

DILATOMETRIC STUDIES ON Ge-Sb-Se CLASSES

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Results of measurements of the thermal expansion coefficient from room temperature upto the softening temperature on several compositions of the Ge-Sb-Se glass system are reported. The α - T data for these glasses have two regions; a region A below T_g where α is essentially constant followed by a region B around T_g where α increases with temperature.

In the region A the composition dependence is identical for the three families of glasses studied, with the α -composition data showing an angularity at the corresponding stoichiometric composition of each family. While changes in α of about eighty per cent are seen for compositions across a family, the change in α over the stoichiometric compositions is about fifteen per cent. An expression of the form $\alpha = \sum \alpha_i x_i$, where α_i and x_i are the expansion coefficients and weight fractions respectively of the individual structural units is found to account satisfactorily for the α -composition data of these glasses.

In the region B, α increases with temperature. The increase in α is greater and begins at about 30 to 40 degrees lower than T_g for the Se-rich glasses as compared to the Ge-rich glasses, where the increase is less and begins at T_g .

1. Introduction

Results of measurements of several properties like the glass transition temperature (T_g), electrical conductivity, density and microhardness, heat capacity and elastic moduli, made on several glasses of the Ge-Sb-Se system have been reported recently [1-5]. These studies covered different families of the Ge-Sb-Se system, with compositions represented by $Ge_xSb_5Se_{95-x}$ ($x = 20$ to 35), $Ge_xSb_{10}Se_{90-x}$ ($x = 15$ to 32), $Ge_xSb_{15}Se_{85-x}$ ($x = 10$ to 28), $Ge_{16.67}Sb_{20}Se_{63.33}$ and $Ge_{12.5}Sb_{25}Se_{62.5}$. Glasses with constant atomic per cent of Sb were classified as belonging to the same family of the Ge-Sb-Se system, while those which fall along the pseudobinary section $(GeSe_2)_{1-c}(Sb_2Se_3)_c$ were referred to as the stoichiometric compositions of the system. The composition dependence of the properties mentioned above showed systematic behaviour for the three families studied. The stoichiometric composition of each family exhibited extrema in several properties [1-5]. It was further seen [1-5] that the composition dependence of these various properties could be explained on the basis of a chemically ordered network model (according to

which maximum number of heteropolar bonds are formed first and the remaining part of the valence requirement is met with by homopolar bonding at random) for the atomic arrangement in these glasses wherein excess Ge and Se are dispersed among structural units (s.u.) of GeSe_2 and Sb_2Se_3 . The various properties show extrema at the stoichiometric compositions because these compositions can be described as made up of completely cross-linked three dimensional s.u. of GeSe_2 and Sb_2Se_3 only, with neither Ge nor Se present in excess. With the stoichiometric composition of each family as a reference, glasses with a greater Ge content than that in the stoichiometric composition were referred to as Ge-rich glasses and those with a lower Ge content than that in the stoichiometric composition as Se-rich glasses of that family.

In order to see if any systematic variation of thermal expansion coefficient (α) with composition exists, dilatometric studies were conducted on several glasses of the Ge-Sb-Se system. The results of these studies are reported in this communication.

2. Experimental

Details of the preparation of these glasses (compositions listed in table 1) are outlined elsewhere [1,2]. Samples were cut into rectangular sections of 4 mm \times 8 mm and of length 8 to 15 mm depending on the piece available in the glass preparation boule. The end faces normal to the length of the sample were ground smooth and parallel by using a hand polishing jig fabricated for this purpose. Before measurement, each sample was annealed *in situ* by holding it for about an hour at a temperature about five degrees higher than the respective T_g and then cooling it slowly.

The expansion measurements were made in a conventional horizontal dilatometer (thermal dilatometric analyser, Harrop Laboratories, USA. Model TDA-H1) which was standardised against an alumina rod supplied with the instrument. The sample temperature was measured using a chromel-alumel thermocouple in contact with the sample. Using an X-Y recorder (sensitivity 0.2 mV/cm, Watanabe model WX 431) in conjunction with the dilatometer, expansions of samples were recorded from room temperature to the respective softening temperature at a heating rate of five degrees per minute. An accuracy of two per cent was possible in the measurement of α and a spread of $\pm 3\%$ was found when α values of different samples of the same composition from different batch preparations were compared: Using the relationship

$$\alpha = \frac{1}{l_s} \frac{\delta l_s}{\delta T},$$

α was calculated from the slope of the l , versus T curve.

