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THERMAL STABILITY OF THE AMORPHOUS SYSTEM As-Se-I

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The effect of adding iodine to the binary systems As-Se on the thermal stability of the ternary glasses thus formed was investigated by DTA and DDTA. The investigated glasses corresponded to different regions of the phase diagram, i.e. they had different contents of As and I and, consequently, contained different types of structural units.

In the investigated ternary systems with iodine, the crystallization effect appears at a lower temperature than in the binary glass $As_{40}Se_{60}$, and the same holds for the temperatures of softening and melting.

For both binary and ternary systems, the activation energies of crystallization were determined. The glass $As_{40}Se_{60}$ exhibited a somewhat higher activation energy, i.e. a somewhat lower tendency to crystallize than the ternary system.

The critical cooling rates of the melts for minimum degree of crystallinity were estimated. The obtained values are approximately equal for the binary (As_2Se_3) and ternary (AsSeI) systems.

Studies of general physical properties of the binary system As-Se and the ternary system As-Se-I, and determination of the short wavelength limit, other optical properties and their microhardness, have recently been reported [1-4].

With the use of Raman spectroscopy, it was established that the As-Se-I glasses with an As content below 2 at% and an I content below 10 at% consist of Se_n chains and Se_8 rings, and of AsI_3 structural units statistically distributed between them.

In a second group of glasses, corresponding to $2<As<20$ and $I<20$ at%, the Se_n chains are linked through As atoms, and these long chains are separated by AsI_3 units.

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A third group of glasses is characterized by 22 < As < 45 and I < 15 at%; their main structural unit is the trigonal pyramid $AsSe_{3/2}$, which is fully realized in the stoichiometric compound As_2Se_3. However, the presence of iodine results in the appearance of AsI_3 and induces changes in the bond lengths and angles [2, 5].

The glasses whose compositions are close to that of the ternary compound AsSeI possess a chain structure which is characteristic of this compound. The structure of these chains remains unchanged in the melt and, together with the layered (or chain) arsenic selenide, they form highly viscous liquids which exhibit a marked tendency to supercooling, which has a favourable effect on glass formation.

The aim of the investigations described here was to contribute further to the elucidation of the effect of adding iodine to the binary system As-Se on the thermal properties of the ternary glasses thus formed.

Experimental

Synthesis

The glasses were synthesized from high-purity starting components in evacuated quartz ampoules [4]. The ampoules were heated at a rate of $1.3 \cdot 10^{-2}$ deg/s to 523 K and held at this temperature for another $(1.4\text{-}1.8) \cdot 10^4$ s. After this, the temperature was raised ($2.7 \cdot 10^{-2}$ deg/s) to 1023 K and this temperature was kept constant during $3.8 \cdot 10^4$ s. The obtained melts were cooled to room temperature at a rate dependent on their chemical composition [6].

Measurement Techniques

Thermogravimetric measurements were carried out on a Paulik-Paulik-Erdey derivatograph in air atmosphere, with Al_2O_3 as standard. The mass of the samples was 100 mg and the heating rate was 10 deg/min. In addition, a special laboratory-built device was used to record DDTA curves, whose characteristics have already been described [7].

The obtained DTA and DDTA curves ar shown in Figs 1-5.

Results and discussion

As a representative sample of the first group of As-Se-I glasses (As<2 at% and I<10 at%), we have investigated the system $As_2Se_{95}I_3$. The corresponding DTA and DDTA curves (Fig. 1) have one broad exothermic and two endothermic (at 318 K and 433 K) maxima (Table 1).

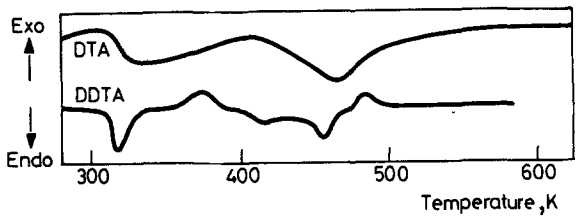

Fig. 1 DTA and DDTA curves of $As_2Se_{95}I_3$

Table 1

Glass	Effect	Process	Temperature, K
$As_2Se_{95}I_3$	endo	softening	318
	exo	crystallization	370
	endo	melting of AsI_3	413
		melting	433
$As_{10}Se_{80}I_{10}$	endo	softening	333
	exo	crystallization	383
	endo	melting	448
$As_{38.5}Se_{54}I_{7.5}$	endo	softening	433
$As_{33}Se_{33}I_{33}$	endo	softening	351
	exo	crystallization	398
	endo	melting	503
$As_{40}Se_{60}$	endo	softening	473
	exo	crystallization	618
	endo	melting	653

Thermal curves for the glass $As_{10}Se_{80}I_{10}$, which is characteristic of the second group of glasses, are shown in Fig. 2. They also exhibit two endothermic and one exothermic peak (Table 1).

