

# Calorimetric studies of glass forming ability and thermal stability in a- $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$ ( $\text{M} = \text{Ag}, \text{Cd}, \text{In}, \text{Sb}$ ) alloys

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**Abstract.** The glass formation and divitrification of a- $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  ( $\text{M} = \text{Ag}, \text{Cd}, \text{In}, \text{Sb}$ ) alloys were studied by Differential Scanning Calorimetry (DSC). A comparison of various simple quantitative methods to assess the level of the stability of these glassy alloys is presented. All of these methods are based on characteristic temperatures such as the glass transition temperature ( $T_g$ ), on-set crystallization temperature ( $T_o$ ) at which crystallization begins, peak crystallization temperature ( $T_c$ ) at which the crystallization rate is maximum and melting temperature ( $T_m$ ). The Hruby number ( $H_r$ ), which is the strong indicator of Glass Forming Tendency (GFT) and thermal stability parameter ( $S$ ) representing resistance to divitrification have also been evaluated for these glassy alloys. The stability criteria based on Arrhenius dependence of rate constant  $K(T)$  are also studied. The stability of these glasses has been evaluated experimentally and correlated with the activation energy of the crystallization by the kinetic  $K(T)$  criteria and it is compared with  $S$  criterion.

**PACS.** 72.80.Ng Disordered Solids – 61.43.Fs Glasses

## 1 Introduction

The study of selenium and selenium-tellurium alloys in the amorphous and glassy states is important in order to understand the physical phenomena occurring in these materials, which are of interest because of their applications in various optoelectronic devices [1–4]. The structure of a-Se [5–8] and the effect of alloying Te into a-Se have been studied by various workers [9–12]. Their results have shown that a-Se contains the long polymeric chains and the eight members rings in various proportions as its structural units, which are dissociated by the addition of Te in a-Se. This makes Se-Te alloys more important due to their attractive advantages (higher photosensitivity, greater hardness and lesser aging effects) as compared to pure a-Se. Due to these advantages, Se-Te alloys can be used as recording layer materials in optical phase change (PC) technique [13–16]. However, these alloys are found to have some significant problems for this type of application. The two serious problems are the limited reversibility [17] and the low glass transition and crystallization temperatures. These problems can be removed by adding a third element as a chemical modifier in Se-Te alloys.

In chalcogenide glasses, GFT of a glassy alloy is related to the ease by which melt can be cooled with the avoidance of crystal formation. On the other hand, the

thermal stability represents the resistance to divitrification of glassy alloy through the nucleation and growth process. The origin of GFT and the thermal stability is, therefore, a subject of great interest [18–20]. In order to evaluate the level of stability of the glassy alloys, different simple quantitative methods have been suggested. Most of these methods [21–24] are based on the characteristic temperatures such as the glass transition temperature ( $T_g$ ), the on-set crystallization temperature ( $T_o$ ), the peak crystallization temperature ( $T_c$ ) and the melting temperature ( $T_m$ ). Some of them [25–27] are based on reaction rate constant  $K$ . These thermal parameters are easily and accurately obtained by DSC technique.

Dietzel [21] introduced the first stability criterion,  $\Delta T = T_c - T_g$ . By the use of the characteristic temperatures, Hruby [23] developed the  $H_r$  criterion,  $H_r = \Delta T / (T_m - T_c)$ . Saad and Poulain [24] obtained another criterion,  $S = \Delta T (T_c - T_o) / T_g$ .

Recently, the effect of incorporation of third element M (chemical modifier) in Se-Te glassy alloys has been reported by our group in a- $\text{Se}_{70}\text{Te}_{20}\text{M}_{10}$  system [18]. Our results showed that GFT and thermal stability are sufficiently changed on addition of third element.

The present work reports on the effect of addition of the third element on GFT and thermal stability in Se-Te-M system at low concentration of M. For this purpose, the above studies have been made in glassy  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$

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(M = Ag, Cd, In, Sb) alloys using DSC technique. The present results show that even a small concentration (0.5 at%) of third element affects GFT and thermal stability significantly.

