

Thermal Properties of $\text{Se}_{100-x}\text{Zn}_x$ Glassy System

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Received November 14th, 2010; revised January 17th, 2011; accepted February 23rd, 2011.

ABSTRACT

The crystallization process in $\text{Se}_{100-x}\text{Zn}_x$ glassy system is investigated using differential scanning calorimeters (DSC). The samples are prepared by conventional melt-quenching technique in the composition range $2 \leq x \leq 20$ (at%). Non-isothermal measurements are carried out for different heating rates. The value of the glass transition temperature T_g , the crystallization temperature T_c and the crystallization peak temperature T_p , are found to be depending upon both heating rate as well as the composition from thermal analytical data. The investigation of crystallization kinetics indicates a single stage crystallization process. The glass transition energy E_g and the crystallization activation energy E_c are also evaluated from thermal analytical data. The analyzer has been used the most reliable non-isothermal kinetic methods. The value of kinetics parameters E_g , E_c and 'n' are calculated using non-isothermal kinetics methods. The analysis shows that the incorporation of Zinc content has a strong influence on the crystallization mechanism for the $\text{Se}_{100-x}\text{Zn}_x$ glassy system.

Keywords: Chalcogenide Glasses, Amorphous, Crystallization Kinetics, DSC, Non-Isothermal

1. Introduction

The thermal behavior of the amorphous glassy alloys plays an important role in determining the transport mechanism, thermal stability and the practical applications. For chalcogenide glasses, crystallization studies are of crucial importance due to some of technical applications of these materials, namely optical recording media and memory switching devices. The differential scanning calorimeter (DSC) technique has so far been played to study the crystallization process in amorphous alloys and has proved to be the very effective method for such characterizing studies [1]. Recently, in thermal analysis studies several temperature control modes are used and a diversification is considered as an aspect of the development in thermal analysis [2]. The most commonly used modes are either isothermal or heating at constant rate. The drawback of the later is that the analysis of non-isothermal. Experiments are generally more complicated than isothermal one [3,4]. However, in isothermal experiments, it is impossible to reach at a test temperature instantly [5]. As comparable study, we have applied selected non-isothermal models reported to be the most reliable for determination of kinetic parameters of the crystallization process. Except some reported thermal studies for the binary $\text{Se}_{100-x}\text{Zn}_x$ system [6,7], the

present contributory goal is studying the crystallization kinetics in $\text{Se}_{100-x}\text{Zn}_x$ system using different preparation method, compositions and non-isothermal analysis methods in detail. The influence of Zinc ratio on the crystallization kinetics is reported. Chalcogenide glasses are a well recognized inorganic group of glassy materials but some chalcogenide elements like as Se, Te and S in conjunction, they are very good electropositive elements. Among the chalcogenide glasses, Se-based glassy alloys are very interesting and unique class of amorphous semiconductors which have large technical applications in electronics and optoelectronics. From the application point of view amorphous Se is very most useful material due to it's currently in use photoreceptors in TV Videocon pickup [8], conventional Xerographic machines and digital X-ray imaging [4-9]. The pure Se has practical application shortcoming like its short lifetimes, low sensitivity and thermal instability. The use of Se-Te, Se-Ge, Se-Sb, Se-Ln and Se-Zn is called binary system [5-10] alloys and is remains of their various properties like greater hardness, higher sensitivity, higher conductivity and smaller aging effect as compared to pure a-Se.

2. Experiment

The melt-quenching technique is adopted to prepare bulk $\text{Se}_{100-x}\text{Zn}_x$ glasses in the composition range of $2 \leq x \leq 20$

($x = 2, 5, 10, 20$). Appropriate amounts of highly pure elements were sealed in evacuated quartz ampoules under a vacuum of 10^{-4} Torr, heated at 850°C for 10 hours and then quenched in ice-cold water. Amorphous nature of these glasses was confirmed using XRD; the result shows the samples to be amorphous. The glassy alloy $\text{Se}_{100-x}\text{Zn}_x$ is prepared to make fine powder for differential scanning calorimeter (DSC) studies. The DSC technique is very important due to the fact that it is easy to carry out, it requires a little sample preparation, it is also very sensitive and it is relatively free of the sample geometry. The thermal properties of glassy alloy $\text{Se}_{100-x}\text{Zn}_x$ are studied using a Model-DSC (Rheumatic Scientific Company, UK) with the temperature correctness of this equipment being ± 0.1 K with average error of about ± 1 K in the measured values of glass transition and crystallization temperature. Non-isothermal runs are carried out

of chosen heating rates, $\beta = 5, 10, 15$ and 20 K/min. The temperature and enthalpy calibrations of the instrument are performed using the well known melting temperature and melting enthalpy of high purity indium supplied with the instrument. The quenched glasses material well grind powder of $\text{Se}_{100-x}\text{Zn}_x$ and is keep into the aluminum pan ~ 10 mg, before loading the (DSC) calorimeter.

3. Results and Discussion

To evaluate the thermal studies of the glassy $\text{Se}_{100-x}\text{Zn}_x$ system, DSC characteristic measurements have been carried out at different heating rates (β) 5, 10, 15, and 20 K/min. The traces of all composition of glassy $\text{Se}_{100-x}\text{Zn}_x$ system are carried out at different heating rates along with the results of all samples are as shown in the **Figure 1**. It is clear that all of the compositions samples show single endothermic and exothermic peaks are observed

