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Studies on $Ge_xSb_{40-x}Se_{60}$ glasses by differential scanning calorimetry and thermomechanical analysis

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Abstract

Calorimetric and dilatometric thermal properties of bulk $Ge_xSb_{40-x}Se_{60}$ glasses ($x = 15$, 20, 25, 27, 32, 35) have been investigated by differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). The variations of the difference in specific heat capacity between glass and undercooled liquid ... Cp and of the glass-transition temperature Tg on the average coordination number Z have been specified. It has been found from the dependence of T_g on the heating rate that the parameter B, related to configurational changes in the structure, reaches a maximum at $Z = 2.67$ (i.e. for Ge_{27} Sb_{13} Se_{60}), while ΔC_p values remain almost constant at $Z \geq 2.67$. The apparent activation energy of glass transition E_t for both the methods has been compared. Threshold-like behaviour at $Z = 2.67$ of the change in the fragility m has also been observed for both the methods. The softening temperature T_s and the coefficient of thermal expansion in glass α_g determined by TMA have exhibited a feature at $Z = 2.67$ as well. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Chalcogenide glasses; Differential scanning calorimetry (DSC); Thermomechanical analysis (TMA); Fragility

1. Introduction

Chalcogenide glasses exhibit unique optical and electrical phenomena that make them perspective for several potential applications, such as infrared transmission and detection through lenses and optical waveguides, threshold and memory switching, inorganic photoresistors, etc. In this connection, the analysis of the compositional dependence of the properties, especially of thermal and mechanical ones, is an important aspect of the study.

Peculiarities in the property–composition relationship of some chalcogenide glasses have been found depending on the average coordination number Z, in particular at $Z = 2.4$ and 2.7. In these materials, the interatomic forces are predominantly strong covalent and refer to the short-range order. It is generally accepted that the coordination number of the covalent atoms in the glass is governed by the (8N) rule [1], where N is the number of the outer-shell electrons in a given atom. The Z concept is useful to describe the cross-linking in such glasses: it is then defined as the atom-averaged covalent coordination of the constituents. Several structural models explaining the above-mentioned peculiarities in these glasses have been presented. Most of them are based on Phillips' con-

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straint theory [2,3] which predicts a transformation from underconstrained or floppy network to overconstrained or rigid network at $Z=2.4$. The features observed at $Z=2.67$ have been mostly understood on the basis of the chemically ordered covalent network (COCN) model [4] and network dimensionality considerations [5,6] which predict a transition from layered structure to three-dimensional network at $Z=2.67$. Recently, another opinion on this question has been suggested to solve the problem of the existence of threshold, accounting the formation energy dE per atom of the glasses [7]. The authors have defined the chemical threshold as the most stable chemical composition and bonding arrangement of a system, where maximal values of $-\mathrm{d}E$ are reached and a tendency to strong chemical order is manifested.

The main purpose of this paper is to determine the basic thermal parameters of bulk $Ge_xSb_{40-x}Se_{60}$ glasses by DSC and TMA, to compare the results and to trace out their variation with Z.

2. Experimental

Bulk $Ge_xSb_{40-x}Se_{60}$ ($x=15$, 20, 25, 27, 32, 35) glasses were prepared by direct synthesis from elements of 5N purity. Pure elements were weighted (total 6 g) into quartz ampoules, subsequently evacuated to a vacuum of 10^{-3} Pa and sealed. After heating at 950°C in a rotary furnace for 24 h the melts in ampoules were quenched in air.

The DSC measurements were performed using a Mettler DSC 13E calorimeter controlled by a computer. The instrument was calibrated with indium, lead and tin standards. Powdered samples (ca. 10 mg) were closed into aluminium pans and measured in the temperature range of 303–673 K with heating rates $\beta=5$, 10, 15, 20 K min^{-1}. The values of T_g were calculated as a midpoint from the ΔC_p curves.

The dilatometric experiments were performed using a TMA CX04R instrument (R.M.I., Czech Republic) on samples of ca. 5 mm × 5 mm × 5 mm polished to optical quality. In the first step, the sample was heated up to a temperature of T_g+20 K with a heating rate of 10 K min^{-1}. Then the sample was cooled to the temperature 373 K with rates 10, 5, 3, 1, 0.5 K min^{-1} and, subsequently, the sample was heated to a temperature of T_g+20 K at the same rates. The maximum heating rate used was limited by the TMA method. The T_g values and the coefficient of thermal expansion in glass α_g were determined from the heating steps for every heating rate. The softening temperature T_s was obtained from the measurement of the sample heated up to the temperature of T_g+50 K at a heating rate of 3 K min^{-1}.

