

Nonisothermal Phase Transformation of the Glassy Composition TeSe₂₀

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Result of differential scanning calorimetry (DSC) at different heating rates $\phi = 5, 15, 20, 40,$ and $50^\circ\text{C}/\text{min}$ on glassy composition TeSe₂₀ are discussed. The characteristic temperatures (the glass transition temperature (T_g), the crystallization temperature (T_c) and the melting temperature (T_m)) and the activation energy of crystallization (E_c) were evaluated by two different models, which are valid to discuss the results of glass-crystalline transformation but with different accuracies. A cyclic scanning method was used to investigate the thermally induced phase during two consecutive heating-cooling cycles covering the temperature range T_g - T_m , which indicates that the glassy compound TeSe₂₀ could be applied as a memory switching compound.

Introduction

Chalcogenide glassies are of interest for both basic researches and technological applications. Recently, it has been pointed out that Se-Te alloys have some additional advantages over amorphous Se as far as their use in xerography is concerned [1-3].

In selenium each atom needs two neighbours to satisfy the valence requirements. This is achieved either by the formation of small molecules Se_8 or linear polymeric chains Se_n . Se can melt without appreciable change within these structural units [4], the required random arrangement of atoms being obtained by the breaking of the weak bonding between units and by increasing flexibility of the chains. The crystallization would appear to require some dissociation of the chains followed by their reformation in an ordered array. Addition of Te has a catalytic effect on the crystallization of Se. The Se-Te bond being weaker than the Se-Se bond. This makes crystallization easier, by facilitating the close packing of a few Se chains to form a nucleation centre.

Studies of the crystallization of a glass upon heating can be performed in several different ways. In calorimetric measurements, two basic methods can be used, isothermal and non-isothermal. In non-isothermal method, the crystallization process can be interpreted in terms of several theoretical models [5,6,7]. The present work is concerned with the evaluation of the activation energy of crystallization using two different models under non isothermal condition.

Experimental Technique

TeSe_{20} composition has been prepared by fusing the highly pure elements (99.99%) in appropriate weight in evacuated quartz ampoule at 500°C under vacuum of 10^{-2} Pa. During synthesis, the ampoule was shaken several times to ensure complete homogenization of the sample. After synthesis, the molten material was quenched in ice water. The thermal behaviour was investigated using differential scanning calorimetries, DSC (Shimatzu instrument, type DSC-50). A 25 mg of the sample in the powdered form was placed in aluminum sample holder and scanned over a temperature range from room temperature to 300°C at uniform heating rates $\phi = 5, 15, 20, 40$ and 50 $^\circ\text{C}/\text{min}$. DSC measurements were conducted on the TeSe_{20} composition to determine the thermodynamic aspects by consecutive thermal cycling covering the temperature range $T_g - T_m$. Several measurements have been carried out on at least two different samples of the same composition to provide the accuracy and test reproducibility measurements.

Results and discussions

The DSC scan of TeSe₂₀ composition obtained at different heating rates is shown in Fig. (1). The values of the glass transition temperature (T_g), the crystallization extrapolated onset (T_b), the crystallization peak (T_p), and the melting temperature (T_m) were determined with accuracy of $\pm 0.1^\circ\text{C}$ (using the microprocessor of the thermal analyser). The values of the observed transition temperature for TeSe₂₀ at different heating rates are given in Table (1). Furthermore, it indicates that the endothermic (glass transition temperature), lies in the range $49.0^\circ\text{C} - 53.0^\circ\text{C}/\text{min}$ by changing the heating rate from $5^\circ\text{C}/\text{min}$ to $50^\circ\text{C}/\text{min}$. After passing the glass softening temperature, the DSC scan shows one peak characterizing the crystallization temperature. The beginning of this exothermic peak has been considered as the temperature characterizing the starting of the crystallization process. It was found that the value of the crystallization peak increases by increasing the heating rate as shown in Table (1).

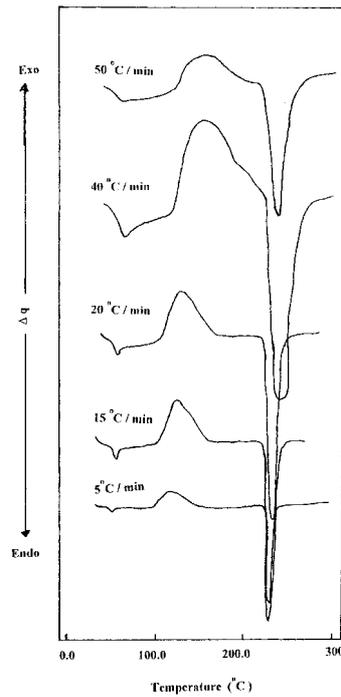


Fig. (1)
DSC thermogram for TeSe₂₀ at heating rate $\phi = 5, 15, 20, 40, 50^\circ\text{C}/\text{min}$.

