A study of crystallization kinetics of $Te_{15}(Se_{100-x}Sb_x)_{85}$ glassy alloys using differential thermal analysis

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Abstract: Thermal crystallization study of $Te_{15}(Se_{100-x}Sb_x)_{85}$ glassy alloys (x= 0, 1, 2, 3 and 4 at. %) has been reported in this communication. Differential thermal analysis (DTA) has been used to carry out the study. DTA has been performed at different heating rates of 10, 15, 20 and 25 K/min. DTA spectra have been analysed for crystallization temperature (T_c) and onset temperature of crystallization (T_o). The crystallization temperature and onset temperature of crystallization have been found to shift to higher value with increase in heating rate (β) and with increase in Sb content (x). The activation energy of crystallization (E_c) has been calculated using the modified Kissinger, Matusita-Sakka, Augis-Bennett and Ozawa's approaches. The activation energy of crystallization has been found to increase with Sb content, implying more crystallization. E_c values calculated using different methods are in good agreement with each other.

Keywords: differential thermal analysis, crystallization temperature, activation energy of crystallization.

1. INTRODUCTION

The chalcogen glasses have applications in optics, optoelectronics, holography and IR lenses etc. [1]. Se in pure form is useful in applications like switching, memory and xerography [2-3]. Pure Se has disadvantages due to its low photosensitivity, low crystalline temperature and short life time. Addition of Te to Se produces higher photo sensitivity, lesser aging effects, higher crystallization temperature and greater hardness [4-5]. Te addition initially resists crystallization but at higher contents the crystallization occurs. The properties of binary alloys can be varied by adding a third element from group 4 or 5 of the periodic table so that the new materials are tailor made for specific purposes. The glass transition temperature and the glass forming ability of Se-Te matrix can be increased by adding the third element [6-8]. It also produces compositional and configurational disorder in the system Applications based on the amorphous to crystalline photo induced phase transition and vice versa require understanding of glass forming tendency and crystallization kinetics. Optical data storage based on laser induced amorphous to crystalline phase transformation of chalcolgenide glasses is an important area of research activity [9-13]. Activation energy of crystallization plays an important role in determining the utility of these glasses for phase change recording on compact discs [14]. Crystallization kinetics of amorphous materials has been studied by various workers [15-17]. Thermal analysis has been used to study the kinetics of chemical reactions [18-20] and crystallization of amorphous alloys [21-22]. Thermal analysis comprises a group of techniques where the properties of the material are studied as they change with temperature. Non isothermal DTA study has been used for the crystallization kinetics of the glasses because it is sensitive, easy to carry out and it require small amount of sample. In DTA the glass transition is exhibited by an endothermic peak and the crystallization by an exothermic peak due to change in specific heat of the sample. In the present paper the E_c has been calculated using DTA scans at different heating rates.

2. EXPERIMENTAL DETAILS

Glassy alloys of $Te_{15}(Se_{100-x}Sb_x)_{85}$ (x = 0, 1, 2, 3 and 4 at%) were prepared by the melt quenching technique. Se, Te and Sb of high purity (99.999%) were weighed according to their atomic percentages and were sealed in quartz ampoules evacuated at 10^{-3} Pa. The sealed ampoules were kept inside a vertical furnace where the temperature was raised up to 1073 K at the heating rate of 3-4 K/min. The ampoules were heated at the highest temperature for 12 h. During this heating the ampoules were frequently rocked to make the melt homogenous. The quenching was done in ice cold water. The quenched samples were obtained by breaking the ampoules. The amorphous nature of the glasses was confirmed as there was no prominent peak in their X-ray diffraction spectra. The prepared glasses were grounded to make fine powder for DTA studies. The thermal behaviour of the samples was recorded using Shimadzu DTG-60 system. In each study approximately 20-25 mg bulk material was used. Four heating rates of 10, 15, 20 and 25 K/min were chosen for the present study to get characteristic temperatures T_c and T_o.

3. RESULTS AND DISCUSSION

Fig.1 shows X-ray diffractogram for $Te_{15}(Se_{100-x}Sb_x)_{85}$ (x = 2) sample. The amorphous nature is confirmed as there is no sharp peak in the X-ray diffraction (XRD) spectra. The other samples also do not show any sharp peak in their XRD spectra. The DTA graphs of $Te_{15}(Se_{100-x}Sb_x)_{85}$ for x = 1 at.% (as reference) at different heating rates of 10, 15, 20 and 25 K/min are shown in Fig. 2.

The characteristic temperatures such as T_c and T_0 were recorded from the DTA data and are listed in Table1 for different heating rates.

