

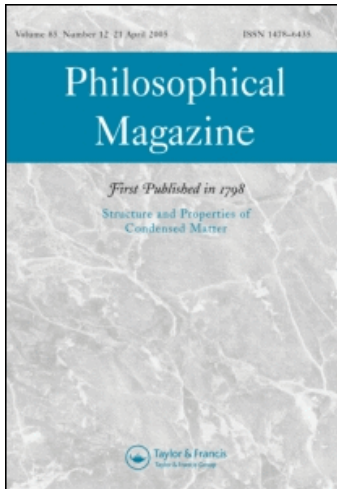
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## Thermal stability and activation energy of some compositions of Ge–Te–Cu chalcogenide system

A. Dahshan<sup>a\*</sup>, K.A. Aly<sup>b</sup> and M.T. Dessouky<sup>c</sup>

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The present study investigates the influence of copper addition on the thermal stability, and the activation energy of the glass transition and crystallization for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x=2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses. Differential scanning calorimetric (DSC) results under non-isothermal conditions for the Ge–Te–Cu system are reported and discussed. From the heating rate ( $\alpha$ ) dependence of the glass transition temperature ( $T_g$ ) and the temperature corresponding to the maximum crystallization rate ( $T_p$ ), the activation energy for both glass transition and crystallization for the studied glasses were obtained. The glass-forming ability of the  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  glasses was evaluated using various thermal stability criteria based on characteristic temperatures. The  $K_i(T)$  criterion has also been considered for the evaluation of glass stability from DSC data. The activation energy for crystallization decreases and thermal stability increases with increasing copper content.

**Keywords:** thermal stability; activation energy; differential scanning calorimetry

### 1. Introduction

Initially, glasses containing chalcogen elements were the subject of study owing to their interesting semiconducting properties, and more recently for their application in optical recording [1,2]. Recording materials must be stable in the amorphous state at low temperature and have a short crystallization time. Recently, promising materials with these characteristics have been studied [3,4]; thus, it is important to know the glass stability of these types of materials.

There is no simple technique of formulating the correlation between the ideal composition and the stability of glasses. Different quantitative methods have been suggested to evaluate the level of stability of glassy alloys. Most, for example the method of Dietzel [5] or Hruby [6], are based on characteristic temperatures, such as the glass transition temperature ( $T_g$ ), the temperature at which crystallization begins ( $T_o$ ), the temperature corresponding to the maximum crystallization rate ( $T_p$ ), or the melting temperature ( $T_m$ ). Some of the suggested methods [7,8] are based on the reaction rate constant ( $K$ ) and the others [9,10] are based on the activation energy for crystallization.

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The characteristic temperatures ( $T_g$ ,  $T_o$ ,  $T_p$  and  $T_m$ ) are easily and accurately obtained by the differential scanning calorimetry [11] during the heating processes of the glass sample. Dietzel [5] introduced the first glass criterion,  $\Delta T = T_o - T_g$ , which is an important parameter to evaluate glass-forming ability. Using characteristic temperatures, Hruby [6] developed the  $H_r$  criterion,  $H_r = \Delta T / (T_m - T_p)$ ; the compositional dependence of the Hruby coefficient were surveyed by Sestak [12]. On the basis of the  $H_r$  criterion, Saad and Poulain [13] obtained two other criteria: weighted thermal stability  $H' = \Delta T / T_g$  and  $S = (T_p - T_o) \Delta T / T_g$  criterion.

In the present work, the effect of addition of Cu on the thermal stability, and the activation energy of glass transition and crystallization for the  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses is investigated.

## 2. Experimental details

Different compositions of bulk  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) chalcogenide glasses were prepared by melt quenching using Ge, Te and Cu elements of high purity (99.999%). The elements were heated together in evacuated ( $10^{-3}$  Pa) silica ampoules to 1250 K, and the temperature kept constant for about 24 h. During the heating process, the ampoules were shaken several times to maintain homogeneity and then quenched in iced water to avoid crystallization.

The amorphous state of the materials was checked using an X-ray diffractometer (Philips type 1710 with Cu as a target and Ni as a filter,  $\lambda = 1.5418 \text{ \AA}$ ). The absence of crystalline peaks confirmed the amorphous state of the prepared samples. The elemental composition of the investigated specimens were checked using energy dispersive X-ray spectroscopy (EDX; Link Analytical, Witney, UK). The compositions agreed with those of the starting materials.

