

Thermal Behaviour and Non Isothermal Kinetics of $Se_{60}S_{40-x}Te_x$

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Differential scanning calorimetry (DSC) of two amorphous alloys of the ternary isoelectronic system $Se_{60}S_{40-x}Te_x$ ($x = 15$ and 25) at different heating rates are reported and discussed. Characteristic temperatures, glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) and the glass forming tendency (K_g), have been estimated. The kinetic parameter (E_c) has been determined using non- isothermal multi-scan technique of Kissinger approach. The calculated order of reaction (n) indicate that bulk crystallization with one-dimensional growth occurs for these glasses. Cyclic scanning technique has been used to demonstrate the structural change during two consecutive heating-cooling cycles.

Introduction

Chalcogenide glasses exhibit unique IR transmission and electrical properties that make these glasses very proper for several potential applications such as threshold switching, memory switching, lenses for IR transmission and detection, and optical waveguide for welding as well as surgery [1-3].

Transport investigations have been made for amorphous selenium and its binary alloys with the isoelectronic elements S or Te [4-7]. The addition of S or Te to amorphous selenium has a miscellaneous effect on the compositional dependence of the different properties [4-7]. In this paper the dual addition effect of the two kinds of atoms S and Te on the crystallization kinetics of amorphous selenium has been studied.

Experimental

High purity (99.999%) Se, S and Te in appropriate proportions were weighted in fused silica tubes. The tubes were sealed under vacuum of 1.3×10^{-2} Pa and heated with rate of 100 °C/h in the following steps: 450 °C and kept at this temperature for 1h. The furnace temperature was then increased to 850 °C for 6h during which the molten solution was occasionally shaken vigorously. This is followed by ice- water quenching [8].

Shimadzu instrument DSC-50 was used for thermal analysis experiments which were elaborated at heating rates of 10, 15, 20, 30 and 40 °C /min under an inert atmosphere and referenced to α -Al₂O₃ powder. The effect of heating and cooling on both the exothermic and endothermic peaks were examined using DSC curves for the prepared ternary glasses. The normal DSC cyclic scan was:

To raise the furnace temperature at a heating rate of 15 °C / min to a maximum temperature which was chosen to be far from the decomposition temperature.

To lower the temperature at a cooling rate of 15 °C/ min to 50°C.

As in step (a)

As in step (b).

Results and discussion

a. Transition temperatures

Figures (1.a & 1.b) show typical DSC traces of the freshly prepared glasses taken at different rates of heating. The traces follow the known common behaviour, where the three characteristic temperatures (T_g), (T_c) and (T_m) are observed, given in Table (1).

