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Kinetic Studies of Bulk $Se_{70}Ge_{30-X}M_x$ { X = 0, 5 & M = Ag, Cd, Pb} Chalcogenide Semiconducting Glasses

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Abstract

The thermal stability and crystallization of Se-Ge and Se-Ge-M alloys (M = Cd, Ag, Pb) were studied by differential thermal analysis (DTA). A comparison of various simple quantitative methods to assess the level of stability of the glassy materials in the above mentioned system is presented. All of these methods are based on characteristic temperatures, obtained by heating of the samples in non-isothermal regime, such as the glass transition temperature, T_g , the temperature at which crystallization begins, T_{in} , the temperature corresponding to the maximum crystalliztion rate, T_p , and the melting temperature, T_m. In this work the thermal stability has been evaluated experimentally and correlated with the activation energies of glass transition and crystallization by this kinetic criterion and compared with those evaluated by other criteria.

Introduction

Glassy alloys of chalcogen elements were the initial subject of study because of their interesting semiconducting properties [1] and more recent importance in optical recording [2]. Recording materials must be stable in the amorphous state at low temperatures and have a short crystallization time. Selinium alloy films, in particular, are used as recording media as they have a low melting temperature and high absorption coefficient for the wavelengths of semiconducting lasers. Infrared transmitting glasses based on Se-Ge and some additive such as Cd, Ag, Pb, and Sb are technologically important because they have a wide IR transmittance range. The applications include fabrication of optical components like IR lenses, windows and filters used in thermal imaging systems. The above mentioned glassy system are also characterized by high sensitivity to UV radiation, and exhibit mechanical, optical and structural changes [3, 4]. Glass-forming regions were studied by several authors [5-10]. Therefore, it is very important to know the glass stability and chemical durability of these materials. However, no simple way presently exists to formulate the correlation between ideal composition and stability of the glasses. With object to evaluate the level of stability of the vitreous alloys, different simple quantitative methods have been suggested. Most of these methods [11-15] are based on characteristic temperatures such as the glass transition temperature, T_g , the crystallization temperature, T_{in} , or the melting temperature, T_m. Some of them [16, 17] are based on the reaction constant, K. some of others [18-20] are based on crystallization activation energy. These thermal parameters are easily and accurately obtained by differential thermal analysis (DTA) during the heating process of glass samples. Dietzel [11] was able to evaluate the glass forming ability of the glasses, by the criterion,

$$H_r = \Delta T / T_m - T_{in}$$

where

$$\Delta T = T_{in} - T_g$$

where T_{in} is the temperature at which crystallization begins, which is often an important parameter.

Saad and Poulain [15] obtained two other criteria, weighted thermal stability; H' and S criterion, $H' = \Delta T / T_g$, $S = (T_p - T_{in})\Delta T / T_g$, respectively.

The present work is aiming at determining the above mentioned criteria determined and applied to the alloys Se-Ge-M (M = Cd, Ag, Pb) and the study of crystallization kinetics in amorphous materials by using several theoretical models and equations suggested to explain the crystallization kinetics.

Experimental Procedure

Bulk glassy $Se_{70}Ge_{30}$ and $Se_{70}Ge_{25}M_5$ alloys (M = Ag, Cd, Pb) were prepared from commercial elements from Blazers company having high purity (5N). Selenium, Germanium, Silver, Cadmium and lead in the appropriate atomic percentage; proportions were weighed using an electric balance and sealed in an evacuated10^{-5} torr silica tube.

The contents of the tube (5g) were heated at 1000 ^{0}C for 24 h. Shaking the ampule frequently during heating improved the homogenity of the melt. Quenching was carried out into iced water to obtain the glass. The amorphicity of the alloy obtained was checked by X- ray diffractometry.

Thermal behavior of the four samples of the system were investigated using a Shimadzu DTA-50 differential thermal analysis. Its runs were taken at four different heating rates, α= 5, 10, 20 and 30 ^{0}C /min on accurately weighed samples taken in a platinum pans. The temperature range covered in DTA was from room temperature to 800 ^{0}C. Through out this paper the experimental data points were taken and the best fit for the results was calculated by the least- square method.

