Journal of Non-Crystalline Solids, 16 (1974) 365–374. © North-Holland Publishing Company

X-RAY INVESTIGATION OF THE CRYSTALLIZATION OF CHALCOGENIDE GLASSES OF THE TYPE $(As_2Se_3)_{1-x} : (Tl_2Se)_x$

C.A. MAJID, P.R. PRAGER, N.H. FLETCHER and J.M. BRETTELL
Department of Physics, University of New England, Armidale, N.S.W. 2351, Australia

Received 6 June 1974

Amorphous and crystalline states of As_2Se_3, $(As_2Se_3)_3 : Tl_2Se$ and $As_2Se_3 : Tl_2Se$ have been studied using X-ray diffraction techniques. Structural changes arise during the process of annealing in the temperature range between their softening and melting points are reported and their rates investigated. The crystallization temperatures were found to be 105 ± 5 °C, 135 ± 5 °C and 180 ± 5 °C respectively. The unit cell parameters are identified for each of the three resulting crystalline phases, that for $As_2Se_3 : Tl_2Se$ being orthorhombic while the other two are monoclinic.

1. Introduction

Studies of the structural changes undergone by the chalcogenide glasses of the type $(As_2Se_3)_{1-x} : (Tl_2Se)_x$ where $x = 0, 0.25$ and 0.50, are discussed. These glasses were synthesized by the conventional method of heating the constituent elements (all of 99.999 % purity) in silicon glass ampoules to high above the melting temperature of the highest melting constituent, followed by air quenching. The silica glass ampoules were sealed after being evacuated to a pressure of the order of 10^{-5} to 10^{-6} torr for about 20 h to ensure the degassing of the atmospheric contents. The glasses thus prepared were completely amorphous and homogeneous.

Of the glasses studied by us, As_2Se_3 has been thoroughly investigated both in the amorphous and crystalline forms. Renninger and Averbach [1, 2] have studied the crystalline structure of this chalcogenide glass while Vaipolin and colleagues [3–6] have reported their investigations on the amorphous as well as crystalline structure of this material. Different values of the glass transition temperature of As_2Se_3 appear in the literature. Kolomiets et al. [7, 8] have reported a value of 187 °C whereas Flasck et al. [9] have reported approximately 180 °C. Information about the crystallization of As_2Se_3 at 240 °C and above is also reported [11, 12]; but no information is available about the structural properties in the range of its softening and melting points. To date no information on the other two glasses of this family has been reported and no information is available in the literature about their structures either in the amorphous or crystalline states.

Table 1
Softening, melting and crystallization temperatures of the semiconducting glasses included in this study.

Glass	Softening temperature (D.T.A.) (°C)	Melting temperature (D.T.A.) (°C)	Crystallization temperature (X-ray) (°C)
As_2Se_3	180	202	180 ± 5
$(As_2Se_3)_3 : Tl_2Se$	135	150	135 ± 5
$As_2Se_3 : Tl_2Se$	104	125	105 ± 5

The semiconducting glasses included in this study, their softening and melting points, as determined from their differential thermal analysis carried out in this laboratory, and their crystallization temperatures T_g determined from the X-ray diffraction studies, are listed in table 1. The measurement of the softening and melting temperatures was carried out with an accuracy of about 3 °C.

Since structural changes affect the optical and electrical properties of the compounds, lack of knowledge about these changes may lead to the misinterpretation of experimental results, particularly when these studies are extended beyond the softening temperatures. Here we present information about such changes in these glasses between their softening and melting points, particularly in relation to the effects of annealing time and of annealing temperature when this is above the softening point.

The studies were carried out with Ni-filtered CuKα radiation since fluorescence precludes the use of MoKα radiation. Experiments were carried out in an evacuated Debye–Scherrer camera of 114.6 mm diameter. These glasses absorb Cu radiation heavily, and the preparation of specimens of optimum thickness is impracticable without subjecting them to some sort of heat treatment. Unfortunately these glasses undergo structural changes almost immediately on heating above their softening points. The specimens prepared by softening the compounds between two clean quartz microscope slides pressed together by a spring clamp in vacuum gave markedly different X-ray diffraction patterns from those prepared in the manner now described.

