JOURNAL OF MATERIALS SCIENCE 25 (1990) 2917–2924

The effect of thallium addition on differential thermal analysis of glassy arsenous selenide. Part 2

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The effect of thallium on the phenomena accompanying the thermally induced structural changes in various glasses of the chalcogenide system $(As_2Se_3)_{1-x}Tl_x$, with $x = 0.0$ to 0.7, has been investigated using DTA measurements. The crystallization kinetic parameters of the glasses (e.g. crystallization mode, n, rate of reaction, K, and activation energy, E) have been evaluated applying a single-scan technique, and compared with those obtained from the shift in the exothermic peaks (Kissinger model). The kinetic parameter results indicate a discontinuity near thallium concentration of 2.25×10^{21} atoms cm^{-3} ($x = 0.25$) where there is a peak in both E(3 eV) and n (2.7) and a corresponding dip in K(6.7×10^{-3}).

1. Introduction

In a previous paper [1], the effect of thallium on the differential thermal analysis (DTA) of glassy selenium has been studied. This study indicated the possibility of preparing massive homogeneous binary glasses of compositions up to 10 at % Tl. However, to improve such a relatively narrow glass-forming region, a third element may be added.

Because glassy As_2Se_3 is known as a stable stoichiometric binary compound, the system $(As_2Se_3)_{1-x}Tl_x$ has been chosen to continue the previous study [1]. Different compositions of this ternary system were prepared by mixing the required quantities of As_2Se_3 and Tl at 450° C for 3 h in evacuated tubes (10^{-5} mm Hg), then quenching in ice–water. The ingots produced up to $x = 0.7$ were confirmed as homogeneous glasses by using X-ray diffractometry (Cu$K\alpha$ source) and DTA (Shimadzu DT-30), [2]. The compositions of $x \geqslant 0.8$ were non-glasses.

The effect of addition of thallium on some electrical and thermal properties of the binary chalcogenide semiconductor As_2Se_3 in the homogeneous glass-forming region, i.e. up to $\sim 10^{22}$ atoms cm^{-3}, has been studied by Kotkata *et al.* [3]. This paper concerns the effect of thallium on the DTA of glassy As_2Se_3. Experimental procedures, details of the measuring arrangements for the DTA and consequences of the applied DTA model to evaluate the crystallization kinetic parameters using a single-scan technique were the same as those described previously [1].

2. Effect of heating rate on the transition temperatures

Fig. 1 shows typical DTA traces of freshly prepared $(As_2Se_3)_{1-x}Tl_x$ alloys taken at a constant heating rate of 10° C min^{-1}. This figure illustrates three phenomena of interest; the glass transition temperature (T_g), the crystallization temperature (T_c) and the melting temperature (T_m). While T_m is independent of heating rate (ϕ), T_g changes slightly (within ± 1° C). On the other

TABLE I DTA data of the glasses investigated in the system $(As_2Se_3)_{1-x}Tl_x$

Composition	T_g (°C)	T_m (°C)	Crystallization temperatures																		T_g/T_m
			2° C min^{-1}			5° C min^{-1}			10° C min			15° C min^{-1}			20° C min^{-1}			30° C min^{-1}			
			Start	Max	End	Start	Max	End	Start	Max	End	Start	Max	End	Start	Max	End	Start	Max	End	
As_2Se_3	177	375	250	303	330	307	327	340	311	333	351	333	360	375	334	361	375	330	367	375	0.47
$x = 0.005$	175	370	220	278	304	260	298	320	285	310	328	296	320	341	305	336	350	310	340	366	0.47
$x = 0.05$	173	369	200	245	262	259	265	270	260	286	290	285	295	300	280	296	305	300	315	320	0.47
$x = 0.1$	160	362	210	229	240	232	244	250	248	266	283	255	266	270	260	265	270	260	280	295	0.44
$x = 0.15$	156	351	208	215	240	223	228	240	240	250	257	242	246	264	246	253	260	250	261	268	0.44
$x = 0.2$	151	346	195	210	235	210	224	240	245	254	258	238	253	258	238	252	260	241	253	260	0.44
$x = 0.25$	148	340	200	230	242	235	244	250	250	255	262	253	266	276	260	274	281	265	283	292	0.44
$x = 0.3$	147	324	195	226	256	228	239	256	254	271	284	244	255	271	246	264	277	256	273	288	0.45
$x = 0.4$	140	290	140	190	225	235	260	280	240	262	280	243	272	285	253	280	290	260	286	290	0.50
$x = 0.5$	130																				
$x = 0.6$	116																				
$x = 0.7$	106	205	140	182	200	142	185	200	150	175	200	146	176	205	150	190	205	170	200	205	0.52