Results

The DTA thermograms were recorded at different heating rate, $\alpha = 5$, 10, 20 and 30 ^{0}C /min, for the $Se_{70}Ge_{30}$ and $Se_{70}Ge_{25}M_5$ (M= Ag, Cd, Pb) chalcogenide glass. A typical DTA trace of the as- prepared samples at a heating rate of 10 ^{0}C/ min is shown in Fig.(1).

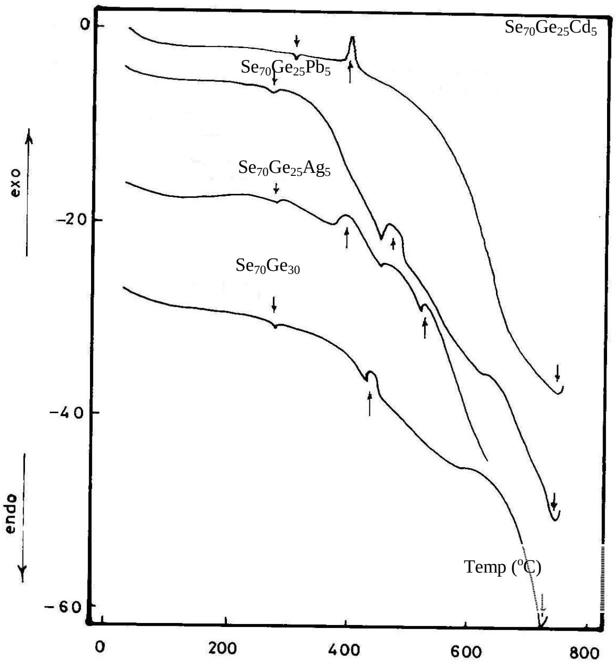

Figure 1: DTA traces of $Se_{70}Ge_{30-x}M_x$ alloys where {M=Ag, Cd, Pb} and {x=5}.

Three characteristic phenomena are resolved in the studied temperature region. The first (T_g) corresponds to the glass transition temperature. The second (T_{in}) corresponds to the peak temperature of the crystallization and the third (T_m) corresponds to the melting temperature of chalcogenide glasses. This behavior is typical for a glass-crystalline transformation.

Fig. (2) shows the DTA traces of the SeGe as an example at different heating rates $\alpha = 5$, 10, 20 and 30 ^{0}C/ min. Obviously, the three characteristic temperatures increase with increasing the heating rate.

Discussion

Two approaches are used for analyzing the dependence of T_g on the heating rate. The first depicts the variation of the glass transition temperature T_g with the heating rate (α) for glasses as shown in Fig. (3) which is found to obey the emprical relation [21]

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

where A and B are characteristic constants. The constant B indicates the response of the configuration changes within the glass transition region to the heating rate.
The values of A and B in Eq.(1) are determined by the least squares line fitting method and listed in Table (1). This relation was originally suggested by Lasocka [22]. The second approach for analyzing T_g is based on the Kissinger's linear dependence [23] in the form

$$\ln\left(\alpha/T_g^2\right) = -E_t/RT_g + \text{constant} \qquad (2)$$

where E_t is the activation energy of the glass transition for homogenous crystallization with spherical nuclei and R is the gas constant. Equation (2) was used by several authors [24-26] to calculate E_t. Fig.(4) shows the variation of $\ln(\alpha/T_g^2)$ versus $1/T_g$ for the glasses $Se_{70}Ge_{30}$ and $Se_{70}Ge_{25}M_5$ (M= Ag, Cd, Pb) .