Under these experimental limitations, the specimens were prepared in the form of thin wafers approximately $6 \times 0.5 \times 0.1$ mm^3. These were cut from slabs of the compound prepared by grinding and polishing the bulk lumps of amorphous material. Annealing of the specimens was carried out in evacuated glass ampoules. These wafers were mounted in the camera with their long sides parallel to the camera axis and with their large faces parallel to the X-ray beam and were oscillated through approximately ± 20° during exposure. The intensity measurements were carried out with a standard microphotometer. No effect of water or of grinding and polishing agents was noted on the diffraction patterns.

2. Comparison of amorphous states

The experimental results are shown in figs. 1–6. The intensity data have been corrected for the background but not for absorption and polarization of the X-rays. Information is presented up to Bragg angle $2\theta = 65^\circ$ in most cases.

Fig. 1 shows the intensity curves of the X-ray diffraction patterns of the three glasses. The spacings of characteristic groups responsible for the bands in each glass are listed in table 2. The accuracy is in each case about ± 0.03 Å.

In fig. 1 curve (a) is the X-ray diffraction pattern of vitreous As_2Se_3. As well as

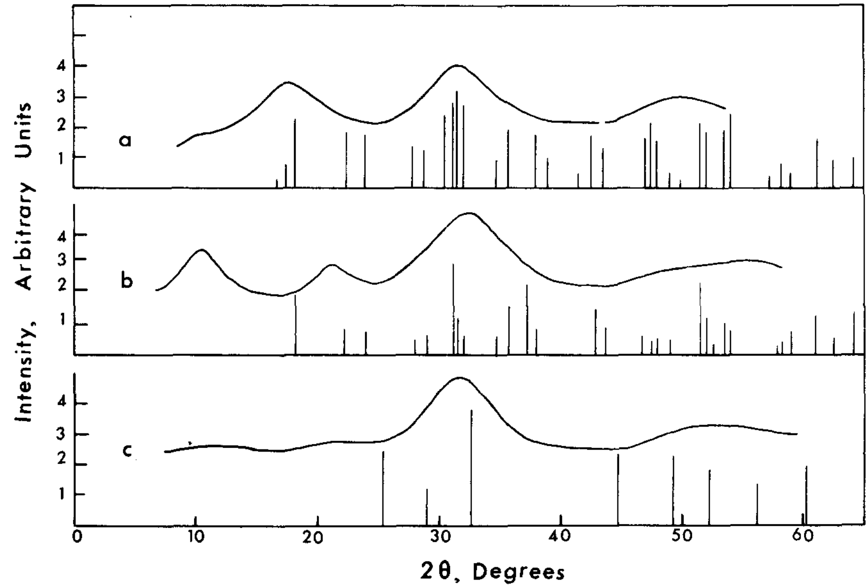

Fig. 1. X-ray intensity curves for glasses (corrected for background) and powder photographs of the corresponding crystalline solids: (a) As_2Se_3; (b) $As_2Se_3)_3$: Tl_2Se; (c) As_2Se_3 : Tl_2Se.

Table 2
Spacings of characteristic groups.

Positions of bands in vitreous As_2Se_3		Positions of bands in vitreous $(As_2Se_3)_3$: Tl_2Se		Positions of bands in vitreous As_2Se_3 : Tl_2Se	
d (Å)	2θ	d (Å)	2θ	d (Å)	2θ
–	–	8.05	10.5°	–	–
4.99	17.75°	4.15	21.5°	–	–
2.84	31.5°	2.77	32.5°	2.82	31.75°
1.82	50.25°	≈1.74	52.5°	≈1.74	52.5°

the three spacings listed above, the intensity curve also suggests the possibility of a shoulder at about $2\theta = 10°$, corresponding to a spacing of 8.1 Å. The positions and the comparative areas under the bands of this glass are in agreement with those reported by the other authors [5].

