Topological and Chemical Thresholds in Glasses of the Ge-Sb-S System

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ABSTRACT

The variation of the molar volume , V , and the glass transition temperature, T_g with the average coordination number , m , for twenty-three glass compositions, belonging to the $Ge_{15}Sb_xS_{85-x}$ and $Ge_{20}Sb_xS_{80-x}$ families of the Ge-Sb-S system, is reported and discussed. The V-m dependence for the $Ge_{15}Sb_xS_{85-x}$ family shows a minimum in V at m=2.4 which is attributed to the floppy-to-rigid transition in network glasses. For both families of the glasses examined, the V-m and T_g-m dependences show peaks at m=2.52 for $Ge_{15}Sb_xS_{85-x}$ and at m=2.56 for $Ge_{20}Sb_xS_{80-x}$, corresponding to the respective stoichiometric composition for each family. These features are found to be consistent with topological and chemically ordered covalent network models proposed for the structure of these glasses.

ملخص

تمت دراسة ومناقشة تغير الحجم الجزيئي الغرامي (V) ودرجة الانتقال الزجاجية (T_g) مع عدد التنسيق المتوسط (m) لثلاث وعشرين تركيبة زجاجية تنتمي للأسرتين Ge_{15} Sb_x S_{85-x} و Ge_{20} Sb_x S_{80-x} . فوجد ان العلاقة V-m للأسره Ge_{15} Sb_x S_{85-x} تظهر قيمة صغرى للحجم (V) عند m= 2.4 تعزى للأنتقال من اللين الى الجاسيء في الزجاجيات الشبكية. لكلتا الاسرتين من الزجاجيات التي درست، وجد ان العلاقات (V-m) و (T_g-m) لهـا قيـم عظمى عندm=2.52 للاسرة Ge_{15} Sb_x S_{85-x}،وعند m= 2.56 للأسرة Ge_{20} Sb_x S_{80-x} وهذه مناظرة للتركيبات النقية لكل أسرة. وقد وجد ان هذه السمات متسقة مع النماذج الطبولوجية ونماذج الشبكات التساهمية المرتبطة كيمائيا التي اقترحت لوصف بنية هذه الزجاجيات .

1. Introduction

The chemically ordered covalent network (COCN) model [1-3], and topological models such as the constraints model [4-7] and the structural transition model [8-10], have been successfully used in the interpretation of property - composition dependence for ternary chalcogenide glasses of the Ge-In-Se [11,12], Ge-Ga-Se [13,14] and Ge-Sb-Se [15-17] systems .

The COCN model emphasises just the relative bond-energies, and thereby favours heteropolar bonding over homopolar bonding. In this model, the properties are discussed in terms of the chemical compositions of the glasses of each system and the structure is assumed to be composed of three-dimensional (3-D) cross-linked structural units of the stable chemical compounds of the system. As a result of the chemical ordering , distinct features , e.g. an extremum or a change in slope , at the stoichiometric or tie-line compositions (also known as the chemical thresholds of the system) , are observed in the property-composition dependence for many glassy systems [11-17] .

In the topological models, the properties are discussed in terms of the average coordination number , m , which is indiscriminate to the species of the valence bond [10] . For the multicomponent chalcogenide glassy system, m is defined simply as the atom-averaged covalent coordination of the constituents [15,16]. Two topological thresholds at m=2.4 and at m=2.67 are present in several covalent glassy systems [10] . For example , in Ge-Se and As-Se systems [18], these thresholds are marked by a minimum in V at m=2.4 and a maximum in V at m=2.67. Using the concept of the glass-forming condition $N_c=N_d$, where N_c is the number of operative constraints per atom and N_d is the number of degrees of freedom per atom ,Phillips [4] showed that m of the most stable glass to be equal to 2.4 . At this m-value the glass network has a mechanical threshold or critical point at which the network changes from a floppy type to a rigid type . The threshold at m=2.67 is ascribed to the transition from an essentially two-dimensional (2-D) layered structure to a 3-D structure due to cross-linking [10] .