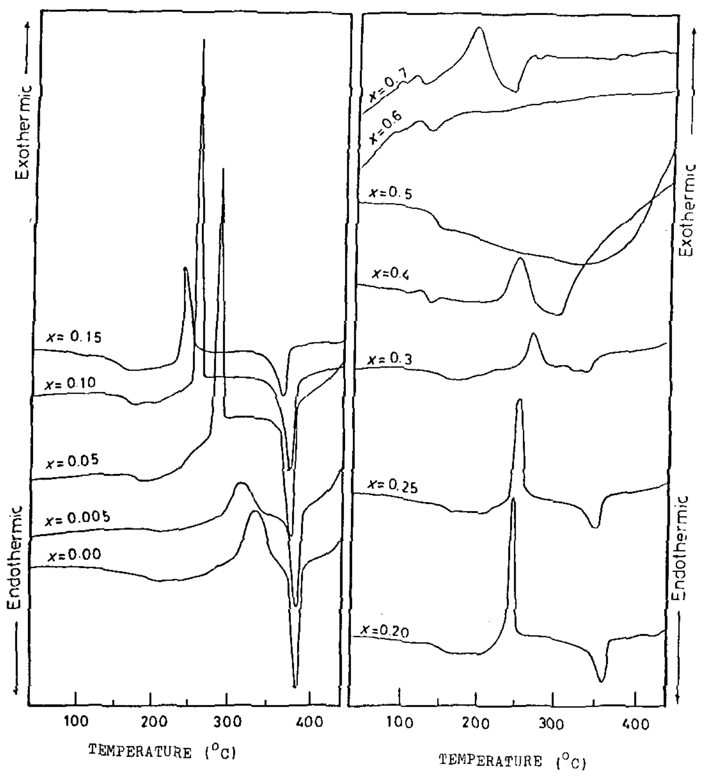

Figure 1 DTA thermograms for $(As_2Se_3)_{1-x}Tl_x$ glasses scanned at a heating rate of $10°C\,min^{-1}$.

hand, the crystallization exotherm location (start-maximum-end) changes markedly with ϕ. Table I shows the characteristic transition temperatures, T_g, T_c and T_m, for pure As_2Se_3 and its alloys with thallium at all rates. For instance, Fig. 2 shows the effect of ϕ on the thermally induced transformation of As_2Se_3. From the figure it is clear that as ϕ increases, the areas under the crystallization and melting peaks of the glassy material As_2Se_3 increase, except at $\phi = 30°C\,min^{-1}$. While the melting peaks are independent of the heating rate, the crystallization peaks move higher temperatures when increasing the heating rate. So, maybe, at $\phi = 30°C\,min^{-1}$, the crystallization temperature overlaps the melting temperature, i.e. the glassy material has reached the melting temperature before it has been completely crystallized.

The results of systematic studies of the effect of heating rate on the thermally induced transformation of the investigated system can be summarized as follows.

1. For all the compositions, the DTA scans at $\phi = 2°C\,min^{-1}$ show small crystallization and melting peaks, i.e. only a small amount of the sample material has been crystallized. The crystallization of an amorphous material proceeds by the processes of nucleation and growth, and the crystallization rate is suppressed by reducing the rate of nucleation or the rate of growth. Because growth follows nucleation, if nucleation is prevented there will be no crystallization. However, even if nucleation occurs, the crystallization rate can still be suppressed by reducing the rate of growth. Experience [4] indicates that the growth rate in liquids with a high viscosity is limited. So, perhaps at the heating rate of $2°C\,min^{-1}$, the liquid will reach its maximum rate of crystallization when the viscosity is still high.

2. At one heating rate (say, $10°C\,min^{-1}$), starting with the composition As_2Se_3, the T_c and T_m peaks are adjacent to each other and the temperature difference between the two peaks ($\delta T = 42°C$ for As_2Se_3) increases with increasing the thallium content up to $x = 0.15$ ($\delta T = 100°C$) and then decreases for a larger thallium content (for $x = 0.7$, $\delta T = 30°C$).

3. For the two compositions $(As_2Se_3)_{0.5}Tl_{0.5}$ and

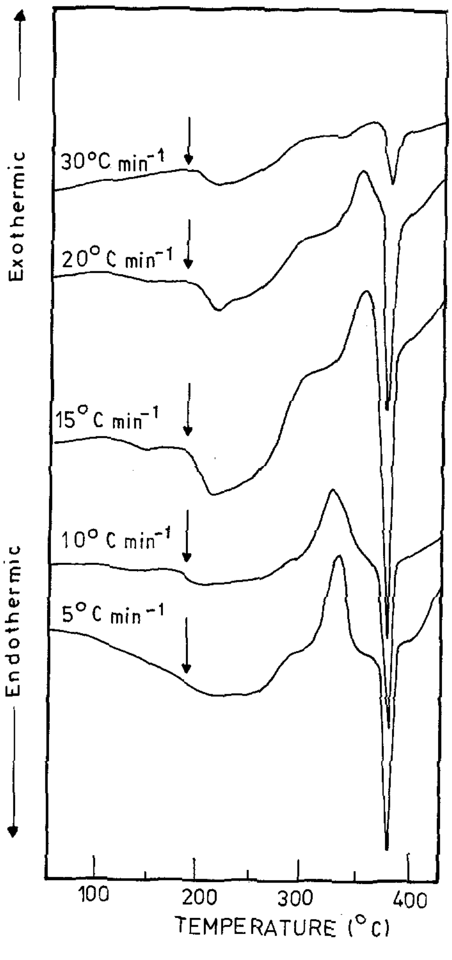

Figure 2 DTA thermogram for As_2Se_3 glass scanned at different heating rates.