3. Results and discussion

A typical example showing the change in sample length Δl_s with temperature along with the corresponding α data is shown in fig. 1. The values of a , T_g and T_s (dilatometric softening temperature) were estimated as shown in fig. 1 and their values for the various compositions are listed in table 1. Also listed in table I are the values of T_g obtained by DSC [4]. The composition dependence of T_g of these glasses has been discussed in detail elsewhere [1,2]. The composition dependence of T_s is essentially the same as that of the T_g of these glasses. For a given family of glasses, the ratio T_s/T_g is seen to decrease (from about 1.28 to 1.1) with increasing Ge content in the glasses. The general behaviour showing an increase of T_s of glasses with the increase of hardness and with the decrease of a [6] is valid for these glasses also.

The α -temperature data (fig. 1) has two regions, a region **A** below T_g , where α is essentially constant, followed by a region **B** around T_g where α increases with temperature. This is followed by softening of the glass as indicated by the peak in Δl_s and in a (fig. 1). The dependence of α on composition in the regions **A** and **B** is discussed separately as they pertain to different states of glass

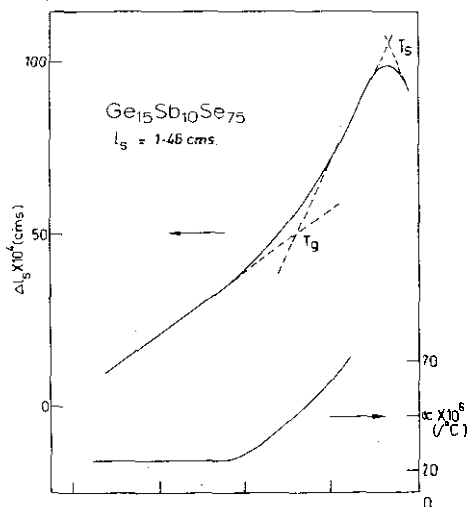


Fig. 1. Typical data showing the change in length Δl_s and α versus temperature for one of the glasses. T_g and T_s are evaluated as indicated.

Table 1
Data on T_g , T_s and α for the Ge-Sb-Se glasses

Composition			T_g ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)	T_s ($^{\circ}\text{C}$)	$\alpha \times 10^6$ ($^{\circ}\text{C}^{-1}$)	$\alpha \times 10^6$ ($^{\circ}\text{C}^{-1}$)
Ge	Sb	Se	DSC	dilat.		measured	calc. ^{a)}
20	5	75	192	195	251	22.4	23.11
25	5	70	259	262	328	18.2	19.21
29.17	5	65.83	355	344	380	15.0	16.05
32	5	63	336	336	380	14.0	15.67 (15.281)
35	5	60	315	323	360	13.0	15.27 (14.88)
15	10	75	172	186	233	22.4	23.85
20	10	70	234	223	264	19.4	20.13
25	10	65	314	322	378	15.2	16.37
30	10	60	291	303	346	14.0	15.73 (14.98)
32	10	58	282	285	324	13.0	15.37 (14.72)
10	15	75	149	150	192	23.0	24.54
15	15	70	187	204	249	19.2	20.93
20.84	15	64.16	286	299	348	15.4	16.69
25	15	60	275	279	321	14.0	16.16 (15.55)
28	15	57	271	273	300	13.4	15.83 (14.74)
16.67	20	63.31	256	275	310	15.6	16.98
12.50	25	62.50	243	258	286	15.8	17.25
28	12	60	285	275	325	13.6	15.91 (15.281)

^{a)} Values in parentheses are those calculated by allowing the maximum number of Ge-Se bond formation.

