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# Composition dependence of the physico-chemical properties in $Ge_{1-x}Sn_xSe_2$ chalcogenide glasses

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$Ge_{1-x}Sn_xSe_2$ chalcogenide glasses, within the composition range $0.1 \leq x \leq 0.6$, were prepared from high purity constituent elements. Differential scanning calorimetry (DSC) measurements on these glasses were undertaken to determine their glass transition ($T_g$) and crystallization ($T_c$) temperatures and to evaluate their thermal stability. It is found that both $T_g$ and $T_c$ decrease upon the increase of Sn concentration in the glass. The temperature interval $\Delta T = T_c - T_g$ is also found to decrease with increasing x which is indicative of the decrease of their thermal stability. The compactness, the number of constraints per atom, the average coordination number, and the overall mean bond energy of the network are also calculated and discussed.

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## 1. Introduction

Chalcogenide glasses are oxygen-free inorganic glasses. They are formed by the alloying of one or more kind of the chalcogen elements with group IV and/or group V of the periodic table. Due to the lack of long-range-order (LRO) in their structure, they provide solid state physicists and material scientists with new challenging fundamental problems. Recently, they have attracted considerable interest from the viewpoint of their exciting actual and potential technological applications in solid state devices [1]. These applications include their use as materials for the preparation of electrical memories [2], of infrared optical fibers, photoconductors, optical memories [3-8] and as solid electrolytes [9]. However, in technical applications the thermal stability of chalcogenide glasses is an important aspect in their characterization to choose the temperature-time modes of manufacturing the homogeneous glasses. Therefore, the determination of their thermal parameters, such as the glass transition ($T_g$) and crystallization ($T_c$) temperatures, with the view of establishing their thermal stability is of great importance. Furthermore, wide glass forming regions in these materials offer ample possibilities for controlling the desired thermal property by means of changing the chemical composition.

The Ge-Sn-Se is a prototypical chalcogenide system and its choice for this study is based on several factors. First, this system is characterized by strong chemical order and very stable building blocks. Second, it offers the possibility of tuning the number of constraints per atom by replacing Ge with Sn. Another attractive feature of this system and other chalcogenides is that their properties generally depend non-linearly on their chemical composition and sudden changes can occur in certain regions of the composition diagram.

## 2. Experimental details

### 2.1. Sample preparation

The standard melt-quenching technique was used to prepare bulk $Ge_{1-x}Sn_x Se_2$ glasses in the composition range $0.1 \leq x \leq 0.6$. The appropriate amounts of high purity elements were vacuum sealed ($10^{-5}$ Torr) in an argon flushed rectangular section silica tubes. The sealed tubes were then heated in an electric rocking furnace up to a temperature 1050 °C for seventy two hours. At this temperature, the tubes were shaken to ensure complete mixing and homogenisation of the melt. Finally, the tubes were quenched, to room temperature, in a water bath to obtain the glass.

### 2.2. Density measurements

The density of the glasses was determined by the Archimedes method using ethyl-methyl ketone as the immersion fluid. The measurements were performed at room temperature. Five separate determinations were made on each sample and the average of them was taken as the measured density of the sample. The accuracy of the measurements, obtained by measuring the densities of some pure elements, was better than ± 1%.

The compactness, δ, of the structure of the glass was calculated by the formula [10-12]

$$\delta = \rho\left(\sum_i x_i A_i \rho_i^{-1} - \rho^{-1} \sum_i x_i A_i\right)\left(\sum_i x_i A_i\right)^{-1} \qquad (1)$$

where $x_i$, $A_i$, and $\rho_i$ are the atomic fraction, the atomic weight, and the atomic density of the ith element of the glass and $\rho$ is the measured density of the glass. Thus, $\delta$ 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 [13] and , therefore, is associated with the free volume and the flexibility of the network. The compactness can assume negative values which correspond to larger free volumes and flexibilities.