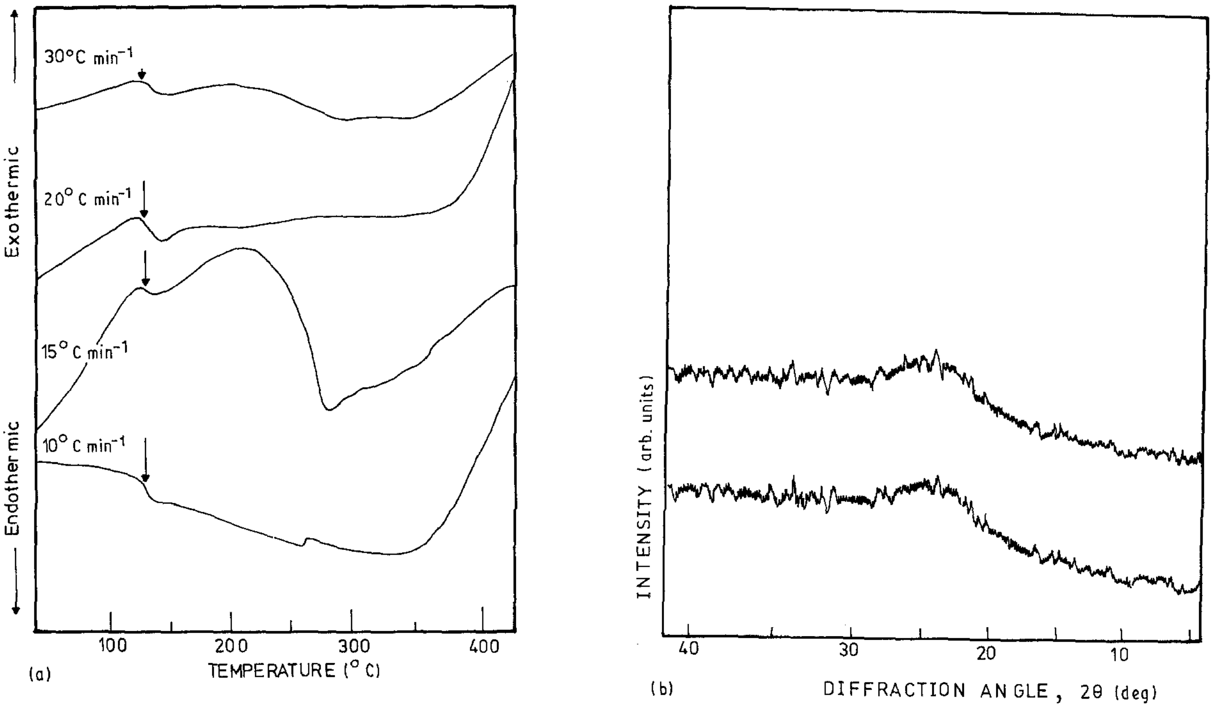

Figure 3 (a)DTA thermograms of $(As_2Se_3)_{0.5}Tl_{0.5}$ glass scanned at different heating rates. (b) X-ray diffraction patterns for the composition of $(As_2Se_3)_{0.5}Tl_{0.5}$. Upper pattern for thermally annealed sample for 30 h at 200° C, and lower pattern for fresh (as-prepared) sample.

$(As_2Se_3)_{0.4}Tl_{0.6}$, only the glass transition peaks appear on all the DTA scans at different heating rates, Figs 3 and 4. An attempt was made to prepare the crystalline phase of the compositions $(As_2Se_3)_{0.5}Tl_{0.5}$ and $(As_2Se_3)_{0.4}Tl_{0.6}$ from their as-prepared quenched materials, by heating ≈ 2 g of each composition for 30 h under vacuum at 200° C. By this type of annealing, a visible change in the annealed material should be detectable after this long-term anneal at a temperature which is higher than the glass transition temperature ($T_g = 130$ and 116° C for $x = 0.5$ and 0.6, respectively) and which is expected to be lower than the melting temperature ($T_m = 290$° C for $x = 0.4$ and $T_m = 205$° C for $x = 0.7$). So, it is difficult, if not impossible, to prepare compositions $(As_2Se_3)_{0.5}Tl_{0.5}$ and $(As_2Se_3)_{0.4}Tl_{0.6}$ in the crystalline form. From Table I it is clear that the temperature difference $\delta T = T_m - T_c$ is rather small for compositions $x = 0.4$ and 0.7 at all heating rates, so perhaps the two compositions have passed the melting temperature before the start of the crystal growth. The normal solution for this type of material is to slow the heating rate, but it is clear from the DTA scans that slow heating rates suppress the growth rate in the system $(As_2Se_3)_{1-x}Tl_x$.

