

## A Study of the Crystallization Kinetics of Ge-Se-Te Glasses

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### Abstract

Bulk  $\text{Ge}_{50-x}\text{Se}_{50}\text{Te}_x$  ( $x = 10, 20, 30, 40$  at %) glasses have been prepared by the melt quenching technique. The crystallization of these glasses has been studied by using differential scanning calorimetry (DSC). The values of the glass transition temperature,  $T_g$ , the crystallization temperature,  $T_c$ , and the crystallization peak temperature,  $T_p$ , were found to be depend on both composition and heating rate. The investigation of crystallization kinetics indicates a double-stages crystallization process. The glass transition energy,  $E_g$ , and the crystallization activation energy,  $E_c$ , were calculated. The determined kinetic parameters have made it possible to discuss the glass forming ability.

### Introduction

Chalcogenide semiconductors have truly emerged as multipurpose materials and have been used to fabricate technologically important devices [1-4]. The electrical properties are influenced by the structural changes associated with thermal effects and can be related to thermally induced transitions [5, 6]. The structural studies of chalcogenide glasses are very important in determining the transport mechanism, thermal stability and practical applications. Different techniques have been used to study the structure of chalcogenide glasses e.g. electron microscopy, x-ray diffraction and scanning calorimetry [7]. Studies of the crystallization kinetics of a glass by thermal differential analysis can be performed in several different ways. In calorimetric measurements, two methods are used, isothermal and non-isothermic. In the isothermal method the sample is brought quickly to a temperature above the glass transition temperature, and the heat evolved during the crystallization process at a constant temperature is recorded as a function of time. In the non-isothermic method,

the sample is heated at a fixed rate,  $\alpha$ , and the heat evolved is recorded as a function of temperature or time.

It has been pointed out that, the Ge-Se-Te system has two glass forming regions; compositions with higher Se % are located in one region and compositions with lower Se % in the other, with the GeSe<sub>2</sub>-Te tie line forming the boundary between these regions. The connectedness varies from two (in Se and Te) to four in (Ge) in these glasses, and the bonding is essentially covalent [8].

There are some characterization studies on several glasses of this system [9, 10]. Hafiz et al [4] reported the effect of the heat treatment on the structure and electrical resistivity of amorphous Ge<sub>20</sub>Se<sub>x</sub>Te<sub>80-x</sub> alloys (where  $x = 15, 30$  and  $50$  at %). Irreversible resistivity changes are observed after heating above the glass transition temperature. The amount of the crystalline phase increases with increasing annealing temperature. On the other hand, crystallization kinetics of chalcogenide glasses is always connected with the concept of activation energy. This activation energy in glass crystallization phenomena is associated with the nucleation and growth processes that dominate the devitrification of most glassy solids. In general, separate activation energies must be identified with nucleation and with growth processes in transformation. They have usually been combined into activation energy representative of the overall crystallization process [11-15].

Husain et al [16] studied the effect of the annealing temperature ( $T < T_p$ ) on the optical energy gap. It has been found that the optical energy gap increases with increasing annealing temperatures. In the present work, the result of crystallization kinetics for Ge<sub>50-x</sub>Se<sub>50</sub>Te<sub>x</sub> for  $x = 10, 20, 30, 40$  at % are reported. The composition dependence as well as the effect of heating rate on the glass transition temperature ( $T_g$ ), the crystallization extrapolated onset temperature ( $T_c$ ) and the crystallization peak temperature ( $T_p$ ) were investigated. Information on some aspects of the crystallization mechanism was discussed.

