

THERMAL EFFECTS ON GLASS $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$

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The DTA trace of the chalcogenide glass $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ shows a single glass transition at 142 °C, a single crystallization exotherm depending on the heating rate, and two melting endotherms, at 290 °C and 312 °C. The X-ray diffraction for a crystallized sample indicates the presence of two solid solution phases: Te in As_2Se_3 (rich in Se) and Se in As_2Te_3 (rich in Te), confirming that the single crystallization peak of the initially homogeneous phase (single T_g) represents two coincident peaks superimposed. The crystallization of the glass phase is also clearly manifested in the time-dependence of the electrical conductivity and microphotography.

The structure and properties of the stoichiometric chalcogenide glass As_2Se_3 have been extensively studied. This compound may readily be prepared in the glassy state, having a definite structure containing only As–Se bonds [1]. Replacement of Se by Te in this compound leads to the formation of As–Te bonds in place of As–Se bonds, and this affects all the structural properties. The degree of change depends on the Te content of the ternary compound $\text{As}_2\text{Se}_3\text{–As}_2\text{Te}_3$ [2, 3]. Such a dependence is linear for the valence bond concentration (As–Te or As–Se), hydrostatic density, dc conductivity and activation energy of conduction, and nonlinear for the Vickers hardness, while there is a discontinuity for the melting temperature, thermal conductivity and activation energy of crystallization. The discontinuity appears at equal proportions of Se and Te, where there is a dip at the composition $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$.

In this paper, the effects of thermal annealing on the electrical conduction and structural changes of the semiconductor glass $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ have been studied. The sample preparation and the measuring arrangements for DTA, X-ray diffraction and dc conductivity were described in previous publications [2–5].

Results and discussion

Figure 1 shows the DTA scan for the glass $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ heated at 5 deg/min. This curve indicates a glass transition (T_g) at 142° , an exothermic peak due to crystallization with a maximum crystallization rate at 225° , and two endothermic peaks due to melting at 290 and 312° . For $\text{As}_4\text{Se}_3\text{Te}_3$ quenched from 600° , El-Fouly and Edmond [6] reported that there is a single T_g , a single crystallization peak and two partially resolved melting peaks. This suggests that the single crystallization peak might be two coincident peaks superimposed. The obtained value of T_g agrees with those obtained by Mackowski [7] ($\sim 143^\circ$) and El-Fouly and Edmond [6] (147°).

The DTA scan in Fig.1 indicates that the initially homogeneous phase (single T_g) separates into two compositions as heating exceeds the T_g cut-off. The two melting peaks are due to non-equilibrium melting of crystalline $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ in two different compositional environments.

Figure 2 shows the X-ray diffraction pattern of crystalline (annealed at 220° for about 6 h) $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$. This pattern is characterized by new lines which do not exist for either pure As_2Se_3 , or As_2Te_3 such as those with d 's (\AA) = 9.600 (20), 9.310 (10), 2.625 (35), 2.430 (15), 1.940 (85), 1.859 (10), 1.614 (25), 1.606 (20) and 1.580 (10). (The values in parentheses are the relative intensities of the lines.) Some of the strongest of these lines are found in the diffraction patterns of solid solutions rich in selenium ($\text{Se} \approx 45\text{--}60$ at. %), while others are found in those rich in tellurium ($\text{Te} \approx 45\text{--}60$ at. %) [3]. This can be justified by lines with d values (\AA) = 4.800 (100), 3.210 (95) and 2.475 (10) for the former condition and with d values (\AA) = 2.980 (40), 2.201 (20), 1.976 (15), 1.668 (20) and 1.622 (5) for the latter one.

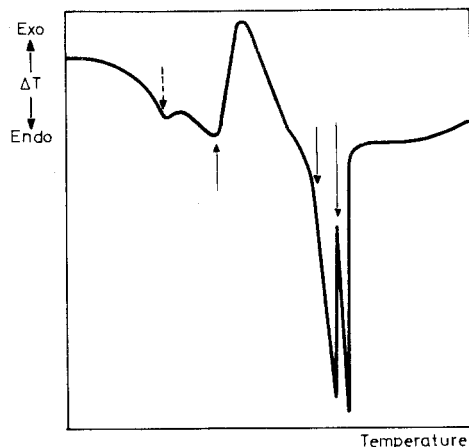


Fig. 1 DTA curve for glass $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ heated at $5^\circ\text{C}/\text{min}$

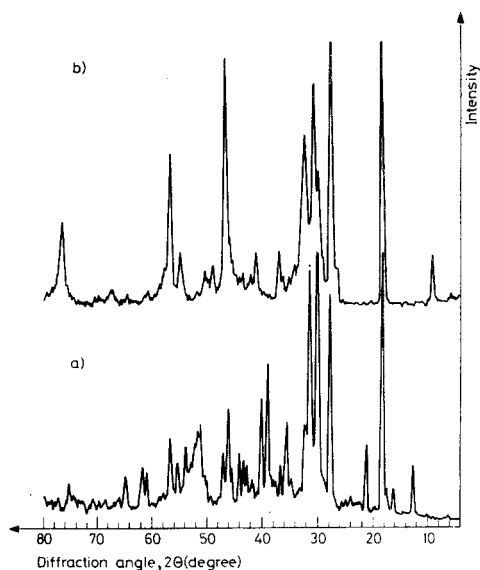


Fig. 2 X-ray diffraction pattern of a) sample prepared by mixing As_2Se_3 and As_2Te_3 crystals (1 : 1), and b) annealed $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ sample

The structure proposed for the composition $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ can be one of the following: (a) an intermediate phase with single-crystal structure containing equal amounts of Se and Te, or (b) two separate solid solution phases, α and γ . Phase α is a solid solution of Te in As_2Se_3 (rich in Se) and phase γ one of Se in As_2Te_3 (rich in Te).

