

# Crystallization kinetics of selenium–tellurium glasses

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Bulk glasses of the compositions  $\text{Se}_{70}\text{Te}_{30}$  and  $\text{Se}_{80}\text{Te}_{20}$  were prepared by the melt quenching technique. Differential thermal analyses were performed at different heating rates. The values of the glass transition temperature,  $T_g$ , the crystallization temperature,  $T_c$ , and the peak temperature of crystallization,  $T_p$ , were found to depend on the composition and the heating rate. The activation energy for the glass transition,  $E_i$ , as well as the activation energy for crystallization,  $E_c$ , were evaluated from the heating rate dependence of  $T_g$  and  $T_p$ . The crystallization mechanism was examined through analysis of the data under non-isothermal conditions. The results indicated that surface crystallization is dominant for both compositions.

## 1. Introduction

Chalcogenide glasses exhibit many useful properties and have recently drawn great attention because of their use in various solid state devices. Crystallization of chalcogenide glasses plays an important role in determining the transport mechanism, thermal stability and practical applications. Different techniques have been used to study crystallization of chalcogenide glasses, e.g. electrical resistivity [1, 2], electron microscopy [3] X-ray diffraction [4] and scanning calorimetry [5]. It has been pointed out [6] that Se–Te alloys have some additional advantages over amorphous selenium as far as their use in xerography is concerned.

The electrical properties are influenced by the structural effects associated with the thermal effects and can be related to thermally induced transitions [7, 8]. The study of the crystallization of a glass upon heating can be undertaken in several ways, according to the particular technique employed. In calorimetric measurement, two basic methods can be used, isothermal and continuous heating crystallization. In the isothermal method, the sample is brought quickly to a temperature above the glass transition temperature,  $T_g$ , and the heat evolved during the crystallization process is recorded as a function of time. In the other method, the sample is heated at a fixed rate and the heat evolved is again recorded as a function of temperature or time. The crystallization process can be interpreted in terms of several theoretical models. The isothermal crystallization data are usually interpreted in terms of the Johnson–Mehl–Avrami–Erofeev (JMAE) transformation equation [9–11], whereas some controversy exists about the correct interpretation of non-isothermal results [12–14].

In this study the dependence of the glass transition temperature,  $T_g$ , the crystallization temperature,  $T_c$ , and the peak temperature of crystallization,  $T_p$ , on the composition and the heating rate have been studied. From the heating-rate dependence of  $T_g$  and  $T_p$ , the

activation energy for the glass transition,  $E_i$ , and the activation energy for crystallization,  $E_c$ , have been evaluated for  $\text{Se}_{80}\text{Te}_{20}$  and  $\text{Se}_{70}\text{Te}_{30}$  glasses. Crystallization studies have been made under non-isothermal conditions. Using a recent analysis developed for non-isothermal crystallization studies, information on some aspects of the crystallization mechanism has been obtained.

## 2. Experimental procedure

Bulk glasses of the compositions  $\text{Se}_{80}\text{Te}_{20}$  and  $\text{Se}_{70}\text{Te}_{30}$  were prepared by the melt-quenching technique. Appropriate amounts of the constituent elements (99.99% purity) were melted together in evacuated sealed quartz ampoules. The ampoules were kept in a rotating furnace at about 1000 K for 20 h, to ensure homogenization of the melt, the ampoules were then quenched in an ice-water mixture. The amorphous nature of the prepared samples was confirmed by X-ray diffraction, using a Philips 1710 diffractometer with a nickel-filtered  $\text{CuK}_\alpha$  radiation source ( $\lambda = 0.154 \text{ nm}$ ).

Differential thermal analysis (DTA) was carried out, using a Du Pont 1090 instrument. Measurements were carried out from room temperature to a temperature above the crystallization exotherms at constant heating rates. Scans at different heating rates ranging from  $1\text{--}50^\circ\text{C min}^{-1}$  were recorded.

