

## **EFFECT OF HEATING RATE AND $\gamma$ -RADIATION ON THE STRUCTURE OF $\text{As}_4\text{Se}_x\text{Te}_{6-x}$ GLASSES**

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The phenomena accompanying the temperature-induced structural changes in five  $\text{As}_4\text{Se}_x\text{Te}_{6-x}$  glasses, with  $x = 1$  to  $x = 5$ , were examined and are discussed. Differential thermal analysis traces of each glass composition at different heating rates from 2 to 50 deg/min were obtained and interpreted. The effect of the Se/Te ratio on the crystallization behaviour is discussed. It is interesting to note that the compositional dependence of the overall behaviour of the crystallization activation energy ( $E$ ) seems to be similar to that of both the melting point ( $T_m$ ) and the thermal conductivity ( $\chi$ ) for the investigated glasses. Created structural defects due to gamma-irradiation have some effects on the crystallization process.

The manner of approach to nucleation is linked to the idea that even a system in a state of thermodynamic equilibrium is subject to thermal fluctuations which can result in temporal and local changes of density in the molecular range. Such fluctuations can lead to the change of processes already in the melt. They usually have an influence on the subsequent structure formation of the glass, as has been confirmed by studies on the relationships between the fluctuations and heterogeneities in the melt structure and the corresponding heterogeneities in the glass structure [1].

The changes in properties of some glasses in the system  $\text{As}_4\text{Se}_x\text{Te}_{6-x}$  on passing from the vitreous to the crystalline state, and the relation of this transition to composition, have been studied by thermal analysis.

### **Experimental methods**

Five bulk glasses in the system  $\text{As}_4\text{Se}_x\text{Te}_{6-x}$ , with  $x = 1$  to  $x = 5$ , were prepared by heating mixtures of the elements (5N purity) with given compositions in vacuum-sealed, fused silica ampoules at 800° for 3 hours, during which the molten solution

was occasionally shaken vigorously; this process was followed by water quenching [2].

A micro-DTA apparatus (Shimazu Model DT-30) was used for the DTA and DSC measurements. The samples consisted of 25 mg of powder in aluminium sample pans.  $\alpha$ - $\text{Al}_2\text{O}_3$  powder in an aluminium pan was used as a reference for all the measurements. These measurements were carried out under a nitrogen atmosphere (flow rate;  $50 \text{ ml min}^{-1}$ ). Heating rates from 2 to 50 deg/min were used.

A gamma cell 220, provided by the Atomic Energy of Canada, was used for gamma-irradiation. The dose rate of the  $^{60}\text{Co}$  source of this cell was  $34 \text{ rad S}^{-1}$ . Exposure doses up to 3.3 Mrad were used.

## Results and discussion

The thermal curves obtained for the systems  $\text{As}_4\text{Se}_x\text{Te}_{6-x}$  ( $x = 1-5$ ) at a rate of 5 deg/min are characterized by the presence of an endothermic effect of softening at  $T = T_g$ . This occurred over the temperature range  $155-124^\circ$ . The value of  $T_g$  decreases with increase of the Te concentration in the glass. This may indicate a tendency for weaker bonding, and hence lower stability in Te-rich glass systems.

Evidence of decreased glass stability for Te-rich samples is shown by measurements of the kinetic crystallization temperature  $T_c$ , which follows  $T_g$  in the DTA traces. The parameter  $T_c$  depends on the heating rate, since crystallization is a kinetic rather than an equilibrium thermodynamic process for the glasses. Further, the value of  $T_c$  decreases with increasing Te/Se ratio at constant heating rate.

Following the exothermic peak of  $\text{As}_4\text{Se}_x\text{Te}_{6-x}$  crystallization, the endotherm due to melting of the crystalline material begins at a temperature  $T_m$  to fluctuate with the Te concentration. Unlike the glass transition or melting temperatures, the features of the exothermic peaks due to crystallization vary remarkably with the heating rate. Table 1 gives the observed transition temperatures as a function of composition at a rate of 5 deg/min, together with the densities of the glasses investigated.