Thermal behaviour was investigated using a calibrated Shimadzu 50 differential scanning calorimeter. About 15 mg of each sample in powdered form was sealed in a standard aluminium pan and scanned over a temperature range from room temperature to about 770 K at different uniform heating rates ( $\alpha = 3, 6, 12, 24$  and  $48 \text{ K/min}$ ).

## 3. Theoretical considerations

The theoretical basis for interpreting kinetic data is provided by the formal theory of transformation kinetics. This theory describes the evolution with time ( $t$ ) of the volume fraction crystallized ( $\chi$ ) by the Kolmogorov–Johnson–Mehl and Avrami Equation [14]:

$$\chi = 1 - \exp(-(Kt)^n) \quad (1)$$

where  $n$  is an integer or half integer depending on the mechanism of growth and the dimensionality of the crystal;  $K$  is the effective (overall) reaction rate constant, which obeys an Arrhenius expression for the absolute temperature:

$$K(T) = K_0 \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where  $K_0$  is the frequency factor,  $T$  is the absolute temperature and  $E$  is the effective activation energy describing the overall crystallization process, which can be expressed as:

$$E = \frac{E_N + E_G}{n} \tag{3}$$

where  $E_N$  and  $E_G$  are the effective activation energies for nucleation and growth, respectively.  $E_N$  can be neglected over the temperature range of concern in the thermo-analytical study [14], then:

$$E \approx \left(\frac{m}{n}\right)E_G \tag{4}$$

where  $n=m$  for the nucleation frequency  $I_v=0$  and  $n=m+1$  for  $I_v \neq 0$  [15]. The rate constant  $K$  in a non-isothermal DSC experiment was found to change continuously with time due to the change in the temperature; therefore Equation (1) can be generalized to:

$$\chi(t) = 1 - \exp\left[-\left(\int_0^t K[T(t')]dt'\right)^n\right] = 1 - \exp(-I^n) \tag{5}$$

where  $K[T(t')]$  is still given by Equation (2), and  $T(t')$  is the temperature at time  $t'$  [15].

The crystallized volume fraction depends on time ( $t$ ) through the temperature,  $T(t)$ , and the same is true for the integral  $I$ . The time integral in Equation (5) is transformed to the temperature integral, yielding:

$$I(T) = \frac{K_0}{\alpha} \int_{T_0}^T \exp\left(\frac{-E}{RT'}\right) dT' \tag{6}$$

which is represented by several approximate analytical expressions [16]. Using the substitution  $y' = E/RT'$ , the above integral has been represented by the sum of the alternating series:

$$S(y') = -\frac{e^{-y'}}{y'2} \sum_{k=0}^{k=\infty} \frac{(-1)^k (k+1)!}{y'^k} \tag{7}$$

Considering that, in this type of series, the error produced is less than the first term neglected and, bearing in mind, that in most crystallization reactions  $y' = E/RT' \gg 1$ . Therefore, it is possible to use only the two first terms of this series and the error introduced is not greater than 1%. By assuming that:

$$T^2(1 - 2RT/E)\exp(-E/RT) \gg T_0^2(1 - 2RT_0/E)\exp(-E/RT_0)$$

Equation (6) can be rewritten in the form of:

$$I = K_0 E (\alpha R)^{-1} e^{-y} y^{-2} (1 - 2y^{-1}) \tag{8}$$

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The maximum crystallization rate in a non-isothermal process, which occurs at the peak of the exotherm at time  $t_p$  and temperature  $T_p$  [14], is found by making  $d^2\chi/dt^2=0$ , thus obtaining the relationship:

$$d^2\chi/dt^2 = nK_p(I^n)_p - (n-1)K_p - \frac{\alpha E(I)_p}{RT_p^2} = 0 \quad (9)$$

$$nK_p(I^n)_p = (n-1)K_p + \frac{\alpha EI_p}{RT_p^2}$$

Substituting for ( $y = E/RT$ ) and ( $K = K_0 \exp(-E/RT)$ ) into Equation (8), one obtains:

