



Thermal stability of Ge–As–Te–In glasses

K.A. Aly^{a,*}, A. Dahshan^b, F.M. Abdel-Rahim^a

^a Physics Department, Faculty of Science, Al-Azhar University, Assiut Branch, Assiut, Egypt

^b Department of Physics, Faculty of Science, Suez Canal University, Port Said, Egypt

ARTICLE INFO

Article history:

Received 24 December 2007

Received in revised form 29 February 2008

Accepted 6 March 2008

Available online 14 April 2008

Keywords:

Thermal stability

Differential scanning calorimetry

Glasses

ABSTRACT

The present paper reports the effect of replacement of Te by In on the crystallization kinetics and the thermal stability for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x = 0, 3, \text{ and } 6 \text{ at.}\%$) glasses. Differential scanning calorimetry (DSC) results under non-isothermal conditions for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ glasses were reported and discussed. The thermal stability of the studied glasses has been evaluated using various thermal stability criteria (ΔT , H_r , H_g and S), based on the characteristic temperatures such as the glass transition temperature (T_g), the temperature at which crystallization begins (T_c), the temperature corresponding to the maximum crystallization rate (T_p), or the melting temperature (T_m). Moreover, in the present work, the $K_f(T)$ criterion has been considered for the evaluation of glass stability from DSC data. A comparison of various simple quantitative methods to assess the level of stability for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x = 0, 3, \text{ and } 6 \text{ at.}\%$) glasses is presented.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Chalcogenide glasses exhibit many useful properties including threshold and memory switching [1–3]. These properties are influenced by the structural changes and could be related to thermally induced transitions [4,5]. Memory switches come from the boundaries of the glass-forming regions, where glasses have a tendency to crystallize when heated or cooled slowly [6–8]. Glasses of chalcogen elements were the initial object of study because of their interesting semi-conducting properties [9,10] and more recent importance in optical recording [11]. Recording materials must be stable in the amorphous state at low temperature and have a short crystallization time. Promising materials with these characteristics have been recently studied [12,13]. Therefore, it is very important to know the glass stability of these types of materials. No simple way presently exists to formulate the correlation between the ideal composition and the stability of the glasses. Different simple quantitative methods have been suggested in order to evaluate the level of stability of the glassy alloys. Most of them as Dietzel [14] and Hruby [15] are based on the characteristic temperatures such as the glass transition temperature (T_g), the temperature at which crystallization begins (T_c), the temperature corresponding to the maximum crystallization rate (T_p), or the melting temperature (T_m). Some of the suggested methods [16–17] are based on the crystallization activation energy. The characteristic temperatures

(T_g , T_c , T_p and T_m) are easily and accurately obtained by the differential scanning calorimetry [18] during the heating processes of the glass sample. Dietzel introduced the first glass criterion, $\Delta T = T_c - T_g$ (T_c is the temperature at which crystallization begins), which is often an important parameter to evaluate the glass-forming ability of the glasses. By the use of the characteristic temperatures, Hruby developed the H_r criterion, $H_r = \Delta T / T_m - T_p$ and the compositional dependence of the Hruby coefficient were surveyed by Sestak [19]. On the basis of the H_r criterion, Saad and Poulain [20] obtained two other criteria, weighted thermal stability $H_g = \Delta T / T_g$ and $S = (T_p - T_0) \Delta T / T_g$ criterion where T_0 is the initial temperature.

In the present work, the above-mentioned criteria have been applied to the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x = 0, 3 \text{ and } 6 \text{ at.}\%$) glasses. It is found that the parameters ΔT , H_r , H_g and S decrease with increasing In content. Bearing in mind that, the values of these parameters increase with increasing stability, it is possible to suggest that, the free In content glass, the greater is its glass thermal stability. In addition, a kinetic parameter, $K_f(T)$, with an Arrhenian temperature dependence, is introduced to the stability criteria. $K_f(T)$ increases with increasing In content which confirms that, the free In content glass is the most stable.