The intensity curve (b) shows the X-ray diffraction pattern of vitreous $(As_2Se_3)_3 : Tl_2Se$. This curve shows three well defined bands along with a widely spread hump. Curve (c) of fig. 1 is the X-ray diffraction pattern of glassy $As_2Se_3 : Tl_2Se$. It shows one broad band near $2\theta = 32°$, the same position at which the strong bands occur in the case of two other glasses. All other bands have nearly disappeared into the background. A comparison of the X-ray diffraction pattern shows that (i) the curve (a) for pure As_2Se_3 is different from the others because of the strong peak at $2\theta = 17.75°$, which is absent from the other two, (ii) the curve (c) for $x = 0.50$ differs from curve (b) in that the low θ maxima have nearly disappeared, suggesting that $As_2Se_3 : Tl_2Se$ is a simpler liquid than the others, and with less long range order. It is, therefore, not surprising that it ultimately crystallizes to a simpler structure.

3. Structural changes during annealing

3.1. As_2Se_3

Fig. 2 shows the results of annealing vitreous As_2Se_3 at 180 ± 5° C for different times. Curve (a) is the X-ray diffraction pattern prior to subjecting the specimen to

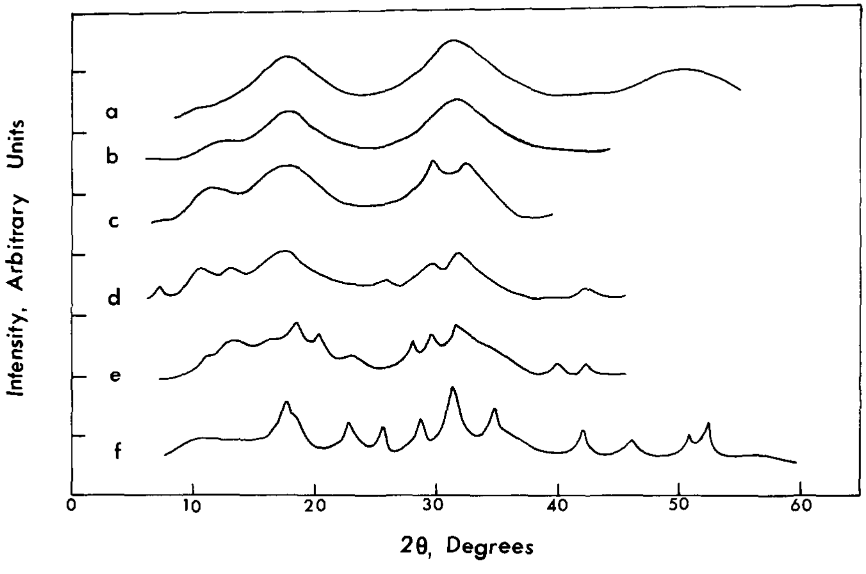

Fig. 2. X-ray intensity curves for As_2Se_3 annealed at 180 ± 5 °C for (a) 0 min; (b) 60 min; (c) 120 min; (d) 200 min; (e) 360 min; (f) 70 h.

heat treatment. These results show that for up to 60 min of annealing at this temperature, little structural change occurs except for an increase in strength of the 8 Å shoulder near $2\theta \simeq 12°$, which becomes a very broad band. When the duration of annealing is doubled, it brings about significant changes in the diffraction pattern, as is shown in curve (c). The strongest band at $2\theta = 31.5°$ has split into two narrow bands; the shoulder at 8 Å near $2\theta \cong 12°$ has developed into a band, and the band at $2\theta = 17.75°$ has started to spread. These changes in the diffraction pattern of the glass indicate the onset of structural changes. Further increasing the annealing time enhances these structural changes and the fraction of amorphous phase diminishes gradually. Complete crystallization of As_2Se_3 at 180 ± 5 °C occurs after ≈70 h.

Fig. 3 shows the results of annealing at temperatures from 170 ± 5 °C to the melting point. Below the softening temperature (180 ± 5 °C) annealing appears to have had no effects since even 40 h annealing at 170 °C has not changed the details of the intensity curve from those prior to annealing.