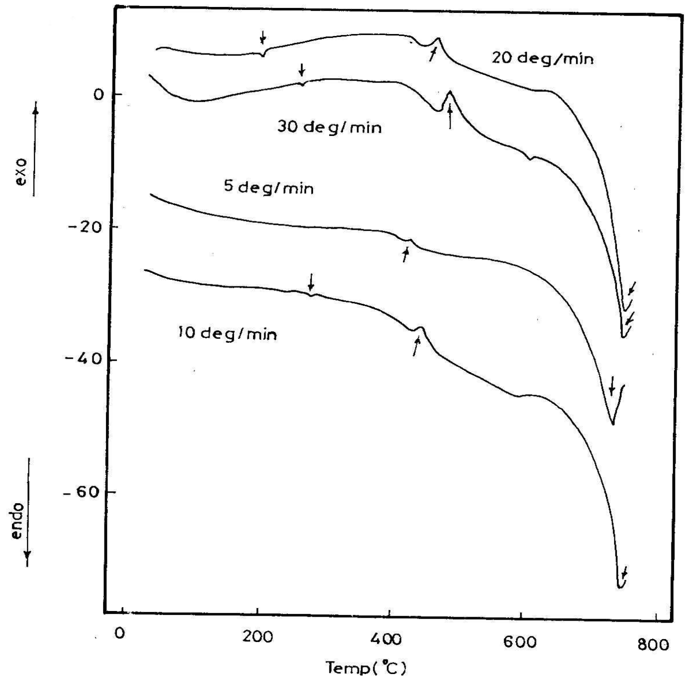

Figure 2: DTA traces of $Se_{70}Ge_{30}$ chalcogenide glass at different heating rates.

Table 1: The flitting parameter to eq. 1 for the glassy alloy.

Glassy alloy	**T_g (K)=A+Blnα**	**T_c (K)= A+Blnα**
SeGe	T_g=721.8-74 lnα	T_c=663.7+18.43lnα
SeGeCd	T_g=787.55-99.2 lnα	T_c=630.7+19.24lnα
SeGePb	T_g=747.9-88.3 lnα	T_c=735.17+3.39lnα
SeGeAg	T_g=865.2-135.6 lnα	T_c=339.21+25.73lnα

The solid lines represent the best straight lines fitting to the experimental data points. The values of E_t for all glassy alloys are calculated from the slope of each straight line and are listed in Table (2).

The Mahedeven et al. approximation [25] could be used. The variation of $\ln(1/T_g^2)$ with ln α is considered to be less than that of $(1/T_g)$ with ln α So the equation (2) can be simplified to

$$\ln \alpha = -\frac{E_t}{RT_g} + \text{constant} \tag{3}$$

Fig. (5) depicts the variation of ln α versus $1/T_g$ for the studied glasses.

The values of E_t for all glassy alloys are calculated from the slope of each straight line and are listed in Table (2).

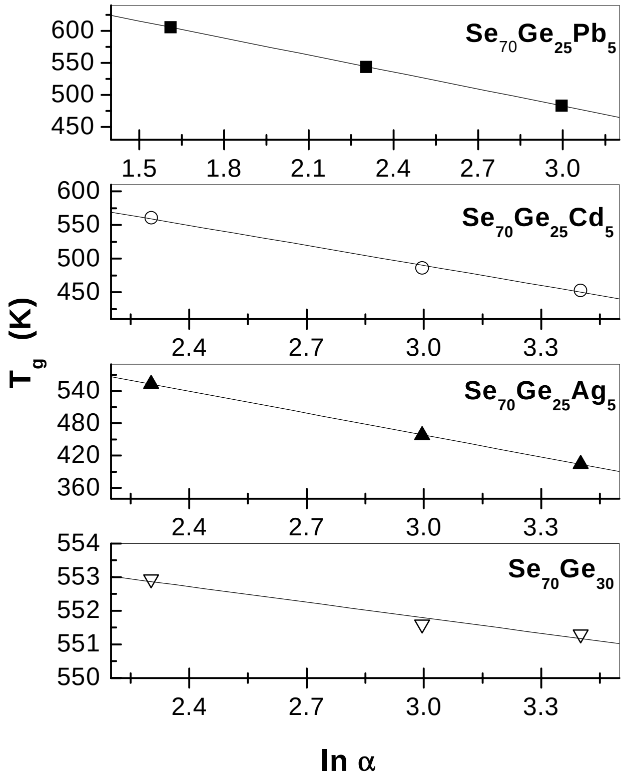

Figure 3: T_g versus ln (α) for $Se_{70}Ge_{30-x}M_x$ alloys, where {M=Ag, Cd, Pb} and {x=5}.

Equation (3) was used by several authors to calculate E_t for different glasses [27, 28]. From Table (2), it can be noticed that the values of E_t calculated from equation (2) and (3) (for each glassy alloy) are in good agreement with each other.