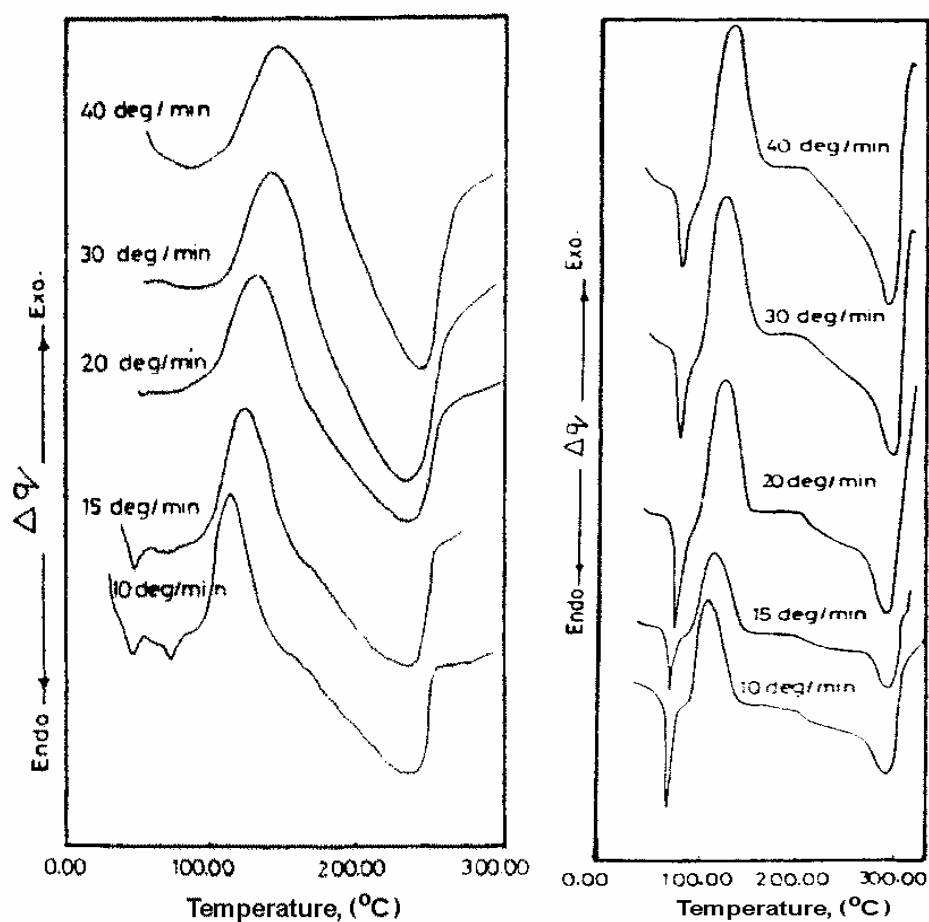


Fig. (1): DSC thermograms of : a) $\text{Se}_{60}\text{S}_{25}\text{Te}_{15}$ glass.
b) $\text{Se}_{60}\text{S}_{15}\text{Te}_{25}$ glass.

For the composition $\text{Se}_{60}\text{S}_{25}\text{Te}_{15}$, two glass transitions are observed at the heating rates of 10, 15 and 30 °C min, but there is only one (T_g) at the heating rate of 20 and 40 °C min. Above (T_g), an exothermic peak due to crystallization (T_c) is occurred in the range 115-142 °C. On melting the crystalline material yields one endothermic peak in the range 234 - 236 °C.

For the composition $\text{Se}_{60}\text{S}_{15}\text{Te}_{25}$ one (T_g) is observed at the different heating rates in the range 72-82 °C. The values of (T_c) and (T_m) lie in the range 110- 135 °C and 295 - 297 °C, respectively.

The data declares that the crystallization peak of the two investigated glasses moves towards higher values of temperature with increasing the heating rate.

b. Glass - forming tendency

Hruby and Stourac (10) suggested an appropriate measure for the glass-forming ability, which can be calculated from DSC scan:

$$K_{gl} = \frac{T_{cl} - T_g}{T_m - T_{cl}},$$

where T_{cl} represents the temperature of the start of crystallization. K_{gl} values of the compositions $Se_{60} S_{40-x} Te_x$ at the different heating rates, are given in Table 1. It reveals that $K_{gl} \geq 0.1$, and is higher for the composition $Se_{60} S_{25} Te_{15}$ than the composition $Se_{60} S_{15} Te_{25}$. This means that the ability to form crystalline solids decreases with increasing the sulphur content. For a given quenching rate, the glass-forming tendency differs for different materials. This is most probably related to the chemical bonds that identify the structure and all the properties of a body in any state of aggregation [9]. For chalcogenide glasses, chemical bonds with lone-pair electrons have a character of flexibility. This flexibility relies on the type, strength and concentration of the possibly existing chemical bonds in the glass.

c. Heat of atomization

The average heat of atomization H_s , is based on chemical bonding aspects, is defined for a compound $A_\alpha B_\beta C_\delta$ as a direct measure of cohesive energy, i.e. of the average bond strength (11). H_s can be given as

$$H_s = \frac{(\alpha H_s^A + \beta H_s^B + \gamma H_s^C)}{\alpha + \beta + \gamma}$$

at standard temperature and pressure, where H_s^A , H_s^B and H_s^C are the heat of atomization of atoms A, B and C, respectively.