## 2 Experimental technique

Glassy alloys of  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  (M = Ag, Cd, In, Sb) were prepared by quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of  $10^{-4}$  mg. The materials were then sealed in evacuated ( $\sim 10^{-5}$  torr) quartz ampoules (length  $\sim 5$  cm and internal diameter  $\sim 8$  mm). Each ampoule was kept inside the furnace at  $1000^\circ\text{C}$  temperature (where the temperature was raised at a rate of  $3\text{--}4^\circ\text{C}/\text{min}$ ). During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly. The ingots of the samples were then taken out by breaking the quartz ampoules.

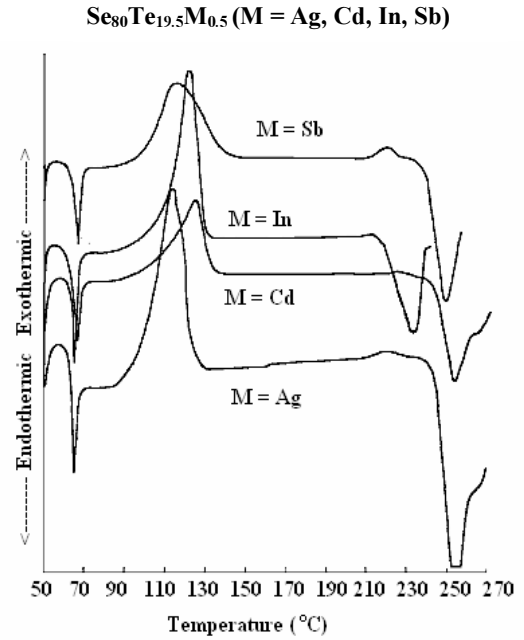
The glasses, thus prepared, were ground to make fine powder for DSC studies. 10 to 20 mg of the powder was heated at constant heating rate and the changes in heat flow with respect to an empty reference pan were measured. DSC 2910 Differential Scanning Calorimeter (T. A. instrument, USA) was used at five different heating rates 5, 10, 15, 20 and  $25^\circ\text{C}/\text{min}$ . Each DSC scan showed a well-defined endothermic peak at the glass transition temperature  $T_g$  and an exothermic peak at the crystallization temperature  $T_c$ .

## 3 Results and discussion

Figure 1 shows typical DSC thermograms at a heating rate of  $10\text{ K}/\text{min}$  for  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  (M = Ag, Cd, In, Sb) alloys. It is clear from Figure 1 that well-defined endothermic peaks are observed at the glass transition temperature  $T_g$  and the melting temperature  $T_m$ . The well-defined exothermic peaks are also obtained between  $T_g$  and  $T_m$  at the crystallization temperature  $T_c$ . The values of  $T_g$  and  $T_c$  at different heating rates for the various glassy alloys are given in Table 1. From this table it is clear that the variation in glass transition temperature  $T_g$  with the change in third element as additive is not significant but the crystallization temperature  $T_c$  is significantly changed with the change in additive.

### 3.1 Glass transition kinetics and glass forming ability

Two approaches are used in the analysis of the dependence of  $T_g$  on the heating rate. The first is the empirical relation



**Fig. 1.** DSC scans of  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  (M = Ag, Cd, In, Sb) alloys at heating rate of  $10\text{ K}/\text{min}$ .

that has been suggested by Lasocka [28] and has the form:

$$T_g = A + B \log \beta \quad (1)$$

where  $A$  and  $B$  are constants. The values of  $A$  and  $B$  for different alloys are given in Table 2. The results shown in Table 2 indicate the validity of this relationship for the various alloys. The plots of  $T_g$  vs.  $\log \beta$  for glassy alloys are shown in Figure 2. The value of  $A$  indicates the glass transition temperature for the heating rate of  $1\text{ K}/\text{min}$ . It has been found by the various workers that the slope  $B$  in equation (1) is related to the cooling rate of the melt: the lower the cooling rate of the melt, the lower the value of  $B$ . The physical significance of  $B$  seems to be related with the response of the configurational changes within the glass transformation region. The values of  $B$  for various alloys have been found to be different, indicating that these glassy alloys undergo different structural changes.