The activation energy for crystallization E_c which depends on the onset temperature of crystallization T_{in} as a function of the heating rate α could be evaluated and discussed using Kissinger's formula [23]. For homogenous crystallization with spherical nucleation, it is shown that the dependence of T_{in} on (α) is given by [26-29]

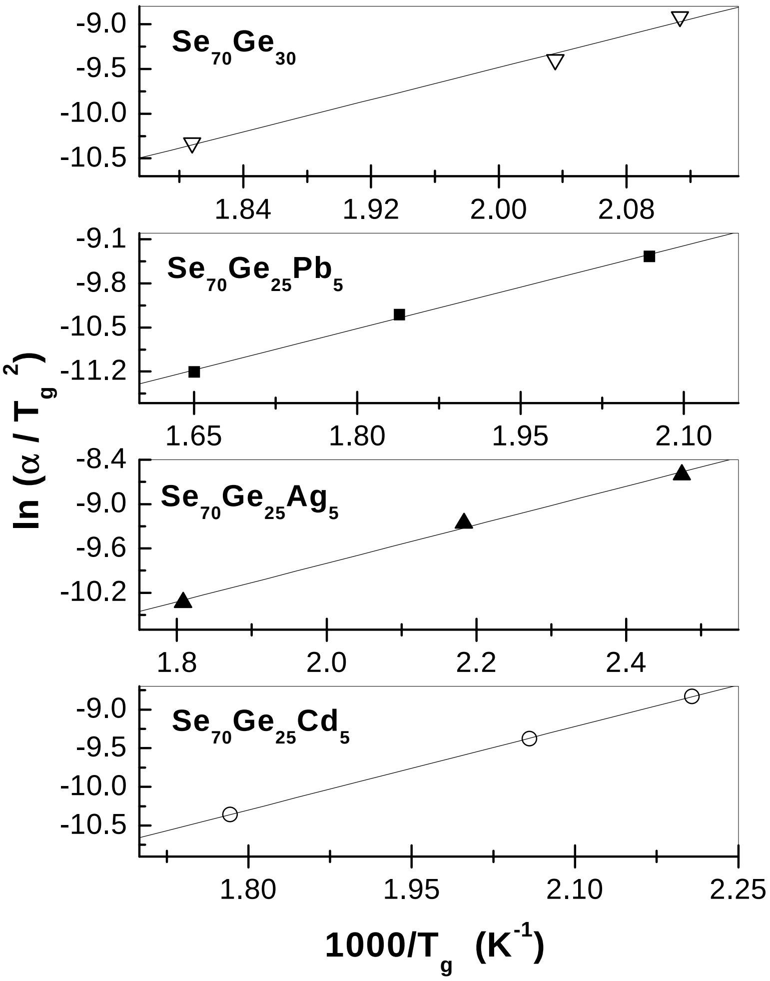

Figure 4: ln (α / T_g^2) versus ($1000/T_g$) for $Se_{70}Ge_{30}$ and $Se_{70}Ge_{30-x}M_x$ alloys where {M=Ag, Cd, Pb} and {x=5}.

$$\ln\left(\alpha \big/ T_{in}^2 \right) = - E_c \big/ RT_{in} + \text{constant} \qquad (4)$$

where E_c is the activation energy of crystallization. Fig. (6) illustrates the variation of $\ln(\alpha/T_{in}^2)$ versus $1/T_{in}$ for the glasses $Se_{70}Ge_{30}$ and $Se_{70}Ge_{25}M_5$ (M= Cd , Ag, Pb)

The solid lines represent the best straight lines fitting to the experimental data points. The value of E_c (for each glassy alloy) was calculated from the slope of each straight line and are listed in Table (3). According to Mahedeven et al. approximation [25]. It should be noted that the change of $\ln(T_{in}^2)$ with α is negligibly small compared with the change of ln α, and therefore, it is possible to write

$$\ln\alpha = - E_c \big/ RT_{in} + \text{constant} \qquad (5)$$

The variation of ln α versus $1/T_{in}$ for all glasses are shown in Fig. (7).

