%) in the former case as compared to the latter case (6 at%). The negative shift in Tanaka's threshold was also previously noted in ternary Ge–Sb–Se [26], Ge–As–Te [5] and Ge–Ga–Se [27] glasses.

The minima exhibited in ρ at Z values of 2.63 and 2.71 for the tie-line compositions with 6 and 12 at% In, respectively, are explained by using the ordered bond network (OBN) model [28 to 31]. This model, which emphasizes just the relative bond energies, favours heteropolar bonding over wrong homopolar bonding at all compositions. According to this model the properties are discussed in terms of the chemical composi-

tions of the glass of each system and the structure is assumed to be composed of three-dimensional (3D) cross-linked structural units (s.u.) of the stable chemical compounds of the system with excess, if any, of the elements dispersed among these units. As a result of the chemical ordering, peculiarities such as extrema, at the tie-line compositions or the chemical thresholds of the system, are observed in the property versus composition dependence of the chalcogenide glasses. The tie-line compositions in the Ge–In–Se system, at which the afore-mentioned minima in ρ occur, are represented by $(\text{GeSe}_2)_c(\text{In}_2\text{Se}_3)_{1-c}$, where c and $1 - c$ are the fractional contents of GeSe_2 and In_2Se_3 , respectively. Any composition with a Ge content larger than that in the tie-line is referred to as Ge-rich composition and that with a larger Se content is called Se-rich one. Based on the OBN model, the structure of the glass for the tie-line composition is built from 3D completely cross-linked GeSe_2 -type tetrahedral s.u. and 3D completely cross-linked In_2Se_3 -type pyramidal s.u., with no excess of Ge or Se. As proposed by Giridhar et al. [32], the large volume requirement for attaining a completely cross-linked 3D network of GeSe_2 and In_2Se_3 present in the tie-line composition as compared with Ge-rich or Se-rich glasses, leads to the observed maxima in molar volume. The maxima in molar volume correspond to minima in ρ and therefore, the minima observed in ρ for the tie-line compositions in Ge–In–Se glasses are due to chemical ordering effects occurring at these compositions.

4. Conclusion

Anomalies observed in the atomic density–composition dependence in glasses of the Ge–In–Se system are found to be consistent with the Phillips-Thorpe model of rigidity percolation, Tanaka’s model of topological transition and the ordered bond network model.

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