$$I = RT^2 K(\alpha E)^{-1} (1 - 2RT/E) \quad (10)$$

Substituting the last expression for  $I$  into Equation (9), one obtains the relationship:

$$I_p = (1 - 2RT_p/nE)^{1/n} \quad (11)$$

When this relationship is equated to Equation (10), this gives:

$$RT_p^2(\alpha E)^{-1} K_0 \exp(-E/RT_p) = (1 - 2RT_p/nE)^{1/n} (1 - 2RT_p/E)^{-1}$$

or in a logarithmic form

$$\ln(T_p^2/\alpha) + \ln(K_0 R/E) - E/RT_p \approx (2RT_p/E)(1 - 1/n^2) \quad (12)$$

where the function  $\ln(1-z)$  with  $z = 2RT_p/nE$  or  $z = 2RT_p/E$  is expanded as a series and only the first term has been taken.

Note that Equation (12) reduces to the Kissinger expression for the  $n=1$  case, as one might have anticipated, since this corresponds to the homogeneous reaction case. Thus, it can be seen that the Kissinger method is appropriate for the analysis not only of homogeneous reactions but also for the analysis of heterogeneous reactions, which are described by the JMA equation in isothermal experiments [14]. The right-hand side (RHS) of Equation (12) is generally negligible in comparison to the individual terms on the left-hand side for  $\alpha \leq 100$  K/min. This approximation in Equation (12) (RHS) implies:

$$\ln(\alpha/T_p^2) = -E_c/RT_p + \ln(K_0 R/E) \quad (13)$$

where the quoted approximation might introduce a 3% error in the value of  $E/R$  in the worst cases. For crystallization processes with spherical nuclei, it has been suggested [14,15] that the dependence of the glass transition temperature on  $\alpha$  may be written as:

$$\ln(\alpha/T_g^2) = -E_t/RT_g + \text{const.} \quad (14)$$

a straight line between  $\ln(\alpha/T_g^2)$  and  $1/T_g$ , whose slope yields the value of  $E_t/R$ .  $R$  is the gas constant.

To evaluate the thermal stability of glassy materials, Surinach et al. [17] and Hu and Jiang [18] introduced two criterion  $K(T_g) = K_0 \exp(-E/RT_g)$  and  $K(T_p) = K_0 \exp(-E/RT_p)$ , respectively. Thus, the values of these two parameters indicate the tendency of glass to devitrify on heating. The larger their values, the greater the tendency to devitrify. The formation of glass is a kinetic process. It is reasonable to assess glass stability by

a kinetic parameter,  $K(T)$ . Also, the  $H_r$  parameter itself is a stability factor based on characteristic temperatures. Here, a stability criterion is defined as:

$$K_r(T) = K_0 \exp\left(\frac{-H_r E}{RT}\right) \quad (15)$$

where  $T$  is any temperature between  $T_g$  and  $T_p$ . The theoretical background for the definition of the parameter  $K_r(T)$  would be based on the analysis of the relation between the parameters  $K(T)$  and  $K_r(T)$ . Differentiating Equations (2) and (15) with respect to temperature and rewriting each parameter per Kelvin we get:

$$\frac{\Delta K_r}{K_r \Delta T} = \frac{H_r E}{RT^2} \quad \text{and} \quad \frac{\Delta K}{K \Delta T} = \frac{E}{RT^2}$$

The above-mentioned variation of the parameter  $K_r(T)$  is  $H_r$  times the variation in parameter  $K(T)$ , which could justify the accuracy of parameter  $K_r(T)$ . Just like the  $K(T)$  criterion, the smaller the values of  $K_r(T)$ , the greater the thermal stability of the glass. The obvious advantage of this method is that it can evaluate glass stability over a broad temperature range rather than at only one temperature, such as  $T_g$  or  $T_p$ .

