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Structural studies of amorphous and crystalline Tl–As–Se compounds

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X-ray diffraction and microstructure studies for amorphous samples of composition $(As_2Se_3)_{1-x}Tl_x$, where x varies between 0 and 0.7, show that up to $x = 0.25$ the short-range order is similar to that of As_2Se_3. A change in the structure is observed as x increases. Diffraction from samples crystallized by annealing confirms that a thallium content up to $x = 0.25$ is not enough to alter a characteristic matrix similar to crystalline As_2Se_3; however, it results in a decrease of crystallization tendency. For $x > 0.25$ up to 0.7 the structural matrix features are almost similar to those of crystalline $TlAsSe_2$. The observed structural changes could rationalize reported changes in the electrical and thermal transport properties of the amorphous ternary system compounds.

1. Introduction

Semiconducting Tl–As–Se glasses are stable, covalent, chemically durable and dielectric. The overall properties of these glasses make them potentially useful for hermetic sealing of semiconductors and other moisture-sensitive electronic components which might be damaged by a high-temperature sealing process.

A determination of the glass-forming region for this system has been carried out by Flaschen *et al.* [1] (Fig. 1). They discovered that the addition of thallium to As_2Se_3 markedly reduces the melt viscosity and they suggested that the structure of these glasses may be based on long chains involving Se–Se linkages, with arsenic entering into the chains. They further hypothesized that the thallium might enter the chains as a weak link, the rupture of which causes low melt viscosities. Bishop and Taylor [2] in their nuclear magnetic resonance studies on these glasses showed that there is a substantial difference between the thallium bonding configurations of the thallium-rich and thallium-poor regions of the system; however, they were not able to relate their results to the structure of the glass, due to lack of detailed knowledge of the structural configuration.

In a study on the effect of thallium addition on the electrical and thermal transport properties of amorphous As_2Se_3, Kotkata *et al.* [3] reported that the thallium in the ternary system $(As_2Se_3)_{1-x}Tl_x$, where x varies between 0.0 and 0.7, tends to decrease the glass transition temperature and melting temperature and to increase the d.c. conductivity in the amorphous phase. A discontinuity in the electrical energy gap, electrical conductivity and heat capacity results was observed at $x \simeq 0.25$.

In this paper, X-ray diffraction from amorphous and crystallized samples of the same compositions was performed for studying possible structural configurations in the glasses, seeking a correlation with the observed changes in viscosity, electrical and thermal properties.

2. Experimental details

Bulk amorphous arsenic triselenide was prepared from highly pure arsenic and selenium (99.999% purity) loaded into a fused silica tube, which was then evacuated (10^{-5} mm Hg) and sealed off. Homogenization was carried out under continuous agitation at 800° C for about 4 h, after which the tube was quenched in ice-water.

Ten different compositions of the system $(As_2Se_3)_{1-x}Tl_x$, with x values from 0.05 to 0.7, were prepared by mixing the required quantities of As_2Se_3 and thallium at 450° C for 3 h in evacuated tubes (10^{-5} mm Hg),

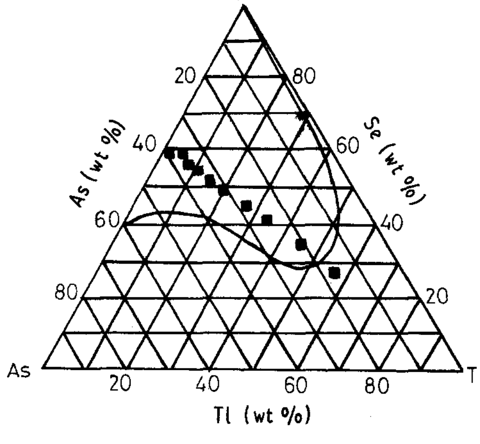


Figure 1 Phase diagram of the system Tl–As–Se according to Flaschen *et al.* [1]; (■) denotes the compositions investigated.