## 3. Results and discussion

For the investigation of the crystallization kinetics in amorphous  $\text{Se}_{70}\text{Te}_{30}$  and  $\text{Se}_{80}\text{Te}_{20}$ , differential thermal analyses were performed at different heating rates (1, 5, 10, 20 and  $50^\circ\text{C min}^{-1}$ ), and the results are shown in Figs 1 and 2. Dependence of  $T_g$  on the heating rate for the compositions studied are given in Table I. The value of  $T_g$  and, therefore, the rigidity of the lattice increases with increasing tellurium content

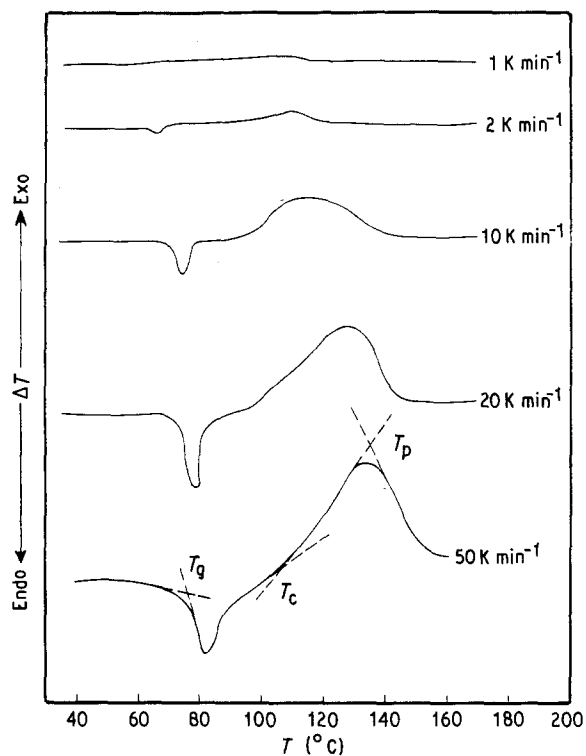


Figure 1 Typical DTA traces for  $\text{Se}_{70}\text{Te}_{30}$  at different heating rates.

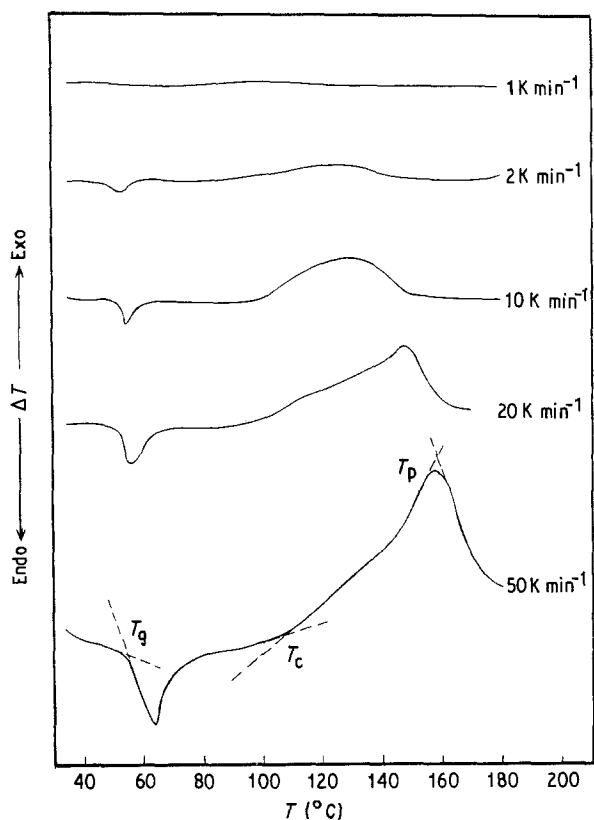


Figure 2 Typical DTA traces for  $\text{Se}_{80}\text{Te}_{20}$  at different heating rates.

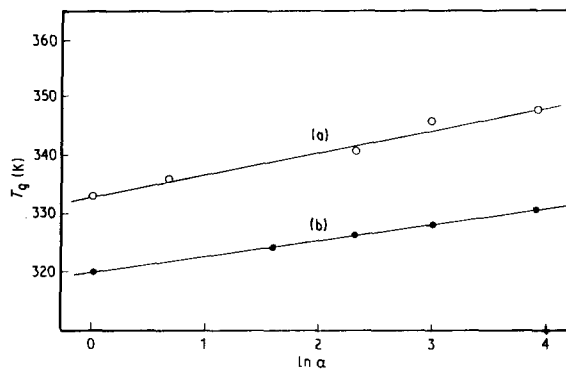


Figure 3  $T_g$  versus  $\ln \alpha$  for the glasses (a)  $\text{Se}_{70}\text{Te}_{30}$  and (b)  $\text{Se}_{80}\text{Te}_{20}$ .

for different heating rates. The results are in good agreement with those obtained by Das *et al.* [15]. The observed increase in  $T_g$  could be attributed either to the increase in the effective molecular weight with increasing tellurium content or to the increase in the concentration of long polymer chains [5].