2. Experimental details

Different compositions of bulk $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x = 0, 3, \text{ and } 6 \text{ at.}\%$) chalcogenide glasses were prepared starting by Ge, As, Te and In elements with high purity (99.999) by the usual melt quench technique. The elements were heated together in an evacuated (10^{-3} Pa) silica ampoule up to 1250 K, then the ampoule temperature kept constant for about 24 h. During the heating process the ampoules were shaken several times to maintain their homogeneity, then the ampoule was quenched in ice-cooled water to avoid the crystallization process. The amorphous state of the materials was checked using X-ray (Philips type 1710 with Cu as a target and Ni as

* Corresponding author.

E-mail addresses: kamalaly2001@gmail.com (K.A. Aly), adahshan73@yahoo.com (A. Dahshan).

a filter, $\lambda = 1.5418 \text{ \AA}$) diffractometer. The absence of the crystalline peaks confirms the amorphous state of the prepared samples. The elemental compositions of the investigated specimens were checked using the energy dispersive X-ray (Link Analytical Edx) spectroscopy. The compositions so determined agreed with those of the starting materials.

The thermal behavior was investigated using calibrated Shimadzu 50 differential scanning calorimeter. About 15 mg of each sample in powdered form was sealed in standard aluminum pan and scanned over a temperature range from room temperature to about 770 K at different uniform heating rates ($\alpha = 2.5, 5, 10, 15, 20$ and 30 K/min).

3. Theoretical background

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 (χ) by Johnson, Mehl and Avrami equation [21]:

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

where n is an integer or half integer depends 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 that can be expressed as

$$E = \frac{E_N + E_G}{n} \quad (3)$$

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 [21] then:

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

where $n = m$ for the nucleation frequency $I_v = 0$ and $n = m + 1$ for $I_v \neq 0$ [22]. The rate constant K in a non-isothermal DSC experiment was found to changes continually with time due to the change in the temperature, therefore Eq. (1) can be generalized to

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

where $K[T(t')]$ is still given by Eq. (2), and $T(t')$ is the temperature at time t' [22]. 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 Eq. (5) is transformed to temperature integral, yielding:

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

which is represented by several approximate analytical expressions [23]. By using the substitution $y = E/RT'$, the above integral has been represented by the sum of the alternating series:

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

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

$T_0^2(1 - 2RT_0/E) \exp(-E/RT_0)$, where T_0 is initial temperature, then Eq. (6) can be rewritten in the form of

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

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 [21] is found by putting $d^2 \chi / dt^2 = 0$, thus obtaining the relationship:

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

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

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

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

Substituting the last expression for I into Eq. (9), one obtains the relationship:

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

When this relationship is equated to Eq. (10) this gives:

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

or in a logarithmic form:

$$\ln\left(\frac{T_p^2}{\alpha}\right) + \ln\left(\frac{K_0 R}{E}\right) - \frac{E}{RT_p} \approx \left(\frac{2RT_p}{E}\right) \left(\frac{1 - 1}{n^2}\right) \quad (12)$$

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

Note that Eq. (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 [21]. The right-hand side (RHS) of Eq. (12) is generally negligible in comparison to the individual terms on the left hand side for $\alpha \leq 100 \text{ K min}^{-1}$. This approximation in Eq. (12) (RHS) implies:

$$\ln\left(\frac{T_p^2}{\alpha}\right) = \frac{E_c}{RT_p} - \ln\left(\frac{K_0 R}{E}\right) \quad (13)$$

where $E_c = E$ (the activation energy for crystallization) and the quoted approximation might introduce a 3% error in the value of E_c/R in the worst cases. For crystallization processes with spherical nuclei, it has been suggested [21,22] that the dependence of the glass transition temperature on α may be written as

$$\ln\left(\frac{T_g^2}{\alpha}\right) = \frac{E_g}{RT_g} + \text{const.} \quad (14)$$

a straight line between $\ln(T_g^2/\alpha)$ and $1/T_g$, whose slope yields the value of E_g/R where E_g is the activation energy for glass transition and R is the gas constant.