Table (1)
Transition temperatures as a function of heating rate for TeSe₂₀.

Rate (ϕ) $^\circ\text{C}/\text{min}$	$T_g(^\circ\text{C})$	Crystallization Exotherm		$T_m(^\circ\text{C})$
		T_b	T_p	
5	49.0	81.3	114.9	229
15	50.0	88	121.0	229
20	50.0	89	127.7	229
40	53.0	100	154.0	233
50	49.0	108	158.4	230

T_b : beginning of the peak
 T_p : top of the peak.

The kinetics of the crystallization process of the examined composition, TeSe₂₀ has been investigated using two different models. The first model is a single scan technique ($\phi = 5^\circ\text{C}/\text{min}$) through an improved DSC or DTA model [8]. According to this model, an estimation of the complex activation energy of the crystallization E_c can be made by using Piloyan's method [9] and Borchard's assumption [10]. This leads to the following two equations [8]

$$\ln [-\ln(1-\alpha)] = n \ln [(k_0^{1/n} E_c)/\phi R] - E_c/RT \quad (1)$$

$$\log [g(\alpha)] = \log [(k_0^{1/n} E_c)/\phi R] - E_c/2.303nRT \quad (2)$$

where

$$g(\alpha) = [-\ln(1-\alpha)]^{1/n} \quad (3)$$

k_0 is considered to be constant with respect to temperature, and n is the order of crystal growth. The transformed fraction ($\alpha\alpha$) at any time t (or temperature T) was calculated using the partial area analysis [7, 11, 12, 13]. Figure (2) illustrates the relation between $\ln[-\ln(1-\alpha)]$ versus $1/T$ for the composition TeSe₂₀. This relation yields a straight line, from its slope the activation energy of crystallization was determined as 18.97 Kcal/mole.

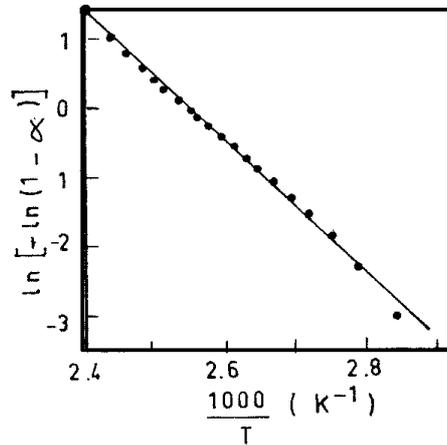


Fig.(2): Plots of $\ln [-\ln (1 - \alpha)]$ Versus $1/T$ for TeSe₂₀

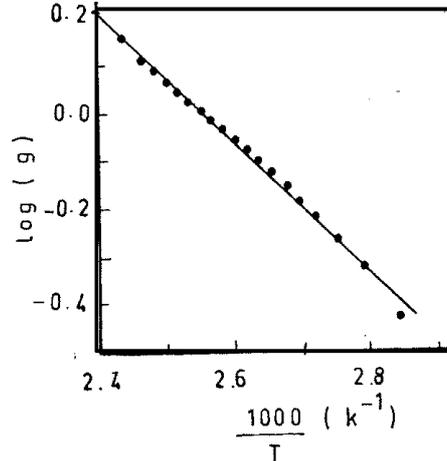


Fig.(3): Plots of $\log g (\alpha)$ versus $1/T$ for TeSe₂₀

A plot of $\log g(\alpha)$ versus $1/T$ yields a straight line (see Fig.(3)) over the entire range of α ($0 < \alpha < 1$) in agreement with the kinetic function ($-\ln(1-\alpha)^{1/2} = kT$)[14] α , then the value of E_c/n can be obtained from the slope. This is done using least-square fit to the straight line. The reaction mode n ,

which depends on the details of the nucleation mechanism, is evaluated from the slope as $n = 1.99$, which means that the crystallization process for TeSe_{20} chalcogenide glass occurs as a two dimension process [7, 15,16,17].