In both cases, the first endothermic effect corresponds to the softening of the main glass matrix. The higher softening temperature of $As_{10}Se_{80}I_{10}$ as compared to that of $As_2Se_{95}I_3$ indicates the presence of branched structural units of the type $(-Se-Se-Se-)_n-As-$.

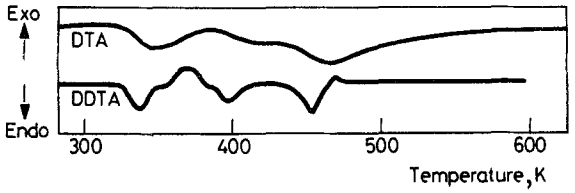

Fig. 2 DTA and DDTA curves of $As_{10}Se_{80}I_{10}$

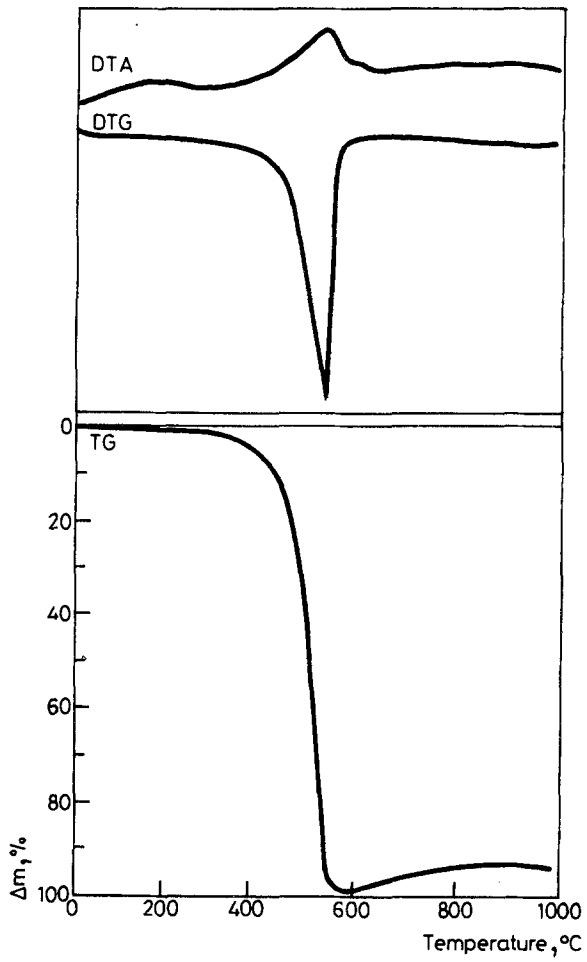

Fig. 3 TG and DTA curves of $As_{38.5}Se_{54}I_{7.5}$

The observed exothermic effect is due to a crystallization process, while the subsequent endothermic effect is due to melting of the crystallization products.

For the glass $As_2Se_{95}I_3$, the latter process is represented by two maxima, the first of which (at 413 K) can be ascribed to melting of the microcrystalline AsI_3 particles.

As a representative example of the behaviour of glasses belonging in the third group, we present results obtained for the system $As_{38.5}Se_{54}I_{7.5}$. The corresponding DTA curve (Fig. 3) also exhibits endothermic peaks characteristic of glass softening (Table 1).

In order to study the effects of iodine in possibly shifting the maxima corresponding to different thermal effects, the DTA curves of the investigated system were compared with those for the binary compound As_2Se_3 (Fig. 4). It is observed that the crystallization effect is much more pronounced in the binary system than in the ternary one and appears at a higher temperature (T_c = 618 K). Additionally, the temperatures of softening and melting are also shifted accordingly. It is obvious that the addition of iodine (or AsI_3) to the binary system yield ternary glasses which are thermally less stable. This indicates that the presence of iodine induces structural changes which result in an increased tendency to crystallization in the system. While small concentrations of iodine cause a deformation of the trigonal structure of the $AsSe_{3/2}$ unit by changing its bond lengths and angles, higher iodine concentrations induce the appearance of macroscopic inhomogeneities in these glasses.

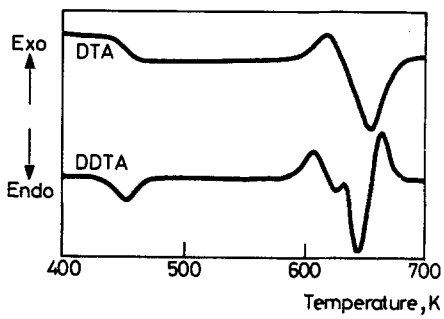

Fig. 4 DTA and DDTA curves of As_2Se_3

The glass $As_{33}Se_{33}I_{33}$, whose composition is identical with that of the ternary compound AsSeI, exhibits the most pronounced thermal effects: softening at 351 K, crystallization at 386 K and melting at 503 K (Fig. 5).

