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Compositional trends of the compactness in ternary chalcogenide glasses of the Ge–In–Se system

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Abstract

Chalcogenide glasses, from the $\text{Ge}_x\text{In}_y\text{Se}_{100-x-y}$ system with $y = 6$ and 12 at%, have been prepared from high purity Ge, In and Se. The compactness, δ , of the structure of the glasses is determined from the measured densities of the glasses. The peculiarities observed in the δ -composition dependence are interpreted by using the ordered bond network model and the topological models proposed to describe the atomic arrangements in these solids. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chalcogenide glasses have recently received considerable attention because they provide solid-state physicists with new challenging fundamental problems and because of their possible technological applications [1,2]. The Ge–In–Se system is of special interest in view of the fact that it forms glasses over a wide domain of compositions [3]. Therefore, it is a suitable model system for the investigation of the variation of a certain physical property with composition, or equivalently, with the average coordination number, Z .

The variation with composition of the plasmon energy losses [4], the glass transition temperature [5], for this system of glasses, was earlier reported by us. Extended X-ray absorption fine structure

(EXAFS) measurements, on some compositions in this system, were also obtained and reported [6].

In this paper we report and discuss the results of the compactness of the structure of these glasses as a function of Z .

2. Experimental details

High purity elemental Ge, In and Se, in the appropriate weight proportions, were vacuum sealed in cylindrical quartz tubes. The tubes were then transferred to an oven and heated to a temperature of 450°C for 24 h. Afterwards the temperature of the oven was raised to 850°C and the tubes were kept at this temperature for another two days. At this temperature the tubes were rigorously shaken to homogenize the melt. To obtain the glasses, the tubes were quenched in iced-water.

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The density of the glasses was measured by the Archimedes method using CCL₄, which has a density of 1.5873 g cm⁻³ at 24°C, as a reference liquid. The density was calculated from the formula

$$\rho = \left(\frac{\omega_0}{\omega_0 - \omega_L} \right) \rho_L, \quad (1)$$

where ω_0 , ω_L and ρ_L are, respectively, the weight of the sample in air, the weight of the sample in the liquid and the density of the reference liquid. The error in the density measurement, and consequently in δ , obtained by measuring the densities of some pure elements was estimated to be less than $\pm 1\%$. The compactness δ was calculated by the formula [7–9]

$$\delta = \frac{\sum_i \frac{c_i A_i}{\rho_i} - \sum_i \frac{c_i A_i}{\rho}}{\sum_i \frac{c_i A_i}{\rho}}, \quad (2)$$

where c_i , A_i and ρ_i are the atomic fraction, the atomic weight and the atomic density of the i th element of the glass and ρ is the measured density of the glass. Thus, δ is a measure of the normalized change of the mean atomic volume due to chemical interactions of the elements forming the network of a given solid [10]. Consequently, it is more sensitive to changes in the structure of the glass network as compared to the mean atomic volume, V_a .

3. Results and discussion

The densities of the investigated compositions, their corresponding compactness values and their respective Z -values are summarized in Table 1. The Z -values for the investigated compositions were calculated using the procedure outlined in Refs. [11,12] where Z is given by

$$Z = 2 + \left(\frac{2x + 3y}{100} \right). \quad (3)$$

The compositional variation of δ , characterized by Z of the investigated glasses, is shown in Fig. 1. The variation of δ with Se-concentration in the glass is depicted in Fig. 2. The prominent features observed in these figures are (i) maxima at Z -values

Table 1

Data of the density, compactness and average coordination number values for the investigated glass compositions