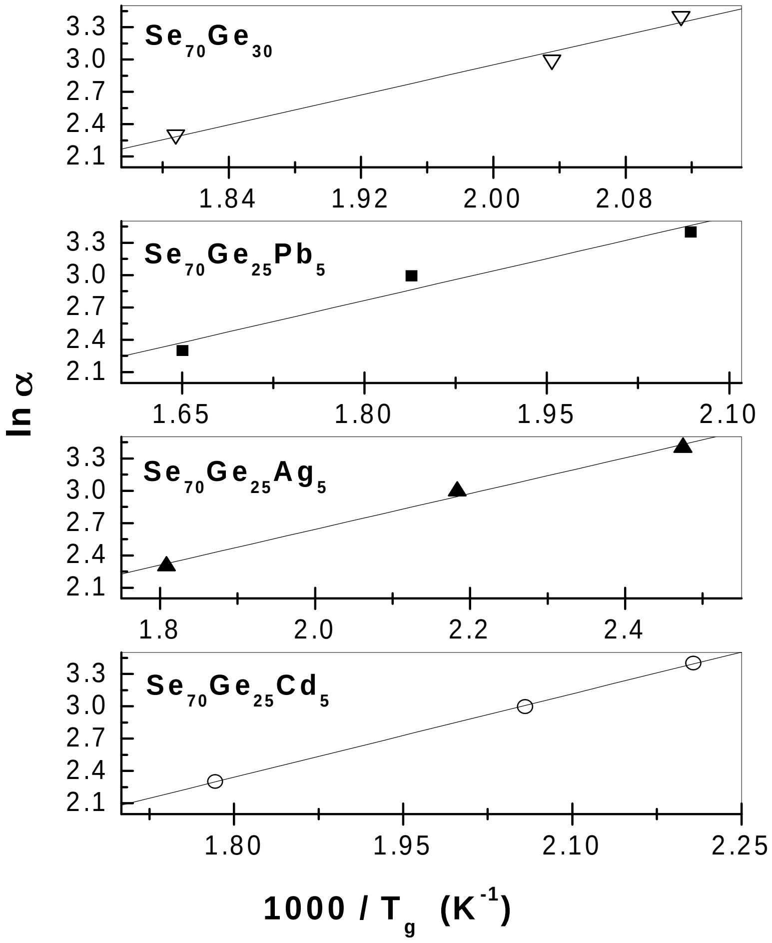

Figure 5: ln (α) versus (1000/T_g) for $Se_{70}Ge_{30}$ and $Se_{70}Ge_{30-x}M_x$ alloys where {M=Ag, Cd, Pb} and {x=5}.

The values of E_c (for each glassy alloy) are calculated and listed in Table Ш. From this table, it can be noticed that the value of E_c calculated from equations (4) and (5) for each glassy alloy, are in good agreement with each other. The range of the values of E_c agree well with those obtained for other chalcogenide glasses [25, 30].

The kinetics of crystallization have been obtained using the method suggested specifically for non- isothermal crystallization, the volume fraction χ of crystals precipitated in a glass heated at a uniform rate α is related to E_c by the expression [31]

$$\ln(-\ln(1-\chi)) = -n\ln\alpha - 1.052mE_c / RT + \text{constant} \qquad (6)$$

where m and n are numerical factors depending on the mechanism of nucleation and growth.

The volume of crystal fraction χ at any temperature T is given by $\chi = (S_t / S)$, where S_t is the area between T_{in} and T, S is the total area of isothermal peak between T_{in} and T_f , where the crystallization is completed. The assumption is made that the extent of crystallization is proportional to the relevant area under the DTA peak.