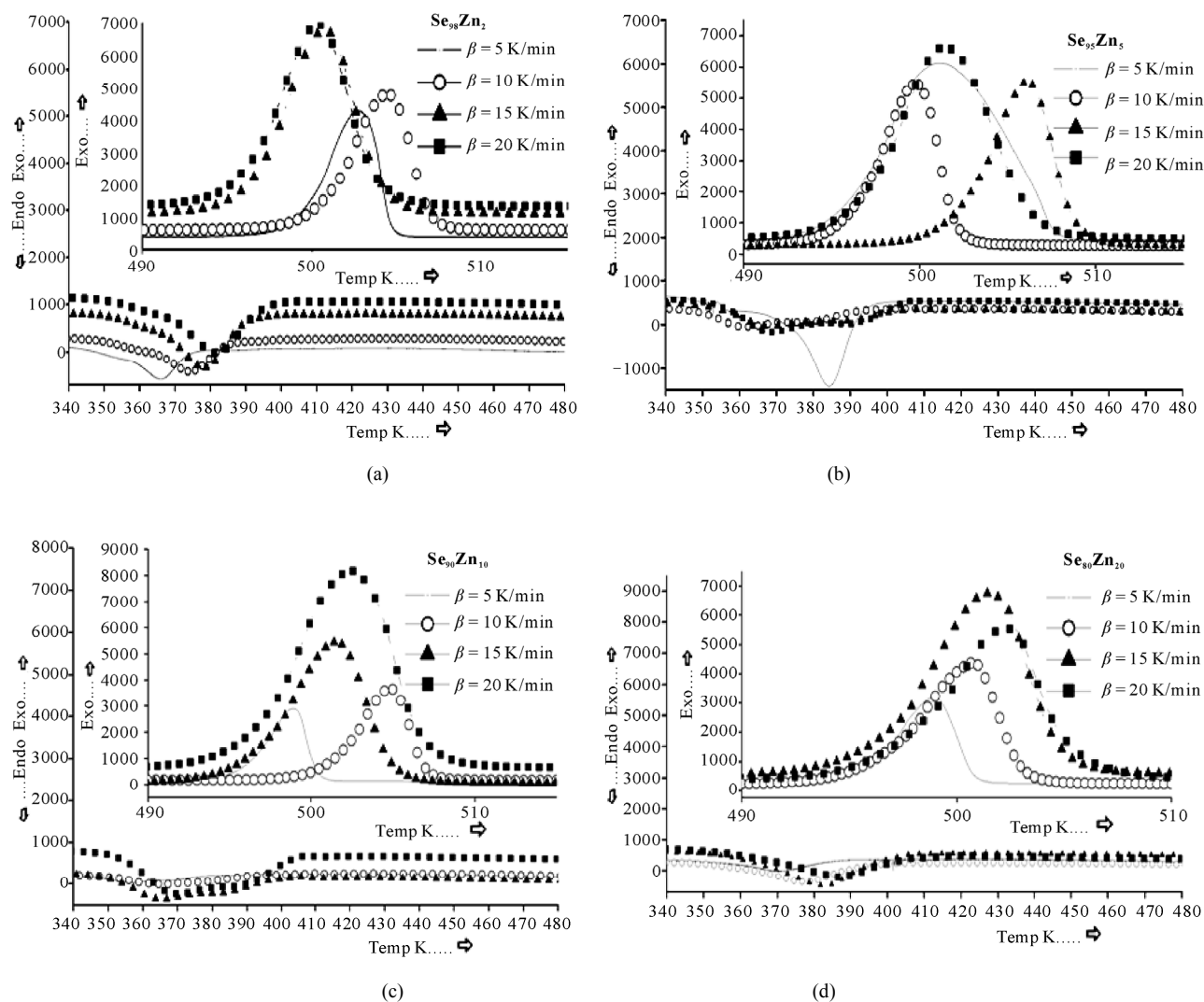


Figure 1. DSC Thermo grams for glassy $\text{Se}_{100-x}\text{Zn}_x$ ($x = 2, 5, 10, 20$) alloys at different heating rates 5, 10, 15 and 20 K/min.

glass transition temperature (T_g), crystallization temperature (T_c) and their values difference are given in the **Table 1(a)**. It is noticeable that those glasses have single endothermic and exothermic peaks, this types of glasses are most stable than which has two or more multiples' endothermic and exothermic peaks in their characteristics. The obtained value of (T_c) at 4% is show maximum crystallized temperature with Zn content, in **Figure 2(a)**. The value of crystallized peak temperatures (T_p) is given in the **Table 1(b)**. The exothermic peak temperature (T_p), is used to identify maximum crystallization rate at 5.8% with different heating rates as well as in composition is given in the **Figure 2(b)**. The value of peak crystallization temperature T_p , the glass transition temperature (T_g) is increase linearly with increasing in the heating rates, and (T_g) is also increases linearly with increase the Zn content for each sample except for 5% Zn in the glassy alloy. The onset crystallization temperatures (T_c) are increases linearly at 5% - 20% for each sample in **Figure 2(a)**, respectively and is decrease at 2% Zn content in the glassy. The exchange in (T_c) may be due to change from one two dimensional structure (bundles to layers) in the glassy systems Se-Zn as given in the **Figure 2(c)**. This type of behavior is typical for glass-crystalline transformation [11]. It is also shows characteristic temperatures are shifted to higher temperatures with increase in the heating rates of the heat flow measurement.

For the determination of crystallization activation energy (ΔE_c) from the data of DSC non-isothermal experiments are use several types of kinetic analysis methods. However, the two types which are broadly applied iso-conversion methods and the peak methods. In an investigation study of the accuracy of known iso-conversion methods, Starink [1] reported that the most accurate methods are Kissinger-Akahira-Sunose (KAS) [9-12] method and the method developed by Author [1-13]. All of the iso-conversion methods require the determination of the onset temperature T_c at which a fixed fraction value α (where $\alpha = A'/A$, It means that A' -Partial Area and A is the total Area in the exothermic peak) of the total amount is transformed. In the KAS method, the relation between the temperatures and the heating rate β is given by

$$\ln(\beta/T_c^2) = -\Delta E_c/RT_c + \text{constant} \quad (1)$$

where R is gas constant and ΔE_c is the crystallization effective activation energy. Plotting of $\ln(\beta/T_c^2)$ vs. $1/T_c$ enables calculation of ΔE_c from the linear fits to experimental data. The results for $\alpha = 0.4, 0.5, 0.9$ and 1.0 are shown in **Figure 3**. The most reliable iso-conversion methods are as reported by Ozawa [13], Flynn-Wall-Ozawa (FWO) [14,15], KAS and the Friedman-Ozawa [15,16]. The FWO model has been developed for non-