It is also shown in Table I, that the value of  $T_g$  varies by about  $15^\circ\text{C}$  for  $\text{Se}_{70}\text{Te}_{30}$  and  $9^\circ\text{C}$  for  $\text{Se}_{80}\text{Te}_{20}$ , as the heating rate increased from 1 to  $50^\circ\text{C min}^{-1}$ . The dependence of  $T_g$  on the heating rate,  $\alpha$ , could be discussed using two approaches. The first is the empirical relationship of the form  $T_g = A + B \log \alpha$ , where  $A$  and  $B$  are constants suggested by Lasocka [16]. Plots of  $T_g$  versus  $\ln \alpha$  for  $\text{Se}_{70}\text{Te}_{30}$  and  $\text{Se}_{80}\text{Te}_{20}$  glasses are shown in Fig. 3, which indicates the validity of the relationship  $T_g = A + B \log \alpha$ .

The calculated value of  $B$  was found to be 3.75 and 3 for the  $\text{Se}_{70}\text{Te}_{30}$  and  $\text{Se}_{80}\text{Te}_{20}$  glass, respectively. It was suggested that the value of  $B$  depends on the cooling rate employed in the preparation of the glass and it decreases with the lower cooling rate of the melt [16]. Both glasses have the same cooling rate during preparation and are isostructural. Therefore, the response of the configurational changes within the glass transition region for both compositions, to the heating rate can be expected to be similar; this is indicated by the constancy of  $B$  observed for these glasses.

The second approach is the evaluation of the activation energy for the glass transition,  $E_i$ , using Kissinger's formula [17] which is valid in a very general case [18–20]. For homogeneous crystallization with spherical nuclei, the dependence of  $T_g$  on  $\alpha$  is given by

$$\ln(T_g^2/\alpha) + \text{const.} = E_i/RT_g \quad (1)$$

where  $\alpha$  is the heating rate,  $E_i$  is the activation energy for the glass transition and  $R$  is the gas constant.

Fig. 4 shows the variation of  $\ln(T_g^2/\alpha)$  with  $1/T_g$  for  $\text{Se}_{70}\text{Te}_{30}$  and  $\text{Se}_{80}\text{Te}_{20}$  glasses. The linearity of the

TABLE I Dependence of  $T_g$  on the heating rate

Composition	$T_g$ ( $^\circ\text{C}$ ) at various heating rates						$E_i$ (kcal mol $^{-1}$ )	$B$ in $T_g = A + B \log \alpha$
	1	2	5	10	20	50		
$\text{Se}_{70}\text{Te}_{30}$	60	63	—	68	73	75	55.7	3.75
$\text{Se}_{80}\text{Te}_{20}$	47	—	51	53	55	56	79.61	3.00

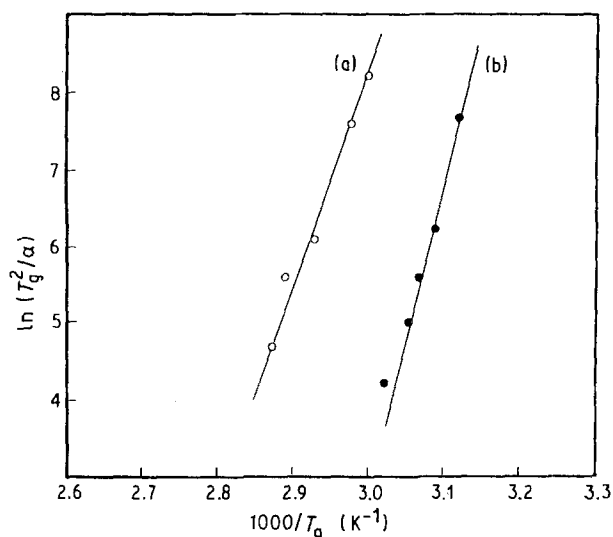


Figure 4  $\ln T_g^2/\alpha$  versus  $1/T_g$  for the glasses (a)  $\text{Se}_{70}\text{Te}_{30}$  and (b)  $\text{Se}_{80}\text{Te}_{20}$ .