The second model is multiscan technique ($\phi = 5, 15, 20, 40$ and $50^\circ\text{C}/\text{min}$) which is commonly used in analysing crystallization data in DSC and DTA experiments, as developed by Kissinger [5,18]. According to his model the rate of reaction is expressed as :

$$d\alpha/dt = nk (1 - \alpha) [-\ln (1 - \alpha)]^{n-1/n} \quad (4)$$

The temperature at the peak of the exotherm is identified in Takhor's method [19], as the temperature of the maximum crystallization rate, i.e., $d^2\alpha/dt^2 = 0$. In taking the derivative with respect to time near the peak, it is convenient to assume that $[-\ln(1-\alpha)]^{n-1/n}$ is constant, denoted B. One then can obtain.

$$d^2\alpha/dt^2 = Bk_0 [E_c/RT_p^2 - \{(Bk_0/\phi) \exp (-E_c/RT_p)\} \phi(1-\alpha_p) \exp (-E_c/RT_p) = 0 \quad (5)$$

$$\text{i.e.} \quad \phi/T_p^2 = (Bk_0R/E_c) \exp (-E_c/RT_p) \quad (6)$$

where the evaluation of the effective activation energy of crystallization E_c could be calculated. In Fig. (4) the relationship of $\ln(\phi/T_p^2)$ versus $1/T_p$ is shown. The value of E_c could be obtained for TeSe_{20} chalcogenide glass deduced from this relation is equal to 12 Kcal/mole. By comparing the deduced values of E_c calculated by using either a single scan or multiple scan, we can conclude that the two methods give results that are different. This means that the two methods are valid to discuss the results of glass-crystalline transformation but with different accuracy.

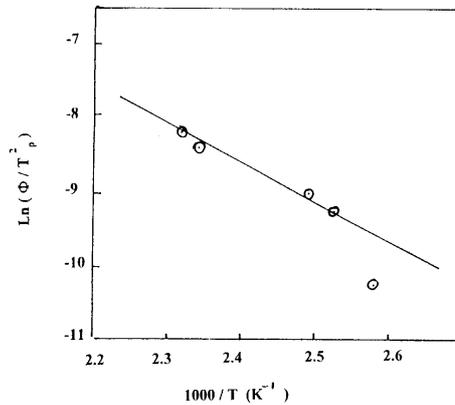


Fig. (4)
Plots of $\ln \phi/T_p^2$ versus $1/T_p$
for TeSe_{20} .

Heating-cooling cyclic scanning

The effect of two consecutive heating and cooling processes on both exothermic and endothermic were also examined, using DSC cyclic scan

covering the temperature up to T_m . The used procedure for DSC cyclic scan was to raise the temperature at heating rate of $15^\circ\text{C}/\text{min}$ to the melting point (T_m), after that the liquid alloy is undercooled into solid state also at cooling rate of about $15^\circ\text{C}/\text{min}$.

The investigation of two consecutive cyclic scans of the examined glassy sample TeSe_{20} shown in Fig. (5) indicates the following behaviours.

1. In the first heating cycle (run a) of amorphous TeSe_{20} , T_g , T_c , and T_m are clearly observed.
2. During cooling cycle (run b), only the exothermic peak was observed, indicating the recrystallization of TeSe_{20} from liquid phase.
3. In the second heating cycle (run c), the same behaviour was observed as shown in run (a) except that the absence of T_g .
4. The second cooling cycle, (run d), the same behavior was observed as shown in run b, including the liquid-crystal transformation.

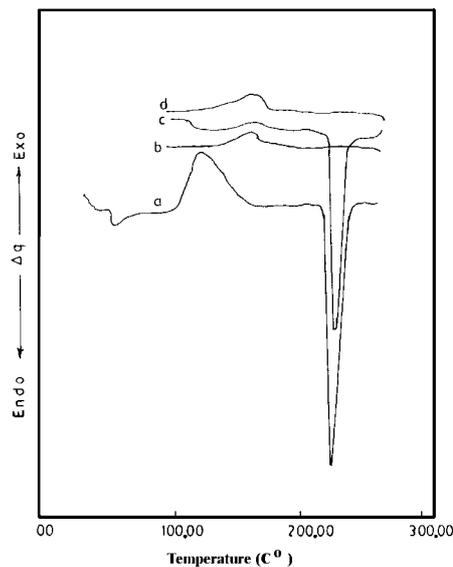


Fig. (5)
DSC heating-cooling cyclic scanning for TeSe_{20} .

In conclusion, we have observed that the recycling of the glassy compound TeSe_{20} , the behaviour of the amorphous-crystal phase transformation depends on thermal treatment, which indicates that the glassy compound TeSe_{20} could be applied as a memory switching compound.

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