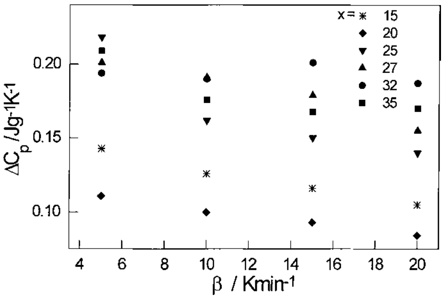

Fig. 1. Dependence of ΔC_p on the heating rate β for the $Ge_xSb_{40-x}Se_{60}$ glasses.

3. Results

The difference of specific heat capacity ΔC_p, between glass and undercooled liquid is an important parameter for the description of glass transition. The dependence of ΔC_p on the heating rate, obtained by DSC measurements, is shown in Fig. 1, where a monotonous decrease is observed. The variation of ΔC_p with Z is non-monotonous in the range 2.55–2.65 and the values remain almost constant at $Z\geq 2.67$ (Fig. 2).

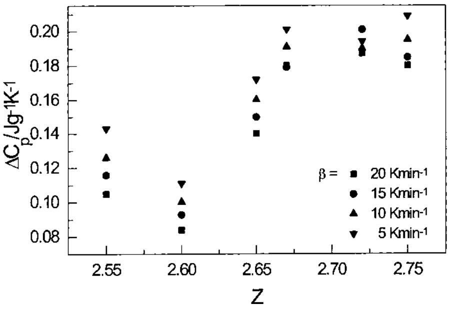

Fig. 2. Dependence of ΔC_p on Z for the glasses studied.

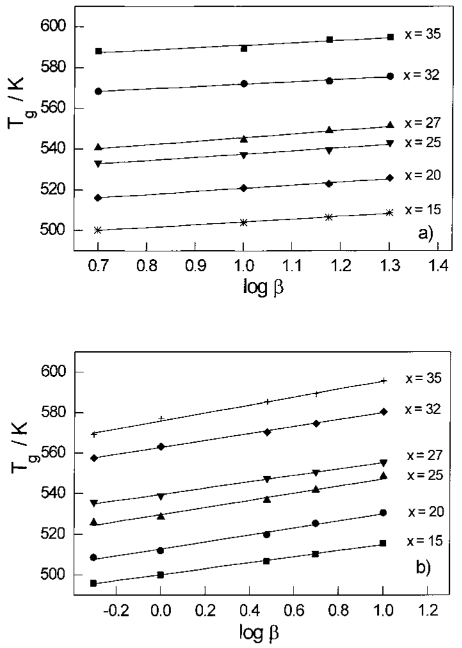

Fig. 3. Dependence of T_g on log β for the glasses studied, obtained from DSC (a) and TMA (b) data.

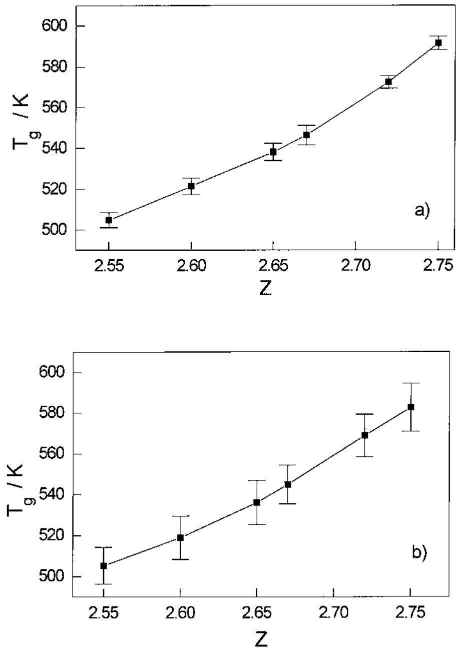

Fig. 4. Dependence of T_g on Z for the glasses studied, obtained from DSC (a) and TMA (b) data.