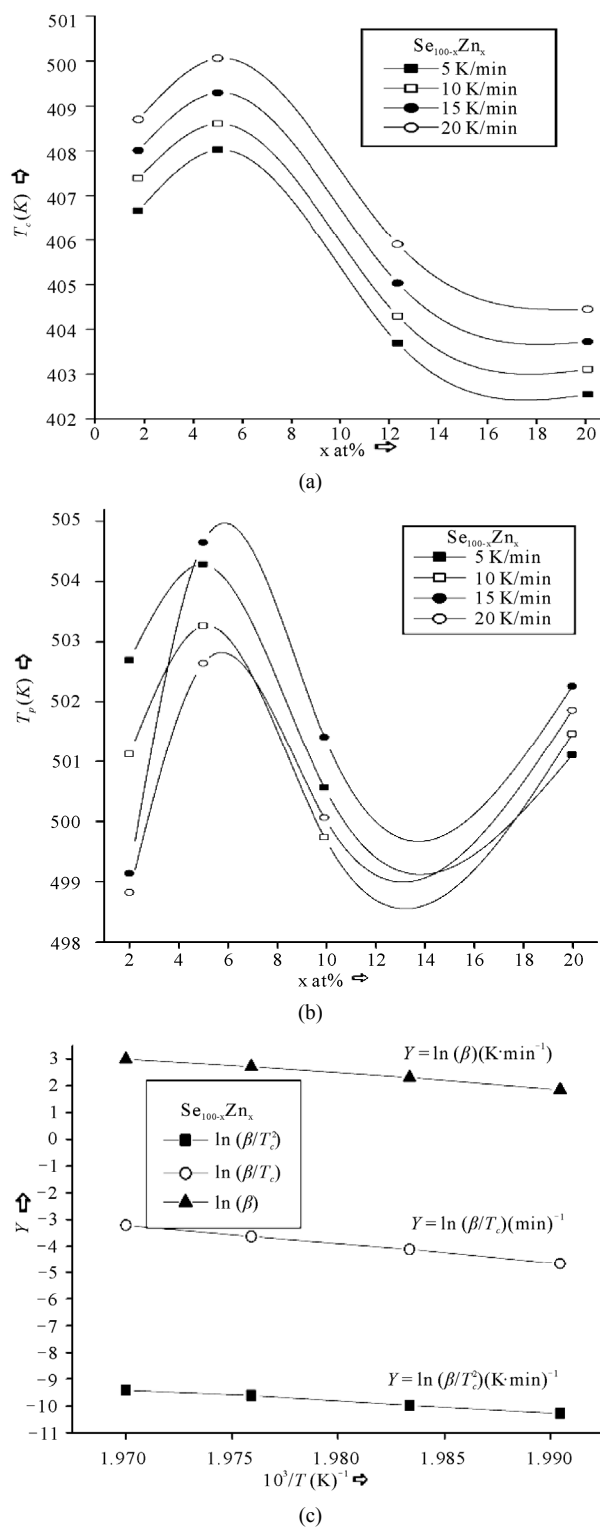


Figure 2. (a) Composition dependence of crystallization temperature T_c for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys. (b) Composition dependence of crystallized peak temperatures T_p for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys. (c) Plots of $10^3/T$ vs. $\ln(10^3/T_c^2)$, $10^3/T$ vs. $\ln(10^3/T_c)$ and $10^3/T$ vs. $\ln(\beta)$ for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys.

Table 1. (a) The value of glass transition, onset temperature and their differences for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys; (b) The value of peak crystallization temperature T_p at different heating rates for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys.

(a)												
Heating Rate (β) K/min	$\text{Se}_{98}\text{Zn}_2$			$\text{Se}_{95}\text{Zn}_5$			$\text{Se}_{90}\text{Zn}_{10}$			$\text{Se}_{80}\text{Zn}_{20}$		
	T_g (K)	T_c (K)	$T_c - T_g$ (K)	T_g (K)	T_c (K)	$T_c - T_g$ (K)	T_g (K)	T_c (K)	$T_c - T_g$ (K)	T_g (K)	T_c (K)	$T_c - T_g$ (K)
5	357.09	497.78	140.69	368.15	496.01	127.86	345.02	495.35	150.33	353.95	494.16	140.21
10	360.09	499.13	139.04	347.96	497.56	149.60	349.59	500.47	150.88	356.33	501.21	144.88
15	361.71	495.73	134.02	354.64	494.68	140.04	350.08	496.82	146.74	359.28	497.8	138.52
20	366.55	495.72	129.17	353.89	494.9	141.01	353.06	496.28	143.22	359.21	496.85	137.64
(b)												
Heating Rate (β) K/min	$\text{Se}_{98}\text{Zn}_2$		$\text{Se}_{95}\text{Zn}_5$		$\text{Se}_{90}\text{Zn}_{10}$		$\text{Se}_{80}\text{Zn}_{20}$					
	T_p (K)		T_p (K)		T_p (K)		T_p (K)					
5	502.69		501.10		499.12		498.82					
10	504.28		503.28		504.62		502.64					
15	500.56		499.73		501.41		500.07					
20	500.10		501.48		502.28		501.87					

isothermal analysis of crystallization in which the final relation is as follows

$$\ln\beta = -1.0518(\Delta E/RT_c) + \text{const} \quad (2)$$

By plotting $(\ln\beta)$ vs. $1/T_c$ for chosen value of fraction transformed α , the effective activation energy ΔE_c have been determined, from the **Figures 4, 5 and 6** with the fixed value of ($\alpha = 0.4, 0.5, 0.9, 1.0$) is given in the **Table 2**.

3.1. Composition Dependence of Crystallization and Peak Temperature in Exothermic Peak

Figure 2(a) indicates the composition dependence of peak crystallization temperature T_c of glassy alloy $\text{Se}_{100-x}\text{Zn}_x$ for four different heating rates. The crystallization kinetics of $\text{Se}_{100-x}\text{Zn}_x$ alloy is characterized by solving the exothermic peak, where T_c is onset temperature and T_p is the peak temperature of the exothermic peak. At lower concentration of Zn the system Gains the unit dissolved in a matrix composed of Se chains with increase of Zn content. The Se-Se bond energy (205.8 kJ/mol) will be replaced by Se-Zn bond energy which has higher bond energy (450.5 kJ/mol) [9], since cohesive energy of the system doesn't decrease with increases in the Zn content. This type of composition is to be considered as a series composition of the system behaving as a chemically ordered alloy by taking the high energy $\text{Se}_{100-x}\text{Zn}_x$ on heteropolar bonds of the system. A comparable turn-around has been found by Tonchev and Kasap [17] in glassy

alloy $\text{Se}_{100-x}\text{Zn}_x$. Under these circumstances the T_c would get converted from one to two dimensional structures (bundles to layers) in the Se-Zn system 5 at% Zn [15]. Further more addition of Zn favors' the formation of (Zn-Zn) bonds, means reducing the bond concentration. This is in turn the results with the decrease of bond energy of (Zn-Zn) – (Se-Zn) = –245.5 kJ/mol. Hence, the cohesive energy decreases with increase of T_c which is shown in **Figure 2(c)**.

3.2. Evaluation of Activation Energy of Crystallization (ΔE_c)

The activation energy of crystallization for the glassy alloy $\text{Se}_{100-x}\text{Zn}_x$ are evaluated by using the method Starink [1] Kissinger-Akahira-Sunose (KAS) [9-12] Flynn-Wall-Ozawa (FWO) [14,15], KAS and the Flynn-Wall-Ozawa [15,16], Kissinger's relation, Augis-Bennett's Approximation, and Approximation method of Mahadevan *et al.* The different kinds of non-isothermal plots for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloy in (**Figures 3, 4 and 5**) are calculated for the present sample by utilizing the five methods as given in the **Table 2**, with the help of Equation (3).

$$\ln(\beta/T_c) = -E_c/RT_c + \ln K_0 \quad (3)$$

The value of activation energy ΔE_c according to Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) varies linearly with systematically and the value very close to each other remaining three *i.e.* Kissinger's relation, Augis-Bennett's and Approximation method of Ma-