As the annealing temperature is increased to 190 ± 5 °C, the glass crystallizes within about 40 h. The diffuse bands are still evident, indicating the presence of some amorphous material as well, and showing that the glass has not crystallized completely. Upon increasing the temperature to close to the melting point, As_2Se_3 crystallizes completely within about 40 h. This behaviour can be explained in terms of nucleation and crystal growth of As_2Se_3. The crystallization process requires first the generation of a population of nuclei of the crystalline phase which then grows at the expense of the metastable vitreous phase. Growth initiates at, and prop-

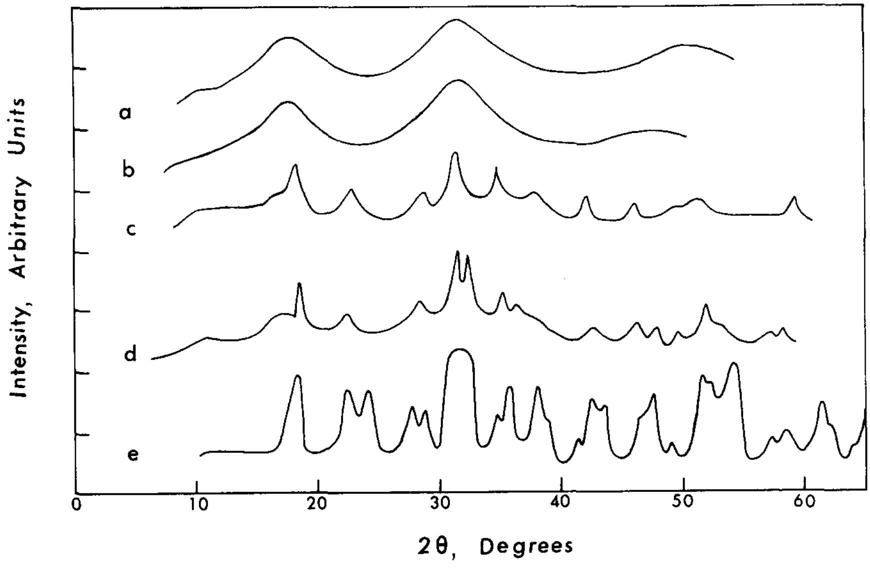

Fig. 3. X-ray intensity curves for As_2Se_3 (a) as prepared, and after annealing at (b) 170 °C for 40 h, (c) 180 °C for 70 h (d) 190 °C for 40 h (e) 210 °C for 40 h. Temperatures maintained ± 5 °C.

agates from, these nuclei, all reaction occurring at the crystal–melt interfaces. The rate of crystallization is thus dependent on the frequency of appearance of crystallization centres and the rate of propagation of the crystal–glass interface from these centres. There is a thermodynamic barrier to the nucleation process because of interfacial energy considerations and a further thermodynamic limit to growth kinetics imposed by the high viscosity of the glass. The resulting crystallization rate, therefore, varies approximately as $K \exp(-Q/kT)$, with a large numerical value for K and with $Q \gg kT$. The onset temperature for crystallization is, therefore, well defined. From these studies, it is apparent that the nucleation period for As_2Se_3 is certainly very large; but there is no evidence at least in this temperature range for the existence of an induction period as reported by other authors [10].

3.2. $(As_2Se_3)_3 : Tl_2Se$

Fig. 4 shows the results of annealing vitreous $(As_2Se_3)_3 : Tl_2Se$ at 135 ± 5 °C for different times. These results show that even with 15 min of annealing at 135 ± 5 °C, structural changes have taken place. The intensity curve (b) appears similar to curve (a) except that the most intense band in the spectrum has started to break up. The band at $2\theta = 10.5°$ has diminished in intensity considerably, while the hump $2\theta \cong 53°$ has become better defined. This point may be regarded as the onset of