#### 4. Results and discussion

Figure 1 shows the DSC thermograms for the  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 7.5$  and  $12.5$  at%) chalcogenide glasses recorded at a heating rate of  $12 \text{ K/min}$ . As shown in this figure, there is a small endothermic peak attributed to the glass transition temperature range of the glass; its minimum refers to  $T_g$ . There is also an exothermic peak originating from the amorphous–crystalline transformation. The exothermic peak has two characteristic points: the first is the onset temperature of crystallization ( $T_o$ ) and the second is the temperature

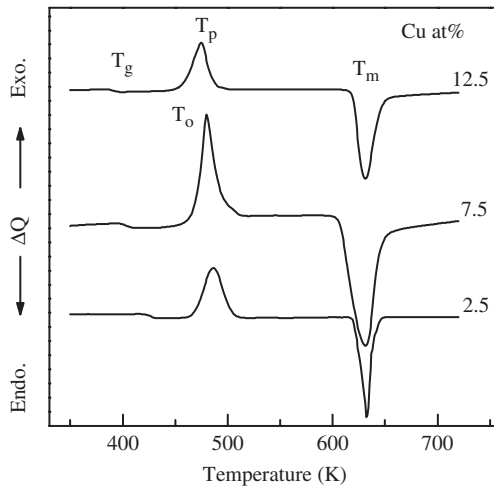


Figure 1. DSC traces for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 7.5$  and  $12.5$  at%) glasses recorded at a heating rate of  $12 \text{ K/min}$ .

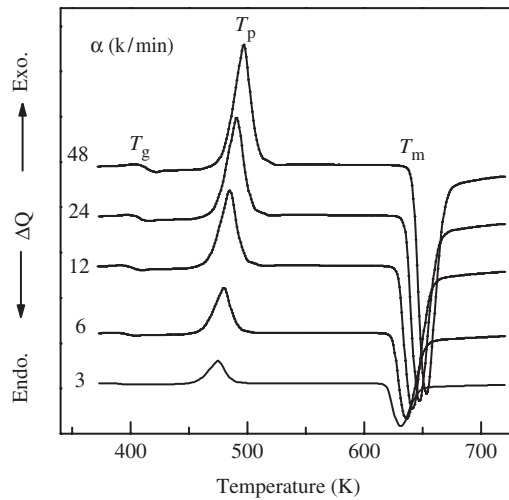


Figure 2. DSC traces for the chalcogenide glass  $\text{Ge}_{26}\text{Te}_{61.5}\text{Cu}_{12.5}$  at different heating rates.

corresponding to the maximum crystallization rate ( $T_p$ ). It can be seen that  $T_p$  decreases with increasing Cu content.

Figure 2 shows the DSC thermograms for  $\text{Ge}_{26}\text{Te}_{61.5}\text{Cu}_{12.5}$  glass recorded at different heating rates ( $\alpha = 3, 6, 12, 24$  and  $48$  K/min.). This figure shows that the characteristic temperatures ( $T_g, T_o, T_p$  and  $T_m$ ) increase with increasing heating rate. The values of  $T_g$  and  $T_p$  for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses recorded at different heating rates (3, 6, 12, 24 and 48 K/min) are given in Table 1. As shown in this table, the glass transition temperature decreases with increasing Cu content. The decrease in  $T_g$  is probably due to the decrease in the mean molecular weight of the glasses as the Cu concentration is increased.

The calculated values of the stability parameters ( $\Delta T, H_r, H'$  and  $S$ ) based on the characteristic temperatures are listed in Table 1. This table shows that  $\Delta T, H_r, H'$  and  $S$  increase with increasing Cu content. These parameters allow one to predict the glass-forming ability of a material. The larger their values, the greater the glass thermal stability should be. Therefore, thermal stability increases with increasing Cu content and the  $\text{Ge}_{26}\text{Te}_{61.5}\text{Cu}_{12.5}$  glass is the most stable. The variation in  $\Delta T$  and  $H_r$  as a function of Cu content (at  $\alpha = 24$  K/min.) for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses is showing in Figure 3. From this figure, it is clear that the increase in both  $\Delta T$  and  $H_r$  for  $x > 7.5$  is much slower than that for  $x < 7.5$  at%.

The dependence of  $T_g$  on the heating rate could be discussed using the empirical relationship, which has the form [15]:

$$T_g = A + B \ln \alpha \quad (16)$$

$A$  and  $B$  are constants for a given glass composition. Plots of  $T_g$  versus  $\ln(\alpha)$  for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses, as shown in Figure 4, indicates the validity of Equation (16) for the studied glasses.

Table 1. Values of glass transition temperatures ( $T_g$ ), temperature corresponding to the maximum crystallization rate ( $T_p$ ) and thermal stability criteria ( $\Delta T$ ,  $H_r$ ,  $H'$  and  $S$ ) at different heating rates for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses.

