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The effect of compositional variations on the glass-transition and crystallisation temperatures in Ge−Se−In glasses

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This work is dedicated to the memory of my beloved mother who passed away in April this year.

Abstract. The glass-transition (T_g) and crystallisation (T_x) temperatures of glassy $Ge_xSe_yIn_{12}$ ($7 \leq x \leq 28$) have been determined from differential scanning calorimetry measurements. The variations of T_g and T_x with composition have been specified. It has been found that T_g reaches a maximum at 614 K for the composition $Ge_{23.33}$ $Se_{64.67}$ In_{12} while T_x passes through a minimum at 740 K for the same composition. The values of the cohesive energies of the studied compositions have also been estimated using the chemical bond approach method. It is found that the composition $Ge_{23.33}Se_{64.67}In_{12}$ possesses the maximum cohesive energy. These results are explained in terms of the structure of Ge−Se−In glasses.

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The glass-forming region in the ternary Ge−Se−In system extends to about 15 at % In and about 60–90 at % Se, with the rest being Ge [1]. The freedom allowed in the preparation of glasses in varied compositions brings about changes in their short-range order (SRO) and thus results in variations in their physical properties. Therefore, it is possible to tailor their various properties to a desired technological application. The applications of these materials in modern technology include optical fibre amplifiers [2, 3], acousto-optic devices [4, 5], and optoelectronic devices [6–8].

Systematic studies of the variation of thermal properties with glass composition have been fruitful in gaining insight into the structural arrangement in the glass. In the present work, we have used differential scanning calorimetry (DSC) to establish T_g and T_x as a function of Ge content in several Ge−Se−In glasses. Our results show that T_g displays a maximum whereas T_x exhibits a minimum for the composition with 23.33 at % Ge. We propose that this observation represents a realisation of a chemical threshold in these covalent-network glasses.

1 Experimental details

1.1 Sample preparation

The appropriate atomic percent proportions of the constituent elements (5 N purity) were sealed under a vacuum of 10^{-5} Torr in carefully degassed, cylindrical silica containers. The silica containers were then transferred to an electric furnace and heated to a temperature of 450 °C for 24 h. Afterwards the temperature of the furnace was raised to 850 °C for 48 h. At this temperature, the containers were frequently shaken to mix the components of the alloy. After the homogenisation is completed, the containers were quenched to 0 °C in an ice–water mixture.

1.2 Differential scanning calorimetry measurements

A DSC instrument, Setaram DSC 92, was used to measure T_gs and T_xs of the samples. The measurements were performed with a heating rate of 10 K/min. Typically, 20–30 mg of the powdered sample was sealed in an Al pan with an empty Al pan used as a reference. The temperature of the sample was then scanned from room temperature to its T_x. T_g was taken as the temperature corresponding to the midpoint of the two linear portions adjoining the transition in the DSC trace, whereas the peak of the crystallisation exotherm was used for the determination of T_x. The values of T_g and T_x were determined to an accuracy of better than ±1 K using the microprocessor of the thermal analyser.

2 Results and discussion

The dependences of T_g and T_x on Ge content in the glass are shown in Fig. 1. It is seen that the T_g-dependence displays a maximum for the composition with 23.33 at %

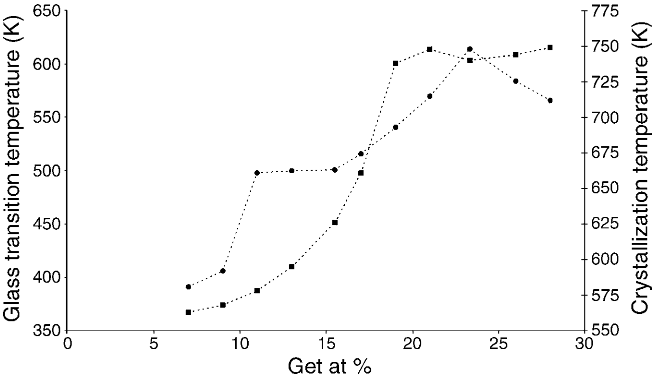

Fig. 1. Glass-transition and crystallisation temperatures (K) as a function of the Ge content (at %) for the investigated compositions. The T_g and T_x values are represented by circles and squares, respectively