3.1. Region A

From the α -temperature data of the glass compositions studied, it was found that the region of essentially constant α extends up to 100 $^{\circ}\text{C}$ or higher for the Se-rich glasses and well beyond this temperature for the Ge-rich glasses of the system. The dependence of α on composition is seen to be similar for the three families of glasses studied (fig. 2) with α decreasing as the Ge content in the glasses is increased. The fall of α is steeper for the Se-rich glasses as compared to the Ge-rich glasses, resulting in an angularity or break at the stoichiometric composition. As discussed in detail elsewhere [1-5] in connection with the other properties of these glasses, this angularity is associated with the change in structural arrangement taking place in glasses with change in composition. In brief, the lowering of n as Ge content is increased is associated with the strengthening of the glass network due to the continuous replacement of chain-like Se s.u. by tetrahedral s.u. of GeSe_2 for the Se-rich glasses and the replacement of GeSe_2 s.u. by Ge for the Ge-rich glasses. By a similar reasoning, the reduction of α (i) as % is replaced by Sb at any given Ge content, and (ii) with increasing GeSe_2 content for the stoichiometric compositions (fig. 2) can be traced respectively to the replacement of some percentage of (i) chain-like Se s.u. by trigonal s.u. of Sb_2Se_3 and (ii) trigonal Sb_2Se_3 s.u. by tetrahedral GeSe_2 s.u.

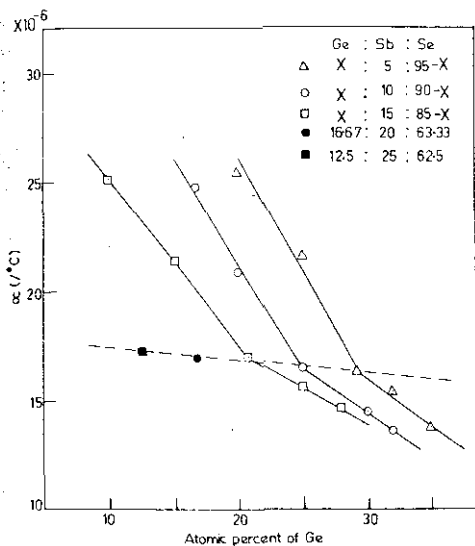


Fig. 2. Variation of α with composition for the Ge-Sb-Se glasses. The dotted line is drawn through the stoichiometric composition of the system.

While a change of over 80% in the magnitude of α is seen (fig. 2) across compositions of a given family, the change in α for the stoichiometric compositions of the system (dotted line, fig. 2) is about 15%. This behaviour is similar to the behaviour of elastic moduli of these glasses [5]. In the Ge-Se system also, the dependence of α on composition exhibits an angularity at the GeSe_2 composition [7,8], while the As-S and As-Se systems. A minimum in α is seen for the compositions As_2S_3 and As_2Se_3 [9,10]. The dotted line running through the stoichiometric compositions (fig. 2) when extrapolated to 33.33 at.% of Ge, gives a value of $15.7 \times 10^{-6}/^\circ\text{C}$ for GeSe_2 . This agrees well with reported value of α for GeSe_2 [7]. A similar extrapolation of the "stoichiometric line" of fig. 2 to zero Ge content gives a value of $18 \times 10^{-6}/^\circ\text{C}$, which can be taken as the value of α for Sb_2Se_3 .

As already indicated, the composition dependence of several properties of the Ge-Sb-Se glasses can be accounted for by using the CONM, wherein GeSe_2 and Sb_2Se_3 s.u. are dispersed among excess Se and Ge. Using the same model for the atomic arrangement, an attempt was made to see if α of these glasses can be calculated using the α of the individual s.u.. For GeSe_2 and Sb_2Se_3 the values of α obtained as indicated above were used. A value of $41.67 \times 10^{-6}/^\circ\text{C}$ was used for the α of Se [11]. As α of amorphous Ge is not available a value of $6 \times 10^{-6}/^\circ\text{C}$ of crystalline Ge [12] was used in the calculation to see the general nature of the behaviour of α with composition. It

is interesting to see that an expression of the form

$$a = \sum \alpha_i x_i$$

where a_i and x_i are the expansion coefficients and weight fractions, respectively, of the individual compounds/elements, the s.u. of which make up the total structure of the glass, gives values of α which agree well with experimental values, as can be inferred from the data in table 1. The agreement is better for Se-rich glasses (within 5%) as compared to the Ge-rich glasses (within 15%). As already pointed out [1], based on the Ge-Se bond energy, the possibility of formation of larger number of Ge-Se bonds in lieu of some Sb-Se bonds cannot be ruled out for the Ge-rich glasses. Values of α were calculated for these Ge-rich glasses allowing for formation of maximum Ge-Se bonds and using a value of $10.88 \times 10^{-6}/^{\circ}\text{C}$ for the a of Sb. Values of α thus obtained (table I) show better agreement with experimental values than those calculated on the basis of Sb_2Se_3 formation.

