

Calorimetric studies on $\text{Ge}(\text{Se}_{1-x}\text{S}_x)_2$ chalcogenide glasses

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Bulk glasses of the system $\text{Ge}(\text{Se}_{1-x}\text{S}_x)_2$ where $x = 0, 0.1, \text{ and } 1$ are prepared by the known melt quenching technique. Non-isothermal differential thermal analysis (DTA) measurements of as quenched $\text{Ge}(\text{Se}_{1-x}\text{S}_x)_2$ $x = 0, 0.1, \text{ and } 1$ chalcogenide glasses reveal that the characteristic temperatures e.g. the glass transition temperature (T_g), the temperature corresponding to the maximum crystallization rate (T_p) are recorded and strongly dependent on heating rate and compositions. Upon heating these glasses show a single transition temperature (T_g) and (T_p). The activation energies of glass transition (E_t) and crystallization E_c are evaluated by different methods. Most of the above mentioned glassy compounds have two-dimensional growth mechanism, according to the average value of avrami index (n). The calculated average values of activation energies of crystallization are used for the estimation of the thermal stability as well as the glass-forming tendency.

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1. Introduction

Great attention has been paid to chalcogenide glasses in recent years, mainly due to their wide range of applications in solid state devices both in scientific and technological fields [2] these glasses exhibit unique IR transmission and electrical properties that make them useful for several applications such as threshold switching, memory switching, inorganic photoreceptors, IR transmission and detection through lenses and optical wave-guides e.g. in welding and surgery, moreover these alloys exhibit the property of reversible transformation. This property makes these systems very useful in optical memory.

Glasses are amorphous in nature i.e. they form a disordered and metastable structure. It is possible to change continuously the elemental ratios in glass compounds due to the lack of translational symmetry; the properties of such substances strongly depend on the character and concentration of chemical bonds, which hold the atoms together in the glassy network. Since the variation of glass transition temperature (T_g) with heating rate [4, 5] and composition [6] is of sufficient importance for amorphous materials. These papers report the differential thermal analysis (DTA) measurements on GeSeS compositions and define the glass transition temperature (T_g) and the crystallization temp. (T_c), both are dependent on heating rate as well as composition.

Kinetics studies are always connected with the concept of activation energy. The activation energy in the glass crystallization phenomena is associated with nucleation and growth processes. Studies of the crystallization of a glass upon heating can be performed in several different ways and the crystallization process can be interpreted in terms of several theoretical models [7-10]. The study of crystallization kinetics using the differential thermal analysis (DTA) methods has been widely discussed in the literature [11-15]. Thermally

activated transformations in the solid state can be investigated by isothermal or non-isothermal experiments [16-18].

There are large varieties of theoretical models and theoretical functions proposed to explain the crystallization kinetics. The application of each of them depends on the type of amorphous material studied and how it is made. For glassy materials obtained in bulk form, which is the case of the alloys submitted to continuous heating experiments, the reaction rate of the process can be expressed as the product of two separable functions of absolute temperature and the fraction crystallized, thus satisfactory kinetic parameters (activation energy, E , and reaction order, n) for describing the crystallization reactions can be obtained.

2. Material preparation

High purity (5N) Ge, Se and S in appropriate proportions were weighted and sealed in evacuated silica tube under a vacuum of 1.33×10^{-3} Pa. The sealed tubes were then heated at 300 °C for 1hr then raised the temperature gradually up to 1000 °C over about 8hrs in rotary furnace, then quenched in ice cold water. The prepared ingots were confirmed to be completely amorphous with X-ray diffraction model (Diano Corporation). On the other hand the chemical composition were determined by energy dispersive X-Ray analysis (EDX) attached to a Scanning electron microscope (Joel - 5400) ensure good homogeneity.

3. Experimental technique

The glasses, thus prepared, were ground to make fine powder for DTA studies. This technique is particularly important due to the fact that: 1) It is easy to carry out; 2)

it requires little sample preparation; 3) it is quite sensitive; 4) it is relatively independent of the sample geometry.