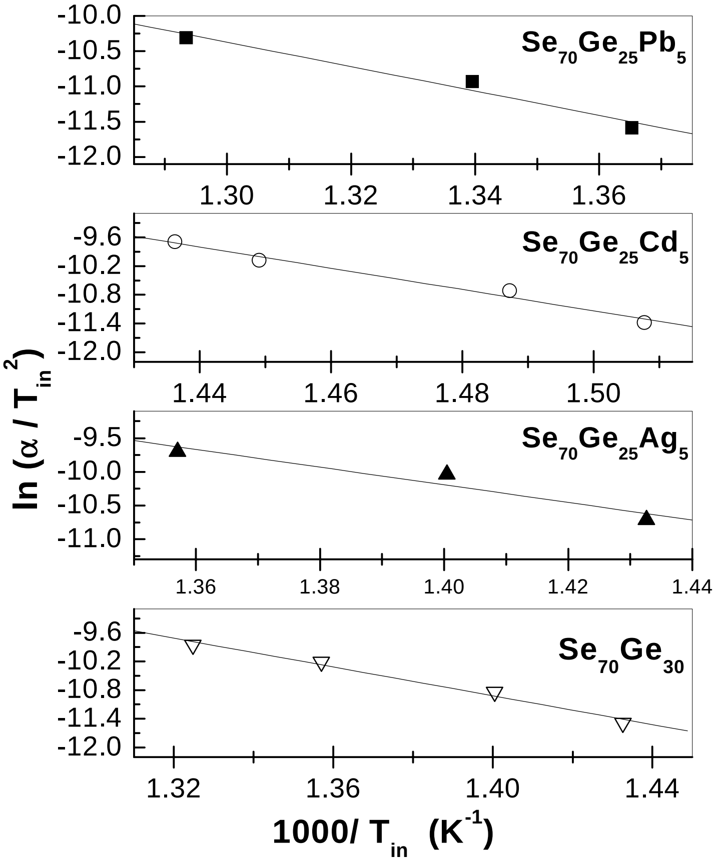

Figure 6: ln (α / T_{in}^2) versus $(1000/T_{in})$ for $Se_{70}Ge_{30}$ and $Se_{70}Ge_{30-x}M_x$ alloys where {M=Ag, Cd, Pb} and {x=5}.

A plot of ln (- ln $(1-\chi)$) vs. (1 / T) data for $Se_{70}Ge_{30}$ glassy alloy as an example, measured at different heating rates, gives straight lines over most of the temperature range as shown in Fig. (8).

From the slope of each straight line the (mE_c) value for these glasses is calculated. The average value of (mE_c) is obtained by considering all of the heating rates. It is also possible to evaluate ln (-ln $(1-\chi)$) as a function of ln α at any fixed temperature as shown in Fig. (9). The slope of the dependence of ln (-ln $(1-\chi)$) versus ln α yields values of exponent n. the average values of n are listed in Table (III).

It is known that $n = m + 1$ [31], in the case when nuclei predominantly form during the heating at constant rate, and $n = m$, in the case, when nuclei are formed before thermal analysis.

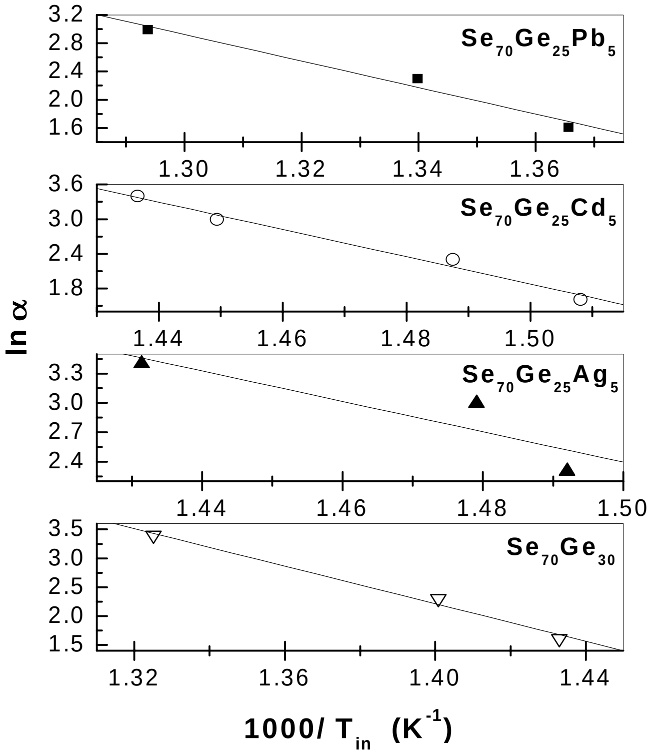

Figure 7: ln (α) versus (1000/ T_{in}) for $Se_{70}Ge_{30}$ and $Se_{70}Ge_{30-x}M_x$ where {M=Ag, Cd, Pb} and {x=5}.