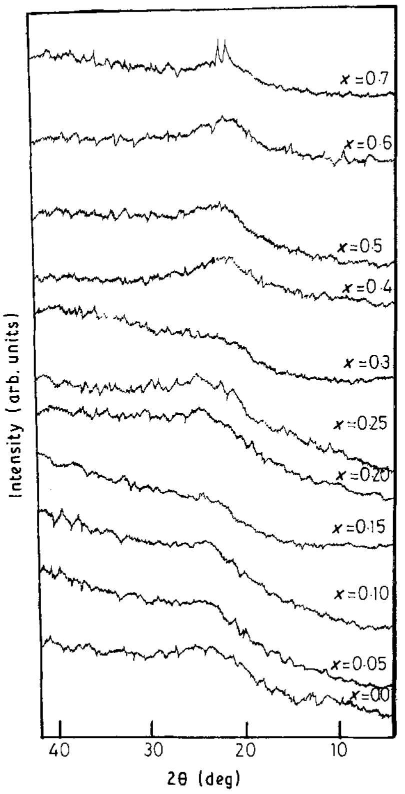


Figure 2 X-ray diffraction patterns of $(As_2Se_3)_{1-x}Tl_x$ ice-water quenched samples having up to 70 at % Tl.

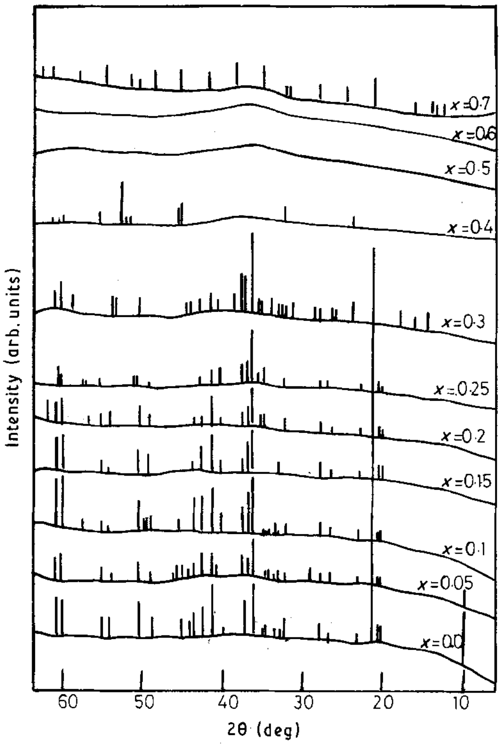


Figure 3 Bragg angle dependence of diffraction line intensities of crystallized $(As_2Se_3)_{1-x}Tl_x$ samples on background diffraction from the amorphous phase present in the samples.

then quenched in ice-water. The ingots produced were confirmed as homogeneously amorphous by using X-ray diffractometry and differential thermal analysis (DTA) [3]. The sample compositions are shown on the phase diagram in Fig. 1.

X-ray diffraction patterns for the amorphous samples obtained by the powder diffractometry method using CuKα radiation are shown in Fig. 2.

For crystallization, the amorphous samples were put into silica tubes, then evacuated (10^{-5} mm Hg) and sealed off, then heated at a temperature corresponding to the end-of-crystallization temperature, measured using DTA and given in Table I, for enough time until the appearance of a crystalline phase was observed. Before complete crystallization occurred the samples were slowly cooled inside the tubes for studying the structural phases of highest crystallization tendency, as an indication of the most probable structural matrix present in the amorphous samples. X-ray diffraction patterns from the crystallized samples were obtained by the powder diffractometry method using cobalt radiation for finer-detailed diffraction patterns. The patterns are shown in Fig. 3 where, on the background diffraction from the amorphous phase, only the highest intensity peaks from crystallized structures are indicated.

3. Results and discussion

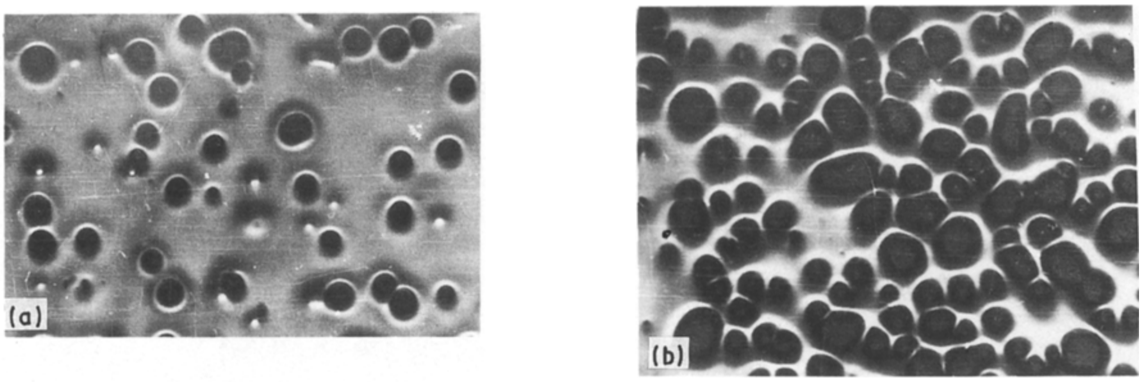
Diffraction patterns from the amorphous samples shown in Fig. 2 show that up to $x = 0.25$ the general features are similar to those of pure As_2Se_3 ($x = 0$). This suggests that the layered structure of crystalline As_2Se_3 which is preserved in the amorphous compound is not much changed in the thallium-poor compositions ($x \leqslant 0.25$) of the ternary structure. This means it is possible that a low percentage of thallium atoms can intercalate between the layered structure of the As_2Se_3 rather than destroying it and forming new bonds. The same sort of behaviour was observed before in low-percentage metal-doped As_2S_3 [4, 5].