Ge whereas a minimum for the same composition is discernible in the T_x-dependence. The maximum observed in the T_g-dependence can be interpreted using the chemical ordered network (CON) model by considering the chemical bond energies. The heteronuclear bond energies, $U_{\text{A-B}}$, between unlike atoms A and B are calculated using homonuclear bond energies, namely $U_{\text{A-A}}$ and $U_{\text{B-B}}$, and the difference in the electronegativities of the two atoms $(x_A - x_B)$ [9]:

$$U_{\text{A-B}} = 0.5[U_{\text{A-A}} + U_{\text{B-B}}] + 23\,(x_A - x_B)^2 \tag{1}$$

where the electronegativities of Ge, Se, and In are 1.8, 2.4, and 1.7, respectively [9]. Using the values of 37.6, 44.0, and 29.9 kcal/mole for the homonuclear bond energies of Ge−Ge, Se−Se, and In−In, respectively [9, 10], one obtains the values of 49.1 and 48.2 kcal/mole for Ge−Se and In−Se bonds, respectively.

It has been recently reported by us [11] from extended X-ray absorption fine structure (EXAFS) measurements, performed at the In K-edge, that In atoms in Ge−Se−In glasses are 3-fold coordinated and only bonded to Se with no evidence of In−Ge or In−In bonds. Because of the fixed amount of In in the glasses, the percentage of In−Se bonds is fixed. For compositions with Ge content < 23.33 at %, the glass contains $\text{GeSe}_{4/2}$ tetrahedral structural units dissolved in a matrix composed of Se chains. With the increase of Ge content in the glass up to 23.33 at %, the concentration of $\text{GeSe}_{4/2}$ units builds up at the expense of Se chains and the replacement of the weak Se−Se bonds by the strong Ge−Se bonds ($U_{\text{Ge−Se}} - U_{\text{Se−Se}} = 5.1$ kcal/mole) leads to an increase in T_g. At the critical composition with 23.33 at % Ge (chemical threshold), the glass becomes chemically ordered, and contains only the strong heteronuclear bonds. It should be noted that the chemical threshold can be written as $(\text{GeSe}_2)_{0.7}(\text{In}_2\text{Se}_3)_{0.3}$ and that it only contains tetrahedral $\text{GeSe}_{4/2}$ as well as pyramidal $\text{In}_2\text{Se}_{3/2}$ structural units. On further addition of Ge (> 23.33 at %), the high-energy Ge−Se bonds would be replaced by the low-energy Ge−Ge bonds ($U_{\text{Ge−Ge}} - U_{\text{Ge−Se}} = -11.5$ kcal/mole), which leads to a decrease in T_g. Thus, T_g decreases on both sides of the chemical threshold, leading to the observed maximum in T_g at the chemical threshold. Similar observations were reported for Ge−Se−Te [12], Ge−Se−Pb [13], Ge−Se−Ga [14, 15], Ge−Se−Sb(As) [16], Ge−Se−In [17], Ge−S [18], Ge−S−Ga [19], and Ge−Te−Ag [20] chalcogenide glasses.

The maximum chemical ordering in the glass containing 23.33 at % Ge (chemical threshold) indicates that it is closest to the crystalline state. Thus, the energy barrier required for crystallisation of the ordered glass is a minimum, resulting in the observed minimum in its crystallisation temperature, T_x. Such a minimum in T_x was recently reported for Ge−Te−Ag glasses [20].

The dependences of T_g and T_x on Ge content, for the glasses under investigation, can be translated into dependences on R using (2) where x, y, and z are the atomic fractions of Ge, Se, and In, respectively:

$$R = \frac{2y}{4x + 3z} \tag{2}$$

Such a plot is shown in Fig. 2, which exhibits a maximum in T_g and a minimum in T_x at $R = 1$. The R value represents the ratio of the covalent bonding possibilities of chalcogen atoms to covalent bonding possibilities of non-chalcogen atoms [21]. Thus $R = 1$ represents the case of the existence of only heteronuclear bonds in a given system, which unequivocally indicates the occurrence of a chemical threshold. Consequently, the extrema observed in T_g and T_x at $R = 1$ are due to chemical ordering effects. The maximum in the $T_g(R)$ dependence at $R = 1$ appears to be common to T_gs in covalent-network glasses [21].

