MOLECULAR STRUCTURE AND CRYSTALLIZATION BEHAVIOR OF CHALCOGENIDE GLASSES

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Isothermal crystallization of ternary $(Ge_2S_3)_{1-x}(Sn_2S_3)_x$ glasses is examined over the glass forming range $0 < x < 0.6$. Time–temperature–transformation (TTT) curves are obtained using scanning calorimetry. The results show that both nucleation and growth processes dominate crystallization of the glasses in the range $0 < x \leq 0.25$, but only growth processes are found to occur once $x \geq 0.25$. The occurrence of this threshold composition correlates quantitatively with changes in glass molecular structure, recently probed by Raman scattering and Mössbauer spectroscopy.

1. Introduction

Crystallization processes can provide important clues to the atomic scale structure of network glasses. In several instances, crystallization of a glass proceeds uniquely at one temperature, T_c, while in others multiple crystallizations $(T_{c1}, T_{c2} \dots)$ can be observed by scanning calorimetry. Furthermore, unique examples of glasses occur like As_2Se_3 and As_2S_3, where the kinetics of crystallization are so retarded that crystallization exotherms cannot be observed using scan rates of a few K/min typical of scanning calorimetry. Generally speaking, glass networks fall in two broad categories, ones that conform to the Ioffe–Regel (IR) rule [1] and others that are exceptions to this rule. In the former instance, the glass network consists of molecular fragments whose morphology derives from that of the corresponding crystals [2,3]. On the other hand, glasses that are exceptions to the IR rule consist of molecular fragments that are peculiar to them. These fragments [3] are not stable in corresponding crystalline (compacted) networks.

Time–temperature–transformation (TTT) curves provide a valuable probe of crystallization processes in network glasses. As discussed by Turnbull and Cohen [4], Uhlmann [5], Angell [6] and others, TTT curves usually possess a parabolic shape (fig. 1) in which at $T > T_h$, the crystallization of a glass is nucleation-dominated, while at $T < T_h$ it is a growth-dominated process. T_h

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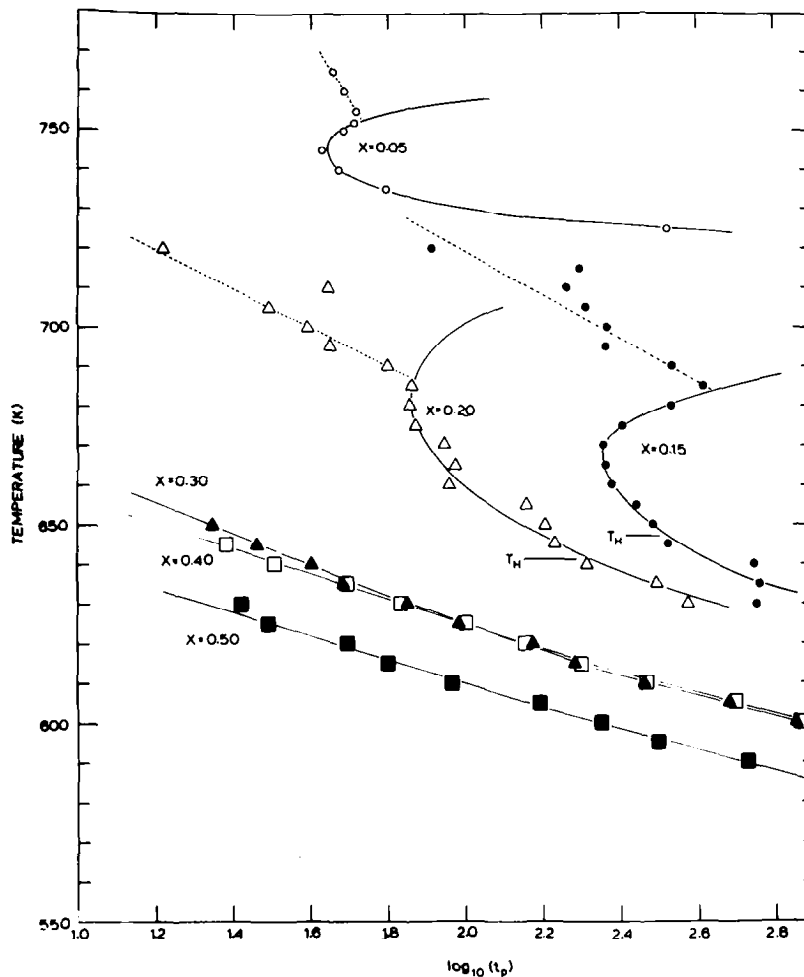
Fig. 1. Time–temperature–transformation curves of $(Ge_2S_3)_{1-x}(Sn_2S_3)_x$ bulk glasses at indicated compositions showing a progressive loss in the parabolic shape of the curves at $x \geq 0.25$. The TTT curves were obtained by studying isothermal crystallization time, t_p.

designates the homogeneous crystallization temperature and is usually close to the compromise temperature representing the nose of the TTT curve.