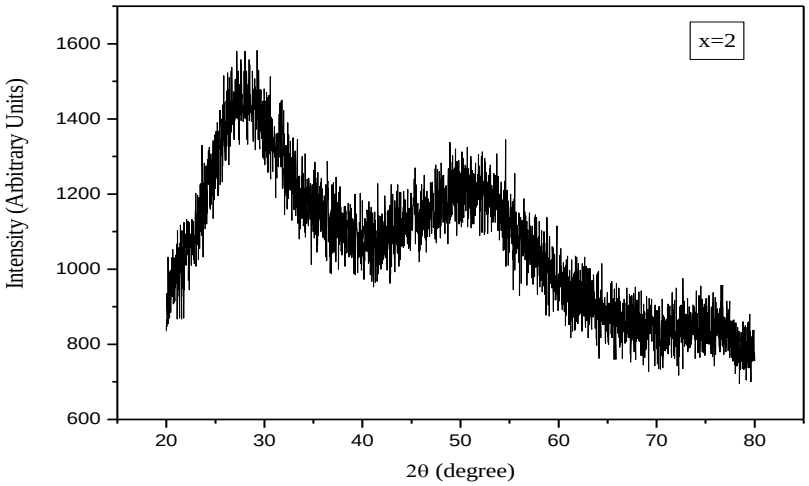

Fig. 1 X-ray diffraction spectra of $Te_{15}(Se_{100-x}Sb_x)_{85}$ (x =2 at.%) glassy alloys.

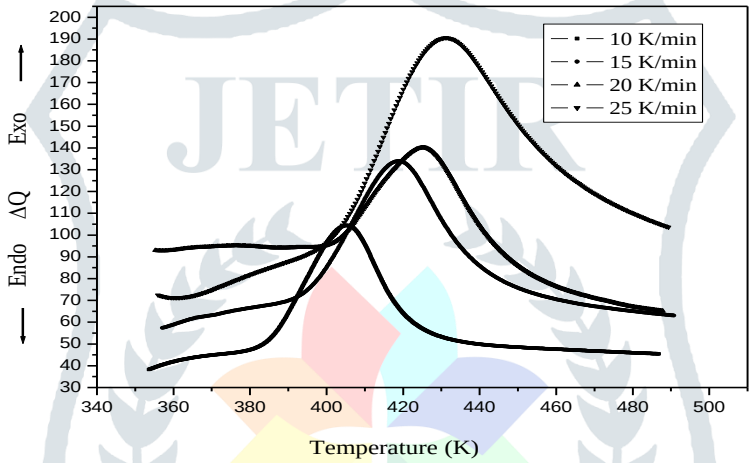

Fig. 2 DTA thermo grams for $Te_{15}(Se_{100-x}Sb_x)_{85}$ glassy alloys for (x = 1 at%) at heating rates of 10, 15, 20, 25 K/min.

Crystallization kinetics has been studied by Johnson-Mehl-Avrami (JMA) for amorphous alloys [23-25].
According to JMA the extent of crystallization (α) can be expressed as function of time by the relation

$$\alpha(t) = 1 - e^{[(-Kt)^n]} \quad (1)$$

where *n* is the Avrami index and *K* is crystallization rate constant given by

$$K = K_0 e^{(-\frac{E_c}{RT})} \quad (2)$$

E_c is activation energy of crystallization, R is universal gas constant.

3.1 Kissinger's method:

The activation energy of crystallization is calculated from variation of peak crystallization temperature (T_c) with heating rate using the modified Kissinger's equation [26-27].

$$\ln(\frac{T_c^2}{\beta}) + const. = \frac{E_c}{RT_c} \quad (3)$$

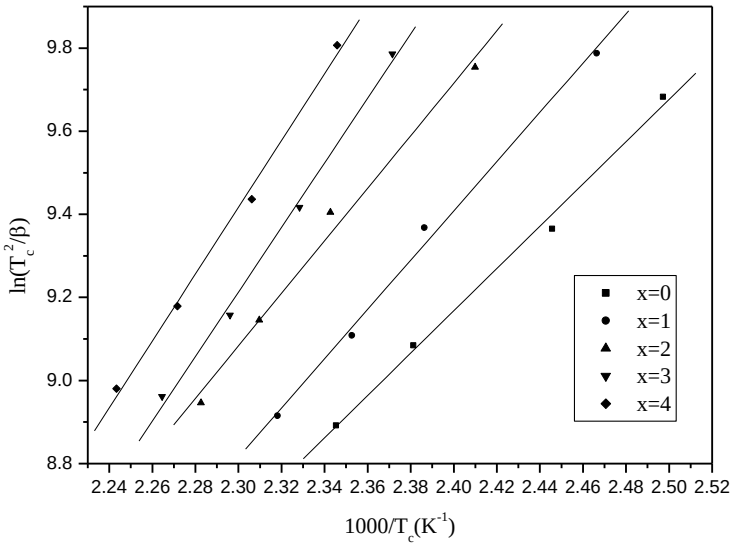

Fig. 3 Plot of ln(T_c^2/β) vs 1000/T_c for $Te_{15}(Se_{100-x}Sb_x)_{85}$ (x = 0, 1, 2, 3 and 4 at.%) glassy alloys.