The second approach concerns the use of the Kissinger's linear dependence [29] in the form:

$$\ln(\beta/T_g^2) = E_g/RT_g + \text{constant}. \quad (2)$$

In addition, when the variation of  $\ln(1/T_g^2)$  with  $\ln \beta$  is much slower than that of  $1/T_g$  then equation (2) converts in to the form [30]:

$$\ln \beta = -E_g/RT_g + \text{constant}. \quad (3)$$

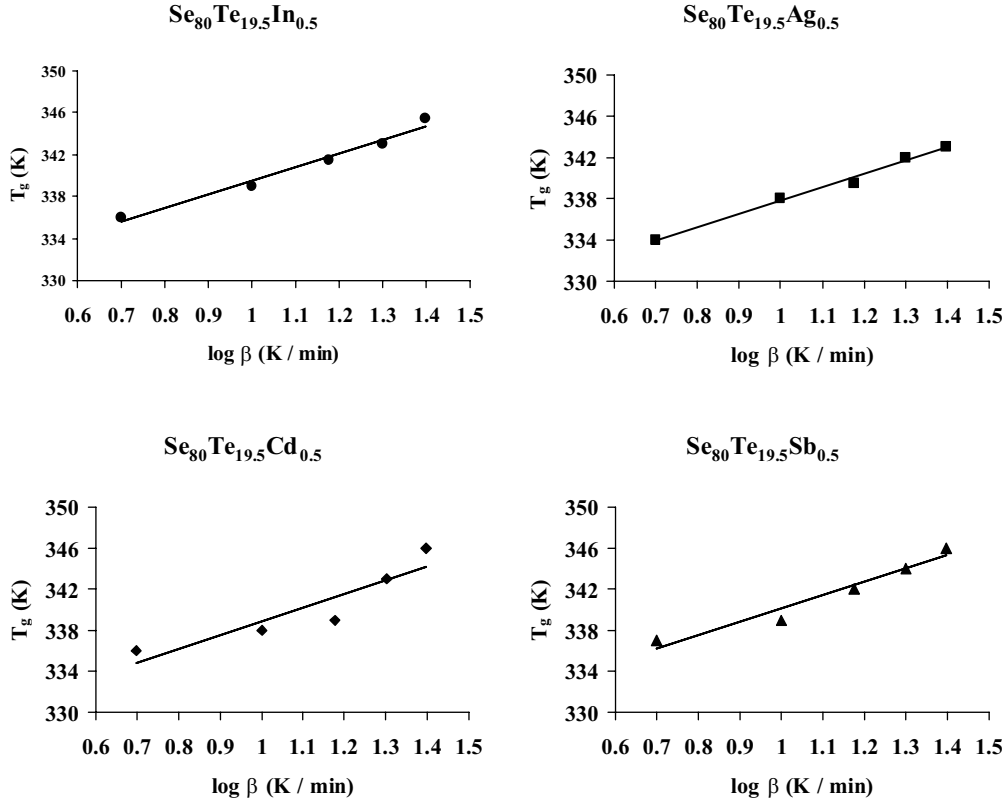
The plots of  $\ln(\beta/T_g^2)$  and  $\ln \beta$  against  $10^3/T_g$  are shown in Figure 3. Using the slopes of these plots, the activation energy of the glass transition process is calculated for the various alloys and is given in Table 2. It is

**Table 1.** Glass transition and peak crystallization temperatures (in  $^{\circ}\text{C}$ ) of various glassy alloys at different heating rates.