From Table (1), it can be seen that H_s decreased by increasing Te content, i.e. the average bond strength of the compound decreased. For Te- rich glasses, the covalent nature of the bond might be weakened by the presence of three - fold coordination Te sites.

Table (1): The heat of atomization and the DSC data of the investigated glasses in the system $\text{Se}_{60}\text{S}_{40-x}\text{Te}_x$

Composition	H_a (Kcal/ gm – atom)	Heating rate (°C / min)	T_g (°C)	T_c (°C)		T_m (°C)	K_{gl}
				Start	Peak		
$\text{Se}_{60}\text{S}_{25}\text{Te}_{15}$	53.04	10	46 , 73	90	115	235	0.3 , 0.11
		15	49 , 73	91	124	235	0.29 , 0.13
		20	52	93	128	235	0.29
		30	53 , 67	103	137	234	0.38 , 0.27
		40	80	101	142	236	0.16
$\text{Se}_{60}\text{S}_{15}\text{Te}_{25}$	51.04	10	72	91	110	295	0.09
		15	75	93	114	295	0.09
		20	76	97	123	296	0.11
		30	80	104	130	297	0.12
		40	82	108	135	297	0.14

* The accuracy in measuring the temperature is ± 3 °C.

d. DSC cyclic scanning

The investigation of the two consecutive cyclic scans of the examined glasses indicated the following behaviours as shown in Figures (2.a & 2.b):

For the composition $\text{Se}_{60}\text{S}_{25}\text{Te}_{15}$, the DSC trace shows in the first heating (run a) three peaks, (T_g) at 49.7 °C, (T_c) at 124 °C and (T_m) at 235 °C. During 1st and 2nd cooling cycle, (runs b and d), no features of interest were observed. In the 2nd heating cycle (run c), one can notice the disappearance of (T_g), (T_c) and (T_m). This is due to the change of the form of the material from the powder form before (run a) to bulk form before (run c). The crystallization can occur more readily in a powdered glass than in a large solid pieces.

For the composition $\text{Se}_{60}\text{S}_{15}\text{Te}_{25}$, the DSC trace shows, (T_g) at 75 °C, (T_c) at 114 °C and (T_m) at 298 °C in the first heating cycle (run a). In (run b) two crystallization peaks at 210 and 220 °C were observed. During the 2nd heating cycle (run c), T_c at 136 °C and (T_m) at 297 °C were only observed, while (T_g) is disappeared. In (run d), one exothermic peak was observed at 256 °C. It can be concluded that the tendency to crystallize in the cooling runs increases by increasing Te content in the composition.