The dependence of T_g on the heating rate β is given in Fig. 3a,b using the empirical relationship [8]:

$$T_g = A + B \log \beta, \qquad (1)$$

where A and B are constants for a given composition. The parameter B is related to the sample preparation and should be responsible for configurational changes during the glass-transition process [8]. From the obtained DSC results (Fig. 3a), it follows that these configurational changes reach a maximum value at $Z = 2.67$, i.e. for the $Ge_{27}Sb_{13}Se_{60}$ composition (Table 1).

The variation of T_g with Z for both the methods is shown in Fig. 4a,b, where an exponential increase by ~100 K is observed with increasing x. Comparing the results for heating rates of 5 and 10 K min^{-1} it is established that the calorimetric T_g values are lower by ca. 10 K as compared with the dilatometric ones.

For calculation of the apparent activation energy of crystallization E_c the Kissinger equation is usually applied [9]:

$$\ln\left(\frac{T_c^2}{a'}\right) + \text{const} = \frac{E_c}{RT_c}, \qquad (2)$$

Table 1
Values of the parameter B Eq. (1) and E_t Eq. (3) of the glasses studied

Composition	Z	B (K)	E_t (kJ mol^{-1})	
			DSC	TMA
$Ge_{15}Sb_{25}Se_{60}$	2.55	13.9	338.9 ± 19.6	320.4 ± 10.1
$Ge_{20}Sb_{20}Se_{60}$	2.60	15.4	325.2 ± 23.4	286.4 ± 27.1
$Ge_{25}Sb_{15}Se_{60}$	2.65	15.7	335.3 ± 39.7	299.5 ± 26.6
$Ge_{27}Sb_{13}Se_{60}$	2.67	17.9	302.5 ± 33.2	353.3 ± 11.6
$Ge_{32}Sb_{8}Se_{60}$	2.72	11.6	514.5 ± 58.1	349.5 ± 10.6
$Ge_{35}Sb_{5}Se_{60}$	2.75	11.9	500.4 ± 65.1	317.1 ± 14.5

where T_c is the crystallization temperature and R the universal gas constant.

It is found that the same equation can be used for calculation of the apparent activation energy of glass transition E_t [10,11]. The values obtained from both the methods are summarized in Table 1. Apparently, the E_t values for glasses of composition $Ge_{32}Sb_8Se_{60}$ and $Ge_{35}Sb_5Se_{60}$ are much higher than the rest, which has not found an explanation so far.

On the basis of the obtained T_g and E_t data, the fragility m is calculated from [12]:

$$m = \frac{E_t}{T_g} R \ln 10. \tag{3}$$

The results show (Fig. 5a and b) that m depends slightly on the heating rate for both the methods, varying from 25 to 45. A threshold-like behaviour in the dependence at $Z \sim 2.67$ is clearly expressed. The observed difference in the fragility for compositions at $Z > 2.67$ can be related to the above-mentioned deviation in E_t values.

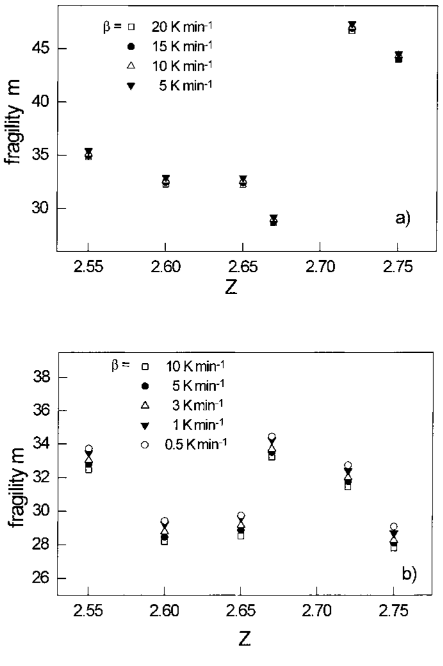

Fig. 5. Dependence of the fragility m on Z for the glasses studied, obtained by DSC (a) and TMA (b) data.