Composition	$\alpha$ (K/min)	$T_g \pm 0.5$ (K)	$T_p \pm 0.5$ (K)	$\Delta T$ (K)	$H_r$	$H'$	$S$ (K)
$\text{Ge}_{26}\text{Te}_{71.5}\text{Cu}_{2.5}$	3	411	476	49	0.378	0.120	1.851
	6	414	481	50	0.380	0.121	1.998
	12	417	486	51	0.382	0.123	2.253
	24	420	491	52	0.385	0.124	2.310
	48	422	495	54	0.386	0.128	2.501
$\text{Ge}_{26}\text{Te}_{69}\text{Cu}_5$	3	402	472	56	0.434	0.139	2.025
	6	405	477	57	0.436	0.140	2.174
	12	408	482	57	0.438	0.140	2.435
	24	411	488	60	0.440	0.145	2.527
	48	413	493	62	0.441	0.149	2.669
$\text{Ge}_{26}\text{Te}_{66.5}\text{Cu}_{7.5}$	3	391	469	64	0.523	0.164	2.361
	6	394	474	65	0.527	0.166	2.478
	12	397	480	67	0.528	0.169	2.733
	24	399	486	68	0.529	0.170	3.248
	48	403	491	69	0.530	0.171	3.443
$\text{Ge}_{26}\text{Te}_{64}\text{Cu}_{10}$	3	385	466	66	0.530	0.171	2.663
	6	388	472	67	0.532	0.173	2.941
	12	390	477	69	0.537	0.177	3.151
	24	393	483	72	0.551	0.182	3.312
	48	396	489	75	0.556	0.188	3.480
$\text{Ge}_{26}\text{Te}_{61.5}\text{Cu}_{12.5}$	3	381	464	68	0.534	0.178	2.793
	6	384	470	69	0.534	0.181	3.056
	12	386	475	72	0.539	0.187	3.209
	24	388	481	75	0.552	0.192	3.522
	48	391	487	77	0.558	0.198	3.677

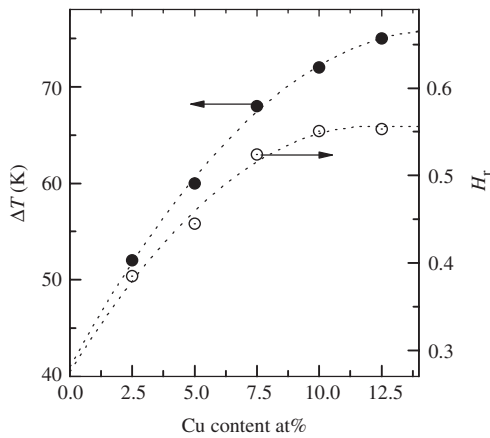


Figure 3. Variation in  $\Delta T$  and  $H_r$  as a function of Cu content at a heating rate 24K/min for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses.

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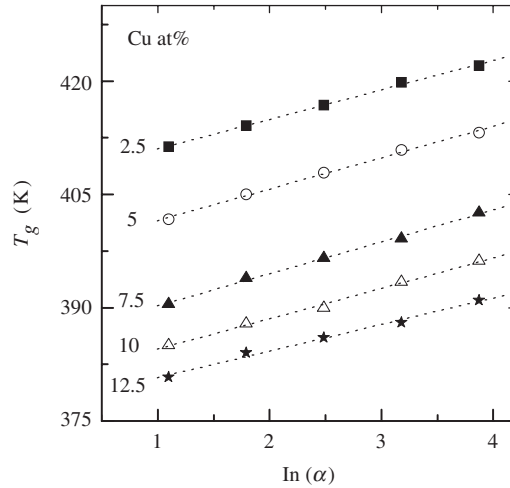


Figure 4. Dependence of glass transition temperature on heating rate for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses.