Glasses that conform to the IR rule provide model examples of networks where nucleation processes cannot play a significant role in crystallization, since nuclei of crystals are native to the glassy networks. For such glasses one may expect the nucleation segment of the TTT curve (i.e. $T > T_h$) to be suppressed in general. On the other hand, crystallization of glasses that are exceptions to the IR rule must involve both nucleation and growth processes. Nuclei of crystals have to form and then grow before such glassy networks can crystallize. For such glasses one may expect to observe the full TTT curve in general.
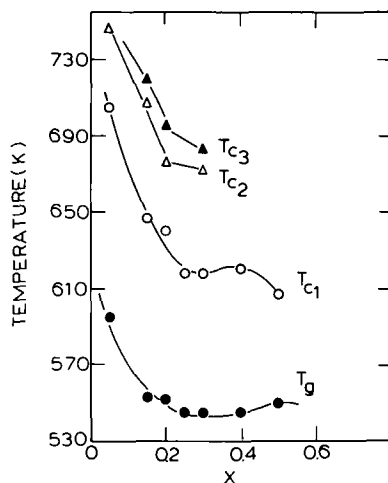
Fig. 2. Glass transition temperature (T_g) and crystallization temperatures T_{c1}, T_{c2} and T_{c3} of $(Ge_2S_3)_{1-x}(Sn_2S_3)_x$ glasses obtained from differential scanning calorimetry. The scan rate was 10 k/min. Note that only one crystallization exotherm is observed once $x \geq 0.25$.

To test these ideas correlating crystallization behavior to glass molecular structure, we have chosen to focus on the ternary chalcogenide $(Ge_2S_3)_{1-x}$ $(Sn_2S_3)_x$ for several reasons. First, homogeneous glasses exhibiting a unique T_g can be prepared [7] in this ternary over the composition range $0 < x < 0.62$. The glass transition temperatures $T_g(x)$ display a characteristic dependence on x which is shown in fig. 2. Second and perhaps most attractive is the molecular structure of these glasses which displays profound changes with composition. These changes were recently elucidated by Raman scattering [8] and Mossbauer spectroscopy [9]. At low $x(x \leq 0.25)$, one found that the glass network consists of two types of molecular phases; a metastable ethane-like Ge_2S_3 phase and a distorted rock salt GeS phase. The ethane-like Ge_2S_3 phase is found to be peculiar to the glasses but not the corresponding crystals. Upon crystallization, this molecular phase disproportionates into c-GeS$_2$ and c-GeS. At higher x ($x \geq 0.25$) the glass network consists of zig-zag chains based on c-SnGeS$_3$ [3,7]. These chains progressively become the more important molecular species in the network with x until, at $x = \frac{1}{2}$, the molecular structure of the glass displays a close similarity to that of the stoichiometric crystals. Thus an attractive feature of the present ternary is the convenience of compositional tuning of the glass molecular structure in a systematic and reproducible manner.

2. Experimental

Bulk glasses of the desired composition were prepared as previously described by Ruffolo and Boolchand [7], using 5-9s pure elements. All measurements in the present work were made using a Perkin Elmer DSC-2C Differen-

tial Scanning Calorimeter. Two types of measurements were made for each composition: (i) glass transition, T_g, and crystallization onset, T_{c1} or T_h, temperatures, and (ii) isothermal crystallization times, t_p. In the first set of measurements, a single crushed sample of the desired composition was placed in the experimental head of the DSC-2 and its temperature raised from ambient room temperature (300 K) to 750 K at a rate of 10 K/min. During each scan, both the glass transition endotherm and crystallization exotherms were observed. T_g was taken to be the temperature at the midpoint in the change in C_p that occurs during the glass transition, and this value was used for comparison to earlier work to confirm the stoichiometry of the sample. At several compositions, multiple crystallization peaks (T_{c1}, T_{c2}, T_{c3}...) were observed to occur. The onset of the first of these peaks at T_{c1} was defined to be the homogeneous crystallization temperature, T_h. This temperature was taken to be the one where homogeneous crystallization of the sample begins. The temperatures at the onset of each of the remaining peaks were measured and labeled T_{c2}, T_{c3}, etc.

To make isothermal crystallization time measurements (t_p), samples were placed in the experimental head of the DSC-2 and their temperatures raised to a predetermined target temperature at the highest controlled rate of the instrument, approximately 160 K/min. At the target temperature, the instrument was placed in a hold mode and the evolution of heat from the sample monitored as it crystallized. The time from the beginning of the hold to the peak in the isothermal crystallization exotherm was defined to be the peak crystallization time, t_p. Target temperatures were selected for their proximity to T_h.

3. Results and discussion

3.1. Differential scanning calorimetry

The principal results of the present work are summarized in figs. 2 and 3. Figure 2 shows our glass transition and crystallization data, which compare well with previous studies [3,7]. Specifically, we observe the reduction in $T_g(x)$ in the range $0 < x < 0.25$, and thereafter an increase toward a local maximum at $x = 0.50$. The local maximum in T_g at $x = 0.50$, as discussed elsewhere [3], is the consequence of a lowering in the configurational entropy of the network as substantial medium range order develops. This behavior in a glass is akin to compound formation in the equilibrium phase diagram of corresponding crystalline alloys.