Extended X-ray absorption fine-structure (EXAFS) measurements on Ge-Sb-S glasses have been performed by [19] and the data obtained was interpreted by excluding the existence of Ge-Sb bonds in these glasses . Recently , EXAFS and X-ray scattering measurements on these glasses have been reported [20].

These structural measurements were used to determine both short-range ordering and medium-range ordering in these glasses. Photostructural changes in two series of the Ge-Sb-S glasses were also investigated [21] . However, the properties of chalcogenide glasses of the Ge-Sb-S system are still not well known . In this study ,the results of the variation of T_g and V with m , for the two families $Ge_{15}Sb_xS_{85-x}$ and $Ge_{20}Sb_xS_{80-x}$, are reported and examined in the light of the COCN and topological models .

2. Experimental Procedures

Appropriate atomic percent proportions of the constituent elements (99.999% purity) were sealed under a vacuum of 10^{-5} Torr in carefully degassed , rectangular-section silica containers (1.5 x 1.5 x 6.0 cm) . The silica containers were then transferred to a rotary furnace and heated to a temperature of 900° C . When this temperature was attained, the containers were agitated to mix the components of the alloy. After homogenizing for 36 hours, the containers were quenched to room temperature in a large volume water bath .

The procedures for measuring the glass transition temperature T_g, and the density are described elsewhere [22]. The molar volume of a given composition was obtained by dividing the average molecular weight by its density .

3. Results and Discussion

The average coordination number for the glass composition $Ge_xSb_yS_z$ is given [23] by :

$$m = x\,N_c(Ge) + y\,N_c(Sb) + z\,N_c(S)$$

where $N_c(Ge)$, $N_c(Sb)$ and $N_c(S)$ are the average coordination numbers of Ge, Sb and S, respectively . Average coordination numbers of 4 for Ge , 3 for Sb and 2 for S , conforming with the so-called '8-N' rule [4,24] (where N is the number of outer-shell electrons), were adopted . The m-values, for the compositions studied in the two families $Ge_{15}Sb_xS_{85-x}$ and $Ge_{20}Sb_xS_{80-x}$, were evaluated using the outlined procedure , and listed in tables 1 and 2, respectively .

In the $Ge_{15}Sb_xS_{85-x}$ family , compositions covering a range of m-values from 2.32 to 2.60 could be prepared . For the $Ge_{20}Sb_xS_{80-x}$ family, the m-values that could be covered ranged from 2.43 to 2.68 . The glass transition temperatures and the molar volumes of the compositions studied in each family are also given in tables 1 and 2 .

The variation of T_g with m (Fig. 1), for both families of the glasses, displays maxima at m=2.52 and 2.56 for the $Ge_{15}Sb_xS_{85-x}$ and $Ge_{20}Sb_xS_{80-x}$ families, respectively . These m-values ,at which the maxima in T_g occur , correspond to the stoichiometric tie-line composition in each family (glass no. 9 in the $Ge_{15}Sb_xS_{85-x}$ family and glass no. 6 in $Ge_{20}Sb_xS_{80-x}$ family) .
The maxima in T_g at these compositions are attributed to the preference of the system for the formation of the energetically favoured heteropolar bonding, and hence to the preference of the COCN model to describe the atomic arrangements at these compositions . According to the COCN model, the stoichiometric compositions of the glasses are assumed to be solely composed of GeS_2-type tetrahedral structural units and Sb_2S_3-type pyramidal structural units . In addition to the maximum at m=2.52 in the $Ge_{15}Sb_xS_{85-x}$ family , there is another distinct feature at m=2.4 , where a marked change in slope in the T_g-m dependence is seen .