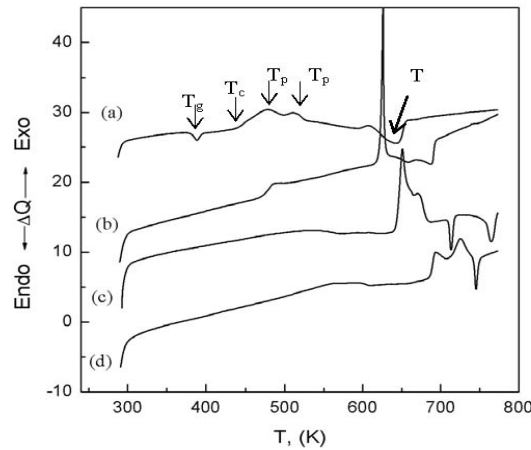
## Experimental

Bulk glasses of Ge<sub>50-x</sub>Se<sub>50</sub>Te<sub>x</sub> system ( $x = 10, 20, 30, 40$  at %) were prepared by the conventional melt-quenching technique. High purity (99.999% pure) Ge, Se and Te in appropriate atomic percentage proportions were weighted into a quartz ampoules. The contents of the ampoules were sealed in a vacuum of  $10^{-4}$  torr and heated in a rotary furnace at 1373 K for 24 h to insure homogeneity of the melt.

Differential scanning calorimetry (DSC) was carried out on 10 mg of the powdered samples using a perkin-Elmer DSC-2 under pure argon atmosphere. The crystallization experiments were carried out through continuous heating rates ( $\alpha$ ) ranging from 5 to 20 K/min. The values of the glass transition temperature ( $T_g$ ), the crystallization extrapolated onset temperature ( $T_c$ ) and the crystallization peak temperature ( $T_p$ ) was determined with accuracy of  $\pm 0.1$  using the microprocessor of the thermal analyzer.

## Results

Differential scanning calorimetry experiments were performed at different heating rates to investigate the crystallization kinetics of  $\text{Ge}_{50-x}\text{Se}_{50}\text{Te}_x$  glasses. Typical DSC traces at the heating rate 10 K/min for different  $\text{Ge}_{50-x}\text{Se}_{50}\text{Te}_x$  (where  $x = 10, 20, 30$  and 40 at %) chalcogenide glasses are shown in Fig.(1). Four characteristic phenomena are clear in the studied temperature region. The first one ( $T_g$ ), corresponds to the glass transition temperature.



**Figure 1:** Typical DSC traces at heating rate (10 K/min) for the chalcogenide glasses: (a)  $\text{Ge}_{40}\text{Se}_{50}\text{Te}_{40}$  (b)  $\text{Ge}_{40}\text{Se}_{50}\text{Te}_{30}$  (c)  $\text{Ge}_{40}\text{Se}_{50}\text{Te}_{20}$  (d)  $\text{Ge}_{40}\text{Se}_{50}\text{Te}_{10}$

The second one ( $T_c$ ) corresponds to the onset crystallization temperature. The characteristics temperatures ( $T_{p1}$  and  $T_{p2}$ ) identify the crystallization peak temperatures, and the last one is melting temperature ( $T_m$ ). The three compositions with ( $x = 10, 20$  and 40 at %) have two stages of crystallization while the sample with ( $x = 30$  at %) has one stage of crystallization. The phenomena of double crystallization have been observed in many glassy systems [17-20]. On other hand all the compositions show that  $T_g$ ,  $T_c$  and  $T_p$  shift towards lower temperatures with increasing Te content. The observed temperatures at different rates ( $\alpha$ ) ranging from 5 to 20 K/min are given in Table (1). The results show that the second peak ( $T_{p2}$ ) for crystallization process appears for the compositions  $\text{Ge}_{10}\text{Se}_{50}\text{Te}_{40}$  at rates (5, 7.5 and 20),  $\text{Ge}_{30}\text{Se}_{50}\text{Te}_{20}$  at rates (10 and 15) and  $\text{Ge}_{40}\text{Se}_{50}\text{Te}_{10}$  at rates (5, 7.5, 10, 20).

## Discussion

Two approaches are used to analyze the dependence of  $T_g$  the heating rate. The first is the empirical relationship, which has originally been suggested by lasocka [21] and has the form:

$$T_g = A + B \ln \alpha \quad (1)$$

where A and B are constants for a given glass compositions. Plots of  $T_g$  versus  $\ln\alpha$  for  $\text{Ge}_{50-x}\text{Se}_{50}\text{Te}_x$  glasses are shown in Fig.(2), and indicates the validity of Eq. (1) for our compositions.

**Table 1:** the glass transition temperature ( $T_g$ ), the onset crystallization temperature ( $T_c$ ), the crystallization temperatures ( $T_{p1}$  and  $T_{p2}$ ) and ( $T_c-T_g$ ) for all compositions at different heating rates.