Of particular interest is our crystallization data. One will note that we observe multiple crystallizations at all compositions $x < 0.30$, but only one crystallization at $x > 0.30$. These results demonstrate the existence of a threshold in the vicinity of $x = 0.30$, above which we also note that the slope dT_g/dx changes both in magnitude as well as sign. We will next show that
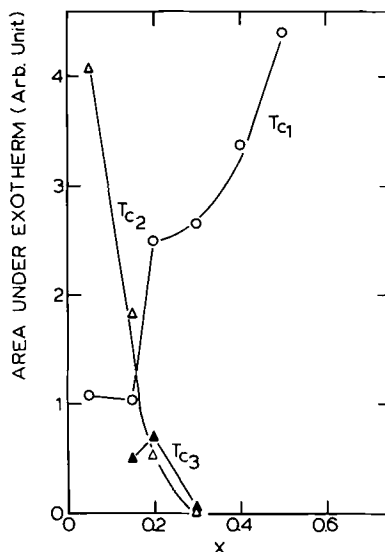
Fig. 3. The heat of transformation associated with various crystallization exotherms in $(Ge_2S_3)_{1-x}(Sn_2S_3)_x$ glasses.

these results, along with our isothermal crystallization results, are a clear signature of the appearance of c-SnGeS$_3$-like zig-zag molecular chains in the glass network above this threshold composition.

The heat of transformation associated with the lowest crystallization temperature T_{c1} is miniscule at $x = 0$, and furthermore is found to rapidly grow with x. Note that at $x \geq 0.20$ this transformation becomes the most important feature in the crystallization of the glasses, as revealed by the largest heat of transformation. We identify $T_{c1} = T_h$ with crystallization of the SnGeS$_3$-like zig-zag chains of the network.

One possible interpretation of the transformations at T_{c2} and at T_{c3} is that these represent crystallization of the ethane-like Ge$_2$S$_3$ and the distorted rocksalt GeS molecular phases respectively. Note that at $x \to 0$, T_{c2} processes are the most important ones as suggested by the heat of transformation (fig. 3). This is a surprising result because previous Mössbauer studies on Ge$_2$S$_3$ glass have shown [3,7] that the fractional population of the ethane-like phase is actually comparable to the distorted rocksalt phase in this glass. Clearly, the integrated areas of the exotherms are determined not only by fractional populations of the molecular phases in the glass network, but also by the heat of transformation associated by bond reformation. Thus, for example, we associate the large heat of transformation of T_{c2} exotherm to the following disproportionation reaction:

$$g\text{-Ge}_2S_3 \to c\text{-GeS} + GeS_2.$$
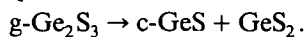
By comparison, the heat of crystallization of the T_{c3} exotherm is probably small because it involves no bond breaking and reformation, but merely minor

changes in bond lengths and bond angles of the microcrystalline GeS molecular phase in order to realize the crystalline GeS phase.

The trends in the heat of transformations of various crystallization events suggest the following broad picture: $SnGeS_3$-like fragments which first appear in the network at low x ($x \leq 0.05$), rapidly grow in population at the expense of the ethane-like Ge_2S_3 and the distorted rocksalt-like GeS molecular fragments. Apparently, alloying Sn progressively promotes formation of $SnGeS_3$-like fragments not only in the ternary glasses but in the ternary crystals as well [7]. The appearance of a single crystallization peak at $x \geq 0.30$ is a manifestation of the structural feature of ternary glass.

3.2. Isothermal crystallization

Figure 1 displays the TTT curves obtained from our isothermal crystallization measurements. These curves appear to be essentially parabolic in shape, an observation made previously by Angell et al. [6] on organic or organometallic systems. Of interest is the qualitative trend in the shape of the curves with composition x. At low values of x, and specifically in the composition range $0 < x < 0.15$, most of the parabola is observable before heterogeneous crystallization processes dominate to form a non-parabolic "tail". With increasing x, and beginning in the vicinity of $x = 0.20$, the upper portion of the parabola is progressively supressed until, at $x \geq 0.30$, the parabolic shape is no longer observed. Thus, we find that the shape of the TTT curves also displays a threshold behavior which coincides with that of $T_g(x)$ and T_c. The disappearance of the upper portion of the TTT curves is a signature of growth processes dominating the crystallization process [6], which we understand in terms of the zig-zag $SnGeS_3$ chains present in the glass network. Below the threshold ($x < 0.25$), it is necessary to nucleate crystallites by disproportioning the ethane-like Ge_2S_3 units before the onset of long-range order. Above the threshold ($x > 0.25$), $SnGeS_3$-like fragments become native to the glass network and thus nucleation events are no longer necessary before crystallization can proceed. Our TTT curves thus reinforce the molecular structure of the present ternary glass deduced earlier from spectroscopic measurements.

4. Conclusions

We have observed a threshold in the isothermal crystallization behavior of these glasses which correlates rather well with $T_c(x)$, as well as the molecular structure of the glasses. Our results show for the first time that it is possible to understand at a basic level the thermal properties such as T_g, T_c of glasses, once their molecular structure has been identified.

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