Systematic studies have been performed on the influence of the heating rate  $\Phi$  on the thermal-induced transformations in the glass systems  $\text{As}_4\text{Se}_x\text{Te}_{6-x}$ . As  $\Phi$  increases, the areas under the crystallization and melting peaks of  $\text{As}_4\text{Se}_5\text{Te}_1$  become smaller. It seems that the viscosity factor suppresses the crystallization rate, so more time is needed for the growth kinetics, which are determined by the heating rate.

The effect of the heating rate on the DTA traces of the glass  $\text{As}_4\text{Se}_4\text{Te}_2$  shows very similar behaviour to that for the glass  $\text{As}_4\text{Se}_5\text{Te}_1$ , but with some differences.

**Table 1** Density and DTA data of the investigated glasses in the system  $As_4Se_xTe_{6-x}$ 

Composition	Density at 20 °C, g/cm <sup>3</sup>	$T_g$ , °C	$T_c$ , °C, $\Phi = 5$ °C/m						$T_m$ , °C	
			1st peak		2nd peak		3rd peak		1st peak	2nd peak
			begin	peak	begin	peak	begin	peak		
$As_4Se_5Te_1$	4.84	155	276	315	—	—	—	—	335	—
$As_4Se_4Te_2$	4.95	146	265	270	294	305	—	—	284	309
$As_4Se_3Te_3$	5.11	137	205	235	—	—	—	—	295	—
$As_4Se_2Te_4$	5.29	128	175	192	251	277	—	—	310	—
$As_4Se_1Te_5$	5.38	124	170	173	223	240	270	319	348	363

The first difference is the phase separation observed at  $\Phi = 2$  and 5 deg/min. El-Fouly and Edmond [3] observed two glass transition temperatures for glass  $As_4Se_4Te_2$  and arrived at the conclusion that phase separation (liquid-liquid separation) had taken place during the cooling phase of the separation. The second observed difference is the vanishing of the peaks from the DTA traces at  $\Phi = 10$  and 15 deg/min. In this case, the effect of the viscosity factor is clearer, as the peaks were originally small, which may be due to the formation of two phases.

The DTA traces of glass  $As_4Se_3Te_3$  show that the transition peaks are sharp and clear at heating rates of 10, 15 and 20 deg/min, but broad at heating rates of 2 and 5 deg/min. Three peaks of crystallization appear in the trace at  $\Phi = 10$  deg/min. Thus, it can be said, with some degree of confidence, that phase separation happens at all heating rates, but the shape of the peaks depends on how far the phases are separated from each other. For example, at a heating rate of 2 deg/min the melting peak is not small, and it is not sharply defined either.

Figure 1 depicts the DTA traces of glass  $As_4Se_2Te_4$  at different heating rates (as an example). It shows that more than two crystallization peaks appear in the DTA traces at low heating rates. The area under the first crystallization peak becomes larger and shifts towards a higher temperature region at higher heating rates. In the meantime, the area under the second crystallization peak becomes smaller at the higher rates. Bagley [4] has pointed out that, because of the multiplicity of phases (any of which may be more fluid or more undercooled than the homogeneous systems) and the extensive interfacial boundary after phase separation, one (or more) of the phases is likely to be more unstable with respect to crystallization than was the initially homogeneous system. Thus, phase separation can result in enhanced crystallization kinetics. From Fig. 1, the melting peak is not sharply defined at  $\Phi = 2$  and 5 deg/min. Again, as in the case of  $As_4Se_3Te_3$ , it depends on the size of the melting peak of each phase and the position of each peak with respect to the others. The final shape of the melting peak will be a result of the superposition of the peaks on each other.

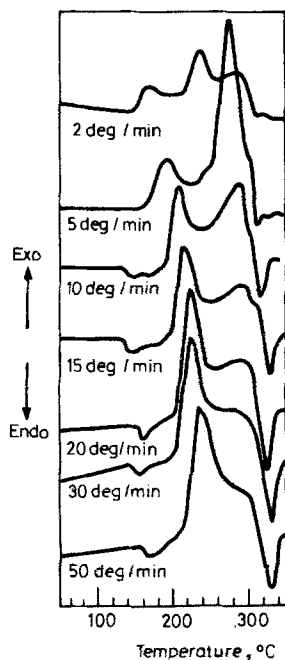


Fig. 1 DTA curves obtained at different rates for the composition of  $\text{As}_4\text{Se}_2\text{Te}_4$