To this end, it would be interesting to calculate the cohesive energy (the stabilisation energy of an infinitely large cluster of the material per atom) for each of the investigated compositions and obtain the cohesive energy-composition dependence to see if this dependence exhibits any peculiar behaviour. This is done using the method suggested by the chemical bond approach [22]. In view of this method, atoms combine more favourably with atoms of different kinds than with the same kind. Consequently, bonds between like atoms will only occur if there is an excess of certain type of atoms. Bonds are formed in the sequence of decreasing bond energy until all the available valences for the atoms are satisfied.

Taking the composition with 23.33 at % Ge as a reference, compositions with less Ge content are referred to as Ge-deficient (chalcogen-rich) and those with more Ge content are Ge-rich (chalcogen-poor). In Ge-deficient compositions, the divalent Se atoms will first fill the available

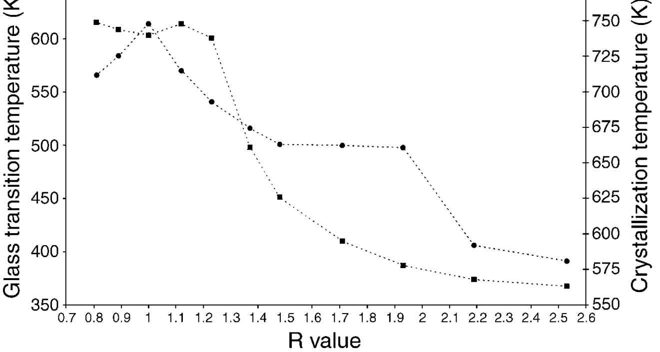

Fig. 2. $T_g(R)$ and $T_x(R)$ dependences for the investigated glasses. R is defined in the text and the key to the data symbols is the same as in Fig. 1.

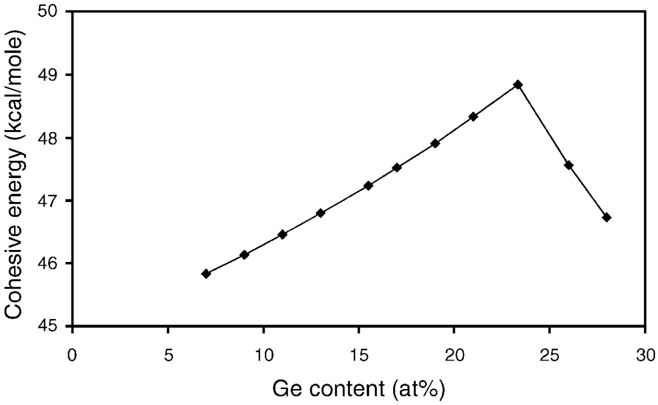

Fig. 3. The dependence of the cohesive energy on Ge content in the glass. The lines through the data points are drawn as a guide for the eye

valences of the tetravalent Ge atoms and then those of the trivalent In atoms. After all these bonds are formed, there are still unsatisfied Se valences, which are satisfied by the formation of Se−Se bonds. Similarly, for Ge-rich compositions and after all the available valences of Se and In atoms are saturated, there are still unsaturated Ge valences, which must be saturated by the formation of Ge−Ge bonds.

Based on the chemical bond approach, the bond energies are assumed to be additive. Thus, the cohesive energies were calculated by summing the bond energies of the bonds present in the glass structure in their relative proportions. The variation of the cohesive energy as a function of Ge content is shown in Fig. 3. This figure shows that the cohesive energy passes through a maximum for the composition containing 23.33 at % Ge (chemical threshold). Therefore, it can be concluded that the energy barrier to matrix rearrangement is a minimum for the chemical threshold. This result is consistent with our observed minimum in T_x for this composition. It is also consistent with the reported minimum in the activation energy of crystallisation for the composition with $x = 15$ at % in $Ge_{20}Se_{80-x}In_x$ glasses [23].

3 Conclusions

We have determined the composition dependences of T_g, T_x, and the cohesive energy for Ge−Se−In network glasses. It is found that these dependences display extrema at the chemical threshold of the system. These extrema are explained in terms of the structural arrangements in the glass.

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