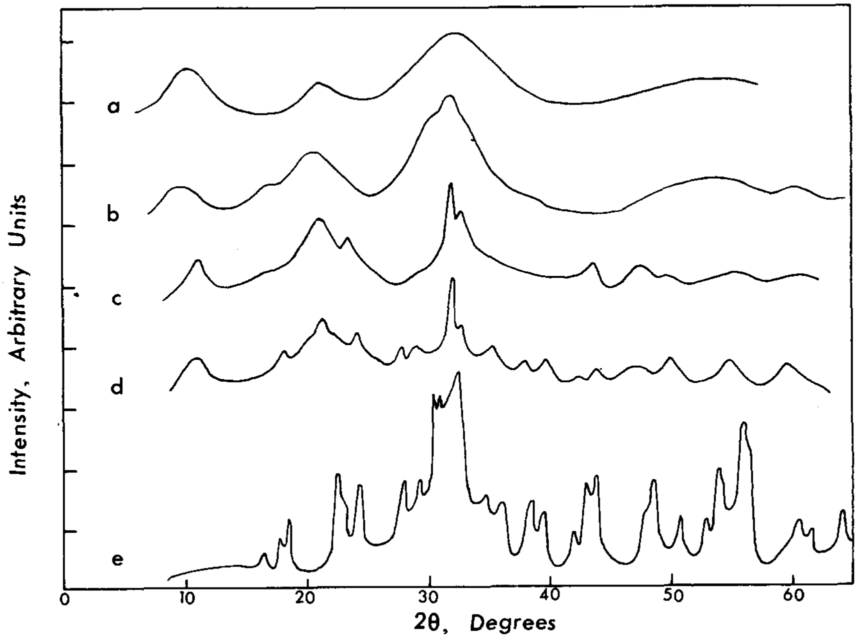

Fig. 4. X-ray intensity curves for $(As_2Se_3)_3 : Tl_2Se$ annealed at 135 ± 5 °C for (a) 0 min; (b) 15 min; (c) 30 min; (d) 60 min; (e) 300 min.

structural changes in this glass. As the annealing time is doubled, a number of spots resulting from diffraction by isolated crystallites appear on the film. There are also some very weak lines superposed on the bands. The hump at $2\theta \cong 53°$ has broken up into several narrow bands. With further increase in the annealing time to 50 min, a number of strong and weak lines appear on the film. The number of spots due to crystallites increases greatly but the film also shows evidence of the amorphous phase. With annealing for 300 min, the compound crystallizes completely and lines grouped together appear. These lines are spotty and broad, the spottiness arising from the large size and small number of crystallites in the irradiated volume.

Fig. 5 shows the results of annealing $(As_2Se_3)_3 : Tl_2Se$ at different temperatures. As with As_2Se_3, annealing below the softening temperature does not affect the structure of vitreous $(As_2Se_3)_3 : Tl_2Se$. However, as the temperature is increased to 135 ± 5 °C, complete crystallization of the glass occurs within about 5 h. With a further increase in temperature to 150 ± 5 °C, the glass crystallizes completely in about 3 h. In the case of annealing at 150 ± 5 °C, in contrast to 135 ± 5 °C, the lines are narrower. They show preferred orientation and remain spotty. The broadness of the lines at 135 ± 5 °C may be due to lattice distortions which disappear as the annealing temperature is increased.

These results may be explained on the same lines as for the case of As_2Se_3. The onset of structural changes is due to crystallization of this glass. At small durations

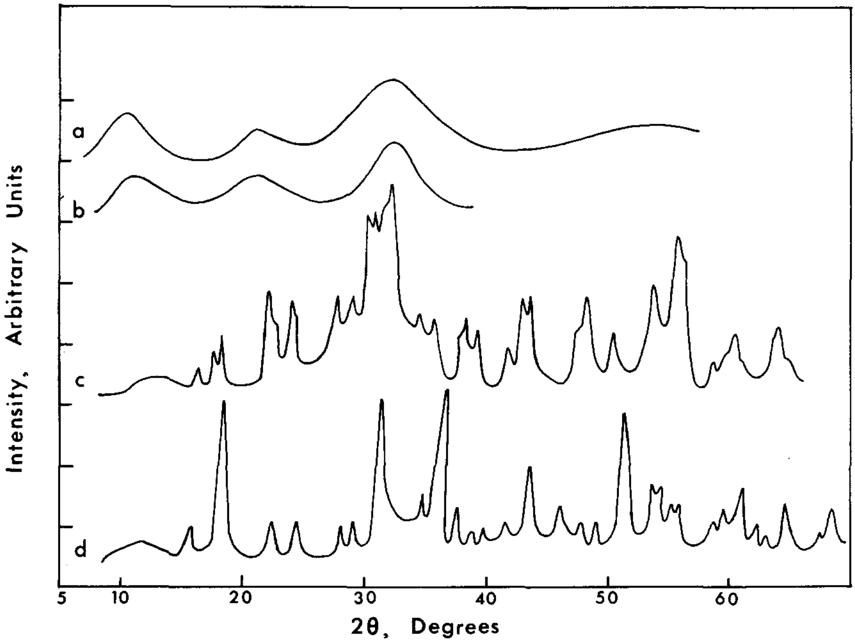

Fig. 5. X-ray intensity curves for $(As_2Se_3)_3 : Tl_2Se$ (a) as prepared, and after annealing at (b) 120 °C for 10 h; (c) 135 °C for 5 h; (d) 150 °C for 3 h. Temperatures maintained ± 5 °C.

of annealing, the size of the crystallites remains but they grow as the annealing time is increased. These results also show that, compared to As_2Se_3, the crystallization and nucleation rates in $(As_2Se_3)_3 : Tl_2Se$ are much faster. The nucleation and crystallization rates for the latter increase very rapidly as the annealing temperature is raised above the softening point.