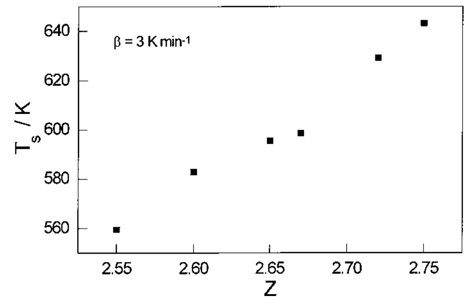

Fig. 6. Dependence of T_s on Z for the glasses studied, obtained by TMA data.

The softening temperature T_s and the coefficient of thermal expansion in glass α_g are measured by TMA and their change with Z is presented in Figs. 6 and 7, respectively. The T_s values exceed by ~60 K those of T_g and, in contrast to the latter, exhibit a threshold at $Z = 2.67$. The same peculiarity is observed in the variation of α_g.

4. Discussion

In order to characterize the medium-range structure (over distances of ca. 20 Å), the term network dimensionality D is used [13], which is defined as the number of dimensions where covalently bonded clusters can be extended. For instance, $D = 1$ for Se corresponds to a chain-like morphology, in which entangled chain molecules are held together mostly with the weak van-der-Waals forces. The layer structures are fully developed at $D = 2$, and $D = 3$ means

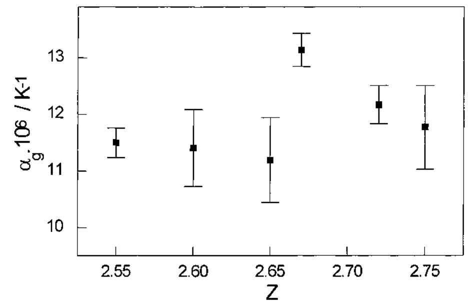

Fig. 7. Dependence of a_g on Z for the glasses studied, obtained by TMA data.

three-dimensional continuos–random networks. Based on the COCN model [4], the chemical threshold is defined as a chemical composition where only heteropolar bonds exist. It is observed at lines joining the stoichiometric compounds, i.e. the so-called tie-line compositions. From this point of view, the $Ge_xSb_{40-x}Se_{60}$ glasses are apparently far from such chemical threshold. Consequently, the observed feature in the Z dependences of ΔC_p, B, E_t, m, T_s and α_g at $Z \sim 2.67$ (Table 1, Fig. 2 and Figs. 5–7) can be explained by a transition from a two (2D) (layered) to three-dimensional (3D) (cross-linked) arrangement, based on the Tanaka' concept [5,6]. However, such change does not probably occur at a fixed value of Z, and covers a narrow range, which is attributable to the structural transformations in network glasses. This is well pronounced in the compositional dependence of ΔC_p (Fig. 2), where at $Z < 2.6$ and $Z > 2.7$ two- and three-dimensional structures are developed, respectively, while in the range of $2.6 < Z < 2.7$ a ($2D \rightarrow 3D$) transition might take place. It is expressed in a narrower interval of Z values for the fragility (Fig. 5) and the coefficient of thermal expansion in glass (Fig. 7). The observed higher values of T_g (Fig. 4) can be related to the cross-linking extension. The variation of the parameter B with the composition confirms the change in the structure (Table 1).

Recently, Tichý and Tichá [7] improved the meaning and definition of chemical threshold as the most stable chemical composition and bonding arrangement. As a rough measure of stability, they have used the formation energy of a given glass dE. In particular, the dependence of dE on Z of $Ge_xSb_{40-x}Se_{60}$ glasses shows a minimum at $Z = 2.7$ owing to the chemical threshold. In other words, this threshold is reached for the chemical composition and bonding arrangements which have the most negative dE value. Accepting the validity of this definition, and having in mind rather closed values of Z (2.67 and 2.7), it could be supposed that the chemical threshold is assisted in the Tanaka threshold.

5. Conclusions

1. Basic thermal characteristics such as the glass transition and softening temperatures, apparent activation energy of glass transition, difference in the specific heat capacity between glass and undercooled liquid, coefficient of thermal expansion in glass and fragility of bulk $Ge_xSb_{40-x}Se_{60}$ glasses have been determined as a function of Z by DSC or TMA and the results obtained have been compared.
2. The observed features in the variation of the parameters B, m, T_s, and α_g at Z arround 2.67 can be explained by a ($2D \rightarrow 3D$) structural phase transition, probably accompanied by a chemical threshold. It should be mentioned that the topological threshold is more general in nature, because it can account for the feature of the chemical one.

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