Sample	$\beta = 5^{\circ}\text{C}/\text{min}$		$\beta = 10^{\circ}\text{C}/\text{min}$		$\beta = 15^{\circ}\text{C}/\text{min}$		$\beta = 20^{\circ}\text{C}/\text{min}$		$\beta = 25^{\circ}\text{C}/\text{min}$	
	$T_g$	$T_c$	$T_g$	$T_c$	$T_g$	$T_c$	$T_g$	$T_c$	$T_g$	$T_c$
$\text{Se}_{80}\text{Te}_{19.5}\text{Ag}_{0.5}$	61.0	107.0	65.0	113.0	66.5	119.0	69.0	123.0	70.0	125.0
$\text{Se}_{80}\text{Te}_{19.5}\text{Cd}_{0.5}$	63.0	117.0	65.0	124.0	66.0	129.0	70.0	134.0	73.0	137.0
$\text{Se}_{80}\text{Te}_{19.5}\text{Sb}_{0.5}$	64.0	107.0	66.0	114.0	69.0	119.0	71.0	122.0	73.0	125.0
$\text{Se}_{80}\text{Te}_{19.5}\text{In}_{0.5}$	63.0	115.0	66.0	122.0	68.5	126.0	70.0	130.0	72.5	133.0

**Table 2.** Values of different kinetic parameters of various glassy alloys.

Sample	$A$ (K)	$B$ (min)	$E_g$ (eV)		$H_r$		$E_c$ (eV)		$S$ (K)
	Eq. (1)	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)
$\text{Se}_{80}\text{Te}_{19.5}\text{Ag}_{0.5}$	324.9	12.8	1.696	1.754	0.34	1.047	1.114	1.081	11.3
$\text{Se}_{80}\text{Te}_{19.5}\text{Cd}_{0.5}$	325.4	13.4	1.394	1.453	0.46	1.024	1.093	1.058	18.0
$\text{Se}_{80}\text{Te}_{19.5}\text{Sb}_{0.5}$	327.2	12.9	1.653	1.711	0.36	1.100	1.058	1.133	8.0
$\text{Se}_{80}\text{Te}_{19.5}\text{In}_{0.5}$	326.4	13.1	1.660	1.719	0.51	1.153	1.042	1.187	7.2

**Fig. 2.** Plots of  $T_g$  vs.  $\log \beta$  for various glassy alloys.

clear from this table that the  $E_g$  values are in good agreement with each other. This shows that one can use any of equations (2) and (3) for the evaluation of  $E_g$ .

The Hruby number ( $H_r$ ), which is the strong indicator of GFT, is defined as the ratio of  $T_c - T_g$  and  $T_m - T_c$  and is given by [23]:

$$H_r = (T_c - T_g)/(T_m - T_c). \quad (4)$$

The values of  $H_r$  are given in Table 2 for the various glassy alloys. From this table, it is clear that the GFT is high in case of glassy  $\text{Se}_{80}\text{Te}_{19.5}\text{In}_{0.5}$  alloy.

### 3.2 Crystallization kinetics and thermal stability

Based on JMA model, different authors have developed very diverse methods for the evaluation of the activation energy of crystallization ( $E_c$ ) of the chalcogenide glasses.

According to Kissinger [29], the peak crystallization temperature  $T_c$ , in terms of the heating rate  $\beta$ , can be expressed as:

$$\ln(\beta/T_c^2) = -E_c/RT_c + \text{constant}. \quad (5)$$

This equation is used to calculate the activation energy of crystallization by plotting  $\ln(\beta/T_c^2)$  vs.  $10^3/T_c$  curve.