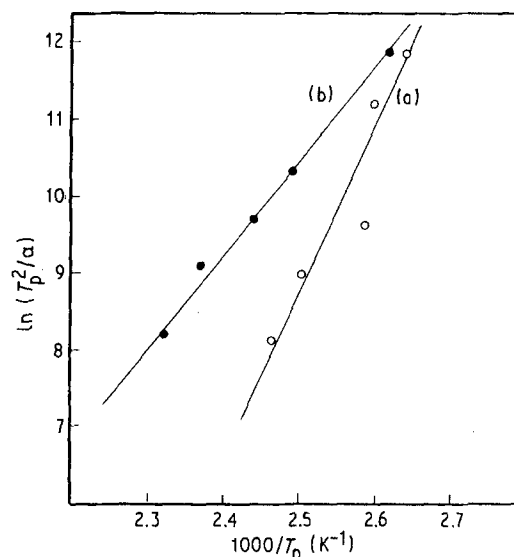


Figure 5  $\ln T_p^2/\alpha$  versus  $1/T_p$  for the glasses (a)  $\text{Se}_{70}\text{Te}_{30}$  and (b)  $\text{Se}_{80}\text{Te}_{20}$ .

plots showed the validity of the relation, the values of  $E_i$  were calculated and are listed in Table I.

The values of the crystallization temperature,  $T_c$ , and the peak temperature of crystallization,  $T_p$ , for the compositions  $\text{Se}_{70}\text{Te}_{30}$  and  $\text{Se}_{80}\text{Te}_{20}$  at various heating rates are listed in Table II. The composition dependence of  $T_c$  of these glasses is similar to that of their  $T_p$ . Both  $T_c$  and  $T_c - T_g$ , which represents the thermal stability of the glasses, decrease with increasing tellurium content [5]. The glass with low ( $T_c - T_g$ ) values can therefore be expected to have higher electrical conductivity [21]. The kinetic resistance to crystallization is increased by increasing selenium content [5].

The activation energy,  $E_c$ , of the amorphous-crystalline transformation was calculated using the equation derived by Kissinger [22]

$$\ln(T_p^2/\alpha) = (E_c/RT_p) + \text{const.} \quad (2)$$

Fig. 5 shows the relation between  $\ln(T_p^2/\alpha)$  and  $1/T_p$  for  $\text{Se}_{70}\text{Te}_{30}$  and  $\text{Se}_{80}\text{Te}_{20}$  glasses. The data are well

fitted by straight lines which show that the crystallization obeys the above-mentioned equation. The obtained values of  $E_c$  are listed in Table III.

The activation energy of the amorphous-crystalline transformation,  $E_c$ , can be calculated also from the following equation, which correlates the shifts in  $T_p$  values of DTA with the heating rate [5]

$$\ln \alpha = -E_c/RT_p + \text{const.} \quad (3)$$

Plots of  $\ln \alpha$  versus  $1/T_p$  for  $\text{Se}_{70}\text{Te}_{30}$  and  $\text{Se}_{80}\text{Te}_{20}$  are shown in Fig. 6. A straight line could be fitted to give the activation energies which are listed also in Table III.

The analysis of the kinetics of phase transformation involving nucleation and growth is usually studied using the JMAF equation [9, 11]. Because of the limitation of the valid heating rates in this method [23], a non-isothermal crystallization method was suggested [24]. For non-isothermal crystallization, the volume fraction,  $x$ , of crystals precipitated in a glass heated at a uniform rate,  $\alpha$ , is shown to be related

TABLE II Crystallization temperature and peak temperature of crystallization

Composition	Heating rate ( $^{\circ}\text{C min}^{-1}$ )						
	1	2	5	10	20	50	
$\text{Se}_{70}\text{Te}_{30}$	106.5	111.5	—	113	128	133	$T_p$
	80	83	—	95	97	105	$T_c$
$\text{Se}_{80}\text{Te}_{20}$	110.0	—	128	135	149	158	$T_p$
	81.5	—	92.5	100	102	112.5	$T_c$

TABLE III Activation energy

Composition	$E_c$ (kcal mol $^{-1}$ )		$\ln[-\ln(1-x)]$ versus $1/T$		
	From Equation 2	From Equation 3	$mE_c$	$m$	$n$
$\text{Se}_{70}\text{Te}_{30}$	39.76	42.74	44.78	1.047	1
$\text{Se}_{80}\text{Te}_{20}$	24.85	26.50	37.83	1.427	1.4