The graph between ln(T^2_c/β) vs 1000/T_c is shown in Fig. 3. The slope of this graph gives the value of activation energy of crystallization (E_c).

3.2 Matusita-Sakka's method:

According to this method the heating rate and T_c can be expressed as [28-29]

$$\ln(\beta) = -\frac{E_c}{RT_c} + const. \quad (4)$$

The value of activation energy of crystallization (E_c) is found from the slope of graph between ln(β) vs 1000/T_c , shown in Fig. 4.

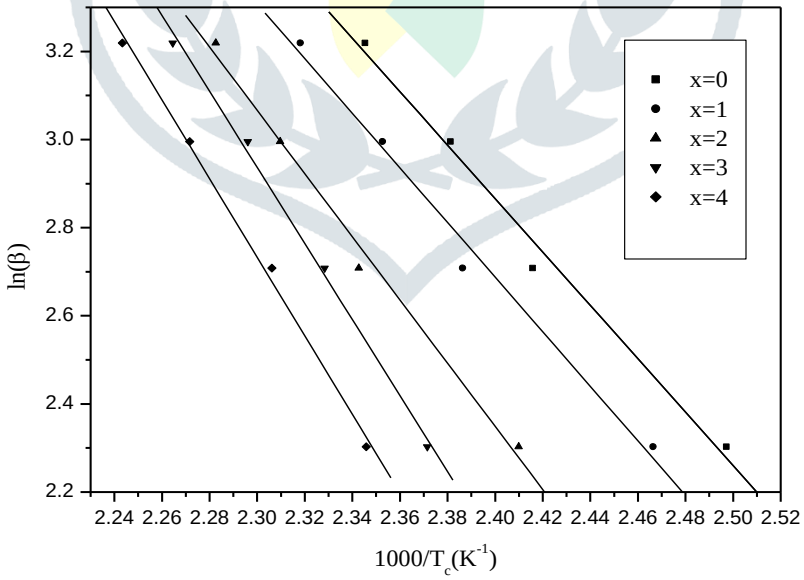

Fig. 4 Plot of ln(β) vs 1000/T_c for $Te_{15}(Se_{100-x}Sb_x)_{85}$ (x = 0, 1, 2, 3 and 4 at.%) glassy alloys.

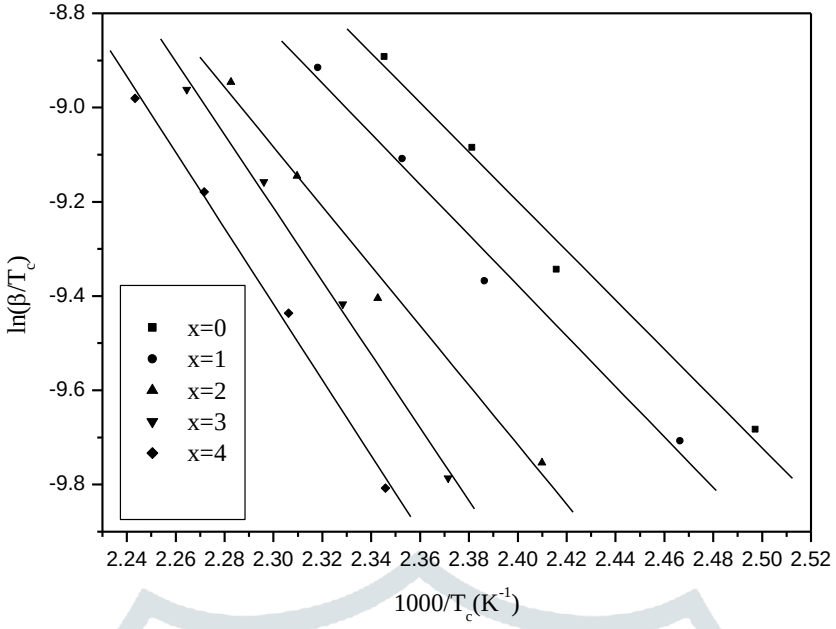

Fig. 5 Plot of ln(β/T_c) vs 1000/T_c for $Te_{15}(Se_{100-x}Sb_x)_{85}$ (x = 0, 1, 2, 3 and 4 at.%) glassy alloys.