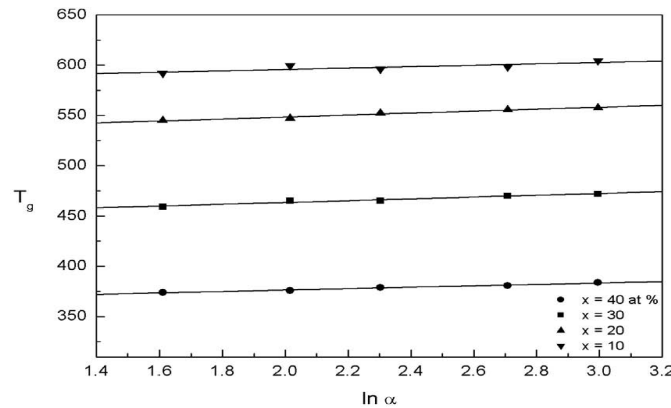
$T_c-T_g$	$T_{p2}$ (K)	$T_{p1}$ (K)	$T_c$ (K)	$T_g$ (K)	Heating rate ( $\alpha$ )	Composition
48.52	493.38	468.55	422.52	374.00	5	$\text{Ge}_{10}\text{Se}_{50}\text{Te}_{40}$
55.25	-	471.72	431.36	376.11	7.5	
55.57	510.39	477.17	434.58	379.01	10	
57.77	-	481.28	438.65	380.88	15	
61.79	518.94	488.50	445.59	383.80	20	
148.81	-	615.72	607.98	459.27	5	$\text{Ge}_{20}\text{Se}_{50}\text{Te}_{30}$
150.06	-	621.08	614.95	464.89	7.5	
152.83	-	626.35	617.83	465.00	10	
151.80	-	630.00	621.80	470.00	15	
154.68	-	634.70	626.68	472.00	20	
89.67	-	640.12	634.67	545.00	5	$\text{Ge}_{30}\text{Se}_{50}\text{Te}_{20}$
89.99	-	646.12	637.13	547.14	7.5	
88.78	669.25	650.75	641.13	552.35	10	
91.50	681.47	656.26	647.19	555.69	15	
93.58	-	662.06	651.38	557.80	20	
78.29	712.42	679.85	670.24	591.95	5	$\text{Ge}_{40}\text{Se}_{50}\text{Te}_{10}$
80.80	717.53	685.66	680.47	599.67	7.5	
90.02	723.01	695.71	686.16	596.14	10	
89.72	-	705.45	688.00	598.28	15	
97.13	737.51	716.59	701.56	604.43	20	

The calculated values of the constant B for the different compositions are listed in Table (2). It was suggested that the parameter B depends on the glass composition [21] and decreases with decreasing the cooling rate of the melt. The same cooling rate was used during the preparation of our systems. Therefore, the response of configurational changes within the glass-transition region for the studied compositions on the heating rates is expected to behave similarly, this could be indicated by the observed constant values of B Table (2).

The second approach is the evaluation of the glass transition activation energy  $E_g$ , using Kissinger's formula [22]. For homogenous crystallization with spherical nuclei the dependence of  $T_g$  on  $\alpha$  is given by

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

where  $\alpha$  is the heating rate,  $E_g$  is the activation energy for the transition and  $R$  is the gas constant. Fig.(3) shows the relation between  $\ln(\alpha/T_g^2)$  and  $(1/T_g)$  for the investigated compositions. The obtained values of for different compositions are listed in table (2).



**Figure 2:** The dependence of  $T_g$  on the heating rate ( $\alpha$ ) for  $\text{Ge}_{50-x}\text{Se}_{50}\text{Te}_x$  ( $X = 10,20,30$  and  $40$  at %) chalcogenide glasses.

**Table 2:** the coordination number ( $Z$ ), the activation energy ( $E_g$ ) and the constant  $B$  for various compositions.