The DTA traces of glass  $\text{As}_4\text{Se}_1\text{Te}_5$  show identical behaviour as in Fig. 1, except for the DTA traces measured at  $\Phi = 2$  deg/min, where the areas under the crystallization and melting peaks are relatively small. This may indicate that only a small amount of the sample material has been crystallized. The viscosity is certainly not a controlling factor for this type of material. Turnbull [5] has pointed out that the resistance of liquids and glasses to nucleation implies something about their structure. If an amorphous material contained microcrystalline regions, there would be no nucleation barrier and the crystallization kinetics would be limited only by grain growth. Thus, at temperatures below the melting point, slow crystallization kinetics would indicate that nucleation was required for that material.

The shift of the exothermic peak temperature was used to determine the activation energies of the crystallization [6]. The peak temperature  $T_p$  is related to the heating rate  $\Phi$  by

$$\frac{d \ln (\Phi / T_p^2)}{d (1 / T_p)} = - \frac{E}{R}$$

where  $R$  is the gas constant.

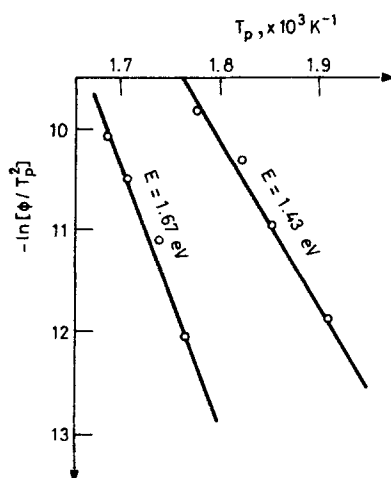


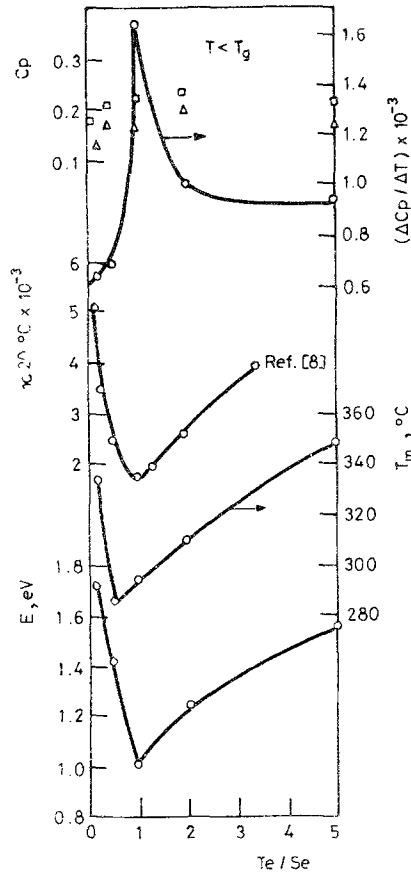
Fig. 2 Determination of the crystallization activation energies for  $\text{As}_4\text{Se}_4\text{Te}_2$  from the shift of the exothermic DTA peaks with the scan rate  $\Phi$

Figure 2 shows plots of  $\ln(\Phi/T_p^2)$  against  $1/T_p$  ( $^\circ\text{K}^{-1}$ ) for the first (lower  $T_p$ ) and second (higher  $T_p$ ) exotherms of the composition  $\text{As}_4\text{Se}_4\text{Te}_2$  (as an example). Similar behaviour was found for the other compositions investigated. A straight line could be fitted in each case to determine the value of  $E$ . The magnitude of  $E$  is found to be minimum (1.08 eV) when  $\text{Te}/\text{Se} = 1$ , as is shown in Table 2.