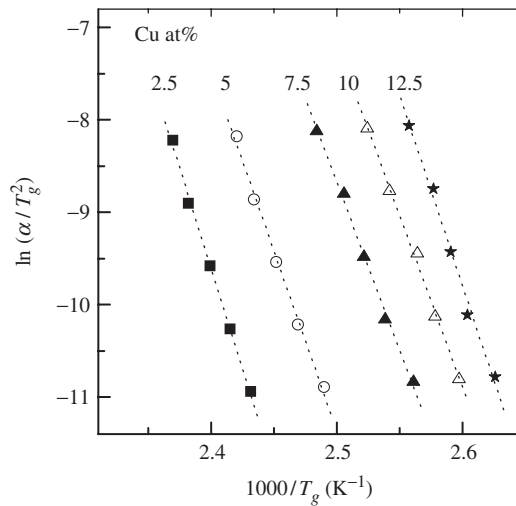


Figure 5.  $\ln(\alpha/T_g^2)$  versus  $1000/T_g$  for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses.

From the heating-rate dependence of  $T_g$ , the values of the activation energy for glass transition ( $E_t$ ) are evaluated, as shown in Figures 5 and 6. Figure 5 illustrate the plots of  $\ln(\alpha/T_g^2)$  versus  $1/T_g$  for the  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses according to Equation (14). The  $E_t$  values can also be deduced using the approximation given by Mahadevan et al. [15]. The variation in  $\ln(1/T_g^2)$  with  $\ln(\alpha)$  is much slower than that  $\ln(1/T_g)$  with  $\ln(\alpha)$ , so Equation (14) can be simplified to:

$$\ln(\alpha) = -\frac{E_t}{RT_g} + \text{const.} \quad (17)$$

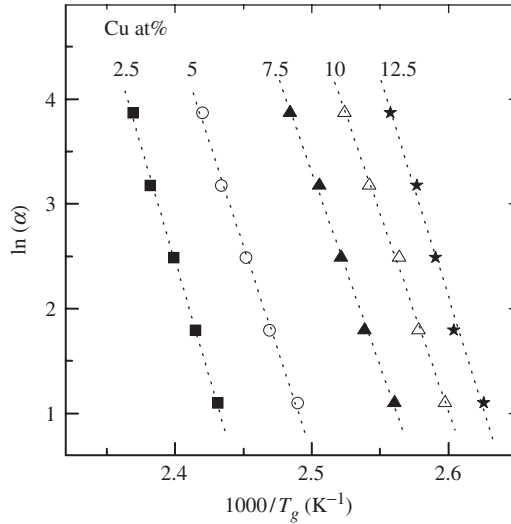


Figure 6.  $\ln \alpha$  versus  $1000/T_g$  for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses.

Table 2. Activation energy of both crystallization ( $E_c$ ) and glass transition ( $E_t$ ) for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses.

Composition	$E_c$ (kJ/mol)		$E_t$ (kJ/mol)	
	Eq. (18)	Eq. (13)	Eq. (14)	Eq. (17)
$\text{Ge}_{26}\text{Te}_{71.5}\text{Cu}_{2.5}$	273.22	277.00	361.05	368.00
$\text{Ge}_{26}\text{Te}_{69}\text{Cu}_5$	244.48	248.22	323.40	330.17
$\text{Ge}_{26}\text{Te}_{66.5}\text{Cu}_{7.5}$	226.56	230.28	301.27	307.86
$\text{Ge}_{26}\text{Te}_{64}\text{Cu}_{10}$	220.25	223.95	308.13	314.63
$\text{Ge}_{26}\text{Te}_{61.5}\text{Cu}_{12.5}$	218.12	221.80	341.85	348.27

Figure 6 shows the plots of  $\ln(\alpha)$  versus  $1/T_g$  for the  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses. The values of  $E_t$  were calculated from the slopes of the plots (Figures 5 and 6) and inserted in Table 2.

Figure 7 illustrates the plots of  $\ln(\alpha/T_p^2)$  versus  $1/T_p$  for the  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses according to Equation (13). The activation energy for crystallization ( $E_c$ ) was calculated from the variation in  $T_p$  with heating rate ( $\alpha$ ) according to this equation.  $E_c$  can be obtained also from the plots of  $\ln(\alpha/(T_p - T_{in}))$  versus  $1/T_p$  (Figure 8) according to the Takhor method [19] following the relation:

$$\ln\left(\frac{\alpha}{T_p - T_{in}}\right) = \frac{1}{n} \ln\left(\frac{n}{n-1}\right) + \ln(k_0) - \frac{E_c}{RT_p} \tag{18}$$

where  $T_{in}$  is the initial temperature. These methods predict a shift in  $T_p$  towards a higher temperature with increasing heating rate. The values of  $E_c$  were calculated from the slopes