The relation between glass transition temperature and the forming glass ability

The first criterion is the difference $\Delta T = (T_{in} - T_g)$ [11]. Usually, unstable glasses show a crystallization peak near to the glass transition temperature, though for stable glasses the crystallization peak is close to the melting temperature. This difference gives an indication of the thermal stability of the glasses [25]. A short temperature interval of (T_{in} - T_g) signifies that the glass contains structural units with a high crystallization tendency. In the first approximation, (T_{in} - T_g) is independent of the heating rate α since both T_{in} and T_g increase with increasing α. Therefore the values of (T_{in} - T_g) for each glass composition are averaged over all heating rates. The values of (T_{in} - T_g) are listed in table (4) for all glassy alloys. From this table, it can be observed that the glassy alloy $Se_{70}Ge_{30}$ is the most stable one, since its value of ($T_{in} - T_g = 229.4$ K) is the largest among all glasses. On the other hand, the glassy alloy $Se_{70}Ge_{25}Cd_5$ is the least stable one ($T_{in} - T_g = 186.21$ K), i.e. it has the highest tendency towards crystallization.

The glass-forming tendency

The coefficient of glass forming tendency could be calculated by the method of Hruby [14] and that modified by Saad and Poulain [15, 32]. The calculations listed in Table (4).

According to the values of H_r which are correlated with the relative ease of forming the material as a glass, it is found that if the value of H_r is equal to or less than 0.1 then the glass is usually difficult to be prepared [33]. Normally H_r should have values equal to or greater than 0.4 for good glass formers. The values of H_r, calculated for all glassy alloys and listed in table (4). It can be noticed from this table that the values of H_r follow the same trend as that of ΔT.

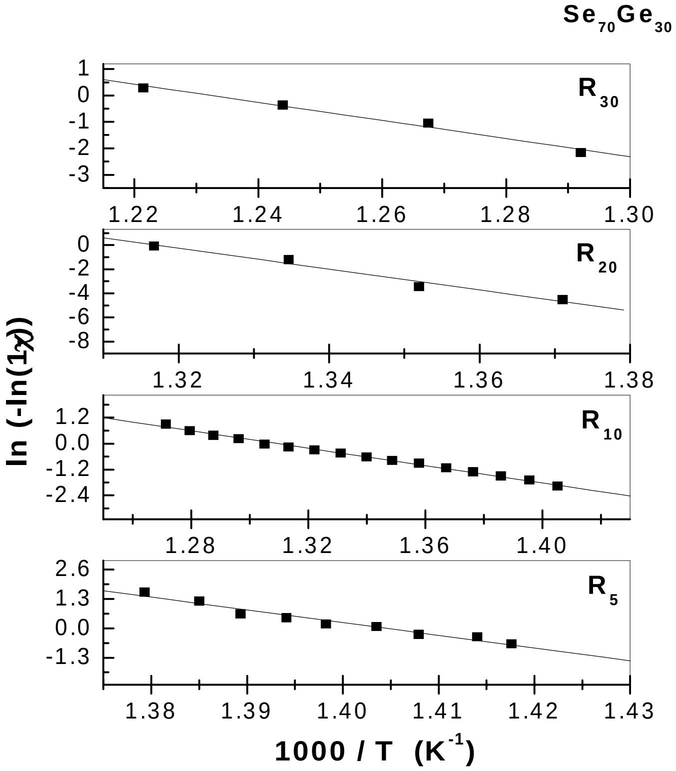

Figure 8: ln[-ln(1-x)] versus (1000/T) for $Se_{70}Ge_{30}$ glassy alloy.

Table 2: The value of the activation energy of the glass transition as determined using two different methods

Method	**SeGe**	**SeGeCd**	**SeGePb**	**SeGeAg**
Kissinger	35.99	28.73 (kJ/mole)	35.07 (kJ/mole)	20.82 (kJ/mole)
Mahedeven	27.78	20.64 (kJ/mole)	20.78 (kJ/mole)	13.26 (kJ/mole)