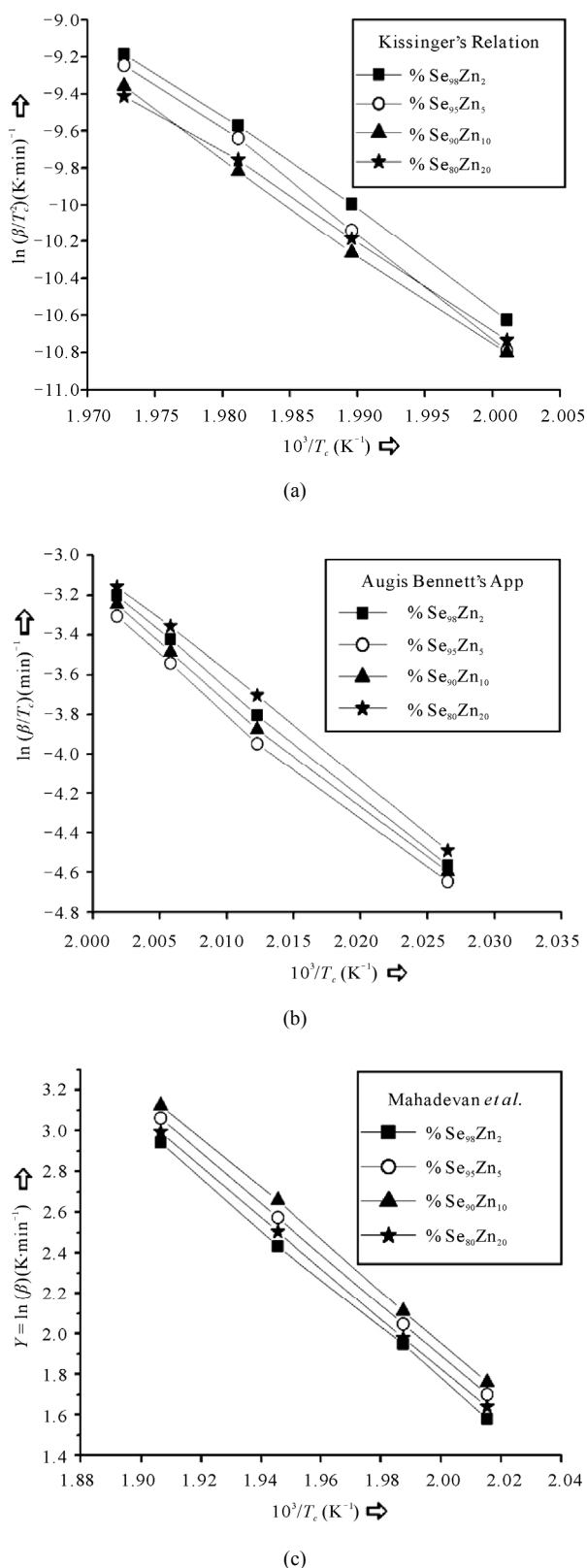


Figure 3. Plots of $(10^3/T_c^2)$ vs. $\ln(\beta/T_c^2)$, $10^3/T_c$ vs. $\ln(\beta/T_c)$ and $10^3/T_c$ vs. (β) for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys.

hadevan *et al.* show much variation in their activation energy for different composition in the glassy $\text{Se}_{100-x}\text{Zn}_x$ alloy. Kissinger's relation, Augis-Bennett's and Approximation method of Mahadevan *et al.* method can be applied in the present analysis as recommended by the Kasap and Juhasz [18]. Comparative values of activation energy ΔE_c is given in the **Table 2**, these values are in well agreement with one another, in the first three cases with each other in the giving two.

3.3. Evaluation of Avrami Index 'n'

To calculate the order parameter 'n' and the activation energy ΔE_c has great helped to evaluate Avrami index 'n' by using the methods Matusita-Ozawa and Vazquez.

$$\ln[-\ln(1-\alpha_T)] = \ln K - \ln(\beta) \quad (4)$$

Figure 6 shows the volume fraction α increases with increases the temperature and variation of $\ln(\beta)$ with $\ln[-\ln(1-\alpha)^{-1}]$ varied in system for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloy at different temperatures with different heating rates [19,20]. The value of Avrami index 'n' have been evaluated from the slopes of these curves at four fixed different temperatures given in the **Table 3**. According to them, Avrami index 'n' basically depends on volume fraction α in the exothermic peaks. It is linearly increases with concentration of Zn and temperature for individual composition of the sample as shown in the **Table 3**. This is an indicate property of the order parameter and for the fluid in the glass transition region, the relaxation times for the molecular movements change into experimental scale. At these circumstances the diffusive movements convert comparable to the experimental timescale. However diffusive motion of the liquid has been trapped and the system is not in the thermal equilibrium [18-21]. At this time, the size of the nuclei does not achieve the critical size required to initiate the nucleation process as the glass is supposed to have no nuclei (of critical size). When the glass is heated in the furnace, the rate of crystal nucleation in the glass reaches the highest value at a temperature than the glass transition temperature and then decrease suddenly with increasing the temperature, during this period the rate of crystal growth is much at a temperature higher than the temperature upon which the nucleation rate is highest. If the glass is heated at a constant rate, the crystal nuclei is formed only at very few temperatures and crystals rise-up in size at higher temperatures without any increase in number. From the **Table 3**, it is show that 'n' decreases with an increase in the temperature. It is very familiar that the crystallization of chalcogenide glasses is connected with nucleation and the growth process and the amount of crystallization α increases with increase in temperature, it approaches to with its standard value 1. Hence, increasing the tempera-