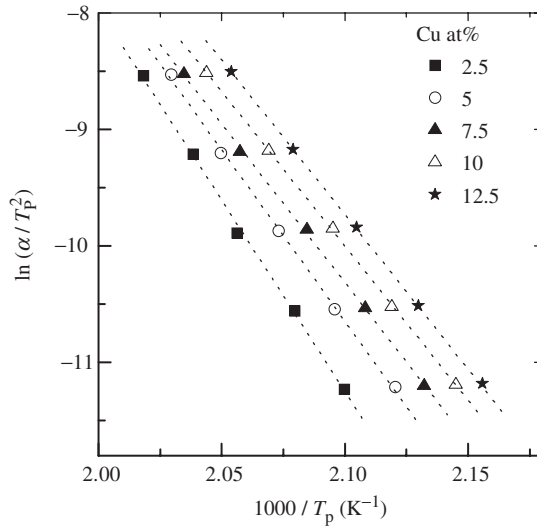


Figure 7.  $\ln(\alpha/T_p^2)$  versus  $1000/T_g$  for  $Ge_{26}Te_{74-x}Cu_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses.

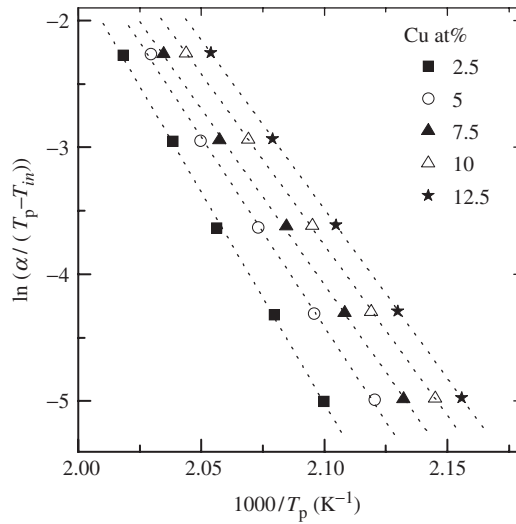


Figure 8.  $\ln(\alpha/(T_p - T_{in}))$  versus  $1000/T_g$  for  $Ge_{26}Te_{74-x}Cu_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses.

of the plots (Figures 7 and 8) and listed in Table 2. From this table, one can notice that  $E_c$  decreases with increasing Cu content.

After knowing the values of  $E$  and  $K_0$ , the kinetic parameters  $K(T)$  and  $K_r(T)$  for the studied glasses were calculated using Equations (2) and (15). These calculations were carried out to compare the thermal stability sequence for the studied glasses. Values of  $K(T)$  and  $K_r(T)$  for the temperatures  $T_g$  and  $T_p$  are listed in Table 3. The smaller the

Table 3.  $K(T_g)$ ,  $K(T_p)$ ,  $K_r(T_g)$ ,  $K_r(T_p)$  criteria at different heating rates for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses.