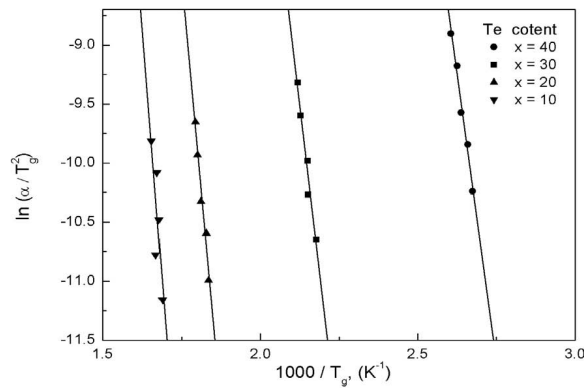
	$\text{Ge}_{10}\text{Se}_{50}\text{Te}_{40}$	$\text{Ge}_{20}\text{Se}_{50}\text{Te}_{30}$	$\text{Ge}_{30}\text{Se}_{50}\text{Te}_{20}$	$\text{Ge}_{40}\text{Se}_{50}\text{Te}_{10}$
<b>Coordination number (<math>Z</math>)</b>	2.2	2.4	2.6	2.8
<b><math>E_g</math> {Eq. (2)} kcal/mol</b>	38.74	44.75	57.67	67.51
<b><math>E_g</math> {Eq. (3)} kcal/mol</b>	40.26	46.59	59.85	69.85
<b>B</b>	6.9	8.9	9.8	6.8

The activation energy of the glass transition  $E_g$  can be deduced also by using the approximation given by Mahadevan et al. [23]. When the variation of  $\ln(\alpha/T_g^2)$  with  $\ln \alpha$  is much slower than that of with Kissinger's equation can be approximated in the form:

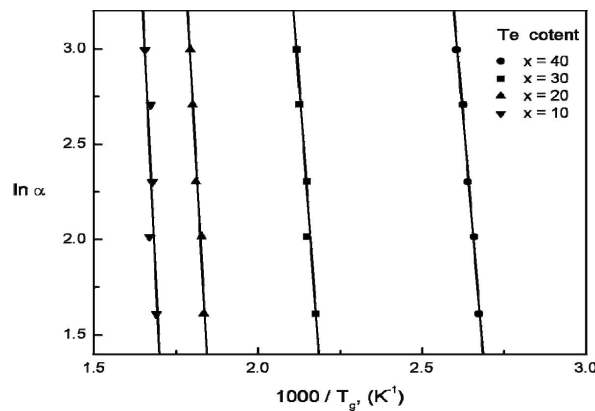
$$\ln \alpha = -E_g/RT_g + \text{const} \quad (3)$$

The relation between and for the studied compositions is shown in Fig.(4). The calculated values of  $E_g$  are listed in table (2) for all compositions. The values of the

activation energy of the glass transition ( $E_g$ ) decrease as the Te content increases as shown in table (2). The decrease of the activation energy ( $E_g$ ) with increasing Te content resulted in an apparent decrease of the glass transition temperature ( $T_g$ ) as shown in table (1). This result are in good agreement with those obtained by Das et al [24]. The glass transition temperature ( $T_g$ ) of a multi component glass is known to be depend on several independent parameters such as the optical band gap, coordination number ( $Z$ ), bond energy, effective molecular weight, and the type and fraction of various structural units formed [25-29]. We attribute the decrease of  $T_g$  to the decrease which occurs in the coordination numbers ( $Z$ ), bond energies and the mean atomic masses of these glasses with increasing Te as shown in table 2. Both  $T_c$  and ( $T_c-T_g$ ) represented the thermal stability of the glass [26,29]. The values of ( $T_c-T_g$ ) for the studied compositions at different heating rates are given in table 1. It is clear the composition  $Ge_{20}Se_{50}Te_{30}$  has the highest value of ( $T_c-T_g$ ) which indicate the composition  $Ge_{20}Se_{50}Te_{30}$  is most stable and the composition  $Ge_{10}Se_{50}Te_{40}$  is less stable.



**Figure 3:** Plot of  $\ln(\alpha/T_g^2)$  versus  $1000/T_g$  for  $Ge_{50-x}Se_{50}Te_x$  ( $x = 10, 20, 30$  and  $40$  at %) chalcogenide glasses.