3.3. $As_2Se_3 : Tl_2Se$

Fig. 6 shows the results of annealing $As_2Se_3 : Tl_2Se$ glass specimens at different temperatures and for different lengths of time at the softening temperature. With only 15 min annealing at the softening temperature vitreous $As_2Se_3 : Tl_2Se$ has started to crystallize. The film shows a number of weak lines, the most intense of these lying on the amorphous band. As the annealing time at 105 ± 5 °C is doubled, the intensity of the lines increases and the amorphous band starts to fade. After about 5 h annealing only a very small amount of amorphous material is left and the film shows a number of lines. Increasing the annealing temperature to 125 ± 5 °C results in complete crystallization of the compound within about 3 h as shown in curve (f).

The onset and development of the structural changes may be explained as for the other two glasses of the family, the rates of nucleation and crystal growth here, however, being much faster and the crystallization temperature lower. Because of the

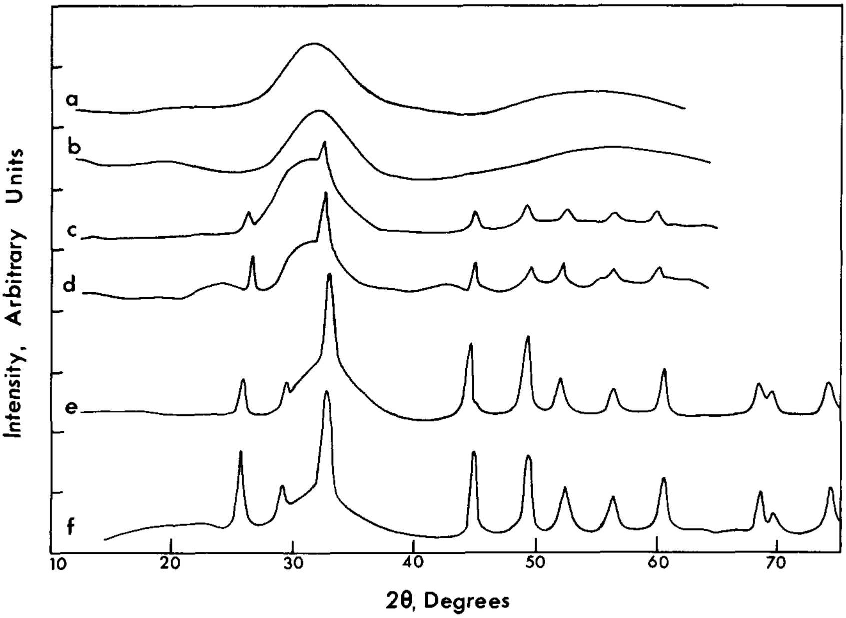

Fig. 6. X-ray intensity curves for $As_2Se_3 : Tl_2Se$ (a) as prepared, and after annealing at (b) 90 °C for 10 h (c) 105 °C for 15 min, (d) 105 °C for 30 min, (e) 105 °C for 5 h, (f) 125 °C for 3 h. Temperatures maintained ± 5 °C.

nature of the transition from glassy to crystalline form there is no precisely defined crystallization temperature for a glass. The crystallization rate varies so rapidly with temperature, however, that an effective crystallization temperature can be specified with reasonable precision. Below this temperature the glassy state persists for a long time while above it crystallization is rapid. Such crystallization temperatures determined from our X-ray results are shown in the last column of table 1. It is clear that they are in good agreement with the temperatures found by DTA measurements.