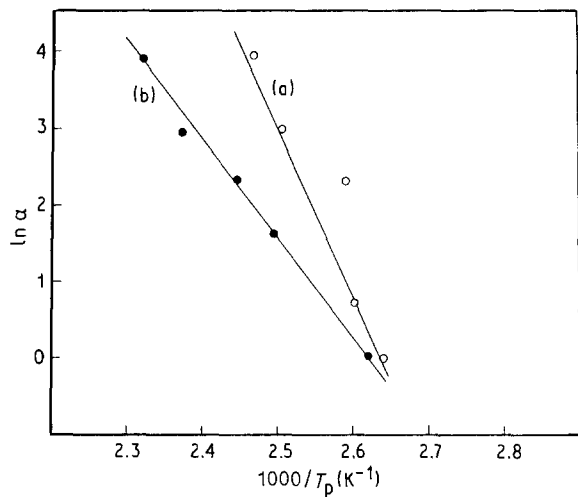


Figure 6  $\ln \alpha$  versus  $1/T_p$  for the glasses (a)  $\text{Se}_{70}\text{Te}_{30}$  and (b)  $\text{Se}_{80}\text{Te}_{20}$ .

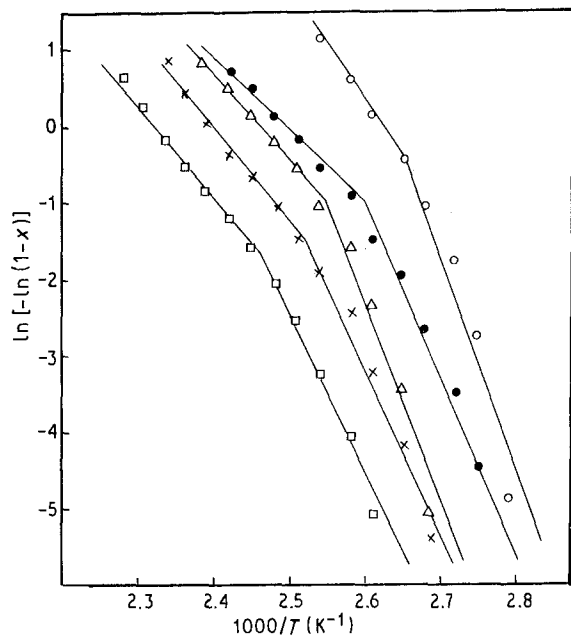


Figure 7  $\ln[-\ln(1-x)]$  versus  $1/T_p$  for  $\text{Se}_{70}\text{Te}_{30}$  at different heating rates: (○) 2, (●) 5, (△) 10, (×) 20, (□)  $50^\circ\text{C min}^{-1}$ .

to  $E_c$  through the expression [25]

$$\ln[-\ln(1-x)] = -n \ln \alpha - 1.052 m E_c / RT + \text{const.} \quad (4)$$

where  $m$  and  $n$  are constants having values between 1 and 4, depending on the morphology of the growth [25].

Figs 7 and 8 show the relation between  $\ln[-\ln(1-x)]$  and  $1/T$  for the compositions  $\text{Se}_{70}\text{Te}_{30}$  and  $\text{Se}_{80}\text{Te}_{20}$  at various heating rates. The plots are found to be linear over most of the temperature range. At high temperature or in regions of large crystallized fractions, a break in the linearity or, rather, a lowering of the initial slope, is observed for all the heating rates, as shown in Figs 7 and 8. Generally this break in slope is attributed to the saturation of nucleation sites in the final stages of crystallization [20, 26]. The values of  $mE_c$  were calculated from the slope of  $\ln[-\ln(1-x)]$  versus  $1/T$ , for different heating rates. The