The thermal behavior was investigated using differential thermal analyzer (shimadzu DTA-50). The melting temperature and melting enthalpy of light purity indium was used to calibrate the temperature and energy of the instrument, and the measurements were carried out under nitrogen atmosphere. The DTA was carried out on powder samples. The accuracy of the heat flow is ± 0.01 mv and the heating rates were varied from 10 to 30° C/min

The glass transition temperature was considered as a temperature corresponding to the intersection of the two linear portions adjoining the transition elbow in the DTA traces, as shown in Fig. 1.

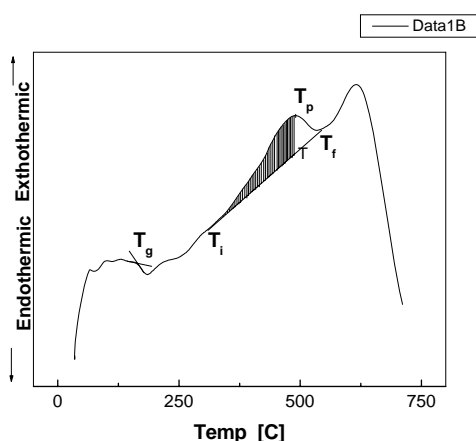


Fig. 1. DTA for GeSe₂ at heating rate 20° c/min.

Table 1. characteristic transition temperature for Ge(Se_{1-x}S_x)₂ and the glass stability factors for different compositions at different heating rate.

Composition	Average Tp-Tg °C/min	10° C/min		1 5° C/min		20° C/min		25° C/min		30° C/min	
		Tg	Tp	g	Tp	Tg	Tp	Tg	Tp	Tg	Tp
GeSe ₂	270.92	275.4	510.2	245.7	491	191.4	455.2	134.	406	99.2	408
Ge(Se _{0.9} S _{0.1}) ₂	242.46	270.6	469.4	212.8	463.6	157.3	436.9	151.8	373.8	142.	304.7
GeS ₂	465.08	257.6	635.5	214.2	535.8	146.8	680	102.	427	119.	733.5

4.1 The activation energy for glass transition.

Two approaches are used to analyze the dependence of T_g on the heating rate. One is the empirical relationship of the form

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

where A and B are constants for a given glass composition [5]. This has been originally suggested based on results for Ge(Se_{1-x}S_x)₂ chalcogenide glasses as in fig.2. For these glasses the empirical relationship can be written in the table [2]. Where a straight regression line is fitted to the experimental data.

The crystallized fraction, χ , at any temperature, T, is given as $\chi = A_t/A$, where A is the total area of the exothermal between the T_i, where the crystallization just begins and the temperature, T_f, where the crystallization is completed and A_t is the area between the initial temperature and a genetic temperature T, see fig. 1.

4. Results and discussion

The typical DTA traces of Ge(Se_{1-x}S_x)₂ chalcogenide glass obtained at heating rate 20° C/min as an example and is plotted in fig. 1 showing the characteristic phenomena in the studied temperature region. The first one corresponds to the glass transition temperature, T_g, and the second detects the peak temperature of crystallization T_p of the above mentioned chalcogenide glass. This behavior is typical for a glass- crystalline transformation. The values of temperature T_g, and T_p decrease by increasing the heating rate, (α) as in table [1]. This behavior opposite the common conception that the transition temp. Increase by heating rate. These phenomena may be due to the exit a large numbers of nuclei that posse the restriction of the growth which accompany by heating rate. This result is in good agreement with Gridhar and Mahadeven (4). This increase of T_g reflects the high rigidity of amorphous GeSe₂ glass network than Ges₂.

Table 2. Kinetic parameters of glass transition

Glassy alloys	Tg =A + Bln(x)
GeSe ₂	- 14.04+2.12ln(x)
Ge(Se _{0.9} S _{0.1}) ₂	- 14.27+2.22ln(x)
(GeS) ₂	- 14.17+2.12ln(x)