4. On increasing the thallium content, it seems that T_c moves to lower values and T_m is nearly constant up to $x = 0.15$. Adding more thallium, up to $x = 0.4$,

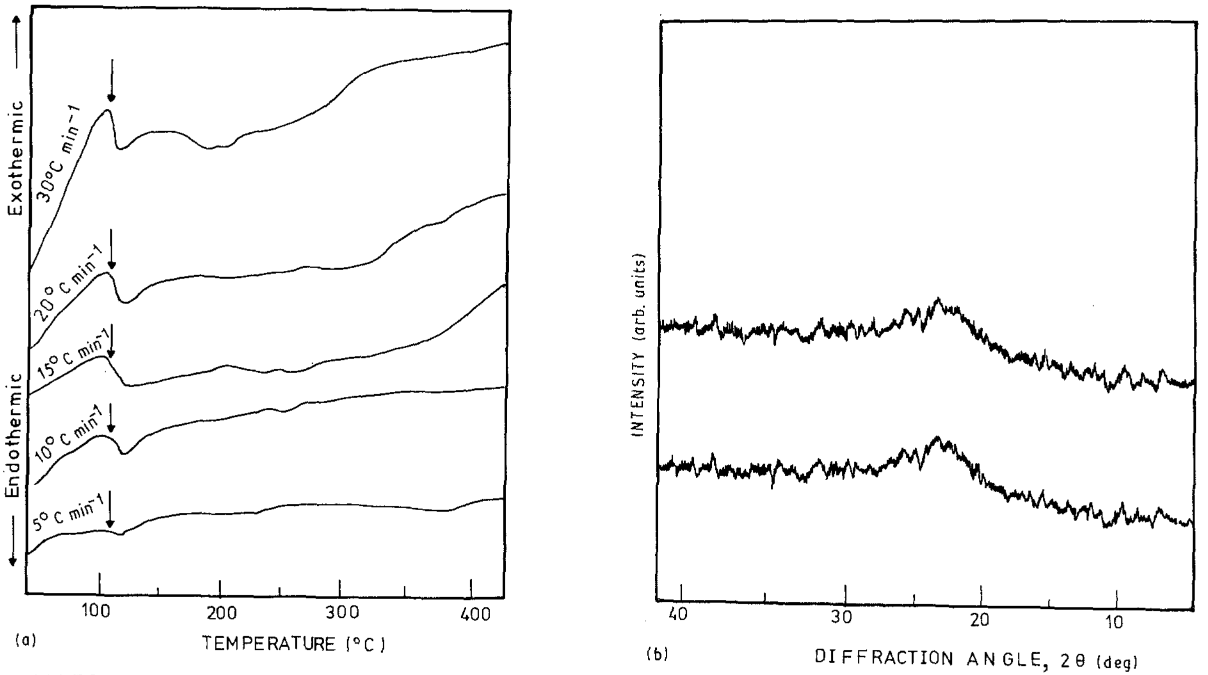

Figure 4 (a) DTA thermograms of $(As_2Se_3)_{0.4}Tl_{0.6}$ glass scanned at different heating rates. (b) X-ray diffraction patterns for the composition of $(As_2Se_3)_{0.4}Tl_{0.6}$. Upper pattern for thermally annealed sample for 30 h at 200° C, and lower pattern for fresh (as-prepared) sample.

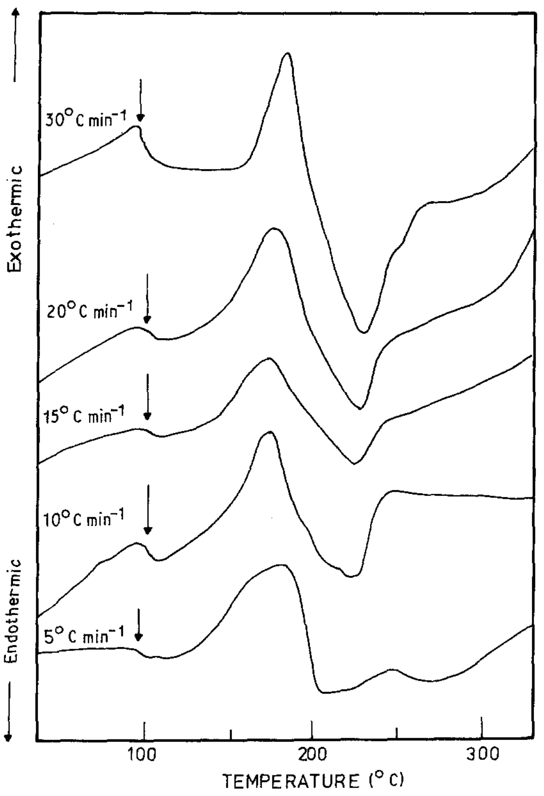

Figure 5 DTA thermograms of $(As_2Se_3)_{0.3}Tl_{0.7}$ glass scanned at different heating rates.

the T_m peaks begin to fall to lower temperatures while T_c is nearly constant, so the T_c and T_m peaks approach each other again. For greater thallium contents, $x = 0.7$, the T_c and T_m peaks move together to lower temperatures, see Fig. 5.

5. Figs 1 and 6 show that the value of T_g decreases with increasing thallium concentration and this may be a tendency for weaker bonding and hence less stability in thallium-rich glasses. Following the glass transition temperature on the same figures, the exotherm due to crystallization, T_c, which appears on the traces, fluctuates with the concentration of thallium. Evidence for decreased glass stability for thallium-rich samples is also shown by the decreasing value of T_m with increasing thallium content. It seems that for high thallium content, the bonding configuration for the thallium atoms in the material is highly covalent, while the thallium site within somewhat less covalent bonding character is introduced for materials of low thallium content. Also, thallium atoms have a small effect on the lattice but enhance the crystallization kinetics ($x < 0.25$). On increasing the thallium content starting from $x = 0.25$ (2.25×10^{21} atoms cm^{-3}), the thallium atoms affect the lattice and the growth process slows down, and perhaps that is one of the reasons for by-passing crystallization at $x = 0.5$ and 0.6. For higher thallium content ($x \geqslant 0.8$), crystallization kinetics depend completely on the metallic impurity, and it is found difficult to prepare the materials in the glassy form, as was verified from the X-ray diffraction [2].