X-ray diffraction patterns from the amorphous

TABLE I DTA data* for glasses in the system $(As_2Se_3)_{1-x}Tl_x$ at heating rate 5° C min^{-1}

Composition	T_g(° C)	T_c(° C) (5° C min^{-1})			Start T_m(° C)
		Begin	Max.	End	
As_2Se_3	176	307	327	329	374
$(As_2Se_3)_{0.95}Tl_{0.05}$	166	259	265	270	367
$(As_2Se_3)_{0.9}Tl_{0.1}$	157	236	244	247	360
$(As_2Se_3)_{0.85}Tl_{0.15}$	151	223	228	237	350
$(As_2Se_3)_{0.8}Tl_{0.2}$	146	218	224	227	346
$(As_2Se_3)_{0.75}Tl_{0.25}$	149	235	244	250	340
$(As_2Se_3)_{0.7}Tl_{0.3}$	143	228	239	254	325
$(As_2Se_3)_{0.6}Tl_{0.4}$	140	240	260	280	280
$(As_2Se_3)_{0.5}Tl_{0.5}$	—	—	—	—	—
$(As_2Se_3)_{0.4}Tl_{0.6}$	116	—	—	—	—
$(As_2Se_3)_{0.3}Tl_{0.7}$	100	145	200	220	230

*T_g = glass transition temperature, T_c = exothermic crystallization temperature, T_m = endothermic melting point.



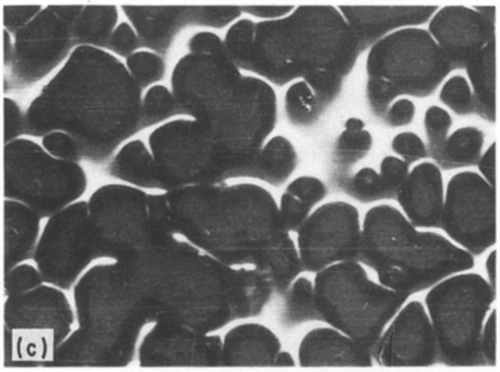


Figure 4 Optical photomicrographs illustrating growth of As_2Se_3 films ($\approx 100\,\mu m$) during isothermal annealing at 260° C for different times, showing (a) distributed centres in the early stages, (b) an increase in their number with time when a sort of ordering is observed, then (c) growth and overlap into regions.

thallium-rich ($x > 0.25$) compounds show a change in the general features of the diffraction pattern, indicating a change in the structure. However, an assessment of the probable structural matrix from these diffraction patterns was not possible and a study of the crystallized phases was carried out.

From the X-ray diffraction patterns shown in Fig. 3, it is found that for the composition containing only arsenic and selenium the diffraction pattern shows a crystalline phase formed mainly of As_2Se_3 crystals. The crystal growth in this composition as followed by photomicrography is shown in Fig. 4. In the diffraction pattern, incomplete crystallization is indicated by the typical amorphous-phase diffraction pattern forming the background.

Addition of thallium at a small percentage up to 15% does not change the main features of the diffraction pattern. Up to that content, it is possible that thallium atoms intercalate or occupy interstitial positions and do not destroy the As_2Se_3-based structure as suggested before. The main effect of adding thallium is a decrease in crystallization tendency.