### 2.3. Differential scanning calorimetry

Thermal analysis have been carried out on single glass chips, about 40 mg, using a Perkin-Elmer DSC-2C differential scanning calorimeter. The measurements were performed with a scan rate of 20 K/min. The sample was sealed in aluminium pan with an empty pan used as a reference. The temperature of the sample was then scanned from room temperature to its $T_c$. The glass transition temperature was taken as the temperature corresponding to the midpoint of the two linear portions adjoining the transition in the DSC curve whereas the onset of the crystallization exotherm was used for the determination of $T_c$.

## 3. Results and discussion

### 3.1. Determination of the average coordination number

Glassy networks are influenced by mechanical constraints associated with atomic bonding and an average coordination number, Z, which is related to the number of these constraints, $N_c$ [14-17]. Two types of constraints due to bond-stretching forces $\alpha$ and bond-bending forces $\beta$ need to be considered. In constraints theory, the number of these constraints per atom arising from bond-stretching, $N_{c\alpha}$, that arising from bond-bending, $N_{c\beta}$, and the total number of constraints, $N_c$, are given by

$$N_{c\alpha}=\frac{Z}{2}$$

$$N_{c\beta}=2Z-3 \qquad (2)$$

$$N_c=\frac{5}{2}Z-3$$

Phillips [18], applied the network constraint theory to the ternary $Ge_{1-x}Sn_xSe_2$ alloy system. He assumed that both bond-bending and bond-stretching constraints to be intact for Ge and Se while only bond-stretching constraints are intact for Sn (i.e. he ignored the bond-bending constraints for Sn because its spring constant is weak compared to Ge and Se). This enabled him to count the number of constraints per atom, $N_c$, which is given in terms of Sn concentration, x, in the glass via the relation

$$N_c=\frac{1}{3}(11-5x) \qquad (3)$$

By equating formulas 2 and 3 for $N_c$, Z has been calculated in terms of x by using the relation

$$Z=2.67-\frac{2x}{3} \qquad (4)$$

which gives the expected average coordination number for $GeSe_2$ (x=0). Table 1 lists the calculated values of $N_c$ and Z for $Ge_{1-x}Sn_xSe_2$ glassy system. As it can be seen from this table, $N_c$ and Z follow the same decreasing trend with increasing Sn content. It is also to be noted that the addition of Sn reduces $N_c$ and allows one to tune the system through $N_c=N_d$ (where $N_d$ is the number of degrees of freedom in 3-D space) from an overconstrained regime $N_c > N_d$ ($x< 0.4$) to an underconstrained regime $N_c < N_d$ ($x> 0.4$).

### 3.2. Compactness

The compactness results (Fig. 1) show that there is a decrease in $\delta$ as x increases. This type of behaviour observed for $\delta$-x dependence indicates that the free volume in the glass network and accordingly its flexibility increase with x. In this regard, network flexibility is defined as the inverse of its rigidity where a measure of the latter is the average coordination number. It can be seen from table 1 that the calculated Z values decrease with increasing x and thus confirming the decrease of network rigidity and the increase in its flexibility. Furthermore, we associate the non-monotonic decrease in $\delta$ with x with the fragmentation of the molecular cluster network which sets on at x=0.2 where a sudden drop in $\delta$ ( an abrupt change of slope), for x=0.2, is observed. Obviously, as the network breaks up accompanied by the increase in the free volume between the fragments, the ratio of surface to volume of the molecular cluster increases which results in the decrease of $\delta$. Our view about the $\delta$-composition dependence is corroborated by the fragmentation model proposed in [19] for the structure of $Ge_{1-x}Sn_xSe_2$ glasses. According to this model, when Sn atoms are added to $GeSe_2$ they substitute preferentially for the Ge atoms situated on the edge of the molecular cluster “outrigger raft”. As the Sn concentration is increased, the average-size cluster can no longer accommodate all the Sn atoms substitutionally in the preferred Ge sites on the edge of the cluster “outrigger sites”. Therefore, the cluster breaks up (fragments) into smaller clusters to create more “outrigger sites” for the Sn atoms to occupy.