In order to evaluate the thermal stability of glassy materials, Surinach et al. [24] and Hu and Jiang [25] 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 are the tendency to devitrify. The formation of glass is a kinetic process. It is reasonable to assess the glass stability by a

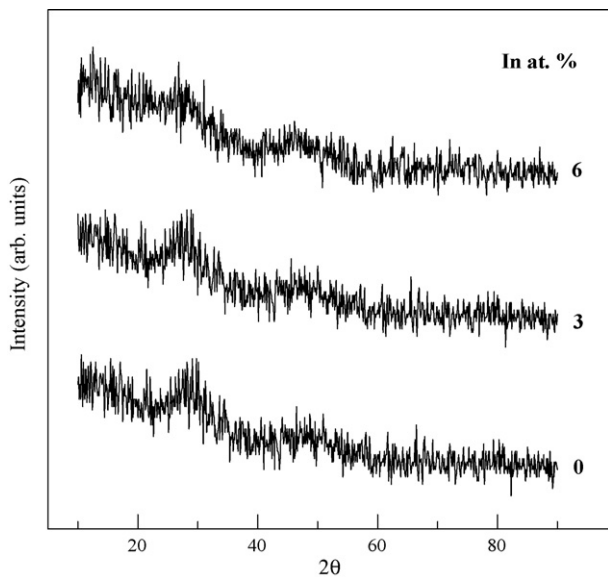


Fig. 1. X-ray diffraction patterns of the amorphous $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x=0, 3$ and 6 at.%) glasses.

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 Eqs. (2) and (15) with respect to temperature and rewrite 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 the parameter $K_r(T)$. Just like the $K(T)$ criteria, the smaller the values of $K_r(T)$, the greater is thermal stability of the glass. The obvious

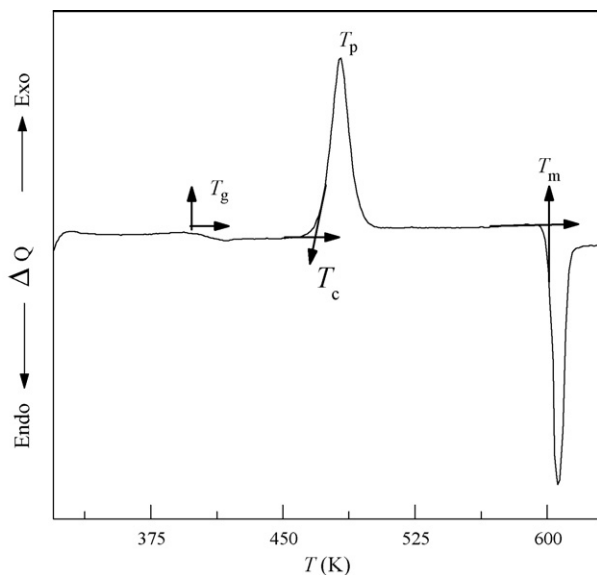


Fig. 2. DSC thermogram of $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65}$ glass recorded at heating rate 10 K/min .

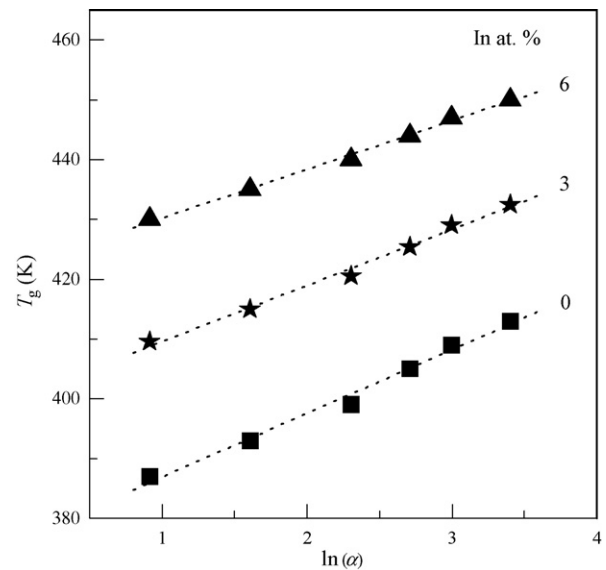


Fig. 3. The plots of T_g vs. $\ln(\alpha)$ for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x=0, 3$ and 6 at.%) glasses.

advantage of this method is that it can evaluate the glass stability over a broad temperature range other than at only one temperature such as T_g or T_p .

4. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x=0, 3$, and 6 at.%) glasses. The absence of the diffraction lines in the X-ray patterns indicates that the glasses have amorphous structures.

Fig. 2 shows the DSC thermogram for the amorphous $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65}$ glass recorded at heating rate 10 K/min . As shown in this figure, there is a very small single endothermic peak. This peak is attributed to the glass transition temperature range which represents the strength or rigidity of the glass structure. Also there is an exothermic peak originating from the amorphous-crystalline transformation. The exo-peak has two characteristic points: the first is

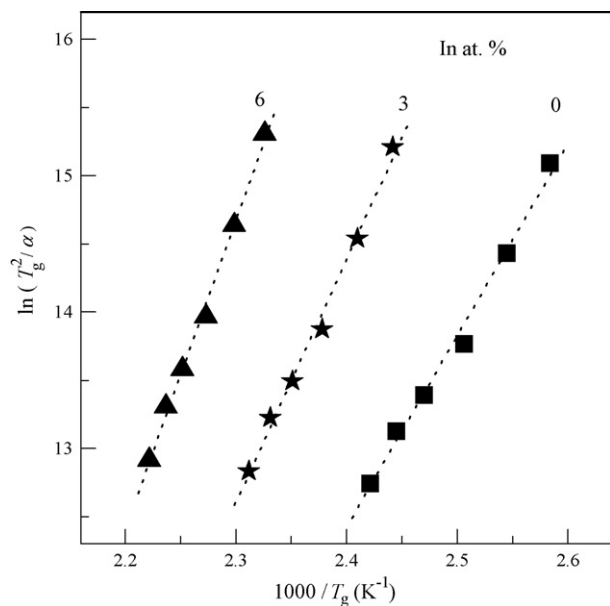


Fig. 4. The plots of $\ln(T_g^2/\alpha)$ vs. $(1/T_g)$ for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x=0, 3$ and 6 at.%) glasses.

Table 1The characteristics temperatures (T_g , T_c , T_p and T_m) and the ΔT , H_r , H_g , S criteria for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x=0, 3$ and 6 at.%) glasses

Composition	α (K/min)	T_g (K)	T_c (K)	T_p (K)	T_m (K)	ΔT (K)	H_r	H_g	S
$\text{Ge}_{15}\text{As}_{20}\text{Te}_{65}$	2.5	387	453	466	580	66	0.579	0.171	2.217
	5.0	393	461	474	590	68	0.586	0.173	2.249
	10	399	469	482	600	70	0.593	0.175	2.281
	15	405	476	490	609	71	0.598	0.176	2.462
	20	409	481	495	615	72	0.600	0.176	2.465
	30	413	486	501	622	73	0.603	0.177	2.651
$\text{Ge}_{15}\text{As}_{20}\text{Te}_{62}\text{In}_3$	2.5	409	462	475	574	52	0.530	0.128	1.731
	5.0	415	469	482	583	54	0.537	0.130	1.757
	10	420	476	490	592	55	0.544	0.132	1.848
	15	425	482	496	599	56	0.549	0.133	1.929
	20	429	486	501	605	57	0.551	0.134	1.943
	30	432	491	506	611	58	0.555	0.135	2.029
$\text{Ge}_{15}\text{As}_{20}\text{Te}_{59}\text{In}_6$	2.5	430	473	484	566	43	0.524	0.100	1.100
	5.0	435	479	490	573	44	0.530	0.101	1.113
	10	440	485	497	581	45	0.536	0.102	1.123
	15	444	490	502	587	46	0.539	0.104	1.243
	20	447	494	506	593	47	0.543	0.105	1.262
	30	450	498	510	598	48	0.545	0.107	1.280

Table 2The coordination number (N_r), the activation energy for glass transition (E_g) and the activation energy for crystallization (E_c) and the frequency factor (K_0) for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x=0, 3$ and 6 at.%) glasses