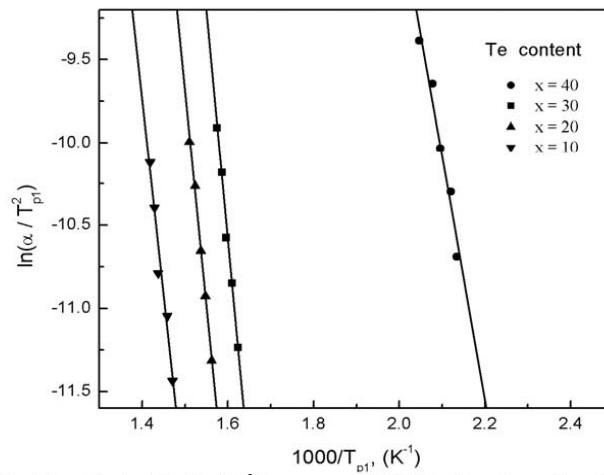
**Figure 4:** Plot of  $\ln \alpha$  versus  $1000/T_g$  for  $Ge_{50-x}Se_{50}Te_x$  ( $x = 10, 20, 30$  and  $40$  at %) chalcogenide glasses.

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

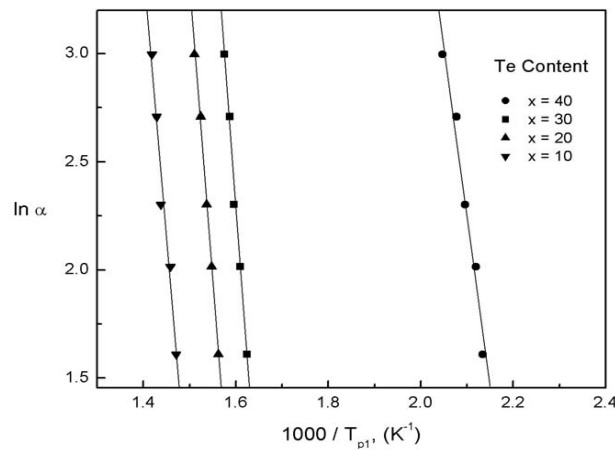
$$\ln(\alpha / T_p^2) = -E_c / RT_p + \text{const} \tag{4}$$

Fig. (5) shows the relation between  $\ln(\alpha / T_{p1}^2)$  versus  $(1 / T_{p1})$  for  $\text{Ge}_{50-x}\text{Se}_{50}\text{Te}_x$  (where  $x = 10, 20, 30$  and  $40$  at %) chalcogenide glasses for the first stage of crystallization. Linear relation was observed and the obtained values of  $E_c$  are listed in Table (3). on the other hand the activation energy of the amorphous-crystalline transformation  $E_c$  can be calculated from the following equation, which correlates the shift in  $T_p$  values with the heating rates [12].

$$\ln \alpha = -E_c / RT_p + \text{const} \tag{5}$$



**Figure 5:** Plot of  $\ln(\alpha / T_{p1}^2)$  versus  $1000 / T_{p1}$  for  $\text{Ge}_{50-x}\text{Se}_{50}\text{Te}_x$  ( $x = 10, 20, 30$  and  $40$  at %) chalcogenide glasses.



**Figure 6:** Plot of  $\ln \alpha$  versus  $1000 / T_{p1}$  for  $\text{Ge}_{50-x}\text{Se}_{50}\text{Te}_x$  ( $x = 10, 20, 30$  and  $40$  at %) chalcogenide glasses.

Fig.(6) shows the Plots of  $\ln \alpha$  versus  $(1/T_{p1})$  for different compositions. The value of deduced by using Eq. (5) for all compositions is listed in table (3).

The activation energy  $E_c$  could be also calculated together with the frequency factor  $K_o$  using the following equation [30].