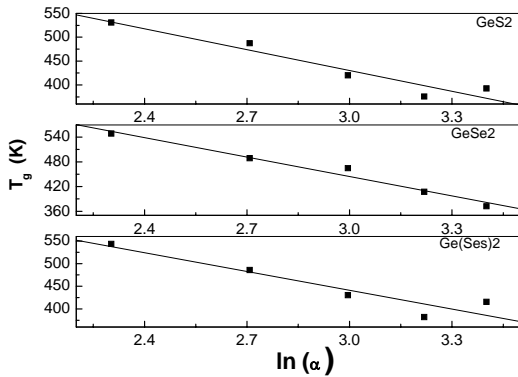


Fig. 2. T_g versus $\ln(\alpha)$ for $Ge(SeS)_2$ chalcogenide glasses

The other approach for analyzing T_g is based on Kissinger's linear dependence (6) in the form

$$\ln(\alpha/T_g^2) = -E_t/RT_g + C \quad \{2\}$$

Table 3. Activation energies for the glass transition (E_t) chalcogenide glasses

method	equation	GeSe ₂ (KJ/mol)	Ge(Se _{0.9} S _{0.1}) ₂ (KJ/mol)	GeS ₂ (KJ/mol)
Augis and Bennet	(6)	17.64	18.87	17.40
Kissinger	(2)	17.64	18.29	17.78
Mahdeven	(3)	10.14	10.87	10.17
average		17.64	16.2	17.64

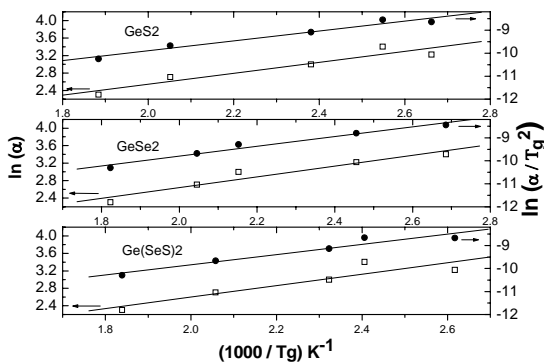


Fig. 3. $\ln(\alpha/T_g^2)$ and $\ln(\alpha)$ against $1000/T_g$ for $Ge(Se_{1-x}S_x)_2$

4.2 The Activation Energy for Crystallization

The theoretical basis for interpreting DTA results is provided by the formal theory of transformation kinetics as developed by Johnson and Meh and Avrami (8-11). In non-isothermal crystallization, the crystallized fraction (χ) precipitated in a glass heated at constant rate (α) is related

Where E_t is the activation energy of the glass transition for homogeneous. C is constant. Plotting $\ln(\alpha/T_g^2)$ versus $1/T_g$ should give straight lines, as shown in fig.3. The values of E_t determined from the slope of the linear relationship are given in table [3]

The approximation of Mahadeven et al (7) is used, where the variation $\ln(1/T_g^2)$ with $\ln(\alpha)$ is much slower than that $\ln(1/T_g)$ with $\ln(\alpha)$. So, the Kissinger equation can be simplified to form.

$$\ln(\alpha) = -E_t/RT_g + c \quad (3)$$

The variation of $\ln(\alpha/T_g^2)$ versus $(1/T_g)$ and $\ln(\alpha)$ against $(1/T_g)$ for the above mentioned glasses is shown in fig. 3, and the deduced values of E_t are listed in table (3). According to the decreasing values of T_g , T_c temperatures as a function of heating rate, consequently the E_t and E_c having values with negative sign but we can take the value as an absolute value.

to the activation energy of crystallization (E_c) through the following expression (12, 13)

$$\ln[-\ln(1-\chi)] = -n \ln(\alpha) - 1.052mE_c/RT + C \quad \{4\}$$

where m and n are integer or half integer which depends on the growth mechanism and the dimensionality of the crystal (14). On the basis of the above, $n = m + 1$, when the nuclei are formed during DTA scanning. Table [4] shows the values of n and m for crystallization mechanisms.

For all heating rates (10,15,20,25, and 30°C/min), plotting of $\ln[-\ln(1-\chi)]$ versus $1/T_p$ gives straight lines as shown in fig.4 for $Ge(Se_{0.9}S_{0.1})_2$ as an example. It's observed that some deviations from linearity at high temperature or in regions of large crystallized fractions are attributed to the saturation of nucleation sites in the final stages of crystallization. From the slope of each straight line mE_c value is calculated and it seems that the mE_c is independent of heating rate, and therefore, the average values of mE_c are obtained by considering all of heating rates, and their corresponding crystallization activation energies are listed in table [4]. crystallization activation energies were listed in table [4].