Composition	N_r	E_g (kJ/mol)	E_c (kJ/mol)	K_0 (s^{-1})
$\text{Ge}_{15}\text{As}_{20}\text{Te}_{65}$	2.50	117.17	125.57	5.53×10^{11}
$\text{Ge}_{15}\text{As}_{20}\text{Te}_{62}\text{In}_3$	2.53	148.72	151.57	1.59×10^{14}
$\text{Ge}_{15}\text{As}_{20}\text{Te}_{59}\text{In}_6$	2.56	190.32	183.63	2.69×10^{17}

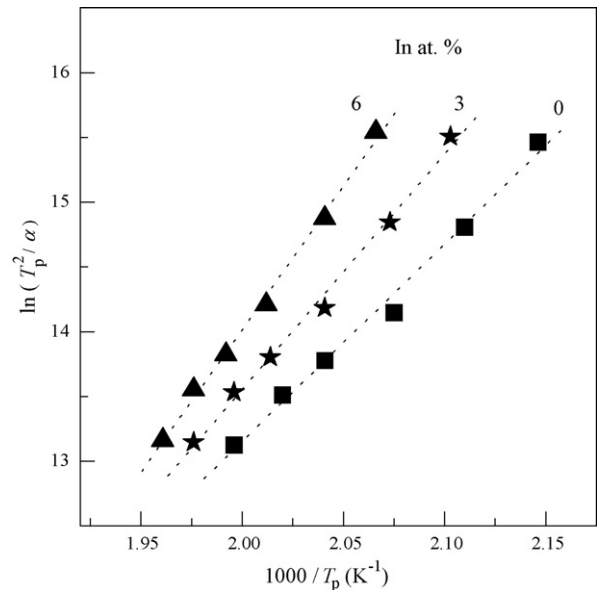
the onset temperature of crystallization (T_c) and the second is the temperature corresponding to the maximum crystallization rate (T_p). The characteristic temperatures (T_g , T_c , T_p and T_m) given by the DSC scans are listed in Table 1.

It is found that the variation of the glass transition temperature as a function of the heating rates follows the empirical relation:

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

where A and B are constants for any given glass composition [26]. Plots of T_g versus $\ln(\alpha)$ for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ glasses as shown in Fig. 3 indicates the validity of Eq. (16) for the studied glasses.

From this figure we can notice that the glass transition temperature increases with increasing the In content. The glass transition temperature is known to depend on several independent parameters such as the average coordination number [27,28]. The average

**Fig. 5.** The plots of $\ln(T_p^2/\alpha)$ vs. $(1/T_g)$, for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x=0, 3$ and 6 at.%) glasses.**Table 3** $K(T_g)$, $K(T_p)$, $K_r(T_g)$, $K_r(T_p)$ criteria for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x=0, 3$ and 6 at.%) glasses

Composition	α (K/min)	$K(T_g)$	$K(T_p)$	$K_r(T_g)$	$K_r(T_p)$
$\text{Ge}_{15}\text{As}_{20}\text{Te}_{65}$	2.5	3.96×10^{-6}	3.191×10^{-3}	65.54	3.16×10^3
	5.0	7.23×10^{-6}	5.550×10^{-3}	70.06	3.44×10^3
	10	1.30×10^{-5}	9.476×10^{-3}	75.45	3.77×10^3
	15	2.25×10^{-5}	0.016	86.19	4.37×10^3
	20	3.31×10^{-5}	0.022	102.07	5.01×10^3
	30	4.75×10^{-5}	0.032	112.22	5.66×10^3
$\text{Ge}_{15}\text{As}_{20}\text{Te}_{62}\text{In}_3$	2.5	7.54×10^{-6}	3.626×10^{-3}	8.98×10^3	2.37×10^5
	5.0	1.36×10^{-5}	6.321×10^{-3}	9.02×10^3	2.45×10^5
	10	2.42×10^{-5}	0.011	9.15×10^3	2.59×10^5
	15	3.98×10^{-5}	0.018	9.86×10^3	2.85×10^5
	20	5.70×10^{-5}	0.025	1.08×10^4	3.11×10^5
	30	8.03×10^{-5}	0.037	1.14×10^4	3.38×10^5
$\text{Ge}_{15}\text{As}_{20}\text{Te}_{59}\text{In}_6$	2.5	1.37×10^{-5}	4.195×10^{-3}	5.48×10^5	1.11×10^7
	5.0	2.44×10^{-5}	7.332×10^{-3}	5.58×10^5	1.14×10^7
	10	4.39×10^{-5}	0.014	5.73×10^5	1.25×10^7
	15	6.89×10^{-5}	0.022	6.11×10^5	1.35×10^7
	20	9.62×10^{-5}	0.030	6.17×10^5	1.40×10^7
	30	1.34×10^{-4}	0.043	6.45×10^5	1.50×10^7