$$\ln(T_p / \alpha) = E_c / RT_p - \ln K_o \quad (6)$$

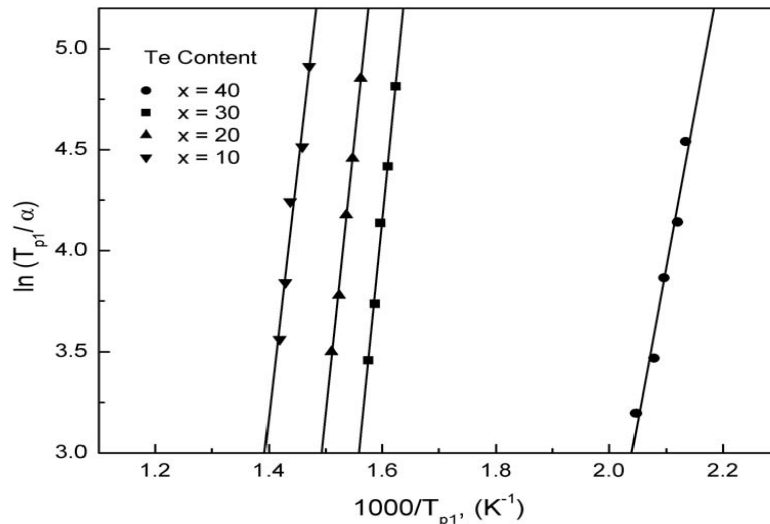
The plot of  $\ln(T_{p1}/\alpha)$  versus  $(T_{p1})$  for the  $Ge_{50-x}Se_{50}Te_x$  glasses for the first peak of crystallization are shown in Fig (7). From the slopes of this function fitted to the data we deduced the values of the activation energy  $E_c$  for the crystallization. In addition, the origin of these straight lines gives the values corresponding to the frequency factor  $K_o$ . The values of  $E_c$  and  $K_o$  are listed in Table (3).

The crystallization reaction rate constant ( $K_p$ ) corresponding to the temperature at which the crystallization rate is maximum, were calculated from the thermograms by using the following condition [31]:

$$\alpha E_c / RK_p T_p^2 = 1 \quad (7)$$

By averaging the values found for each exothermic peak at different heating rates, the values of  $\langle K_p \rangle$  for all studied compositions are listed in table (3).

Glass-forming ability (GFA) can be evaluated in terms of  $\langle K_p \rangle$  [22]. The obtained values indicated the crystallization ability increases with increasing Te concentration, which agree with the conclusions reached by others [32-34]. On the other hand, the frequency factor (which measures the probability of effective molecular collisions for the activated complexes in case), decreases with increasing Te content. This implies high crystallization ability for glasses containing high concentration of tellurium.



**Figure 7: Plot of  $\ln(T_{p1}/\alpha)$  versus  $1000/T_{p1}$  for  $Ge_{50-x}Se_{50}Te_x$  ( $x=10,20,30$  and  $40$  at %) chalcogenide glasses.**

**Table 3:** The activation energy of crystallization ( $E_c$ ), the frequency factor ( $K_o$ ) and The crystallization reaction rate constant  $\langle K_p \rangle$  for various compositions.

	$Ge_{10}Se_{50}Te_{40}$		$Ge_{20}Se_{50}Te_{30}$		$Ge_{30}Se_{50}Te_{20}$		$Ge_{40}Se_{50}Te_{10}$	
	Peak1	Peak2		Peak2	Peak2	Peak2	Peak1	Peak2
$E_c$ {Eq.(5)} kcal/mol	29.263	24.35	54.63	-	51.45	27.39	47.036	53.21
$E_c$ {Eq.(6)} kcal/mol	31.17	26.36	57.11	-	54.03	30.07	49.78	56.12
$E_c$ {Eq.(7)} kcal/mol	29.8	25.36	55.88	-	52.74	28.72	48.40	54.67
$\ln K_o$	28.01	21.23	40.83	-	36.6	17.39	30.92	33.21
$\langle K_p \rangle$	0.0142	-	0.0124	-	0.0114	-	0.0089	-

## Conclusions

- Thermal analysis studies showed that  $Ge_{50-x}Se_{50}Te_x$  (where  $x = 10, 20$  and  $40$  at %) chalcogenide glasses have two overlapping crystalline phases but composition with ( $x = 30$  at %) has one crystalline phase.
- The glass transition temperatures for Ge-Se-Te glasses depend on both heating rate and composition. The observed heating dependence of  $T_g$  was used to evaluate  $E_g$ .
- The calculated values for the activation energies indicate the glass forming ability (GRA) increases with decreasing Te content for Ge-Se-Te glasses.
- The crystallization ability of the system  $Ge_{50-x}Se_{50}Te_x$  chalcogenide glasses increases with increasing Te concentration.

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