Glass composition			Density (g cm ⁻³)	Compactness	Z
Ge (at%)	In (at%)	Se (at%)			
4	6	90	4.297	-0.1341	2.26
6	6	88	4.367	-0.1219	2.30
8	6	86	4.463	-0.1045	2.34
11	6	83	4.487	-0.1025	2.40
14	6	80	4.487	-0.1054	2.46
16	6	78	4.493	-0.1060	2.50
18	6	76	4.495	-0.1075	2.54
20	6	74	4.476	-0.1132	2.58
22	6	72	4.461	-0.1180	2.62
24.5	6	69.5	4.438	-0.1248	2.67
26	6	68	4.435	-0.1268	2.70
28.33	6	65.67	4.396	-0.1366	2.75
32	6	62	4.453	-0.1287	2.82
34	6	60	4.503	-0.1207	2.86
7	12	81	4.535	-0.1159	2.50
9	12	79	4.592	-0.1066	2.54
11	12	77	4.628	-0.1015	2.58
13	12	75	4.646	-0.0998	2.62
17	12	71	4.636	-0.1055	2.70
19	12	69	4.620	-0.1104	2.72
21	12	67	4.607	-0.1147	2.78
23.33	12	64.67	4.565	-0.1248	2.83
26	12	62	4.653	-0.1104	2.88

of 2.4 (the corresponding Se-concentration is 83 at%) and 2.62 (the corresponding Se-concentration is 75 at%) for compositions with 6 and 12 at% In, respectively and (ii) minima at Z -values of 2.75 (the corresponding Se-concentration is 65.67 at%) and 2.83 (the corresponding Se-concentration is 64.67 at%) for compositions with 6 and 12 at% In, respectively. Fig. 1 also shows the δ - Z dependence for the binary Ge_{*x*}Se_{1-*x*} system where δ passes through a minimum at $Z = 2.67$ corresponding to the GeSe₂ stoichiometric composition. The δ - Z data for Ge_{*x*}Se_{1-*x*} system were generated from the mole volume-composition data of [13].

The maximum observed at $Z = 2.4$ for glasses with 6 at% In is understood in light of the constraint theory and the rigidity percolation concept [14–17]. In the constraint theory, where only short-range order covalent structures are considered, the number of interatomic force-field

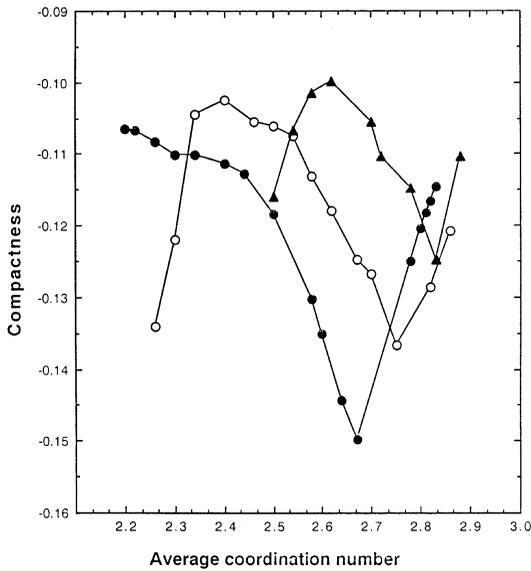


Fig. 1. Variation of the compactness with the average coordination number for compositions with 6 at% In (open circles), 12 at% In (filled triangles), and $\text{Ge}_x\text{Se}_{1-x}$ (full circles). The lines drawn are a mere connection of the data points to guide the eye.

constraints per atom (N_c) exhausts the number of degrees of freedom per atom (N_d) for the ideal glass. The aforementioned balance condition ($N_c = N_d$) led Phillips [14] to conclude that the mechanical stability for the network with $Z = 2.4$ is optimised. The same result was arrived at by Thorpe [15] by counting the number of zero-frequency modes. Networks with $Z < 2.4$ (polymeric glasses) contain large floppy regions with a few rigid inclusions. For networks with $Z > 2.4$ (amorphous solids), the rigid regions percolate to form a rigid solid with a few floppy inclusions. The stability of the network with $Z = 2.4$, where the floppy-to-rigid transition takes place, can be associated with atomic arrangements that become more tightly bound and with shorter bond lengths resulting in the smallest mean atomic volume of the network and hence with a maximum in its compactness. Consequently, the maximum observed in δ at $Z = 2.4$ for glasses with 6 at% In, is attributed to the floppy-to-rigid transition occurring in these networks.

The δ -composition dependence for the glasses with 12 at% In exhibits a maximum at $Z = 2.62$.