Composition	$\alpha$ (K/min)	$K(T_g) \times 10^{-7}$ (s)	$K(T_p) \times 10^{-2}$ (s)	$K_r(T_g)$ (s)	$K_r(T_p)$ (s)
$\text{Ge}_{26}\text{Te}_{71.5}\text{Cu}_{2.5}$	3	1.34	0.7	$5.32 \times 10^{14}$	$3.24 \times 10^{16}$
	6	2.29	1.4	$5.43 \times 10^{14}$	$3.56 \times 10^{16}$
	12	3.86	3.0	$5.51 \times 10^{14}$	$4.08 \times 10^{16}$
	24	6.75	5.4	$5.64 \times 10^{14}$	$4.33 \times 10^{16}$
	48	10.15	10.5	$5.98 \times 10^{14}$	$5.14 \times 10^{16}$
$\text{Ge}_{26}\text{Te}_{69}\text{Cu}_5$	3	1.16	0.6	$1.23 \times 10^{11}$	$1.40 \times 10^{13}$
	6	2.26	1.3	$1.39 \times 10^{11}$	$1.66 \times 10^{13}$
	12	3.75	2.6	$1.46 \times 10^{11}$	$1.93 \times 10^{13}$
	24	6.34	5.1	$1.67 \times 10^{11}$	$2.41 \times 10^{13}$
	48	9.48	9.3	$1.86 \times 10^{11}$	$2.94 \times 10^{13}$
$\text{Ge}_{26}\text{Te}_{66.5}\text{Cu}_{7.5}$	3	0.53	0.6	$1.52 \times 10^7$	$0.69 \times 10^{10}$
	6	1.01	1.2	$1.59 \times 10^7$	$0.76 \times 10^{10}$
	12	1.55	2.3	$1.90 \times 10^7$	$1.02 \times 10^{10}$
	24	2.39	4.5	$2.17 \times 10^7$	$1.39 \times 10^{10}$
	48	4.29	8.8	$2.77 \times 10^7$	$1.83 \times 10^{10}$
$\text{Ge}_{26}\text{Te}_{64}\text{Cu}_{10}$	3	0.37	0.5	$6.73 \times 10^6$	$2.40 \times 10^9$
	6	0.62	1.1	$7.19 \times 10^6$	$2.88 \times 10^9$
	12	0.98	2.1	$7.48 \times 10^6$	$3.01 \times 10^9$
	24	1.67	4.2	$8.23 \times 10^6$	$4.93 \times 10^9$
	48	2.79	8.6	$9.03 \times 10^6$	$5.10 \times 10^9$
$\text{Ge}_{26}\text{Te}_{61.5}\text{Cu}_{12.5}$	3	0.22	0.5	$2.34 \times 10^6$	$0.82 \times 10^9$
	6	0.37	1.0	$3.15 \times 10^6$	$1.04 \times 10^9$
	12	0.57	2.0	$5.05 \times 10^6$	$1.68 \times 10^9$
	24	0.83	4.1	$5.62 \times 10^6$	$2.53 \times 10^9$
	48	1.40	8.3	$7.12 \times 10^6$	$3.31 \times 10^9$

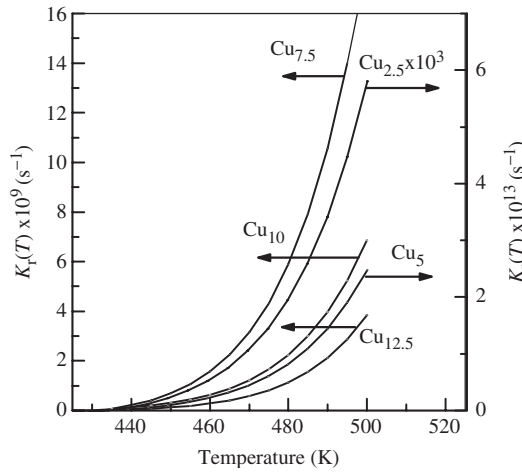


Figure 9.  $K_r(T)$  as a function of temperature  $T$  at a heating rate of 12 K/min for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses.

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values of the two criteria  $K(T)$  and  $K_r(T)$ , the better the thermal stability of glass should be. Figure 9 represents the plots of  $K_r(T)$  versus  $T$  for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses at a heating rate of  $12 \text{ K/min}$ . From this figure, one can notice that the values of  $K_r(T)$  decrease with increasing Cu content, so thermal stability increases with increasing Cu content.  $K_r(T)$  for the  $\text{Ge}_{26}\text{Te}_{61.5}\text{Cu}_{12.5}$  glass varies slowly with increasing the temperature, indicating a relatively high stability.

## 5. Conclusions

From analyses of DSC results under non-isothermal conditions for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  ( $x = 2.5, 5, 7.5, 10$  and  $12.5$  at%) glasses, it can be concluded that the values of the glass transition temperature and the temperature corresponding to the maximum crystallization rate depend on heating rate and Cu content. The glass transition temperature decreases with increasing Cu content; this decrease is probably due to the decrease in the mean molecular weight of the glasses as Cu concentration is increased. The composition dependence of  $\Delta T$ ,  $H_r$ ,  $H'$ ,  $S$ ,  $K(T)$  and  $K_r(T)$  for  $\text{Ge}_{26}\text{Te}_{74-x}\text{Cu}_x$  glasses shows that the thermal stability increases with increasing Cu content.

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