Table 1 : Data of m, T_g and V for the compositions examined in the $Ge_{15}Sb_xS_{85-x}$ family . T_g is in K ; V in cm^3 ; and compositions are in at%

Glass Number	Ge at%	Sb at%	S at%	m	T_g(K) ±1	V (cm^3) ±0.001
1	15	2	83	2.32	498	16.496
2	15	5	80	2.35	535	16.509
3	15	8	77	2.38	575	16.516
4	15	10	75	2.4	600	16.409
5	15	12	73	2.42	606	17.106
6	15	15	70	2.45	615	17.251
7	15	18	67	2.48	623	17.388
8	15	20	65	2.5	630	17.449
9	15	22	63	2.52	635	17.495
10	15	25	60	2.55	629	17.359
11	15	27	58	2.57	625	17.336
12	15	30	55	2.6	620	17.314

Table 2 : Data of m, T_g and V for the compositions examined in the $Ge_{20}Sb_xS_{80-x}$ family . T_g is in K ; V in cm^3 ; and compositions are in at%

Glass Number	Ge at%	Sb at%	S at%	m	T_g(K) ±1	V (cm^3) ±0.001
1	20	3	77	2.43	611	16.321
2	20	5	75	2.45	616	16.399
3	20	8	72	2.48	626	16.508
4	20	10	70	2.5	631	16.573
5	20	12	68	2.52	637	16.633
6	20	16	64	2.56	647	16.744
7	20	18	62	2.58	641	16.662
8	20	20	60	2.6	632	16.582
9	20	22	58	2.62	621	16.497
10	20	25	55	2.65	610	16.456
11	20	28	52	2.68	603	16.411

Figure 1 : T_g-m dependence for the $Ge_{15}Sb_xS_{85-x}$ family □ and for the $Ge_{20}Sb_xS_{80-x}$ family △ . Solid lines are drawn through data points to guide the eye .

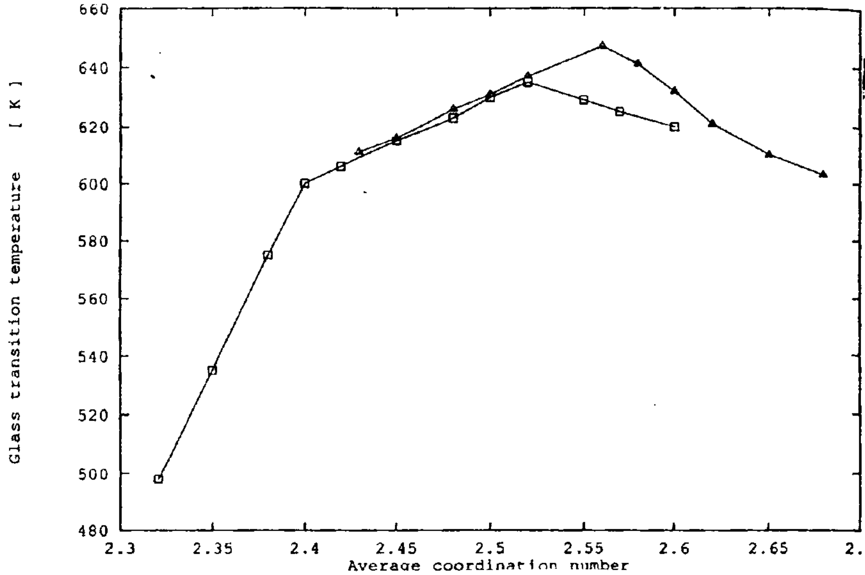
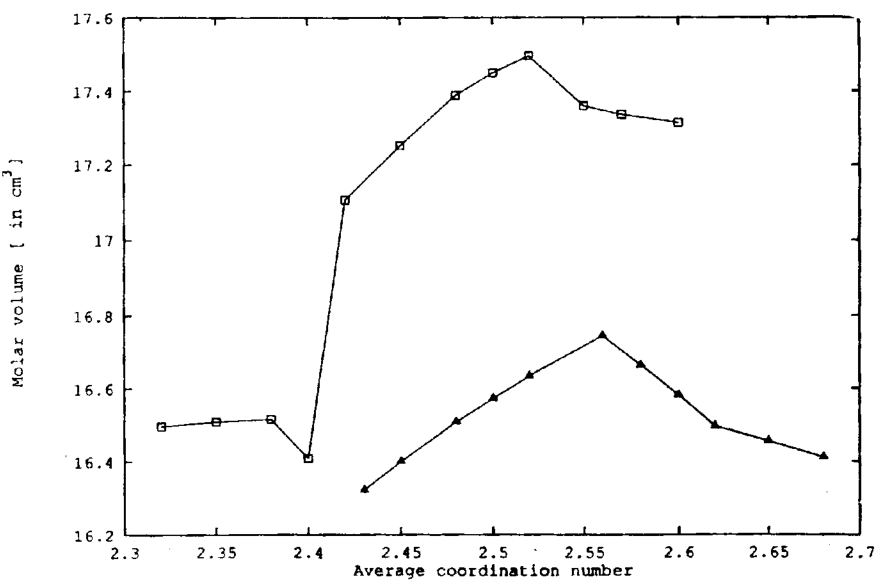