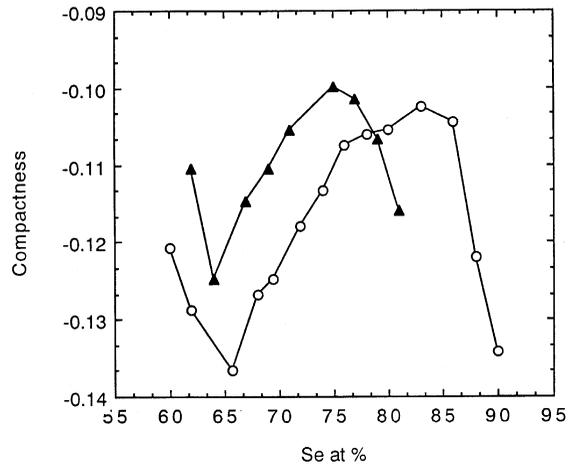


Fig. 2. Variation of the compactness with the content of Se at% in the glass for compositions with 6 at% (open circles) and 12 at% In (filled triangles), respectively. The lines drawn are a mere connection of the data points to guide the eye.

This maximum can be accounted for by using the structural transition model proposed by Tanaka [18–20]. He showed, by including medium-range structures into the Phillips balance condition, that the mechanical threshold occurring at $Z = 2.4$ is shifted to $Z = 2.67$. At this Z -value, two-dimensional (2D) layered structures are fully evolved and that a transition from 2D structures to 3D networks is taking place due to the increase of the number of cross-linked sites. Therefore, the maximum in δ at $Z = 2.62$, for the glasses with 12 at% In, is attributed to a structural 2D \rightarrow 3D transition. The small negative shift in the Z -value marking the 2D \rightarrow 3D transition may be associated with the inclusion of a relatively high concentration of the heavy metal In into the covalent Ge–Se network. This enhances the possibility of the formation of iono-covalent bonding and hence Tanaka's prediction of the threshold at $Z = 2.67$, obtained for networks with purely covalent bonding, will not be valid. Such a small negative shift in Tanaka's threshold was observed in Ge–As–Te glasses from high pressure resistivity measurements [21], in Ge–Sb–Se glasses from surface toughness measurements [22], in Ge–In–Se [23] and Ge–Ga–Se [24] glasses from mean atomic volume results.

The minima in δ at $Z = 2.75$ and 2.83 for the tie-line compositions with $y = 6$ and 12 at%, respectively, and at $Z = 2.67$ for the stoichiometric GeSe_2 composition, are explained using the ordered bond network (OBN) model [25–27]. In this model atoms bond favourably with atoms of different kinds than with the same kind thus maximizing the amount of chemical ordering. Due to this ordering, features such as extremum or a change in slope, are observed at the tie-line compositions (also known as the chemical thresholds of the system), in the compositional dependence of the various properties of chalcogenide glasses. The tie-line compositions are represented by $(\text{GeSe}_2)_{1-c}(\text{In}_2\text{Se}_3)_c$ where $1 - c$ and c are the fractional contents of GeSe_2 and In_2Se_3 , respectively. The compositions with Ge content/Se content greater than that of the chemical threshold are called Ge-rich/Se-rich compositions. Conversely, those with Ge content/Se-content less than that of the chemical threshold are called Ge-deficient/Se-deficient. The OBN model pictures the glass structure to be composed of 3D cross-linked GeSe_2 -type tetrahedral structural units (s.u.) and In_2Se_3 -type pyramidal (s.u.) with excess of Se (for Se-rich compositions) or excess of Ge (for Ge-rich compositions). The tie-line composition (chemical threshold) is solely built of completely cross-linked 3D GeSe_2 -type (s.u.) and In_2Se_3 -type (s.u.) which consist of heteropolar bonds only. The attainment of the completely cross-linked 3D network of GeSe_2 and In_2Se_3 requires the largest mean atomic volume, V_a [28]. The maxima in V_a for the tie-line compositions correspond to minima in δ and hence it is concluded that the observed minima in δ , at the respective tie-line compositions for the investigated ternary as well as for the binary glasses, are of chemical origin.

4. Conclusions

It is concluded from the δ - Z dependence that thresholds of topological as well as of chemical nature exist in this system of glasses. These obser-

vations accentuate our earlier results obtained from the compositional dependence of T_g [5] for this system.

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