A conventional experiment to reach a rough representation of the state present was carried out by mixing pure crystalline As_2Se_3 and As_2Te_3 in equal proportions. The prepared mixture sample was examined and its diffraction pattern is given in Fig. 2. It is worth mentioning that the set of diffraction lines for the mixture sample is almost identical with the sum of the lines for the annealed compositions $\text{AsSe}_{1.15}\text{Te}_{0.35}$ and $\text{AsSe}_{0.35}\text{Te}_{1.15}$ [3], i.e. the solid solution α and γ phases mentioned above. However, as can be seen in Fig. 2, the annealed sample (upper pattern) differs from that of the mixture (lower pattern). The differences involve both the disappearance of several lines and the variation in intensity of analogous lines. The main high-intensity lines are present in both patterns. A complicated problem of interference can arise in such systems of two solid solution phases. It is possible to assume that the structure of $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ ($\text{As}_4\text{Se}_3\text{Te}_3$) is that of the α and γ phases, i.e. state (b) is considered preferable.

The dc electrical conductivity of the glass $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ is exponentially dependent on $1/T$ (K), and can be satisfactorily described between $\approx 20^\circ$ and 120°

(i.e. below T_g) by the thermal activation formula: $\sigma = \sigma_0 \exp(-E_\sigma/2KT)$. A least squares fit for the function $\log \sigma = f(1/T)$ indicates that the specific conductivity at 20° is $3.16 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$, the pre-exponential factor σ_0 is $912 \text{ ohm}^{-1} \text{ cm}^{-1}$, and the activation energy of conduction E_σ is 1.25 eV.

The fraction of a crystalline phase increases at the expense of the amorphous phase when appropriate heat treatment is applied. Therefore, in order to follow the changes in electrical conduction of the glass $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ during the crystallization process, the stepwise technique is considered. That is, the sample is conducted for a given time and then removed from the oven and subsequently quenched in air, at room-temperature, to stop possible crystal growth in the sample. Next, the sample is polished gently to eliminate the effect of surface crystallization, and the function $\sigma = f(T)$ can be measured below T_g to preserve quenching of the transformation process in each annealing step. Aging of the sample was carried out in a preheated oven adjusted to a temperature between T_a and T_m , viz. 180° . The linear relationship obtained for the function $\log \sigma = f(1/T)$ at the different stages indicates the semiconductor character of the investigated material in the glassy, crystalline or intermediate states.

The annealing time-dependences of the characteristic electrical quantities $\sigma_{20^\circ\text{C}}$, E_σ and σ_0 of $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ are given in Fig. 3. The Figure reveals that the value of each of the quantities changes from one corresponding to the initial amorphous state to a limiting value corresponding to the crystallized mode. Table 1 gives the values of the characteristic properties at the beginning and the end of the isothermal