Table 2 Activation energy for the vitreous-crystalline transformation of the compositions of  $\text{As}_4\text{Se}_x\text{Te}_{6-x}$

Composition	Activation energy of crystallization $E$ , eV		
	First peak	Second peak	Third peak
$\text{As}_4\text{Se}_5\text{Te}_1$	1.73	2.15	—
$\text{As}_4\text{Se}_4\text{Te}_2$	1.43	1.67	—
$\text{As}_4\text{Se}_3\text{Te}_3$	1.08	—	—
$\text{As}_4\text{Se}_2\text{Te}_4$	1.24	2.05	—
$\text{As}_4\text{Se}_1\text{Te}_5$	1.56	2.62	3.25

It is interesting to plot the melting point ( $T_m$ ), the thermal conductivity ( $\chi$ ) and the slope of the specific heat vs. temperature curves ( $\Delta C_p/\Delta T$ ) against the composition in one Figure with the plot of the crystallization activation of the first peak against the composition. Figure 3 shows such plots where the overall behaviour of the crystallization activation energy seems to be similar to both the  $T_m$



**Fig. 3** Compositional dependence of different thermal characteristic properties of  $\text{As}_4\text{Se}_x\text{Te}_{6-x}$ .  
 $\Delta$  50 °C,  $\square$  90 °C

and  $\chi_{20}$  behaviour and the reverse of that for  $\Delta C_p/\Delta T$ . The latter is obtained from plotting the relation of  $C_p$  against  $T$  for each composition. This relation was found to be linear with positive slope below  $T_g$ . However, at any particular  $T$ , the value of  $C_p$  showed behaviour independent of the composition of the glasses investigated (Fig. 3).

Samples from bulk glass  $\text{As}_4\text{Se}_3\text{Te}_3$  were subjected to gamma-irradiation (at a temperature around  $T_g$ ). It is interesting to note that the defects created by gamma-irradiation influence the mechanism of the crystallization process detected by DTA (Fig. 4). The Figure shows that at the saturation dose [7] the material displayed an ability to crystallize earlier than the fresh one (i.e. at 205° instead of 235°), with

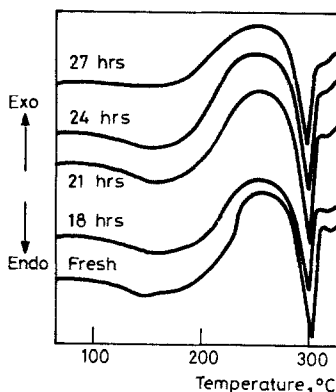


Fig. 4 DTA traces of glass  $\text{As}_4\text{Se}_3\text{Te}_3$  subjected to gamma-irradiation at 413 K for different periods

broadening of the crystallization peak as well. This may be due to the fact that structural defects (such as broken or dangling bonds, vacancies, non-bridging atoms, or chain ends) causing the growth of nucleation arise earlier.

## References

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**Zusammenfassung** — Die die temperaturbedingten strukturellen Veränderungen von 5 Gläsern der allgemeinen Zusammensetzung  $\text{As}_4\text{Se}_x\text{Te}_{6-x}$  ( $x = 1-5$ ) begleitenden Phänomene wurden untersucht und diskutiert. Die von jedem Glas bei unterschiedlichen Aufheizgeschwindigkeiten zwischen 2 und 50 Grad pro Minute erhaltenen DTA-Kurven werden interpretiert. Der Effekt des Se/Te-Verhältnisses auf das Kristallisationsverhalten wird diskutiert. Von Interesse ist, daß die Abhängigkeit der Aktivierungsenergie ( $E$ ) der Kristallisation von der Zusammensetzung der des Schmelzpunktes ( $T_m$ ) und der Wärmeleitfähigkeit ( $\chi$ ) der untersuchten Gläser ähnelt. Durch  $\gamma$ -Bestrahlung hervorgerufene strukturelle Defekte haben einen gewissen Einfluß auf den Kristallisationsprozeß.

**Резюме** — Исследованы и обсуждены структурные изменения, вызванные термической обработкой пяти стекол состава  $As_4Se_xTe_{6-x}$  с  $x = 1-5$ . Для каждого стекла при различных скоростях нагрева (от 2 до 50°/мин) измерены кривые дифференциального термического анализа и приведена их интерпретация. Обсуждено влияние соотношения Se/Te на кристаллизацию стекол. Установлено, что сложный характер влияния этого соотношения на энергию активации процесса кристаллизации, подобен таковому для температуры плавления ( $T_m$ ) и удельной теплопроводности ( $\chi$ ). Структурные дефекты, вызванные гамма-облучением, оказывали некоторое влияние на процесс кристаллизации.