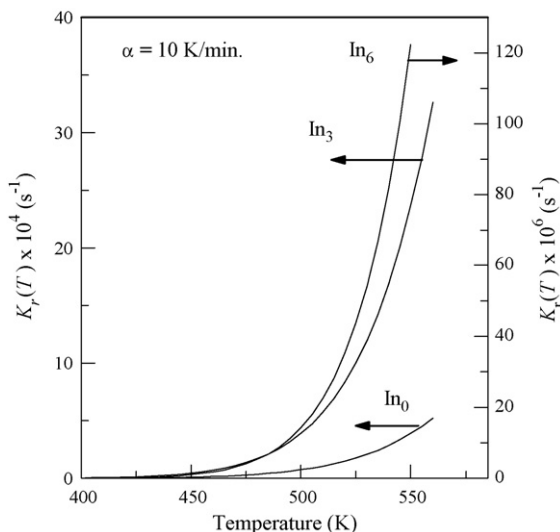


Fig. 6. $K_r(T)$ as a function of temperature T at heating rate $\alpha = 10$ K/min for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x = 0, 3$ and 6 at.%) glasses.

coordination number (N_r) for the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ glasses can be written as [29]:

$$N_r = 4X_{\text{Ge}} + 3X_{\text{As}} + 2X_{\text{Te}} + 3X_{\text{In}} \quad (17)$$

where X is the mole fraction, by using the values of N_r for Ge, As, Te and In as 4, 3, 2, and 3, respectively [30,31], the values of N_r for the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ glasses are obtained. Values of N_r for the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ glasses are listed in Table 2. It can be seen that N_r increases with increasing In content. The increase in the glass transition temperature which is accompanied by an increase in the coordination number can be ascribed to the increase of the rigidity (strength) of the system with increasing the In content.

The thermal stability for the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ glasses can be estimated by using the characteristic temperatures (T_g , T_c , T_p and T_m). The stability criterion parameters (ΔT , H_r , H_g and S) based on the characteristic temperatures are calculated for the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x = 0, 3$, and 6 at.%) glasses and listed in Table 1.

The stability criterion parameters allow the prediction of the glass forming ability of a material. The larger their values, the

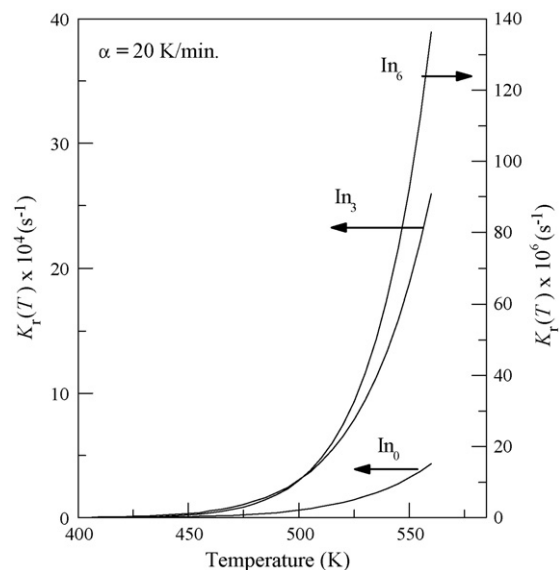


Fig. 7. $K_r(T)$ as a function of temperature T at heating rate $\alpha = 20$ K/min for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x = 0, 3$ and 6 at.%) glasses.

greater the glass thermal stability should be. Table 1 show that ΔT , H_r , H_g and S decrease with the increase of In content, so we can say that the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65}$ glass is the most stable one.