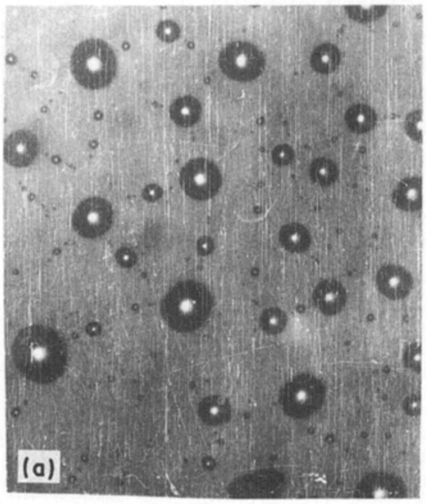
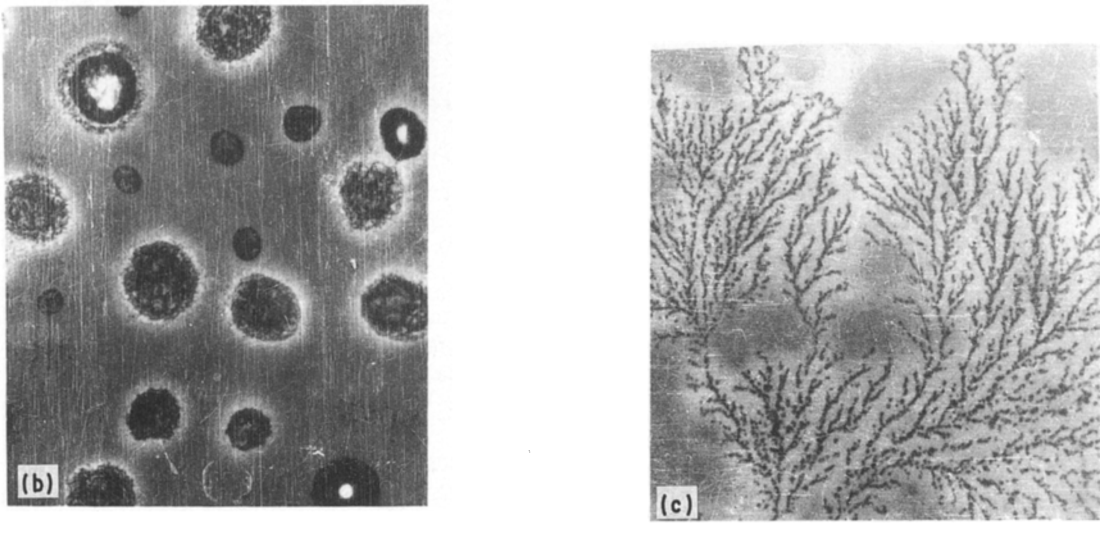


Figure 5 Optical photomicrographs illustrating the growth of $(As_2Se_3)_{0.6}Tl_{0.4}$ films ($\approx 100\,\mu m$) during isothermal annealing at 260° C for different times showing (a) distributed centres which grow with time forming (b) spheroids and then change to (c) fractals.