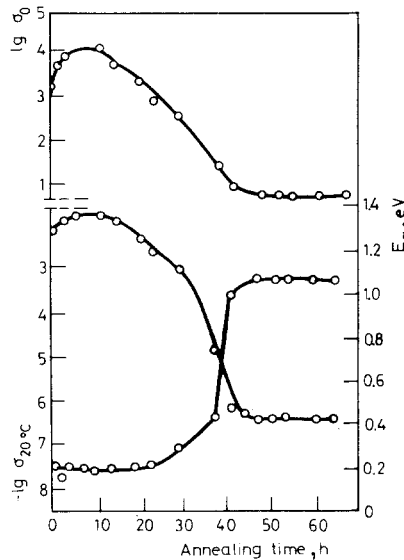


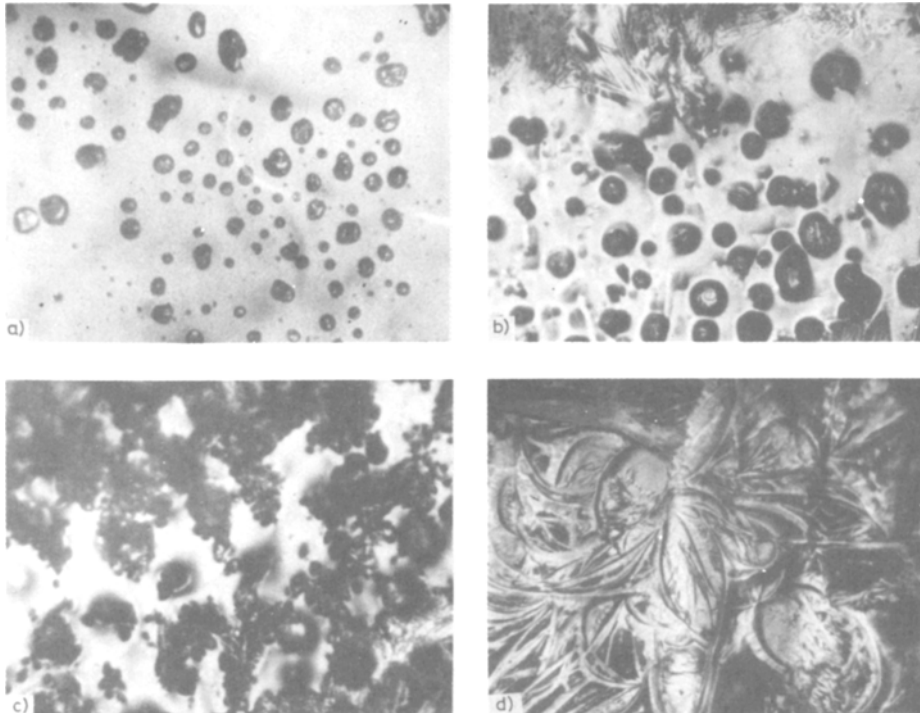
Fig. 3 The annealing time dependence of $\log \sigma_{20^\circ\text{C}}$, E_σ and $\log \sigma_0$ for glass $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$

Table 1 Values of the electrical characteristic quantities at the start and end of the transformation process of the glass $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ at 180°

Stage	$-\log \sigma_{20^\circ\text{C}}$	E_σ , eV	$\log \sigma_0$
Start	7.5	1.25	2.96
End	3.25	0.44	0.70

annealing process. It shows that the conductivity increases by about four orders of magnitude, while the activation energy decreases from 1.25 eV to 0.44 eV due to integral annealing of the glass for about 45 h at 180° . Any further annealing does not greatly alter the values of $\sigma_{20^\circ\text{C}}$, E_σ or σ_0 (Fig. 3).

Myuller [8] has reported that the process of crystallization may be separated into two successive processes: diffusional redistribution of structural units, and local transformation of chemical bonds. However, the two processes overlap between the process of appearance of centres of crystallization (nucleation) and their growth.

**Fig. 4** Optical photomicrographs showing the nucleation at the early stages and further growth of $\text{As}_2\text{Se}_3 \cdot \text{As}_2\text{Te}_3$ films ($\approx 100 \mu\text{m}$) during the time of isothermal annealing, under vacuum, at 180°C

All these processes are limited to a definite degree by the same activation energy of the transformation of covalent bonds. Accordingly, the observed changes in the considered electrical characteristic quantities can be explained by the process of structural ordering occurring during the isothermal treatment and, as a consequence, the crystallization of the glass $As_2Se_3 \cdot As_2Te_3$.

To follow the morphological changes in the investigated composition, amorphous films of about 100 μm were annealed inside a preheated oven adjusted to 180°. Figure 4 shows reflection photographs of $As_2Se_3 \cdot As_2Te_3$ annealed for different times. The nucleation in the early stages is observed in micrograph (a). The nuclei formed are grown spherulitically till the formation of larger grains in micrograph (b), and ultimately these grains coalesce with each other in micrograph (c). Micrograph (d) shows the state after complete crystallization (~ 80 h) of the $As_2Se_3 \cdot As_2Te_3$ film.

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Zusammenfassung — Die DTA-Kurve von chalcogenidem Glas $As_2Se_3 \cdot As_2Te_3$ läßt eine Glastransformation bei 142 °C, eine von der Aufheizgeschwindigkeit abhängige exotherme Kristallisation und zwei endotherme Schmelzvorgänge bei 290 und 312 °C erkennen. Röntgendiffraktometrie der kristallisierten Probe zeigt das Vorliegen von zwei Phasen fester Lösungen: Te in As_2Se_3 (reich an Se) und Se in As_2Te_3 (reich an Te). Das steht in Übereinstimmung damit, daß der Kristallisationspeak der ursprünglich homogenen Phase (ein T_g -Wert) zwei sich überlagernde Peaks repräsentiert. Die Kristallisation der Glasphase ist klar an der Zeitabhängigkeit der elektrischen Leitfähigkeit und durch Mikrophotographie zu erkennen.

Резюме — ДТА измерения халькогенидного стекла $As_2Se_3 \cdot As_2Te_3$ показали единственный переход в стеклообразное состояние при температуре 142 °C, он экзотерму кристаллизации в зависимости от скорости нагрева и две эндотермы плавления при 290 и 312 °C. Рентгеноструктурное исследование кристаллического образца показало наличие двух твердых растворов: Te в As_2Se_3 (обогащенного селеном) и Se в As_2Te_3 (обогащенного теллуром), подтвердив тем самым, что единственный пик кристаллизации исходной гомогенной фазы (одна T_g), представляет собой наложение двух совпадающих пиков. Кристаллизация стеклообразной фазы ясно показывает временную зависимость электропроводности и микрофотографии.