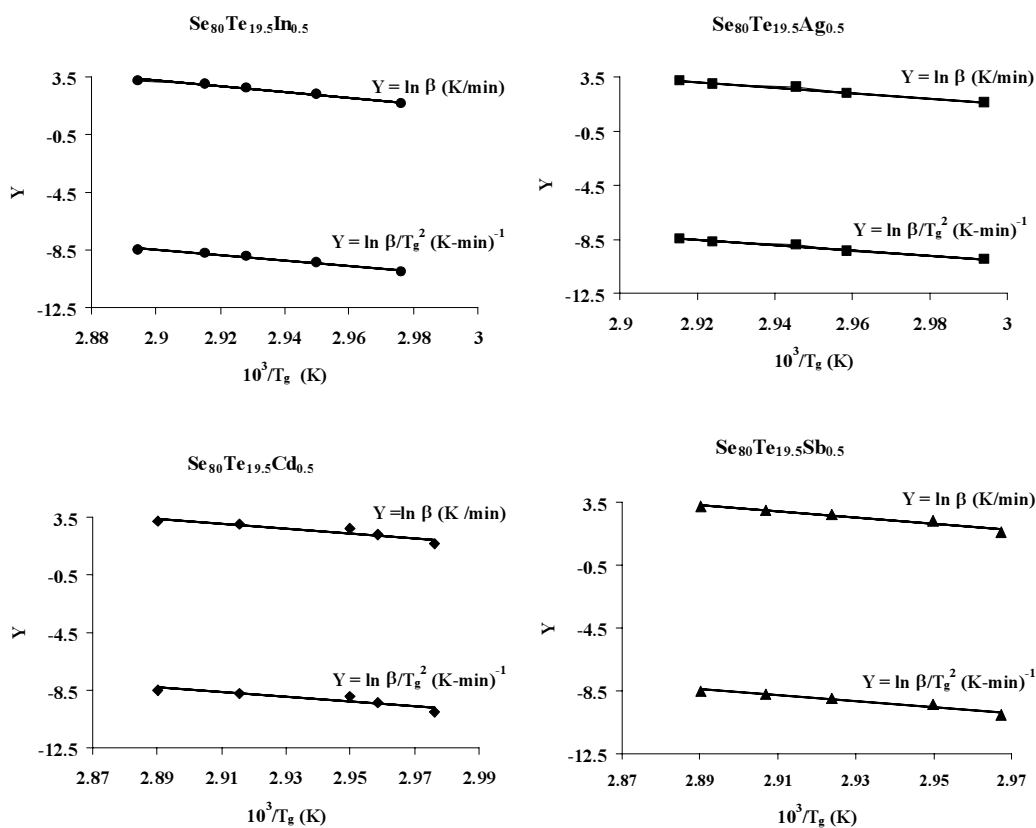


Fig. 3. Plots of  $\ln \beta$  and  $\ln (\beta/T_g^2)$  against  $10^3/T_g$  for various glassy alloys.