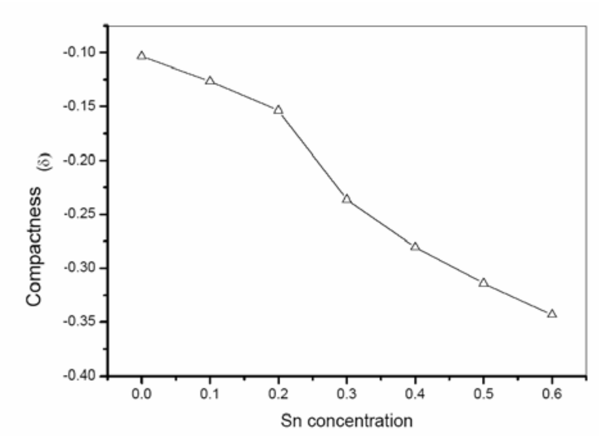

*Fig. 1. The dependence of the compactness, δ, on the amount of Sn concentration in the glass. Solid lines between data points are drawn as a guide for the eye.*

### 3.3. Differential scanning calorimetry

The $Ge_{1-x}Sn_xSe_2$ glasses undergo a single glass transition and a single crystallization on heating. This indicates that these glasses are homogeneous. Numerical values of $T_g$, $T_c$, and $\Delta T=T_c-T_g$ are listed in Table 1. The value of $T_c$ for $GeSe_2$ is taken from [20 ]. As it can be seen from table 1, both $T_g$ and $T_c$ decrease with the decrease of Z (increase of Sn content in the glass composition). This is as expected for $T_g$ because the lower coordination number indicates weaker bonding between atoms ( i.e. weakening of the glass structure by Sn). This view is also consistent with an increase in the ratio of the surface to volume of the molecular clusters, which would occur as the "rafts" break up and their sizes decrease, as predicted by our compactness results and the fragmentation model [19]. The observed decrease of $T_c$ with increasing Sn content indicates that the Sn addition facilitates the crystallization of the glass, thus rendering the glass less thermally stable.

*Table 1. Values of the number of constraints/atom ($N_c$) ; the average coordination number (Z); the glass transition temperature ($T_g$); the onset crystallization temperatures ($T_c$), the temperature interval ($\Delta T$); the mean bond energy of the average cross-linking per atom ($<E_c>$, of the remaining matrix ($<E_{rm}>$), the overall mean bond energy ($<E>$); and the compactness (δ) for the investigated Ge-Sn-Se glasses.*

| Glass composition (x) | $N_c$/atom | Z | $T_g$ ($^0C$) | $T_c$ ($^0C$) | $\Delta T$ ($^0C$) | $<E_c>$ kcal/mole | $<E_{rm}>$ kcal/mole | <E> kcal/mole | δ |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 3.67 | 2.67 | 414 | 533 | 119 | 65.46 | 0 | 65.46 | -0.1037 |
| 0.1 | 3.50 | 2.60 | 389 | 428 | 39 | 62.05 | 1.13 | 63.18 | -0.1266 |
| 0.2 | 3.33 | 2.54 | 369 | 402 | 33 | 58.67 | 2.26 | 60.93 | -0.1538 |
| 0.3 | 3.17 | 2.47 | 349 | 379 | 30 | 55.28 | 3.63 | 58.91 | -0.2364 |
| 0.4 | 3.00 | 2.40 | 335 | 363 | 28 | 51.90 | 4.89 | 56.79 | -0.2806 |
| 0.5 | 2.83 | 2.34 | 319 | 346 | 27 | 48.52 | 6.22 | 54.74 | -0.3142 |
| 0.6 | 2.67 | 2.27 | 315 | 342 | 27 | 45.12 | 7.82 | 52.94 | -0.3433 |

Another parameter usually used to judge the thermal stability of the glasses or, equivalently, the relative ease with which a glass can be formed (inverse of the crystallization tendency) is the temperature difference $\Delta T$ between $T_c$ and $T_g$ [21]. A high $\Delta T$ has been associated with thermally stable glasses wherein a small $\Delta T$ signifies that the glass contains structural units with a high crystallization tendency. The values of $\Delta T$ for the studied Ge-Sn-Se compositions are given in Table 1 which shows a decrease with increasing x. Thus, once more we have a further support for the conclusion that the increase of Sn concentration in the glass leads to the reduction of its thermal stability, increases its glass-forming difficulty, and its crystallization tendency. This conclusion is in agreement with the results reported in [19] where an increase in x beyond 0.7 leads to the crystallization of the prepared material.