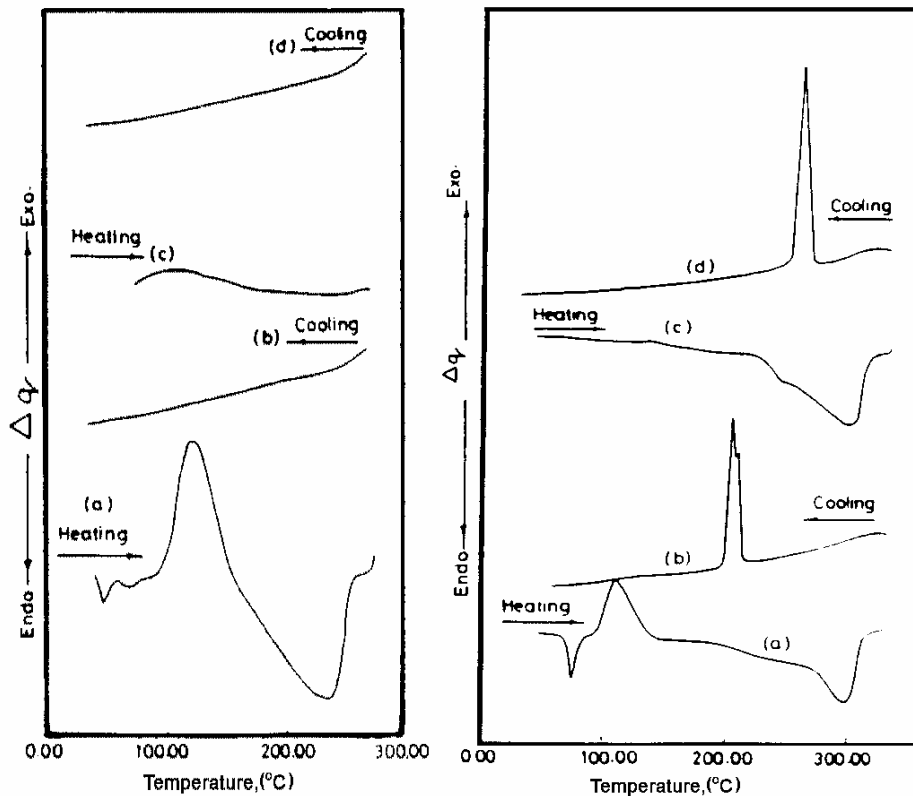


Fig. (2): DSC scanning of : a) $\text{Se}_{60}\text{S}_{25}\text{Te}_{15}$ glass.
b) $\text{Se}_{60}\text{S}_{15}\text{Te}_{25}$ glass.

It is well mentioned that chalcogenide glasses exhibit many useful electrical properties including threshold and memory switching. The electrical properties are influenced by the structural changes associated with thermal effects and can be related to thermally induced transitions [12]. The glasses which exhibit no exothermic peaks in the cooling runs, display very little tendency to crystallization. This is usually belongs to threshold switching type. But the glasses, which exhibit an exothermic crystallization peak in cooling runs, display high tendency to crystallize, and, hence, they are memory switching type [13].

e. Crystallization kinetics

Kissinger [14] quoted a relationship between the peak position ($T = T_p$) of the exotherm and the heating rate (Φ) for a series of DSC or DTA thermograms carried out at different scan rates. The effective activation energy of reaction (E_c) can be derived using such relation:

$$d(\ln \Phi / T_p^2) / d(1/T_p) = -E_c / R,$$

considering that the order of reaction (n) remains constant through the greater part of the reaction, and so it was disregarded in the derivation of the relation. A plot of $\ln(\Phi / T_p^2)$ versus $1/T_p$ is shown in Fig. (3). A line was fitted by least-square for the data of each composition to obtain the value of E_c . The latter is found to be 0.63 eV for the composition $\text{Se}_{60} \text{S}_{25} \text{Te}_{15}$ and 0.61 eV for the composition $\text{Se}_{60} \text{S}_{15} \text{Te}_{25}$. The data showed that increasing Te content decreased the activation energy of crystallization. This means that the composition $\text{Se}_{60} \text{S}_{25} \text{Te}_{15}$ has higher crystallization capacity.