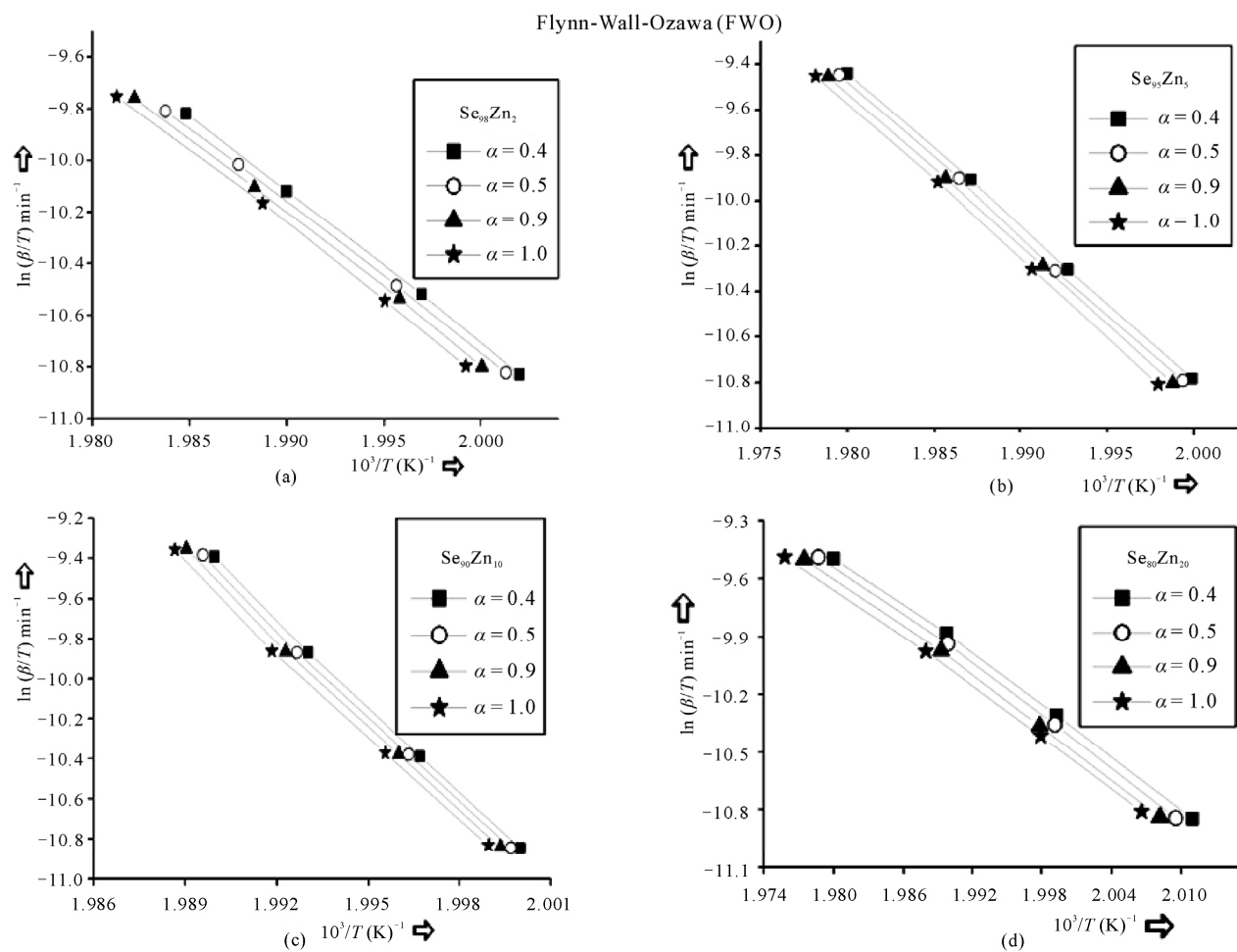


Figure 4. Plots of $(10^3/T)$ vs. $\ln(\beta/T)$ at fix value of crystallized fraction α for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys.

Table 2. The values of activation energy of crystallization (ΔE_c) and the activation energy structural relation ΔE_g of glassy $\text{Se}_{100-x}\text{Zn}_x$ alloy evaluated by using non-isothermal methods.

Non-isothermal method	Activation Energy of crystallization ΔE_c (kJ/mol)			
	Se ₉₈ Zn ₂	Se ₉₅ Zn ₅	Se ₉₀ Zn ₁₀	Se ₈₀ Zn ₂₀
Kissinger's relation	205.61	409.46	540.91	1052.39
Augis-Bennett's app.	286.83	307.53	321.17	1044.82
Approximation method of Mahadevan <i>et al.</i>	369.47	263.55	386.19	744.10
FWO	451.48	150.02	315.88	795.76
KAS	483.22	149.43	340.60	828.66
Non- isothermal method	The activation Energy of structural relation ΔE_g (kJ/mol)			
Kissinger's relation	152.39	281.59	155.39	333.47
Approximation method of Mahadevan <i>et al.</i>	156.55	206.10	160.38	238.19
FWO	95.34	101.70	92.22	101.26
KAS	94.09	100.78	90.76	100.22

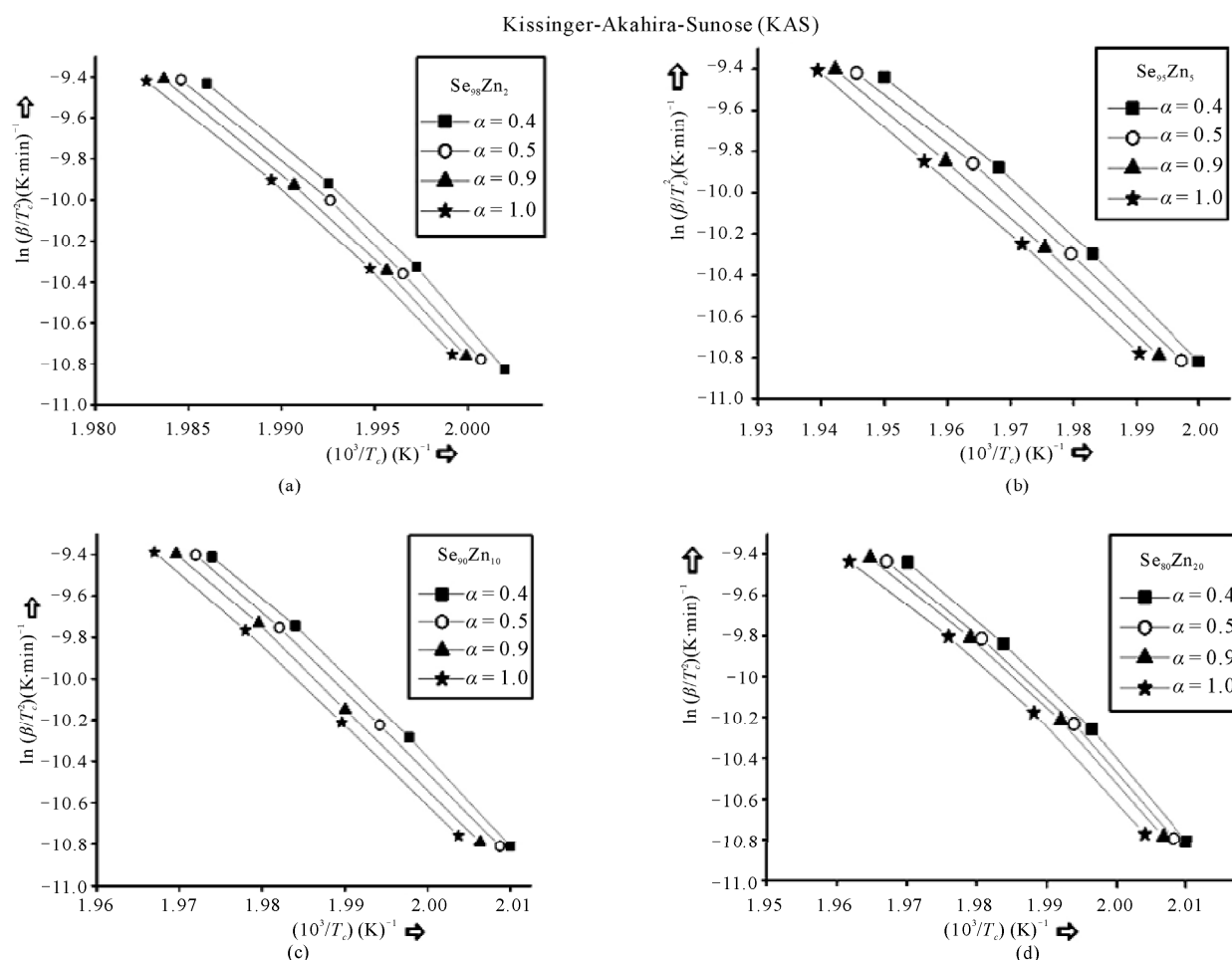


Figure 5. Plots of $(10^3/T_c)$ vs. $\ln(\beta/T_c^2)$ for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys.

Table 3. Temperature dependence of Avrami index (n).

$\text{Se}_{98}\text{Zn}_2$		$\text{Se}_{95}\text{Zn}_5$		$\text{Se}_{90}\text{Zn}_{10}$		$\text{Se}_{80}\text{Zn}_{20}$	
Temp (K)	'n'	Temp(K)	'n'	Temp (K)	'n'	Temp (K)	'n'
476.0	1.04	478.0	1.43	480.0	1.00	494.0	1.23
476.5	1.08	478.5	1.44	480.5	1.14	494.5	1.30
477.0	1.14	479.0	1.48	481.0	1.24	495.0	1.65
477.5	1.16	479.5	1.58	481.5	1.33	495.5	1.75

ture with increase in the order of the glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys suggests that the character of characterization converts from a nucleation-driven system at the beginning to a growth-driven system by the crystallization process [13-21].