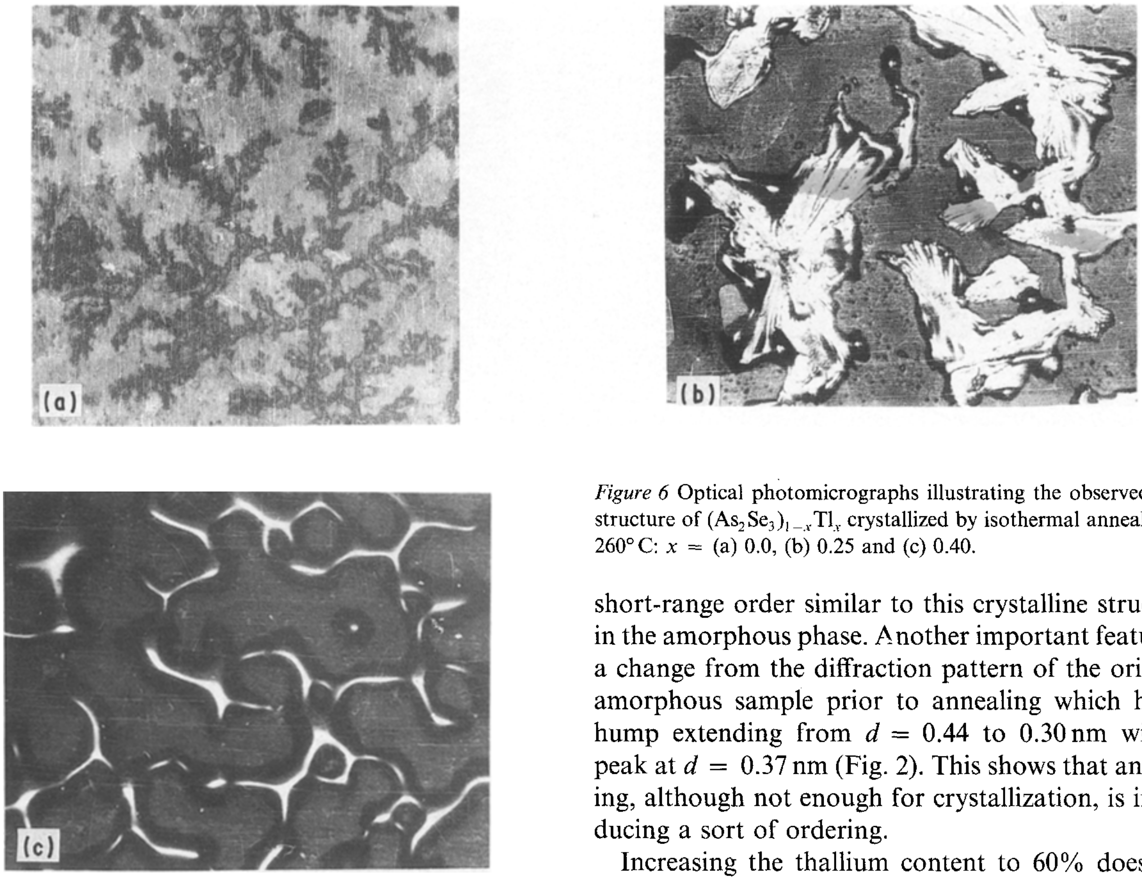


Figure 6 Optical photomicrographs illustrating the observed final structure of $(As_2Se_3)_{1-x}Tl_x$ crystallized by isothermal annealing at 260° C: x = (a) 0.0, (b) 0.25 and (c) 0.40.

Increasing the thallium-content to 20%, one observes slight changes in the diffraction pattern. In addition to the previously observed crystalline phase of As_2Se_3, traces of crystalline $TlAsSe_2$ are present. Also, a small hump around $2\theta \approx 37°$ (d = 0.28 nm defined by $2d \sin\theta = \lambda$) appears, indicating a higher percentage of the disordered amorphous phase in the sample. The same features are preserved when the thallium content reaches 25%.

Major changes in the features of the diffraction pattern, and hence the structure, are only observed when the thallium content is greater than 25%. For 30% thallium the main changes are a smaller percentage of the As–Se-based crystalline phase and a higher percentage of the Tl–As–Se crystalline phase. From the amorphous portion of the sample, a wide hump extending from 32 to 48° in 2θ appears in the diffraction pattern background.

On increasing the thallium content to 40% the crystallization tendency was greatly decreased and only a few peaks corresponding to crystalline phases were observed. However, it was possible to follow the growth process in this composition as illustrated by the optical photomicrographs shown in Fig. 5. In Fig. 6 the observed final crystalline structures of $(As_2Se_3)_{1-x}Tl_x$ are shown for x = 0.0, 0.25 and 0.40.

As the thallium content was increased to 50% it was not possible to obtain any crystalline structure by annealing and the diffraction pattern shows a 100% amorphous phase content. A hump extends from 24 to 48° in 2θ corresponding to 0.43 to 0.22 nm in d. The location of the hump peak at d = 0.27 nm is identical to the position of largest peak in the $TlAsSe_2$ crystal diffraction pattern. This suggests the presence of a short-range order similar to this crystalline structure in the amorphous phase. Another important feature is a change from the diffraction pattern of the original amorphous sample prior to annealing which has a hump extending from d = 0.44 to 0.30 nm with a peak at d = 0.37 nm (Fig. 2). This shows that annealing, although not enough for crystallization, is introducing a sort of ordering.

Increasing the thallium content to 60% does not change the main features of the annealed amorphous-phase diffraction pattern and no crystallization is observed. A major change in the structure is observed as the thallium content is increased to 70%. The diffraction pattern amorphous background largely changes and crystallization is possible. The main component of the crystalline phase is crystalline $TlAsSe_2$ together with a small percentage of crystalline As_2Se_3.

4. Conclusion

X-ray diffraction study of glassy and crystallized samples of the ternary system $(As_2Se_3)_{1-x}Tl_x$ shows that for the thallium-poor amorphous compounds ($x \leqslant 0.25$) the structure is generally similar to the amorphous As_2Se_3 layered structure. For the thallium-rich compounds ($x > 0.25$) a change in the structure is observed and a matrix similar to that found in crystalline $TlAsSe_2$ is most probable. The results completely rationalize the observed changes in the viscosity, electrical and thermal properties of the glasses, where the change in the properties is associated with the formation of more covalent thallium bonding configurations.

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