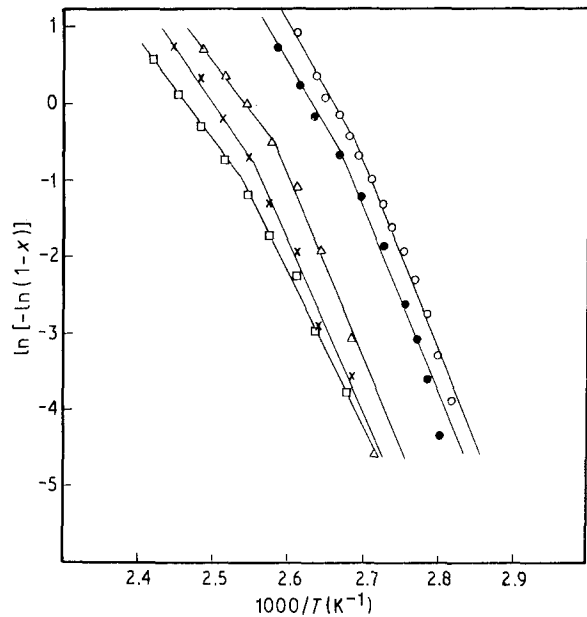


Figure 8  $\ln[-\ln(1-x)]$  versus  $1/T_p$  for  $\text{Se}_{80}\text{Te}_{20}$  at different heating rates. For key, see Fig. 7.

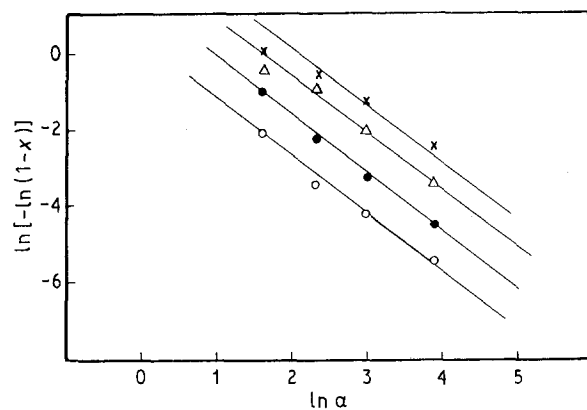


Figure 9  $\ln[-\ln(1-x)]$  versus  $\ln \alpha$  for the  $\text{Se}_{70}\text{Te}_{30}$  at fixed temperatures:  $T =$  (○) 377, (●) 384.5, (△) 392, (×) 400 K.

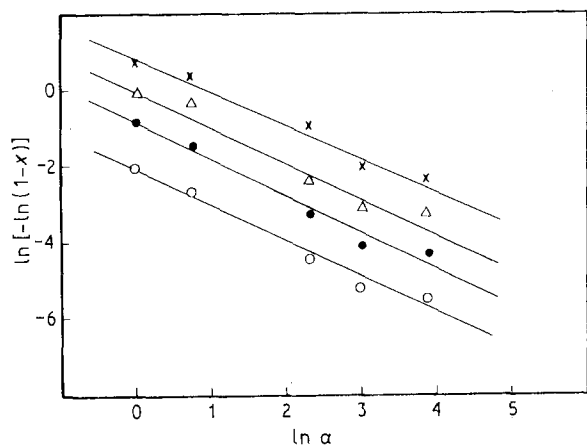


Figure 10  $\ln[-\ln(1-x)]$  versus  $\ln \alpha$  for the  $\text{Se}_{80}\text{Te}_{20}$  at fixed temperatures:  $T =$  (○) 363.6, (●) 370, (△) 377, (×) 384.5 K.

calculated values of  $mE_c$  are shown to be independent of the heating rate, and therefore an average value of  $mE_c$  was calculated by considering all the heating rates. The values of  $E_c$  obtained from the linear relation between  $\ln \alpha$  and  $1/T_p$  are used for calculation of

$m$ . The calculated values of  $mE_c$  and  $m$  for the two compositions are listed in Table III.

Figs 9 and 10 show linear plots of  $\ln[-\ln(1-x)]$  versus  $\ln \alpha$  at four fixed temperatures, for the compositions  $\text{Se}_{70}\text{Te}_{30}$  and  $\text{Se}_{80}\text{Te}_{20}$ . The  $n$  value was calculated from the slope of the straight lines of Figs 9 and 10 according to Equation 4. The values of  $n$  and  $m$  obtained are closer to unity as shown in Table III. The values of  $m$  and  $n$  obtained indicated that for the powdered samples of the glasses  $\text{Se}_{70}\text{Te}_{30}$  and  $\text{Se}_{80}\text{Te}_{20}$ , surface nucleation is dominant [25].

## Conclusions

Results of thermal analyses show that the glass transition temperature  $T_g$ , the crystallization,  $T_c$ , and the peak temperature,  $T_p$ , are dependent on the heating rates for the two compositions. The crystallization mechanism was analysed using a recent analysis developed for a non-isothermal crystallization process. The results indicate that surface nucleation is dominant for the compositions investigated.

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