3.4. Rate of Crystallization Glassy $\text{Se}_{100-x}\text{Zn}_x$ Alloys

After knowing the calculated parameters as ΔE_c is used

to Equations (1), (3), and K_0 with the help of Equation (3), and the value of rate constant K are evaluated from the Equation (4). Finally, the frequency factor K_0 is obtained by using this relation and with the help of JMA model of authors [7].

$$K = K_0 \exp(-\Delta E_c/RT) \quad (5)$$

Therefore, the values of $\ln K$ at different temperatures in the crystallization region are given in the Table 4, for

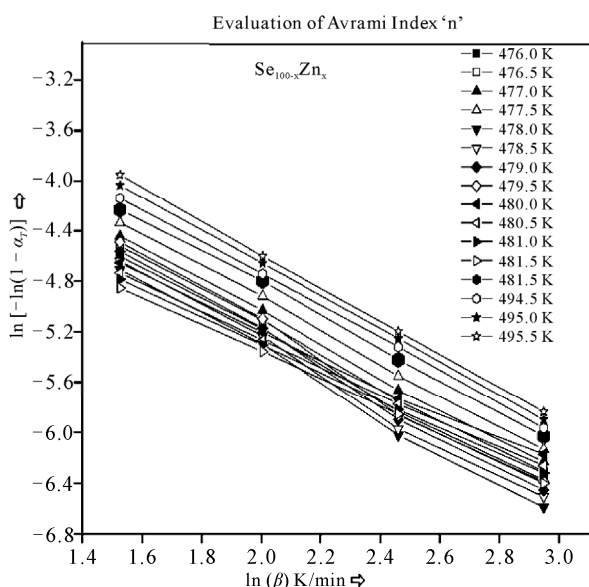


Figure 6. Plots of $\ln(\beta)$ vs. $\ln[-\ln(1 - \alpha_T)]$ for four constant temperature for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys.

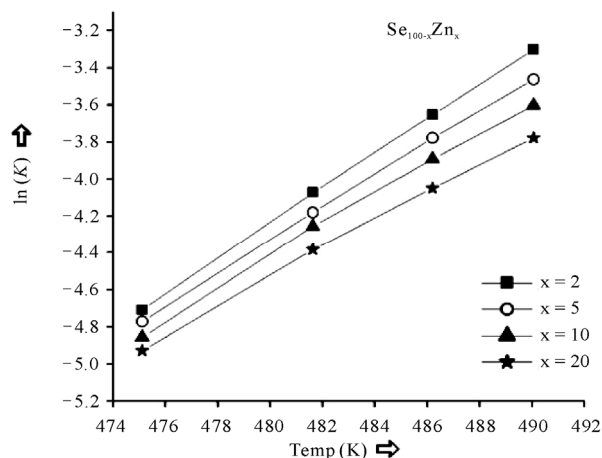
Table 4. Temperature dependence of rate constant K in the crystallization region.

Temp (K)	$\ln K$ $\text{Se}_{98}\text{Zn}_2$	$\ln K$ $\text{Se}_{95}\text{Zn}_5$	$\ln K$ $\text{Se}_{90}\text{Zn}_{10}$	$\ln K$ $\text{Se}_{80}\text{Zn}_{20}$
475	-4.71	-4.79	-4.86	-5.12
480	-3.96	-4.09	-4.17	-4.41
485	-3.59	-3.71	-3.75	-4.01
490	-3.31	-3.41	-3.47	-3.72

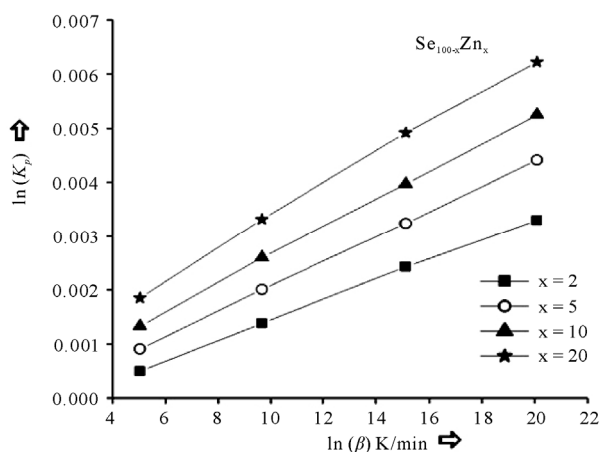
glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys, It shows that K increases with increase in temperature in the **Figure 7(a)**. It is clear that the crystallization rate is highest for glassy $\text{Se}_{80}\text{Zn}_{20}$ alloy. To know more information about morphology of growth, the given Equation (5) from the Gao-Wang model [22] leads to the Equation (5) is

$$K_p = (\beta E_c) / (RT_c^2) \quad (6)$$

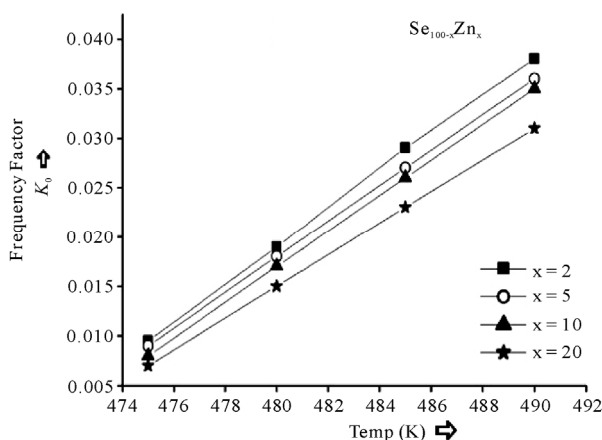
where K_p being the value of the rate constant K at peak crystallization temperature T_c for the constant heating rate. Therefore, the heating rate dependence of K_p is given in the following **Table 4**. The value of K_p is increases with increasing in the x at% and with increasing the heating rates in **Table 5**. It is clear that the crystallization rate constant is highest for glassy $\text{Se}_{80}\text{Zn}_{20}$ alloy as given in the **Figure 7(b)**. The value of K_0 increases with increases the x at% and with increase in the heating rates. It is clear that the frequency factor K_0 is highest for glassy $\text{Se}_{80}\text{Zn}_{20}$ alloy as given in the **Figure 7(c)**. **Figure 8(a)** shows the rigidity of glass sample [22]. **Figure 8(b)**



(a)



(b)