Fig. 4 shows the plots of $\ln(T_g^2/\alpha)$ versus $1/T_g$ according to Eq. (14) for the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x = 0, 3$, and 6 at.%) glasses. From this figure we can obtain the values of the activation energy for glass transition (E_g) of $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ glasses. Values of E_g for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x = 0, 3$, and 6 at.%) glasses were listed in Table 2. Values of E_g for the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ glasses lie within the observed values for chalcogenide glasses [32–34]. As shown in this table E_g increases with the increase of In content. The increase in E_g is due to the increase in T_g (increasing the rigidity) with increasing In content. This result is in good agreement with Cofmenero and Barandiaran [35].

The linear relation of $\ln(T_p^2/\alpha)$ versus $1/T_p$ for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x = 0, 3$, and 6 at.%) glasses are plotted in Fig. 5 to obtain the activation energy of crystallization (E_c) and the frequency factor K_0 . The obtained values of the activation energy of crystallization and the frequency factor are listed in Table 2. It is found that E_c increases with increasing In content, this increase is a result of the increase of T_p with increasing In content.

After known the values of E and K_0 , the kinetic parameters $K(T)$ and $K_r(T)$ for the studied glasses were calculated by using Eqs. (2) and (15). These calculations were carried out to compare the stability sequence of the studied materials. Values of $K(T)$ and $K_r(T)$ for the temperatures T_g and T_p are listed in Table 3. The smaller the values of the two criteria $K(T)$ and $K_r(T)$, is the better the thermal stability of glass should be. The obtained data of these criteria (Table 3) indicates that the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65}$ glass is the most stable one, and the stability orders at different heating rates are $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65} > \text{Ge}_{15}\text{As}_{20}\text{Te}_{62}\text{In}_3 > \text{Ge}_{15}\text{As}_{20}\text{Te}_{59}\text{In}_6$.

Figs. 6 and 7 represent the plots of $K_r(T)$ versus T for $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ ($x = 0, 3$, and 6 at.%) glasses at heating rates 10 and 20 K/min, respectively. From these figures, one can notice that, $K_r(T)$ for the first composition, $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65}$, varies slowly with increasing the temperature indicating a relatively high stability, while it varies more rapidly with increasing T for the other two compositions, which signifies a less stability.

5. Conclusions

The addition of In at the expense of Te in $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ glasses results in an apparent increase in the characteristic temperatures (T_g , T_c and T_p), the activation energy for glass transition and the activation energy for crystallization. The thermal stability for the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65-x}\text{In}_x$ glasses has been evaluated by using various criteria. The $K_r(T)$ criterion has been considered in the present work for the evaluation of glass stability by using DSC data. The obtained results of the $K(T)$ and $K_r(T)$ agree satisfactorily with the ΔT , H_r , H_g and S criteria for the studied glasses. The obtained data of the thermal stability criteria indicates that, the $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65}$ glass is the most stable, and the stability orders at different heating rates are $\text{Ge}_{15}\text{As}_{20}\text{Te}_{65} > \text{Ge}_{15}\text{As}_{20}\text{Te}_{62}\text{In}_3 > \text{Ge}_{15}\text{As}_{20}\text{Te}_{59}\text{In}_6$.

Acknowledgement

The authors thank Al-Azhar University for financial support.

References

- [1] S.R. Ovshinsky, H. Fritzsche, Met. Trans. 2 (1971) 641.
- [2] D. Alder, Sci. Am. 236 (1977) 36.
- [3] E.A. Davis, N.F. Mott, Electronic Processes in Non-Crystalline Materials, Clarendon, Oxford, 1979.
- [4] J.R. Bosnell, C.B. Thomas, Solid State Electr. 15 (1972) 1261.
- [5] C.B. Thomas, A.F. Fratang, J. Bosnell, Philos. Mag. 26 (1972) 617.
- [6] J.A. Savage, J. Mater. Sci. 7 (1972) 64.