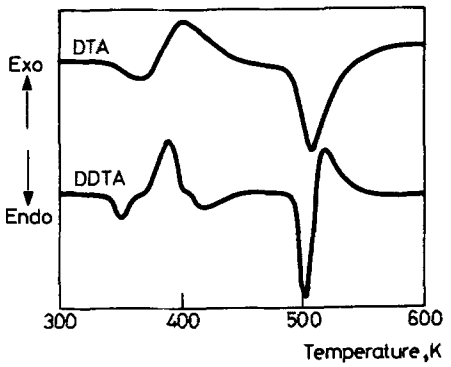

Fig. 5 DTA and DDTA curves of $As_{33}Se_{33}I_{33}$

With a known procedure [8], we determined the activation energies of crystallization, ΔG_{AN} and ΔG_{AM}, for both AsSeI and As_2Se_3. To a first approximation, for a crystallization process taking place in two stages, we can assume that ΔG_{AB} consists mainly of the activation energy of nucleation, while ΔG_{AM} predominantly corresponds to the crystal growth.

For the system AsSeI, we obtained $\Delta G_{AN} = 125$ and $\Delta G_{AM} = 100$ kJ/mol. It can be supposed that the rate of formation of chains in this system is small in comparison with the rate of chain growth. As a result, the corresponding crystallization peak in the DTA curve is broadened, which suggests that the main role is played by the crystallization of the surface, and not in the volume [9, 10]. Therefore, an increase in the free surface brings about favourable conditions for a relatively fast growth of the crystalline AsSeI chains on the glass surface.

The glass $As_{40}Se_{60}$ exhibits a somewhat lower tendency to crystallize than the above system. The corresponding activation energies (at the temperature corresponding to the beginning of crystallization and its higher rate) are $\Delta G_{AN} = 158$ and $\Delta G_{AM} = 146$ kJ/mol. On the basis of the values obtained, it can be presumed that a higher energy barrier is to be surmounted when the layers consisting of $AsSe_{3/2}$ pyramids are formed than in the case of formation of the crystallization centres of the AsSeI chains. Further, the rate of AsSeI crystal growth is somewhat higher than that for As_2Se_3.

The given examples of glass crystallization permit estimation of the critical rate of cooling of the melt, b^-, for the minimum degree of crystallinity ($\alpha \approx 10^{-6}$), according to the semi-empirical relation [11]:

$$\alpha = \frac{4}{3}\frac{\pi}{b^-}\int_{T_g}^{T_m} J(T)\,\mathrm{d}T \left| r_k^*(T^-) + \frac{1}{b^-}\int_{T_g}^{T'} U(T)\,\mathrm{d}T \right|^3$$

where $J(T)$ and $U(T)$ are the rate of formation of crystallization centres and the linear rate of crystal growth, respectively, and $r_k^*(T')$ is the critical radius of the crystalline nucleus.

The estimated b^- values for the systems AsSeI and As_2Se_3 are equal and amount approximately to 10^{-2} deg/s. It is obvious that a decisive role is played in the crystallization process not only by the activation barriers ΔG_{AN} and ΔG_{AM}, but also by the difference in free energies for the crystalline and glassy states.

On the basis of the thermal analysis of the system As-Se-I, it can be concluded that the addition of iodine to the binary system As-Se yields a more complex structure and, to some extent, causes an increase in its tendency to crystallize, which is obviously reflected in some properties of these glasses.

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Zusammenfassung — Mittels DTA und DDTA wurde untersucht, wie die Zugabe von Jod zu dem binären System As-Se die thermische Stabilität der so gebildeten ternären Gläser beeinflußt. Die untersuchten Gläser entsprechen verschiedenen Regionen des Phasendiagrammes, d.h. sie besitzen einen unterschiedlichen As- bzw. I-Gehalt und enthielten unterschiedlich geartete Struktureinheiten.

Bei den untersuchten jodhaltigen ternären Systemen tritt der Kristallisationseffekt bei niedrigeren Temperaturen auf als bei den binären Gläsern $As_{40}Se_{60}$, das gleiche gilt für die Schmelz- als auch für die Erweichungstemperatur.

Sowohl bei den binären als auch bei den ternären Systemen wurde die Aktivierungsenergie für den Kristallisationsprozeß ermittelt. Das Glas $As_{40}Se_{60}$ zeigte eine etwas höhere Ak-

tivierungsenergie, d.h. eine etwas geringere Neigung zur Kristallisation als das ternäre System.

Für die kritische Abkühlgeschwindigkeit der Schmelzen zum Erreichen eines minimalen Kristallinitätsgrades wurden bei den binären (As_2Se_3) und ternären (AsSeI) Systemen annähernd gleiche Werte bestimmt.