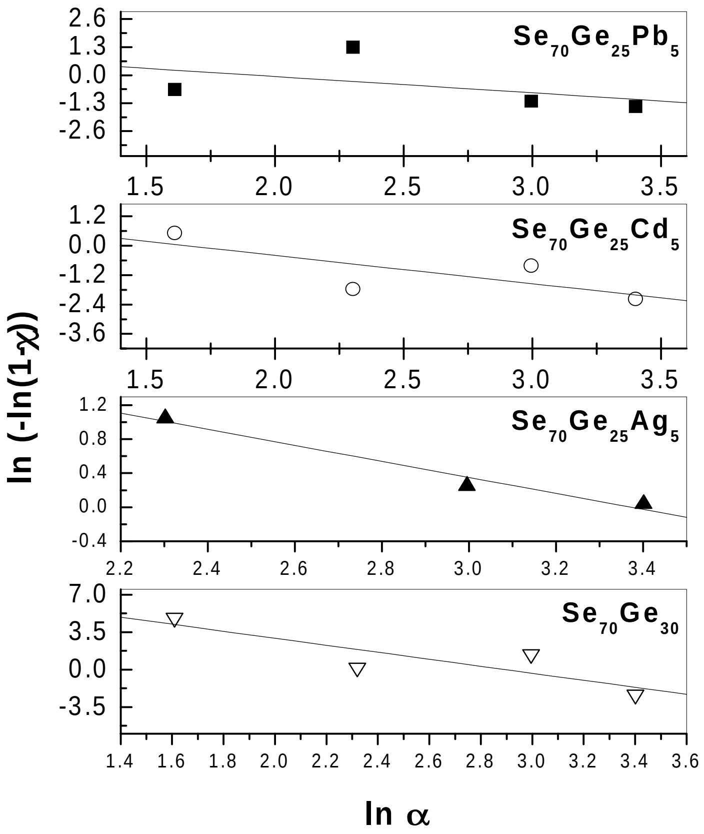

Figure 9: ln[-ln(1-x)] with ln (α) at constant temperature for $Se_{70}Ge_{30}$ and $Se_{70}Ge_{30-x}M_x$ alloys where {M=Ag, Cd, Pb} and {x=5}.

Table 3: The value of the activation energy of crystallization obtained from different methods

Method	SeGe	SeGeCd	SeGePb	SeGeAg
Kissinger	120.58	177.99	138.22	113.34
Mahedeven	129.85	188.88	150.25	124.12
Matusita	132.54	235	208.36	138.82
Ozwa n=	2.28	1.15	0.78	1.19

The relation between T_g and T_m

A simple theoretical relationship between T_g and T_m was suggested by Kauzmann [34]. When T_g and T_m are expressed in degree Kelvin, Kauzmann found that the ratio between T_g and T_m is almost constant and equals 2/3, or $\frac{T_g}{T_m} \approx \frac{2}{3}$

This is also known as the “two-third rule”. It is found that the value of T_g/T_m is the same for all glassy alloys, hence the “two- third rule” seems to be applied as indicated in table (4). It was found that the “two- third rule” holds fairly well for other chalcogenide glasses such as Ge-Bi-Se-Te [35], $Se_{98-x}S_xSn_2$(x=8,18) and $Se_{77}S_{20}X_3$ [36].

Table 4: The values of ΔT, T_m-T_{in}, H_r, T_g/T_m, H' and S for different samples

Glassy alloy	**SeGe**	**SeGeCd**	**SeGePb**	**SeGeAg**
$\Delta T=T_{in}-T_g$ (K)	229.41	186.21	206.09	191.43
T_m-T_{in} (k)	307.43	315.6	264.82	116.15
$H_r= \Delta T/T_m-T_{in}$	0.75	0.59	0.78	1.6
T_g/T_m	0.54	0.57	0.53	0.69
$H' = \Delta T/ T_g$	0.98	0.82	0.76	0.61
$S=(T_p–T_{in})\Delta T/T_g$	18.94	12.45	17.93	24.61

Conclusions

The obtained results of DTA measurements on the glass of the system $Se_{70}Ge_{30-x}M_x$ with (x = 0 and 5), where (M= Ag, Cd, Pb), show that:

1 The characteristic crystallization parameters T_g, T_{in}, T_p, E_t, and E_c for these glasses are dependent on both the glass composition and heating rates.

2 The average value of Avrami index $n \approx 2$ for glass $Se_{70}Ge_{30}$ indicates volume nucleation and one dimensional growth mechanism, while $n \approx 1$ for the ternary glasses indicates surface nucleation in one dimensional crystal growth.

3 The calculated value of activation energy and the glass transition reflect the high rigidity for Se-Ge compared with Se-Ge-Cd.

4 The dependence of T_p on the heating rate reveals the crystallization of these glasses is a thermally activated process.

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