6. According to Turnbull [4], the effect of increasing the ratio T_g/T_m is to decrease the rate of nucleation, sharpen its dependence on temperature and shift its maximum to smaller undercooling, all of which aid in glass formation. From Fig. 6, as the thallium increases, the ratio T_g/T_m decreases until $x = 0.25$ and the tendency to crystallize increases. For a greater thallium

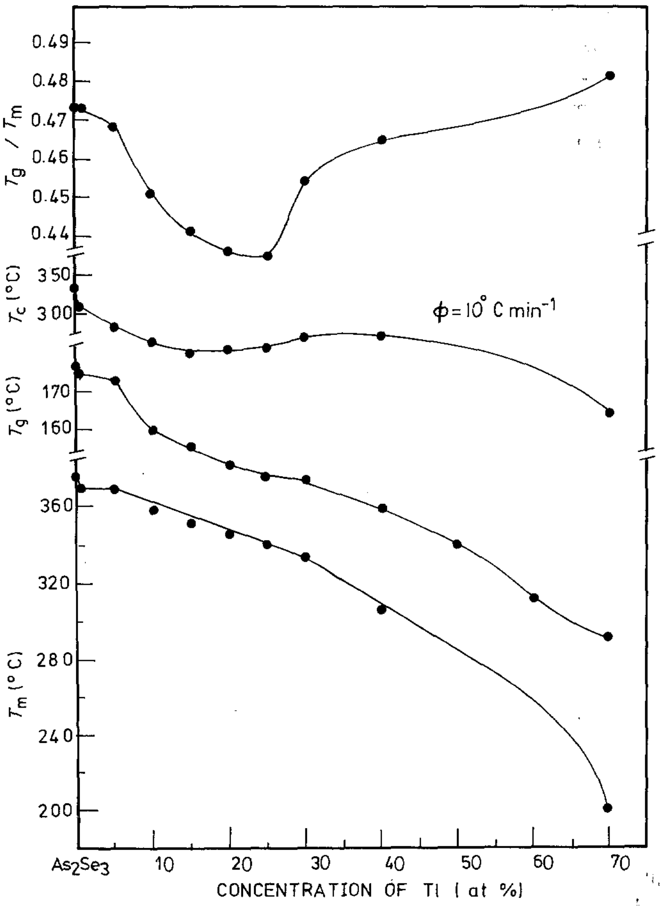

Figure 6 Dependence of melting point (T_m), glass transition temperature (T_g), crystallization temperature (T_c), and the ratio T_g/T_m, on thallium content in the system $(As_2Se_3)_{1-x}Tl_x$.