To get a better understanding of the behaviour of $T_g$ in this system, we have calculated the overall mean bond energy <E> of the glass network using the method suggested by the covalent bond approach (CBA) [22]. In CBA, the mean bond energy of the average cross-linking per atom, $<E_c>$, in a glass $A_{1-x-y}B_xC_y$ at the chalcogen-rich region, as in our case, is given by

$$<E_c> = x r_B E_{A-B} + y r_C E_{A-C} \quad (5)$$

where the symbol A refers to Se, and x, $r_B$, y and $r_C$ correspond, respectively, to the atomic concentration and coordination number of Ge and Sn atoms. The heteropolar bond energies for Ge-Se and Sn-Se have been calculated from Pauling [23] using the relation

$$E_{a-b} = 0.5\,(E_{a-a} + E_{b-b}) + 23\,(X_a - X_b)^2 \quad (6)$$

where $X_a$, $X_b$, $E_{a-a}$ and $E_{b-b}$ correspond to the electronegativity and homopolar bond energy of a and b atoms, respectively. Next, the average bond energy per atom of the 'remaining matrix', $<E_{rm}>$, is defined as:

$$< E_{rm} > = \frac{2\left(\frac{Z}{2} - x r_B - y r_C\right) E_{A-A}}{Z} \quad (7)$$

Finally, <E> is the sum of the two contributions and given by

$$< E > = < E_c > + < E_{rm} > \quad (8)$$

Thus, <E> is determined by the degree of cross-linking, the bond energy, the average coordination number, and the bond type. It is also known that all these factors influence the $T_g$ of the glass network.

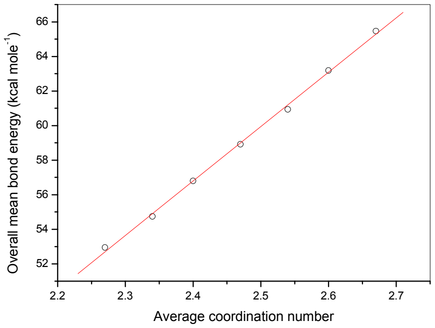

*Fig. 2. The variations of the overall mean bond energy, <E>, with the average coordination number, Z. Full line indicates a least-squares fit.*

The calculated values of $<E_c>$, $<E_{rm}>$, and <E> are listed in table 1. As it is seen from this table, <E> decreases with increasing x (decreasing Z) and thus following the same pattern as $T_g$ for this glassy system. This further confirms the increased weakness of the glass structure and consequently the decrease in its stability upon increasing the Sn content. Furthermore, a plot of <E> versus Z in these glasses, depicted in Fig. 2, shows a linear dependence. A highly significant correlation between <E> , in units of kcal/mole, and Z of the form

$$<E>=31.5Z-18.8 \tag{9}$$

is obtained, where a least squares line has been fitted to the calculated data. We are quite fortunate that this empirical formula correctly predicts the single bond energy for Se ( the glass backbone with Z=2) at 44.2 kcal/mole which is in close agreement with the Pauling value of 44.0 kcal/mole [23].

## 4. Conclusions

It is found that the thermal stability of the studied glasses decreases with increasing Sn content. The cluster size, as evidenced from the compactness results, also decreases with the increase of Sn concentration in the glass. Thus, it may be presumed that the decrease of the cluster size is indicative of a less thermally stable structure and vice versa. An empirical formula relating the calculated overall mean bond energy and the average coordination number for these glasses is obtained. This formula correctly predicts the Se-Se Pauling bond energy.

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