- [7] J. Cornet, *Ann. Chem.* 10 (1975) 239.
- [8] S.C. Moss, J.P. Deneufville, *Mater. Res. Bull.* 79 (1972) 423.
- [9] K. Tanaka, Y. Osaka, M. Sugi, S. Iizima, M. Kikuchi, *J. Non-Cryst. Solids* 12 (1973) 100.
- [10] A.A. Othman, K.A. Aly, A.M. Abousehly, *Thin Solid Films* 515 (2007) 3507–3512.
- [11] Y. Sugiyama, R. Chiba, S. Fugimori, N. Funakoski, *J. Non-Cryst. Solids* 122 (1990) 83.
- [12] S. Fugimori, S. Sagi, H. Yamazaki, N. Funakoski, *J. Appl. Phys.* 64 (1988) 100.
- [13] Y. Maeda, H. Andoh, I. Ikuta, M. Magai, Y. Katoh, H. Minemura, N. Tsuboi, Y. Satoh, *Appl. Phys. Lett.* 54 (1989) 893.
- [14] A. Dietzel, *Glasstech. Ber.* 22 (1968) 41.
- [15] A. Hruby, *Czech. J. Phys. B* 22 (1972) 1187.
- [16] A. Marotta, A. Buri, F. Branda, *J. Non-Cryst. Solids* 95/96 (1987) 593.
- [17] X. Zhao, S. Sakka, *J. Non-Cryst. Solids* 95/96 (1987) 487.
- [18] Z.U. Borisova, *Glassy Semiconductors*, Plenum, New York, 1981.
- [19] J. Sestak, *J. Therm. Anal.* 33 (1988) 75.
- [20] M. Saad, M. Poulain, *Mater. Sci. Forum* 19/20 (1987) 11.
- [21] W.A. Johnson, K.F. Mehl, *Trans. Am. Inst. Min. Eng.* 135 (1981) 315.
- [22] S. Mahadevan, A. Giridhar, A.K. Singh, *J. Non-Cryst. Solids* 88 (1986) 11.
- [23] M. Abramowitz, I.E. Stegun, *Handbook of Mathematical Functions*, Dover, New York, 1972.
- [24] S. Surinach, M.D. Baro, M.T. Clavaguera-Mora, N. Clavaguera, *J. Mater. Sci.* 19 (1984) 3005.
- [25] L. Hu, Z. Jiang, *J. Chin. Ceram. Soc.* 18 (1990) 315.
- [26] M. Lasocka, *Mater. Sci. Eng.* 23 (1976) 173.
- [27] J.J. Tauc, in: F. Abeles (Ed.), *The Optical Properties of Solids*, North Holland, Amsterdam, 1970, p. 227.
- [28] Ch. Hurst, E.A. Davis, in: J. Stuke, W. Brenig (Eds.), *Amorphous and Liquid Semiconductors*, Taylor and Francis, London, 1974, p. 349.
- [29] N. Yamaguchi, *Phil. Mag.* 51 (1985) 651.
- [30] L. Tichy, H. Ticha, *J. Non-Cryst. Solids* 189 (1995) 141.
- [31] J.M. Saiter, J. Ledru, G. Saffarini, S. Benazeth, *Mater. Lett.* 35 (5/6) (1998) 309.
- [32] A.A. Othman, K.A. Aly, A.M. Abousehly, *Phys. Stat. Sol. a* 203-5 (2006) 837.
- [33] P.L. Lopez-Aleman, J. Vazquez, P. Villares, R. Jimenez-Garay, *J. Mater. Process. Technol.* 143/144 (2003) 512.
- [34] A.A. Othman, H.H. Amer, M.A. Osman, A. Dahshan, *J. Non-Cryst. Solids* 351 (2004) 130.
- [35] J. Cofmenero, J.M. Barandiaran, *J. Non-Cryst. Solids* 30 (1979) 263.