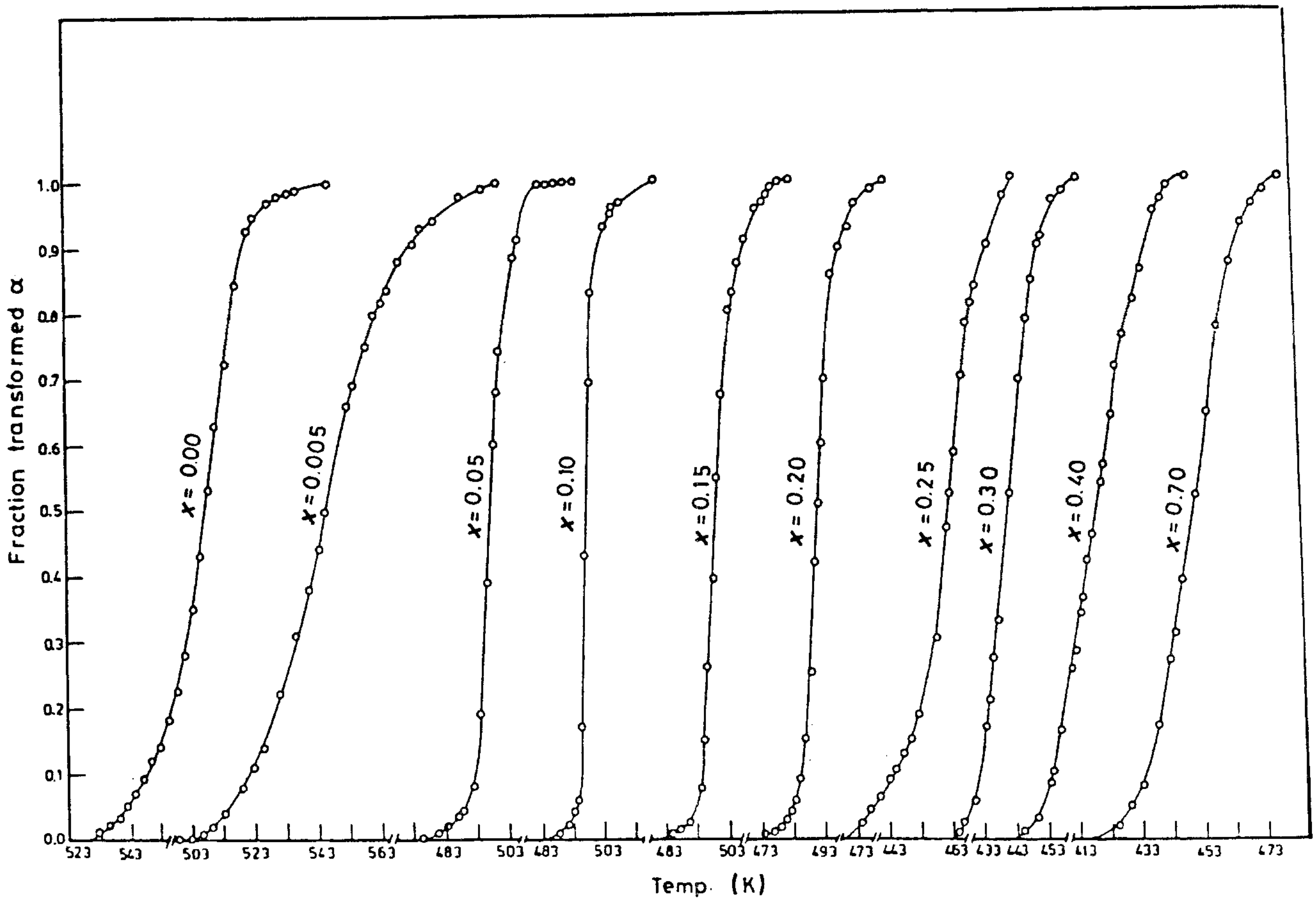

Figure 7 Variation of fraction transformed (α) with temperature, calculated from the area under DTA exothermic peak for glasses of the system $(As_2Se_3)_{1-x}Tl_x$.

content ($x > 0.25$), the ratio T_g/T_m increases and the tendency for crystallization decreases, up to a certain limit, as is clear from Fig. 6.

7. The T_c and T_m peaks, at all heating rates, are sharp and clear for thallium contents up to $x = 0.25$, and for higher contents, the peaks are broad and not clear.

3. Crystallization kinetics

A single-scan technique [1, 5] is applied to calculate reaction mode (n), reaction rate (K) and activation energy on crystallization (E). In this model, the assumption is made that the extent (α) of crystallization is proportional to the relevant area under the exothermic DTA peak. The variation of α with the heating temperature for the system As–Se–Tl glasses is shown in Fig. 7. A plot of log $[g(\alpha)]$ against $1/T$ should give a straight line over the whole range of $\alpha(0 < \alpha < 1)$ when the appropriate mathematical description of the reaction is employed [1, 5]. From the slope of the straight line, the value of E/n can be obtained.

In Fig. 8, log $[g(\alpha)]$ is plotted against $1/T$ for all As–Se–Tl alloys studied. The value of E/n can be obtained from the slope of the straight line. In this figure, only the most probable reaction mechanism for the devitrification process of each composition is presented. The function $A_3(\alpha)$ was found to approximate linear behaviour closely over the entire range of α for all compositions except the two compositions of $x = 0.0$ and 0.005 where the function $A_2(\alpha)$ gives better fitting.

According to Avrami's equation [6–8]

$$\alpha = 1 - \exp(-Kt^n) \qquad (1)$$

which can be written in a logarithmic form as

$$\ln[-\ln(1 - \alpha)] = \ln K + n \ln t \qquad (2)$$

So, a plot of $\ln[-\ln(1 - \alpha)]$ against $\ln t$ should yield a straight line whose slope is n and intercept on the ordinate at $\ln K$, as shown in Fig. 9. The value of E can be calculated from the slope of log $[g(\alpha)]$ against $1/T$ which yields E/n, and knowing n one can calculate E. Here, it is worth noting that the fitting of log $[g(\alpha)]$ or $\ln[-\ln(1 - \alpha)]$ curves of some compositions can be achieved through two distinct slopes. This indicates that the crystallization process proceeds at two different rates. Accordingly, the values of kinetic parameters n, K and E have been evaluated for the different compositions investigated, see Fig. 10.

The value of n, which depends on the mechanism of crystal growth, changes in a non-monotonic way with the addition of thallium to As_2Se_3 and lies in the range of 1.2 to 4.3. Fractional values of the experimentally obtained n can be theoretically explained by Evans principle [9] suggesting a linear change of the number of nuclei with time. With an increase in the rate of increase of nuclei, the Avrami exponent n can acquire increasing values. That is, n can acquire continuous values up to 4 instead of 3 in the case of sporadic three-dimensional growth. In the case of predetermined processes, n can take only three integer values, 1, 2 or 3, depending on whether it is one-, two-, or three-dimensional growth, respectively. Hay [10], taking