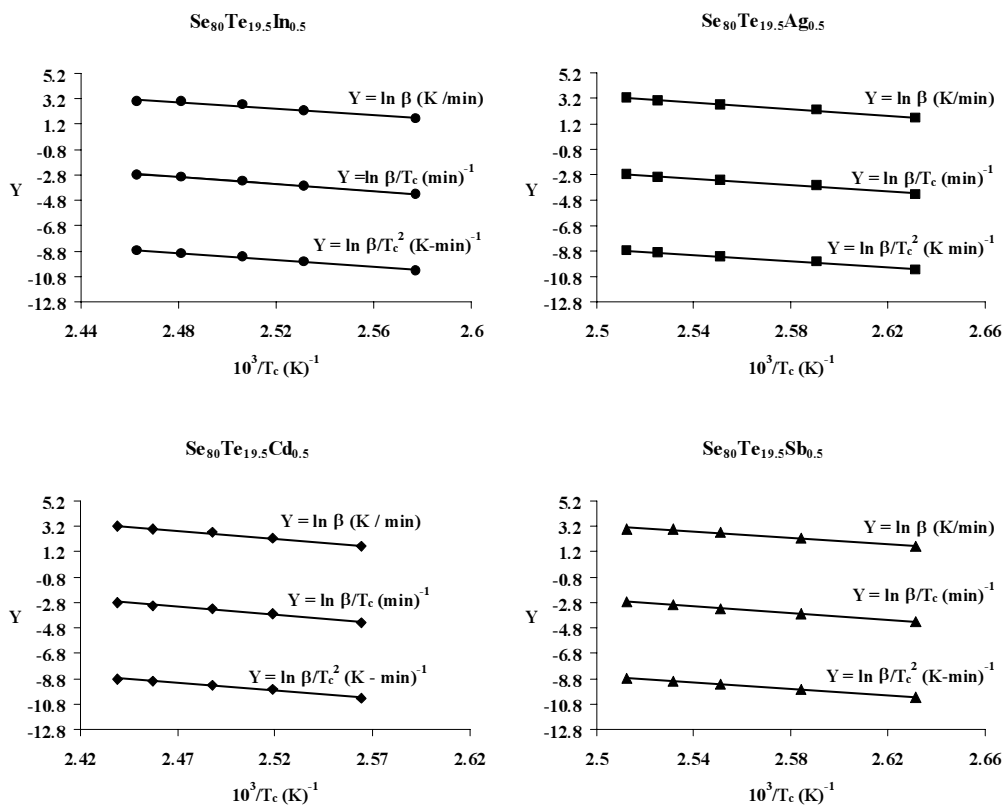


Fig. 4. Plots of  $\ln \beta$ ,  $\ln (\beta/T_c)$ ,  $\ln (\beta/T_c^2)$  against  $10^3/T_c$  for various glassy alloys.

**Table 3.** Kinetic parameters of various glassy alloys showing stability criteria of Surinach et al. and Hu et al.

Heating Rate	Se <sub>80</sub> Te <sub>19.5</sub> Ag <sub>0.5</sub>		Se <sub>80</sub> Te <sub>19.5</sub> Cd <sub>0.5</sub>		Se <sub>80</sub> Te <sub>19.5</sub> Sb <sub>0.5</sub>		Se <sub>80</sub> Te <sub>19.5</sub> In <sub>0.5</sub>	
	$K(T_g) \times 10^{-12}$	$K(T_c) \times 10^{-12}$	$K(T_g) \times 10^{-11}$	$K(T_c) \times 10^{-11}$	$K(T_g) \times 10^{-13}$	$K(T_c) \times 10^{-13}$	$K(T_g) \times 10^{-13}$	$K(T_c) \times 10^{-13}$
5	2.816	2.829	6.165	6.197	1.357	1.363	3.298	3.315
10	2.817	2.830	6.167	6.200	1.358	1.364	3.299	3.317
15	2.818	2.832	6.167	6.202	1.358	1.364	3.300	3.318
20	2.818	2.833	6.170	6.205	1.358	1.365	3.300	3.319
25	2.819	2.833	6.172	6.206	1.359	1.365	3.301	3.320

**Table 4.** Kinetic parameters of various glassy alloys showing stability criteria of Vazquez et al.

Heating Rate	Se <sub>80</sub> Te <sub>19.5</sub> Ag <sub>0.5</sub>		Se <sub>80</sub> Te <sub>19.5</sub> Cd <sub>0.5</sub>		Se <sub>80</sub> Te <sub>19.5</sub> Sb <sub>0.5</sub>		Se <sub>80</sub> Te <sub>19.5</sub> In <sub>0.5</sub>	
	$K_r(T_g) \times 10^{-12}$	$K_r(T_c) \times 10^{-12}$	$K_r(T_g) \times 10^{-11}$	$K_r(T_c) \times 10^{-11}$	$K_r(T_g) \times 10^{-13}$	$K_r(T_c) \times 10^{-13}$	$K_r(T_g) \times 10^{-13}$	$K_r(T_c) \times 10^{-13}$
5	2.886	2.891	6.288	6.303	1.390	1.392	3.361	3.488
10	2.887	2.891	6.289	6.304	1.390	1.393	3.362	3.487
15	2.887	2.892	6.289	6.305	1.390	1.393	3.362	3.486
20	2.887	2.892	6.290	6.306	1.391	1.39	3.363	3.486
25	2.887	2.892	6.291	6.307	1.391	1.393	3.363	3.486

Matusita and Sakka [31,32] established the following equation for the evaluation of  $E_c$  from the classical JMA equation:

$$\ln \beta = -E_c/RT_c + \text{constant}. \quad (6)$$

This equation is used to calculate the activation energy of crystallization by plotting  $\ln \beta$  vs.  $10^3/T_c$  curve.