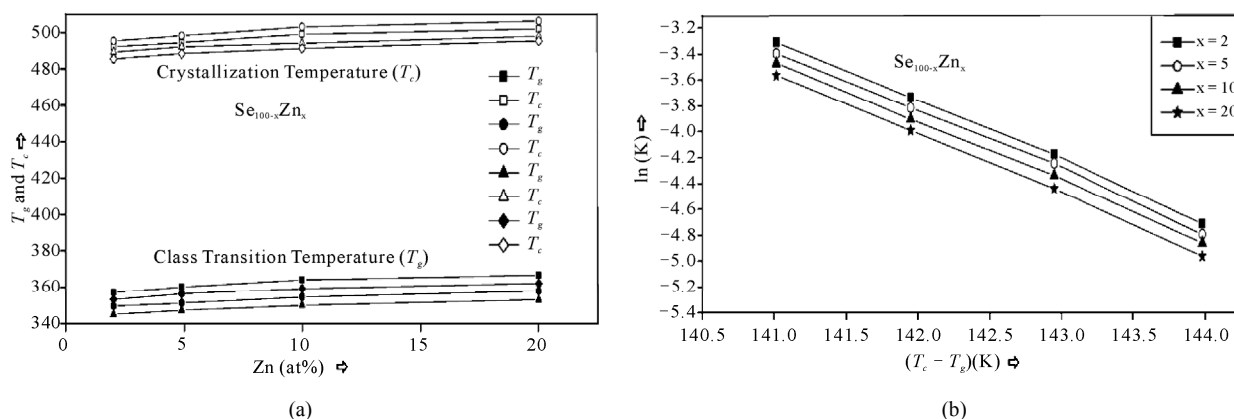


(c)

Figure 7. Plots of Temperature $T(\text{K})$ vs. Rate constant ($\ln K$), $\ln(\beta)$ K/min vs. rate constant $K_p \text{ min}^{-1}$ and Temperature (T) K vs. K_0 for glassy $\text{Se}_{100-x}\text{Zn}_x$ alloys as shown in the above figure.

Table 5. Heating rate dependence of rate constant K_p .

Heating rate(β)/K/min	K_p (min^{-1}) $\text{Se}_{98}\text{Zn}_2$	K_p (min^{-1}) $\text{Se}_{95}\text{Zn}_5$	K_p (min^{-1}) $\text{Se}_{90}\text{Zn}_{10}$	K_p (min^{-1}) $\text{Se}_{80}\text{Zn}_{20}$
5	4.95×10^{-4}	10.05×10^{-4}	13.28×10^{-4}	25.83×10^{-4}
10	9.93×10^{-4}	20.02×10^{-4}	26.02×10^{-4}	51.87×10^{-4}
15	15.08×10^{-4}	29.43×10^{-4}	39.66×10^{-4}	77.81×10^{-4}
20	20.18×10^{-4}	39.88×10^{-4}	52.47×10^{-4}	102.90×10^{-4}

**Figure 8.** Plots of Zn content vs. glass transition temperature, (T_g) crystallization Temperature T_c and $T_c - T_g$ (K) vs. $\ln K$, for glassy $\text{Se}_{100-x}\text{Zn}_x$ glasses at different heating rates 5, 10, 15, and 20 as Mention in the above Figure (a) and (b).

the glass alteration temperatures T_g represents the power or strictness of the glass structure in chalcogenide glasses. Since thermal stability depends on the T_g value in the glassy state [20-23]. From the **Figure 8(b)** T_g individual doesn't give the information about the thermal stability [24] but the difference value $T_c - T_g$, is give in the thermal stability for all composition with different heating rates [25]. The maximum value of $T_c - T_g$ is giving the information of highest thermal stability for the sample $\text{Se}_{90}\text{Zn}_{10}$ at 10 K/min as shown in the **Table 1**. It is very important to know the composition $\text{Se}_{90}\text{Zn}_{10}$ is more stable than other composition of the alloy $\text{Se}_{100-x}\text{Zn}_x$. It is obvious from the **Figure 8(a)** and **Table 1** in first the crystallization temperature increases with increase in the Zn content up-to 10% and then decreases up-to 20 at% of Zn content in the $\text{Se}_{100-x}\text{Zn}_x$ system. Therefore, it is said that the rate of crystallization is highest at 10% of Zn content in the glassy system [26].

4. Conclusions

The kinetics parameter of crystallization has been investigated under the non-isothermal methods in glassy $\text{Se}_{100-x}\text{Zn}_x$ ($2 \leq x \leq 20$). The DSC thermograms are used to evaluate the data of kinetic parameters. There are three best fit methods Kissinger's relation, Augis-Bennett's app and Approximation method of Mahadevan *et al.*, the activation energy (ΔE_c) is increases as increased the Zn

concentration in the glassy. According to Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), the activation energy ΔE_c also increases linearly on (5 - 20) at% Zn concentration systematically in the glassy. The activation energy of structural relation ΔE_g is increase non-linearly with increases in the composition of the alloy. Avrami index 'n' is increases linearly with increasing the temperature and non-linearly with Zn concentration in the glassy $\text{Se}_{100-x}\text{Zn}_x$. The rate constant K increases with the temperature increases in the composition of the glassy. The rate of crystallization is highest in the glassy $\text{Se}_{98}\text{Zn}_2$ alloy. The thermal stability on the basis of experimental data is highest for the glassy $\text{Se}_{90}\text{Zn}_{10}$. The rate of crystallization constant is high because of the highest difference of $T_c - T_g$ in $\text{Se}_{90}\text{Zn}_{10}$; furthermore it indicates that thermally is most stable this glass in the range of composition. It has been seen that the crystallization is to deliberate for the chalcogenide glasses by taking the maximum thermal stability. Finally the frequency factor K_0 is also increases with increase the temperature in the glassy $\text{Se}_{100-x}\text{Zn}_x$.

5. Acknowledgements

Thanks are due to Department of Physics (Materials Sciences Lab-2) of JMI, New Delhi (India) for providing financial assistance in the form of major research programmed.