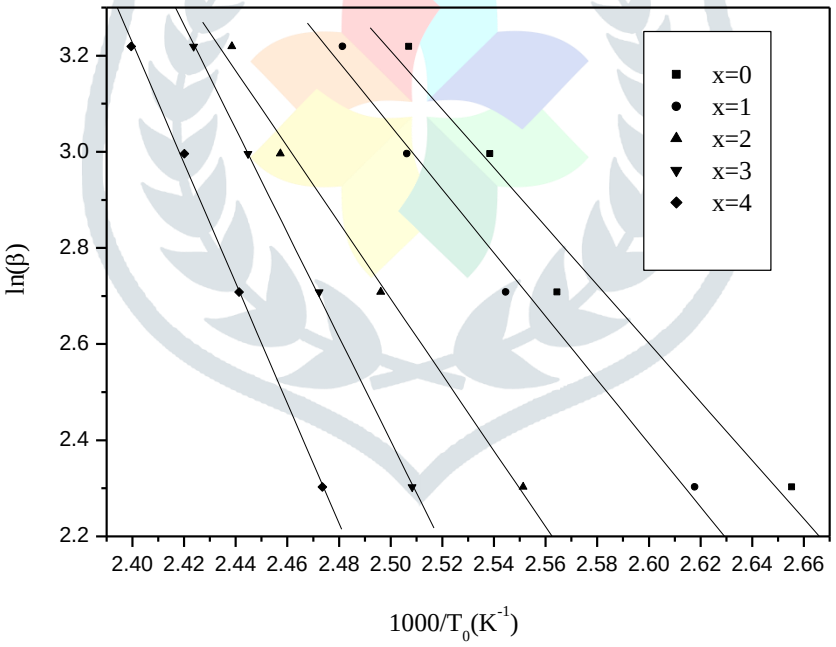

Fig. 6 Plot of ln(β) vs 1000/T_0 for $Te_{15}(Se_{100-x}Sb_x)_{85}$ (x = 0, 1, 2, 3 and 4 at.%) glassy alloys.

3.3 Augis-Bennett's method:

The value of E_c is also calculated from the relation used by Augis and Bennett [28] using the relation [30]

$$\ln\left(\frac{\beta}{T_c}\right) = -\frac{E_c}{RT_c} + \ln(K_0) \qquad (5)$$

The graph between ln(β/ T_c) vs 1000/T_c is shown in Fig. 5. The slope of this graph gives the value of activation energy of crystallization (E_c).

3.4 Ozawa's method:

E_c was also calculated from heating rate (β) dependence of on-set temperature of crystallization T_0. According to this method β and T_0 are related by equation [31]

$$\ln(\beta) = -\frac{E_c}{RT_0} + const. \qquad (6)$$

The slope of plot of ln(β) vs. $1000/T_0$, Fig.6, gives the value of activation energy of crystallization (E_c). The values of E_c in all the methods are found to increase with increase in Sb content. This increase in activation energy of crystallization with Sb content is probably due to increase in temperature of crystallization. The calculated E_c values using all the methods are reported in Table 1.

Table 1 Values of T_c, T_0, and E_c for $Te_{15}(Se_{100-x}Sb_x)_{85}$ (x = 0, 1, 2, 3 and 4 at.%) glassy alloys at the heating rate of 10, 15, 20 and 25 K/min.

Sample	Heating rate β (K/min)	T_c (K^{-1})	T_0 (K^{-1})	E_c (kJ/mol)			
				Kissinger	Matusita-Sakka	Augis-Bennett	Ozawa
x=0	10	400.45	376.45	41.64	50.37	43.51	50.58
	15	413.95	389.95				
	20	419.94	393.94				
	25	426.39	398.89				
x=1	10	405.45	382.11	49.28	51.52	46.94	54.94
	15	419.05	393.08				
	20	425.05	399.13				
	25	431.39	403.04				
x=2	10	414.95	391.95	52.54	59.62	48.05	65.72
	15	426.85	403.85				
	20	432.96	406.96				
	25	438.09	410.09				
x=3	10	421.67	398.67	64.60	71.77	56.08	89.90
	15	429.48	404.48				
	20	435.53	409.03				
	25	441.59	412.59				
x=4	10	426.28	404.18	66.84	74.13	67.21	103.90
	15	433.62	409.52				
	20	440.2	413.28				
	25	445.76	416.79				

4. CONCLUSION

The crystallization temperature and on-set crystallization temperature increases with increase in heating rate (β) and with Sb addition for $Te_{15}(Se_{100-x}Sb_x)_{85}$ (x = 0, 1, 2, 3 and 4 at %) system under investigation. Activation energy of crystallization (E_c) is calculated using Kissinger, Matusita-Sakka, Augis- Bennett and Ozawa's approaches. E_c has been found to increase with increase in Sb content in all methods in all the samples. E_c values calculated in all the approaches are in fairly good agreement indicating any of the four methods can be used for crystallization kinetics study.

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