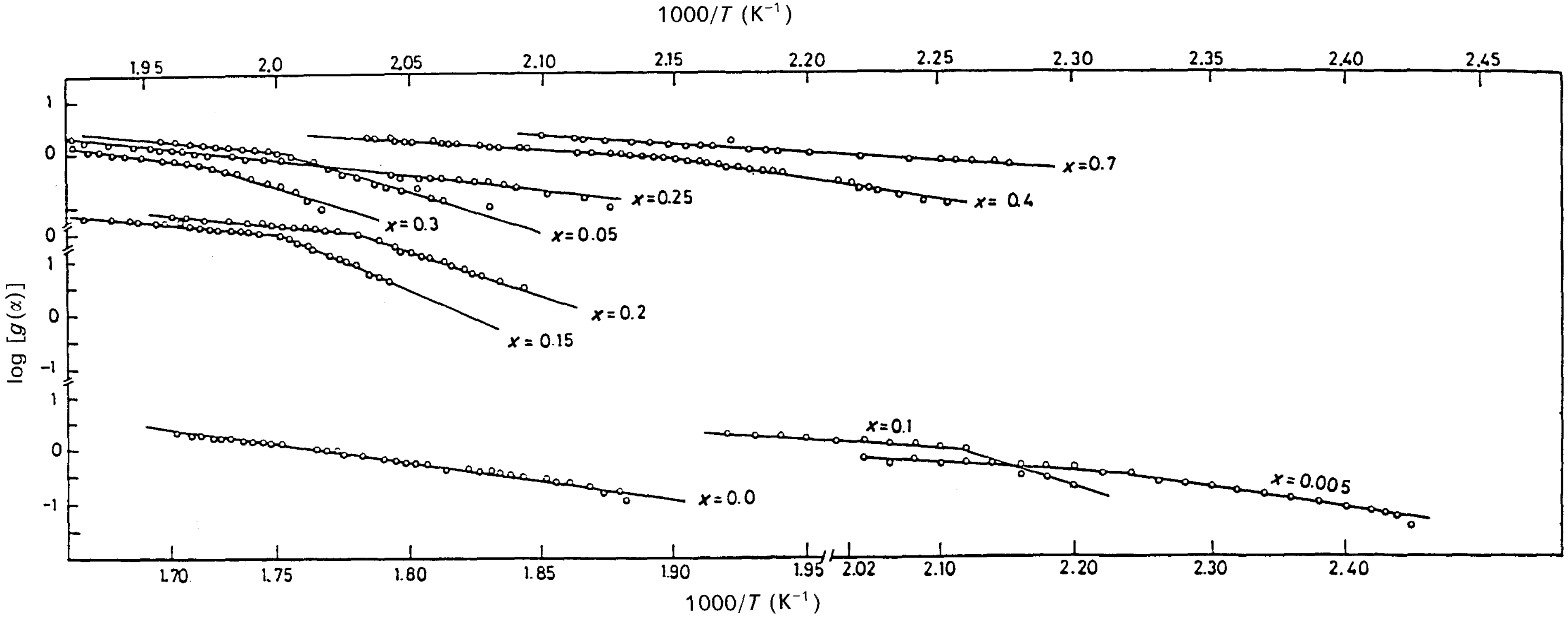

Figure 8 Plots of log [$g(\alpha)$] against $1/T$ for the reaction kinetic function $A_2(\alpha)$ or $A_3(\alpha)$ for glasses of the system $(As_2Se_3)_{1-x}Tl_x$. $A_2(\alpha):[-\ln(1-\alpha)^{1/2}] = Kt$, $A_3(\alpha):[-\ln(1-\alpha)^{1/3}] = Kt$.