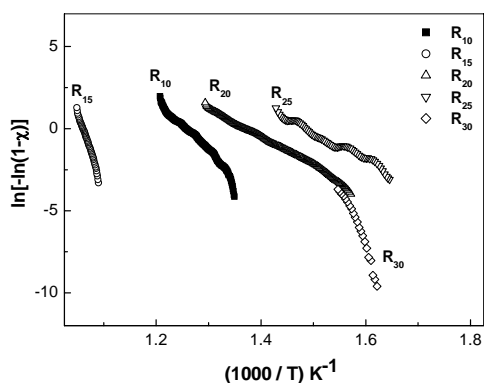


Fig.4. $\ln[-\ln(1-\chi)]$ versus $1000/T_p$ for different heating rate For $Ge(SeS)_2$.

At any constant temperature, the relation $\ln[-\ln(1-\chi)]$ versus $\ln(\alpha)$ is plotted as shown Fig.5. From the slope of this relation, the order of crystallization mechanism or Avrami index (n) can be calculated and listed in table [4]. On the other hand, Ozwa method (15) can be utilized to deduce the Avrami exponent (n), can be calculated by plotting $\ln[-\ln(1-\chi)]$ versus $\ln(\alpha)$ as in fig.5.

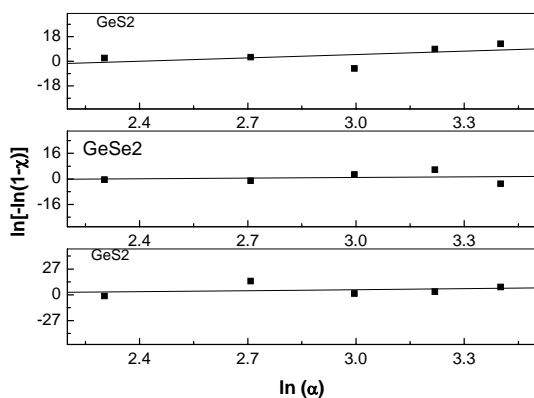


Fig. 5. $\ln[-\ln(1-\chi)]$ $\ln(\alpha)$ for chalcogenide glasses at fixed temperature

$$\ln[-\ln(1-\chi)] = -n \ln(\alpha) + n \ln[k(T-T_0)] \quad (5)$$

Table [4] Average values of the activation energy for crystallization E_c , deduced from different methods and values of (m) and (n) for $Ge(SeS)_2$.

Methods	equation	GeSe ₂ (KJ/mol)	Ge(Se _{0.9} S _{0.1}) ₂ (KJ/mol)	GeS ₂ (KJ/mol)
Augis and Bennet	(6)	44.72	20.52	17.54
Kissinger	(2)	44.72	31.23	25.86
Mahdeven	(7)	44.72	20.52	26.1
Avrami	(4) unacceptable	84.48	60.804	56.44
n(orderofcrystallization)		3.19	3.47	3.04
M(orderofgrowth)		2.19	2.47	2.92

The activation energy for crystallization (E_c) can also be deduced using the formula suggested by Augis and Bennett (16) where

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

By Plotting $\ln(\alpha/T_p)$ versus $1/T_p$ as shown in fig (6). The activation energy for crystallization (E_c) can be calculated. Kissinger (6, 17) developed a method which commonly used for analyzing the crystallization data of DTA. The value of E_c can be obtained from the slope of

$$\ln(\alpha/T_p^2) = -E_c / RT_p + C \quad (7)$$

A plot of $\ln(\alpha/T_p^2)$ against $(1/T_p)$ is shown in fig.7 and the deduced value of E_c is listed in table [4]. According to the approximation of Mahadeven et al (7), it should be noted that the change of $\ln(T_p^2)$ with α is small compared with the change of $\ln(\alpha)$, and therefore, it is possible to write the following expression(7,18)