REFERENCES

- [1] M. J. Starink, "Analysis of Aluminum Based Alloys by Calorimetric: Quantitative Analysis of Reactions and Reaction Kinetics," *International Materials Reviews*, Vol. 49, No. 3-4, 2004, pp. 191-226. [doi:10.1179/095066004225010532](https://doi.org/10.1179/095066004225010532)
- [2] T. Ozawa, "Temperature Control Modes in Thermal Analysis," *Pure and Applied Chemistry*, Vol. 72, No. 11, 2000, pp. 2083-2099. [doi:10.1351/pac200072112083](https://doi.org/10.1351/pac200072112083)
- [3] N. Mehta, M. Zulfequar and A. Kumar, "Kinetic Parameters of Crystallization in Glassy $\text{Se}_{100-x}\text{Zn}_x$," *Physica Status Solidi (A)*, Vol. 203, No. 2, 2005, pp. 236-246.
- [4] E. Maruyama, "Amorphous Built-in-Field Effect Photoreceptors," *Japanese Journal of Applied Physics*, Vol. 21, No. 2, 1982, pp. 213-223. [doi:10.1143/JJAP.21.213](https://doi.org/10.1143/JJAP.21.213)
- [5] D. C. Hunt, S. S. Kirby and J. A. Rowland, "X-Ray Imaging with Amorphous Selenium: X-Ray to Charge Conversion Gain and Avalanche Multiplication Gain," *Medical Physics*, Vol. 29, No. 11, 2002, p. 2464. [doi:10.1118/1.1513157](https://doi.org/10.1118/1.1513157)
- [6] T. Ozawa, "Non-Stoichiometry of $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ Observed by Repeated Temperature Scanning," *Journal of Thermal Analysis and Calorimetry*, Vol. 72, No. 1, 2003, pp. 337-345. [doi:10.1023/A:1023960928871](https://doi.org/10.1023/A:1023960928871)
- [7] H. S. Chen "A Method for Evaluating Viscosities of Metallic Glasses from the Rates of Thermal Transformations," *Journal of Non-Crystalline Solids*, Vol. 27, No. 2, 1978, pp. 257-263. [doi:10.1016/0022-3093\(78\)90128-X](https://doi.org/10.1016/0022-3093(78)90128-X)
- [8] N. Mehta, P. Agarwal and A. Kumar, "Calorimetric Studies on $\text{Se}_{0.6}\text{Ge}_{0.22}\text{M}_{0.10}$ ($\text{M} = \text{Cd, In, Pb}$)," *Turkish Journal of Physics*, 29, 2005, pp. 193-200.
- [9] H. E. Kissinger, "Reaction Kinetics in Differential Thermal Analysis," *Analytical Chemistry*, Vol. 29, 1957, pp. 1702-1706. [doi:10.1021/ac60131a045](https://doi.org/10.1021/ac60131a045)
- [10] S. O. Kasap, In: A. S. Diamond, Ed., *Handbook of Imaging Materials*, Marcel Dekker, New York, 1991, p. 355.
- [11] M. A. El-Oyoum, "Determination of the Crystallization Kinetic Parameters of $\text{Ge}_{22.5}\text{Te}_{77.5}$ Glass Using Model-Free and Model Fitting Methods," *Journal of Alloys and Compounds*, Vol. 486, No. 1-2, 2009, pp. 1-8. [doi:10.1016/j.jallcom.2009.06.137](https://doi.org/10.1016/j.jallcom.2009.06.137)
- [12] T. Akahira and T. T. Sunuse, "Joint Convention of Four Electrical Institutes," Research Report, Chiba Institute of Technology, Chiba, Vol. 16, 1971, pp. 22-31.
- [13] T. Ozawa, "Estimation of Activation Energy by Isoconversion Methods," *Thermochimica Acta*, Vol. 203, 1992, pp. 159-165. [doi:10.1016/0040-6031\(92\)85192-X](https://doi.org/10.1016/0040-6031(92)85192-X)
- [14] T. Ozawa, "A New Method of Analyzing Thermo Gravitric Data," *Bulletin of the Chemical Society of Japan*, Vol. 38, No. 11, 1965, pp. 1881-1886. [doi:10.1246/bcsj.38.1881](https://doi.org/10.1246/bcsj.38.1881)
- [15] J. H. Flynn and L. A. Wall, "A Quick, Direct Method for the Determination of Activation Energy from Thermo-gravimetric Data," *Journal of Polymer Science Part B: Polymer Letters*, Vol. 4, No. 5, 1966, pp. 323-328. [doi:10.1002/pol.1966.110040504](https://doi.org/10.1002/pol.1966.110040504)
- [16] H. L. Friedman, "Kinetics of Thermal Degradation of Charforming Plastics from Hermogravimetry. Application to a Phenolic Plastic," *Journal of Polymer Science Part C: Polymer Symposia*, Vol. 6, No. 1, 1964, pp. 183-185.
- [17] D. Tonchev and S. O. Kasap, "Thermal Properties of $\text{Sb}_x\text{Se}_{100-x}$ Glasses Studied by Modulated Temperature Differential Scanning Calorimetric," *Journal of Non-Crystalline Solids*, Vol. 248, No. 1, 1999, pp. 28-36. [doi:10.1016/S0022-3093\(99\)00100-3](https://doi.org/10.1016/S0022-3093(99)00100-3)
- [18] S. O. Kasap and C. Juhasz, "Theory of Thermal Analysis of Non-Isothermal Crystallization Kinetics of Amorphous Solids," *Journal of the Chemical Society, Faraday Transactions*, Vol. 81, 1985, pp. 811-831. [doi:10.1039/f29858100811](https://doi.org/10.1039/f29858100811)
- [19] J. Vázquez, C. Wagner, P. Villares and R. Jiménez-Garay, "Glass Transition and Crystallization Kinetics in $\text{Sb}_{0.18}\text{As}_{0.34}\text{Se}_{0.48}$ Glassy Alloy by Using Non-Isothermal Techniques," *Journal of Non-Crystalline Solids*, Vol. 235-237, 1998, pp. 548-553. [doi:10.1016/S0022-3093\(98\)00661-9](https://doi.org/10.1016/S0022-3093(98)00661-9)
- [20] K. Matusita, T. Konastu and R. Yokota, "Kinetics of Non-Isothermal Crystallization Process and Activation Energy for Crystal Growth in Amorphous Materials," *Journal of Materials Science*, Vol. 19, No. 1, 1984, pp. 291-296. [doi:10.1007/BF02403137](https://doi.org/10.1007/BF02403137)
- [21] T. Ozawa, "Kinetics of Non-Isothermal Crystallization," *Polymer*, Vol. 12, No. 3, 1971, pp. 150-158. [doi:10.1016/0032-3861\(71\)90041-3](https://doi.org/10.1016/0032-3861(71)90041-3)
- [22] Y. Q. Gao and W. Wang, "On the Activation Energy of Crystallization in Metallic Glasses," *Journal of Non-Crystalline Solids*, Vol. 81, No. 1-2, 1986, pp. 129-134. [doi:10.1016/0022-3093\(86\)90262-0](https://doi.org/10.1016/0022-3093(86)90262-0)
- [23] K. Singh, N. S. Saxenaa, O. N. Srivastava, D. Patidara and T. P. Sharmaa, "Energy Band Gap of $\text{Se}_{100-x}\text{In}_x$ Chalcogenide Glasses," *Chalcogenide Letters*, Vol. 3, No. 3, 2006, pp. 33-36.
- [24] A. Hurby, "Evaluation of Glass-Forming Tendency by Means of DTA," *Czechoslovak Journal of Physics*, Vol. 22, No. 11, 1972, pp. 1187-1193.
- [25] S. A. Khan, F. S. Al-Hazmi, A. S. Maida and A. A. Al-Ghamdi, "Calorimetric studies of the crystallization process in $\text{a-Se}_{75}\text{S}_{25-x}\text{Ag}_x$," *Current Applied Physics*, Vol. 9, No. 3, 2009, pp. 567-572. [doi:10.1016/j.cap.2008.05.004](https://doi.org/10.1016/j.cap.2008.05.004)
- [26] N. Mehta and A. Kumar, "Thermal Characterization of Glassy $\text{Se}_{70}\text{Te}_{20}\text{M}_{10}$ Using DSC Technique," *Journal of Materials Science*, Vol. 39, No. 21, 2004, pp. 6433-6437. [doi:10.1023/B:JMSE.0000044880.99215.be](https://doi.org/10.1023/B:JMSE.0000044880.99215.be)