3.2. Region B

The dependence of α on temperature for $\text{Ge}_x\text{Sb}_{10}\text{Se}_{90-x}$ glasses is shown in fig. 3. It is seen (fig. 3) that the change in α during glass transition ($\Delta\alpha$) is

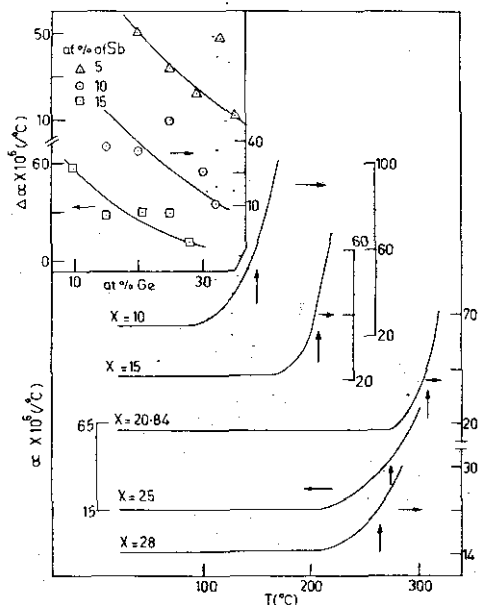


Fig 3. Dependence of α or T for five glasses of the $\text{Ge}_x\text{Sb}_{10}\text{Se}_{90-x}$ family. The inset shows the variation of α during transition of different compositions for the three families of glasses studied.

much larger for the Se-rich glasses as compared to the Ge-rich. Also, the increase in α begins at temperatures of 30 to 40°C lower than T_g for the Se-rich glasses. For the Ge-rich glasses on the other hand, the region of essentially constant α extends almost upto T_g and these glasses register an increase in α at T_g . This general variation of α with composition was found to be similar for the other two families $Ge_xSb_3Se_{95-x}$ and $Ge_xSb_{15}Se_{85-x}$ studied. While for Se-rich glasses an increase in α of 40 to 60 $\times 10^{-6}/^\circ C$ (compared to its value below T_g) is seen during glass transition, the increase for the Ge-rich glasses is about 15 to 30 $\times 10^{-6}/^\circ C$ (inset fig. 3). The value of $\Delta\alpha$ for Se, as inferred from the data of ref. 13 is about 97 $\times 10^{-6}/^\circ C$. $Se_{80}Te_{20}$ glasses which have a large concentration of Se also show a large change in α ($\Delta\alpha$ of about 100 $\times 10^{-6}/^\circ C$) during glass transition and this increase begins at a temperature lower than T_g [14]. Thus in the case of network glasses Ge-Sb-Se studied presently, the value of $\Delta\alpha$ is seen to reduce by a factor of about two for the Se-rich glasses and about five for the Ge-rich glasses as compared to the value in pure Se. Qualitatively it is possible to rationalise this behaviour based on the chain like arrangement of excess Se in Se-rich glasses compared to the network arrangement of excess Ge in Ge-rich glasses.

4. Conclusions

Dilatometric studies have been performed on several glasses of the Ge-Sb-Se systems. The α -temperature data has two regions. a region A below T_g where α is essentially constant with change of temperature, followed by a region around T_g where α increases with increase of temperature.

In the region A, the composition dependence of α is identical for the three families of glasses studied, with the α -composition data exhibiting an angularity at the corresponding stoichiometric composition of each family. The results are explicable based on the CONM model, with which it was possible to understand the behaviour of the other properties of this system. An expression of the form $\alpha = \sum \alpha_i x_i$ where α_i and x_i are the expansion coefficient and weight fraction respectively of the various compounds/elements which form the s.u. in the glasses gives values of α agreeing well with experimental data.

In the region of glass transition, α increases with temperature. This increase is larger (40 to 60 $\times 10^{-6}/^\circ C$ more compared to the value of α below T_g) and begins at temperatures below T_g for the Se-rich glasses as compared to the Ge-rich glasses where the increase is smaller (about 15 to 30 $\times 10^{-6}/^\circ C$) and begins at T_g .

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