Figure 2 : V-m dependence for the $Ge_{15}Sb_xS_{85-x}$ family □ and for the $Ge_{20}Sb_xS_{80-x}$ family △ . Solid lines are drawn through data points to guide the eye .



This feature , which is coincident with Phillips rigidity percolation threshold , is taken as a signature of the transition from a floppy-type to a rigid-type glass .

In the V-m dependence for the $Ge_{15}Sb_xS_{85-x}$ family (Fig.2) , a minimum in V is observed at m=2.4, corresponding to the $Ge_{15}Sb_{10}S_{75}$ composition. The occurrence of this minimum in V is understood using the topological arguments of [4,7], which optimize covalent bonding at m=2.4 in such network glasses . It has been mentioned in the Introduction that the condition $N_c=N_d$ gives an m value of 2.4 for the most stable glass . This stability can be associated with atomic arrangements that become more tightly bound and having shorter bond lengths, thus resulting in the smallest molar volume for the most stable glass . A marked change in slope at m=2.42 , in the V-m dependence of the $Ge_{15}Sb_xS_{85-x}$ family, could also be attributed to the floppy-to-rigid transition in network glasses . The V-dependenc for both families of the glasses (Fig. 2) shows maxima at m=2.52 and m=2.56 for $Ge_{15}Sb_xS_{85-x}$ and $Ge_{20}Sb_xS_{80-x}$, . These maxima, as mentioned previously , correspond to the stoichiometric tie-line compositions of each family in the system and are due to the effects of chemical ordering at these compositions . The increase in V between m=2.4 and 2.52 for $Ge_{15}Sb_xS_{85-x}$ and between m =2.43 and 2.56 $Ge_{20}Sb_xS_{80-x}$ can be attributed to the increase in the interlayer separation of the layered structure proposed for these glasses in this range of m [10] . The decrease in V and T_g for m=2.52 and m= 2.56 for $Ge_{15}Sb_xS_{85-x}$ and $Ge_{20}Sb_xS_{80-x}$ families, respectively, may be explained by suggesting that the transition to 3-D structures is probably occurring at m =2.52 for $Ge_{15}Sb_xS_{85-x}$ and at m =2.56 for $Ge_{20}Sb_xS_{80-x}$, rather than at the constant m =2.67, as argued by Tanaka [9,10] .

4. Conclusions

Chemical thresholds for glasses of the Ge-Sb-S system occur at m-values other than m=2.4 and m=2.67. Similar observations have been recently reported for glasses of the Ge-In-Se [11,12] and the Ge-Sb(As)-Se [17] systems. The floppy-to-rigid transition in the $Ge_{15}Sb_xS_{85-x}$ family is identified by (i) a marked change in slope in the T_g-m dependence at m=2.4, and (ii) by a minimum in V in the V-m dependence at the same m. The transition to 3-D structures is probably occurring at m=2.52 for $Ge_{15}Sb_xS_{85-x}$ and at m=2.56 for $Ge_{20}Sb_xS_{80-x}$.

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