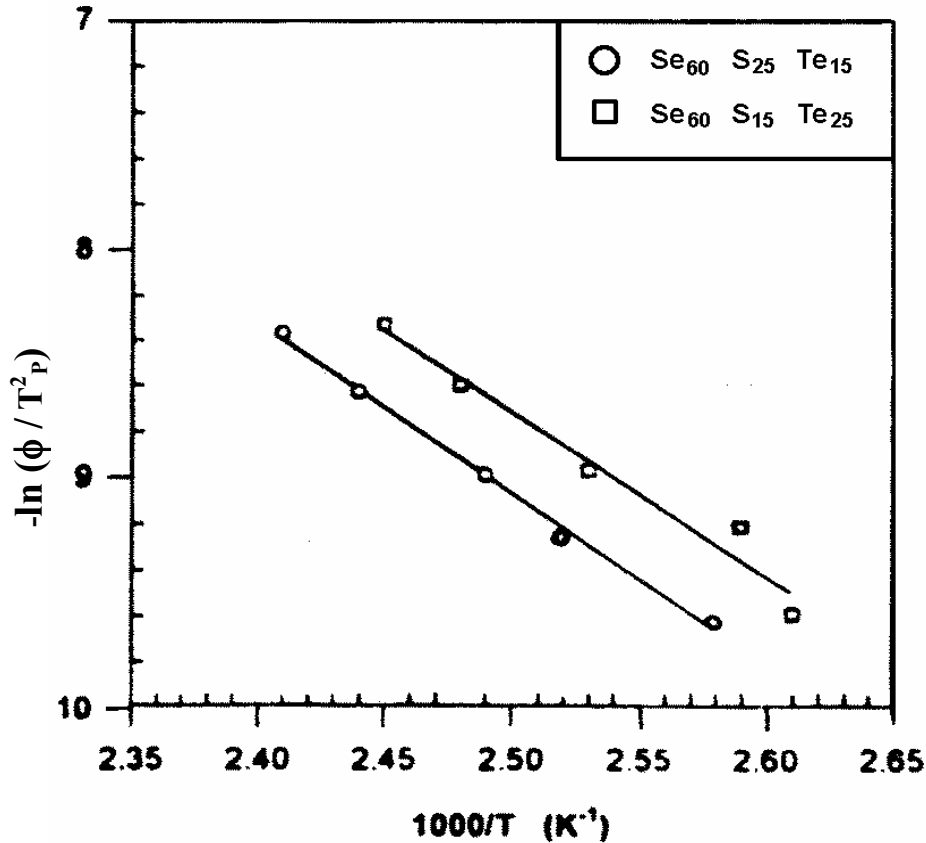


Fig. (3): The relation between $-\ln(\Phi / T_p^2)$ and $10^3 / T_p$.

Applying the shape index method (14), the order of reaction n was calculated. It is found to lie between 0.96 - 0.97, i.e. ≈ 1 . This means that the growth occurs at one dimension.

Conclusions

The DSC analysis reveals that increasing Te content leads to the increase of the transition temperatures (T_g , T_c , T_m). Using the non - isothermal kinetic analysis, it was found that the activation energy of crystallization decreases by increasing Te content. This means that the composition $Se_{60}S_{15}Te_{25}$ has a high crystallization capacity.

References

1. S.R. Ovshinsky, Phys. Rev. Letters, **21**, 1450 (1988).
2. L.A. Wahab, Proceeding of 2nd international conference (Science, Development & Inviroment) Cairo, pp 215 (1997).
3. A.F. Maged, L.A. Wahab, I.A. El Kholy, J. Materials Science, **33**, 3331 (1998).
4. M.F. Kotkata et al., Indian J. Technology, **20**, 390 (1982).
5. M.F. Kotkata et al., J. Non - cryst. Solids, **33**, 13 (1979).
6. M.F. Kotkata & E.A. Mahmoud, J. Mat. Sci. Eng., **54**, 163 (1982).
7. M.H. El- Fauly, L.A. Wahab and M.F. Kotkata, J. Thermal Analysis, **42** , 1285 (1994).
8. M.F. Kotkata and A. El. Dib, Mater. Sci. Eng., **67**, 39 (1984).
9. M.F. Kotkata, J. Mater. Sci., **26**, 4869 (1991).
10. Hruby and L. Stourac, Mat. Res. Bull., **6**, 465 (1971).
11. M. Yamaguchi, Phil. Mag., **51** (1985) 651.
12. H. Fritzsche and S.R. Ovshinsky, J. Non- cryst. Solids, **2** , 148 (1970).
13. S. Mahadevan, A. Giridhar and A.K. Singh, J. Non- cryst. Solids, **88**, 11 (1986).
14. H.E. Kissinger, Anal. Chem., **29**, 1702 (1957).