4. Comparison of the crystalline structures

Line intensities measured from the X-ray powder photographs of polycrystalline As_2Se_3, $(As_2Se_3)_3 : Tl_2Se$ and $As_2Se_3 : Tl_2Se$ are shown in fig. 1. Comparison of these shows that the crystal structures of As_2Se_3 and $(As_2Se_3)_3 : Tl_2Se$ are quite similar. In both cases the number of lines is the same, their positions correspond very well, and strong and weak lines appear in the same order. Comparison of these two photographs with that of $As_2Se_3 : Tl_2Se$, shows that the crystal structure of $As_2Se_3 : Tl_2Se$ is very different from that of the other two members of the family, the small number of lines on the powder photograph of $As_2Se_3 : Tl_2Se$ evidencing a much smaller unit cell. In all cases the strong lines appear approximately in the positions of the bands in the amorphous state.

The pattern for As_2Se_3 is consistent with a monoclinic unit cell. The space group is assigned as P21/c and the lattice parameters are estimated to be:

$$a_0 = 4.30 \pm 0.02\ \text{Å}; \qquad b_0 = 9.92 \pm 0.04\ \text{Å}; \qquad c_0 = 12.84 \pm 0.04\ \text{Å};$$

$$\beta = 109.1 \pm 0.1^\circ .$$

These values are in good agreement with those proposed by Renninger and Averbach [1]. $(As_2Se_3)_3 : Tl_2Se$ is also monoclinic and has nearly the same cell parameters as As_2Se_3. The third member of the family viz., $As_2Se_3 : Tl_2Se$ crystallizes in the orthorhombic system. From preliminary studies, the space group is assigned as $P_{21}22$ and the cell parameters are estimated to be:

$$a_0 = 5.50 \pm 0.01\ \text{Å}; \qquad b_0 = 6.17 \pm 0.01\ \text{Å}; \qquad c_0 = 7.01 \pm 0.01\ \text{Å}.$$

Detailed analysis of the structure of crystalline $As_2Se_3 : Tl_2Se$ will be published elsewhere.

5. Conclusion

This study has shown that certain chalcogenide glasses, while stable at low temperatures, tend to crystallize rapidly at temperatures within about 20 °C of their melting points. For the system based on As_2Se_3, the addition of Tl_2Se lowers both the melting point and the crystallization temperature and hastens the kinetics of crystallization when this occurs. The detailed study traces the progress of the crystallization from a structural point of view.

Crystallization of these glasses is accompanied by a thermal anomaly which is readily detected. Studies carried out in this laboratory, which will be reported later, also show the existence of an anomaly in the behaviour of the electrical conductivity σ at the crystallization temperature. This shows up clearly when $\ln \sigma$ is plotted against $1/T$.

We believe that the recognition of these structural changes as an important determinant of the detailed behaviour of these materials is a matter of some importance.

Acknowledgements

This study has been supported by the Australian Research Grants Committee and the Radio Research Board. One of us (C.A. Majid) is also grateful to the University of New England for a research scholarship, during tenure of which this work was done.

References

[1] A.L. Renninger and B.L. Averbach, Acta Cryst. B29 (1973) 1583.
[2] A.L. Renninger and B.L. Averbach, Phys. Rev. B8 (1974) 1507.
[3] A.A. Vaipolin and E.A. Porai-Koshits, Soviet Phys. –Solid State 2 (1960) 1500.
[4] A.A. Vaipolin and E.A. Porai-Koshits, Soviet Phys. –Solid State 5 (1963) 178, 186.
[5] A.A. Vaipolin and E.A. Porai-Koshits, Soviet Phys. –Solid State 5 (1963) 497.
[6] A.A. Vaipolin, Soviet Phys. –Crystallography 10 (1966) 509.
[7] B.T. Kolomiets and V.P. Pozdnev, Soviet Phys. –Solid State 2 (1960) 23.
[8] B.T. Kolomiets, Phys. Status Solidi 7 (1964) 359.
[9] R. Flasck and H.K. Rockstad, J. Non-Crystalline Solids 12 (1973) 353.
[10] S.A. Dembovskii and A.A. Vaipolin, Soviet Phys. –Solid State 6 (1964) 1388.
[11] E;V. Shol'nikov, M.A. Rumsh and R.L. Myuller, Soviet Phys. –Solid State 6 (1964) 620.
[12] M. Kitao, N. Asakura and S. Yamada, Japan J. Appl. Phys. 8 (1968) 499.