$$\ln(\alpha) = -E_c/RT_p + c \quad (8)$$

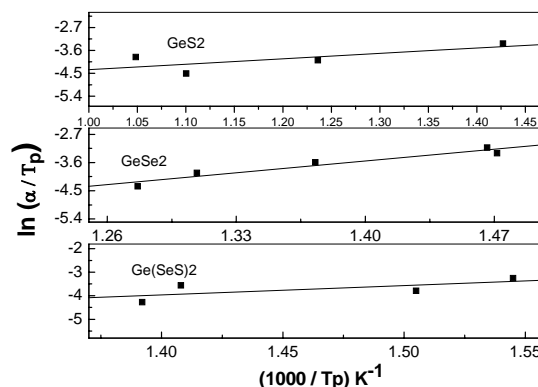


Fig.6 $\ln(\alpha/T_p)$ versus $1000/T_p$ for $Ge(SeS)_2$ chalcogenide glasses.

Based on this method, the slope of $\ln(\alpha)$ versus $1/T_p$ is shown in fig.(7), yielding the activation energy for crystallization (E_c) which are listed in table 4.

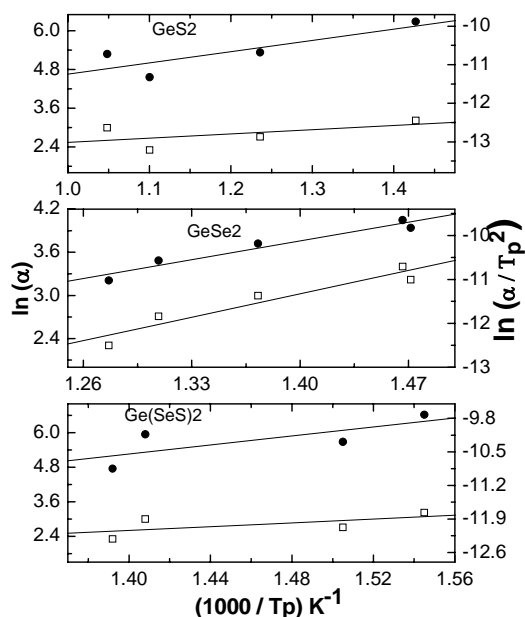


Fig.7 $\ln(\alpha/T_p^2)$ and $\ln(\alpha)$ versus $1000/T_p$ for $Ge(SeS)_2$ chalcogenide glasses.

4.3 The Temperature Difference ($T_p - T_g$)

The kinetic resistance to crystallization increases with increasing the difference between T_c and T_g . This difference gives an indication of the thermal stability of the glasses (7). A short temperature interval of ($T_p - T_g$) signifies that the glass contains structural units with a high crystallization tendency. In the first approximation α is independent of the heating rate (α), since both T_p and T_g decreases almost with increasing α . Therefore the values of ($T_p - T_g$) are listed in table [1] for all glassy alloys. From this table, it can be observed that the value ($T_p - T_g$) is the largest for GeS_2 indicating that it has the highest stability.

5. Conclusion

Calorimetric measurements are performed on the chalcogenide glasses $GeSe$, GeS , and $GeSeS$. Crystallization kinetics of the chalcogenides has been successfully determined under non-isothermal experiment using methods deduced specifically for isothermal conditions. The activation energy for crystallization (E_c) was calculated using several equations. The average value for E_g is found to vary from 10.87 to 17.78 KJ/mol and the average value of E_c was found from 37 up to 84KJ/mol, depending on the sample composition. The average value of avrami index $n=3$ indicates the existence of the volume nucleation and two-dimensional growth mechanism. The existence of volume nucleation and the three dimensional growth mechanisms. Both were explained in terms of the

mechanically stabilized structure at a particular coordination. The calculated average values of activation energies of crystallization and the glass transition reflect the rigidity.

The characteristic crystallization parameters T_g , T_p , E_t and E_c for these glasses are dependent on both glass composition and heating rates.

The calculated average values of activation energies of crystallization and glass transition reflect the high rigidity of the glass $GeSe_2$ compared to GeS_2 and $Ge(SeS)_2$.

The discrepancy in the values of E_c evaluated by John, Mehl and Avrami may be attributed to the different approximations that have adopted, is arriving to the final equation.

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