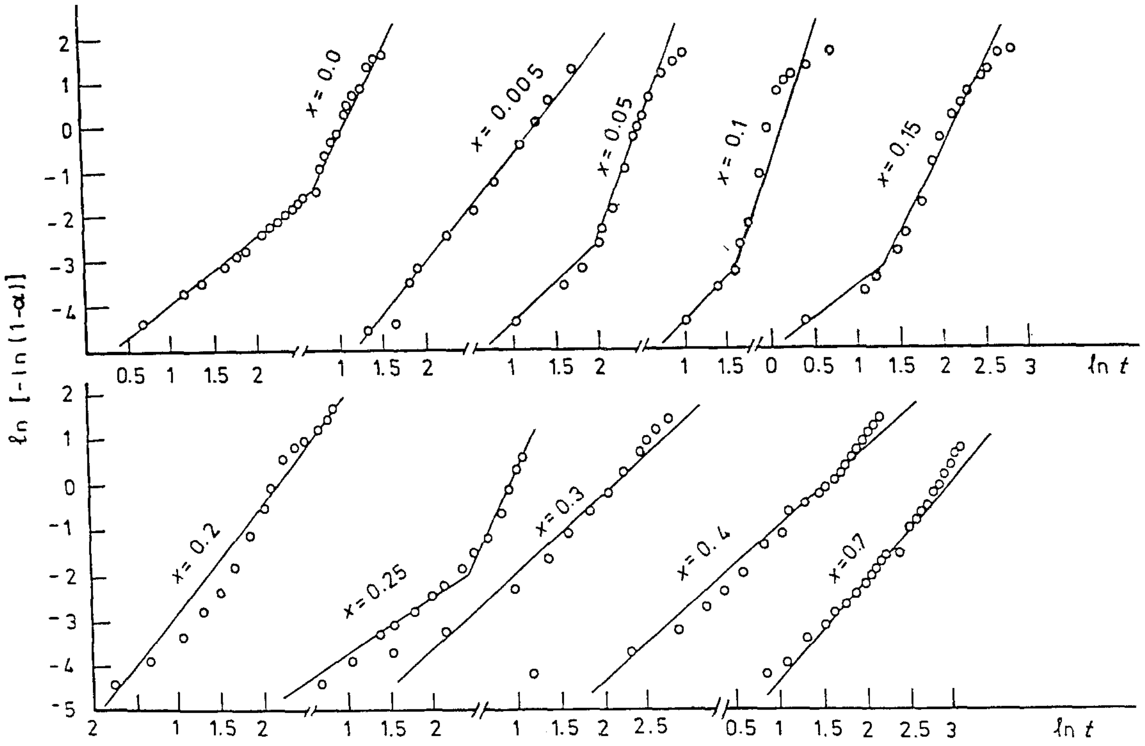

Figure 9 Avrami's plots, ln [$-$ln (1 $-$ α)] against ln t, for glasses of the system $(As_2Se_3)_{1-x}Tl_x$.

into consideration the experimental data obtained for polymer crystallization, proved the possibility of half integer values of n in the case of lateral growth and in the case of growth controlled by diffusion.

The evaluation of kinetic parameters [11] indicates that the reaction rate K lies in the range 1.1×10^{-1} to 8.0×10^{-6}, and the relative corresponding variation for E is 0.7 to 6.6 eV. The corresponding controlling mechanism (one out of nine [12]) as well as the corresponding valid range of α for the fitting of both $\log [g(\alpha)] = f(1/T)$ and $\ln[-\ln(1-\alpha)] = f(\ln t)$ with respect to each composition have been carried out using the computer facilities to check the reliability and limitation of the lines.

The increasing value of E for some phases could be an indication of the increased thermal stability of the composition. However, values of E higher than 3 eV are often unreasonable. Regarding such high values of E and the wide valid range of α, Fig. 10 shows the thallium concentration dependence of the parameters n, K and E. The values of E calculated from the shifts in the exothermic peaks [3] (multi-scan technique, known as the Kissinger method [13, 14]) assuming that the reaction mode n remains constant throughout the reaction, which is not always the case, are represented on the figure. Although the figure indicates that the features of the discontinuity of the values of E calculated using both techniques (single-scan and multi-scan) are alike, the present representation is proved to be more accurate. Fig. 10 also shows that the thallium concentration dependence of n is almost a mirror for that of K. In addition, there is a peak in both E and n and a dip in K near the composition of 25 at % Tl, i.e. near the thallium concentration of 2.25×10^{21}

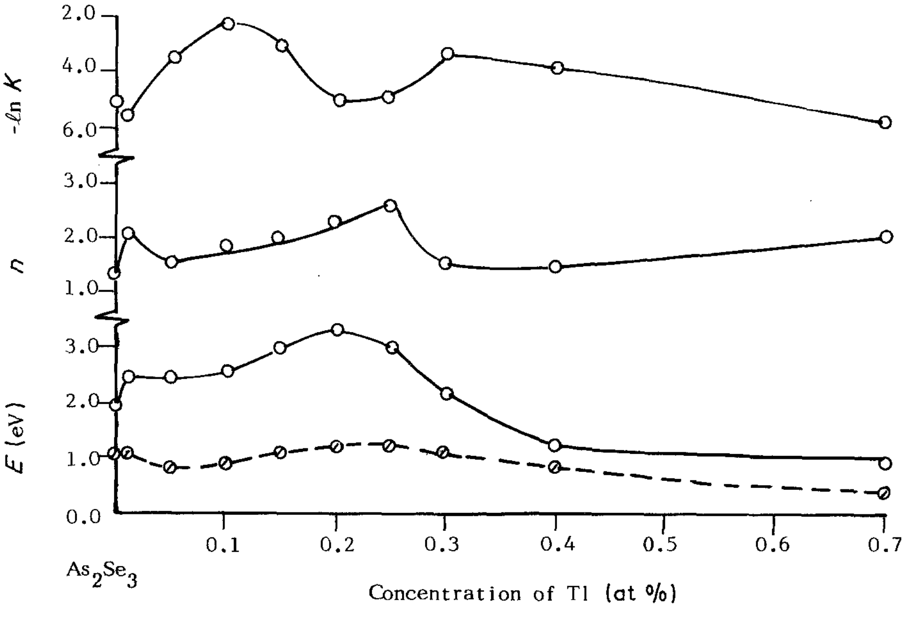

Figure 10 Composition dependence of the crystallization parameters n, K and E. (○) Present data, and (⊘) data from [3].

atoms cm^{-3}. This argument is strongly confirmed by the authors through their study of the compositional dependence of different electrical and thermal properties for glasses of the system $(As_2Se_3)_{1-x}Tl_x$ [3]. Such behaviour is correlated with the substantial difference between the thallium bond configurations of thallium-rich ($x > 0.25$) and thallium-poor ($x \leqslant 0.25$) regions of the ternary glasses investigated in the system As–Se–Tl.

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Received 27 February
and accepted 30 August 1989