The activation energy of crystallization  $E_c$  can also be determined by an approximation method developed by Augis and Bennett [33]. The relation used by them is of the form:

$$\ln(\beta/T_c) = -E_c/RT_c + \ln K_o. \quad (7)$$

The activation energy of crystallization can be evaluated by this equation using the plots of  $\ln(\beta/T_c)$  against  $10^3/T_c$ . This method has an extra advantage that the intercept of  $\ln(\beta/T_c)$  vs.  $1/T_c$  gives the value of pre-exponential factor  $K_o$  of Arrhenius equation.

The plots of  $\ln(\beta/T_c^2)$ ,  $\ln \beta$  and  $\ln(\beta/T_c)$  against  $10^3/T_c$  are shown in Figure 4. Using the slopes of these plots, the activation energy of the crystallization process is calculated for the various alloys and is given in Table 2. It is clear from this table that the  $E_c$  values are in good agreement with each other. This shows that one can use any of equations (5–7) for the evaluation of  $E_c$ .

The thermal stability parameter [24]:

$$S = [(T_c - T_o)(T_c - T_g)]/T_g, \quad (8)$$

reflects the resistance to divitrification after formation of the glass. Higher values of  $(T_c - T_g)$  delays the nucleation process and the small values of  $(T_m - T_c)$  retards the growth process. On the other hand,  $(T_c - T_o)$  is related to the rate of divitrification transformation of the glassy phases. The values of  $S$  are also given in Table 2 for the various glassy alloys.

In order to evaluate the stability in glasses, Surinach et al. [25] introduced  $K(T_g)$  criterion and Hu et al. [26]

developed  $K(T_c)$  criterion:

$$K(T_g) = K_o \exp[-E_c/(RT_g)] \quad (9)$$

$$K(T_c) = K_o \exp[-E_c/(RT_c)]. \quad (10)$$

Since  $H_r$  parameter itself is a stability factor, Vazquez et al. [27] defined the stability criterion in the following forms:

$$K_r(T_g) = K_o \exp[-(H_r E_c)/(RT_g)] \quad (11)$$

$$K_r(T_c) = K_o \exp[-(H_r E_c)/(RT_c)]. \quad (12)$$

The values of these stability criteria are given in Tables 3 and 4 for the present glassy alloys at all the five heating rates. The plots of  $\ln(K)$  vs. temperature using equations (9–12) are shown in Figure 5. From these plots it is clear that values of  $\ln(K)$  increases in the sequence  $[\ln(K)]_{Cd} < [\ln(K)]_{Ag} < [\ln(K)]_{Sb} < [\ln(K)]_{In}$  for all the above four criteria. High values of  $K$  or  $\ln(K)$  means poor stability of glass. This is also confirmed from the values of the thermal stability parameter  $S$  as the decreasing sequence of  $S$  is  $(S)_{Cd} > (S)_{Ag} > (S)_{Sb} > (S)_{In}$ . Thus, the stability results of the above four criteria based on the Arrhenius dependence of the rate constant  $K$  agrees with  $S$  criterion. Hence one can conclude that the rate of crystallization is related to thermal stability in the present glasses. This result is consistent with our previous results [18] at higher concentration of additive.

## 4 Conclusions

The GFT and thermal stability of glassy Se<sub>80</sub>Te<sub>19.5</sub>M<sub>0.5</sub> ( $M = Ag, Cd, In, Sb$ ) alloys have been studied by non-isothermal DSC technique. The activation energies of the glass transition and crystallization processes for the chalcogenide glasses Se<sub>80</sub>Te<sub>19.5</sub>M<sub>0.5</sub> ( $M = Ag, Cd, In, Sb$ ) have been calculated using the different non-isothermal methods.

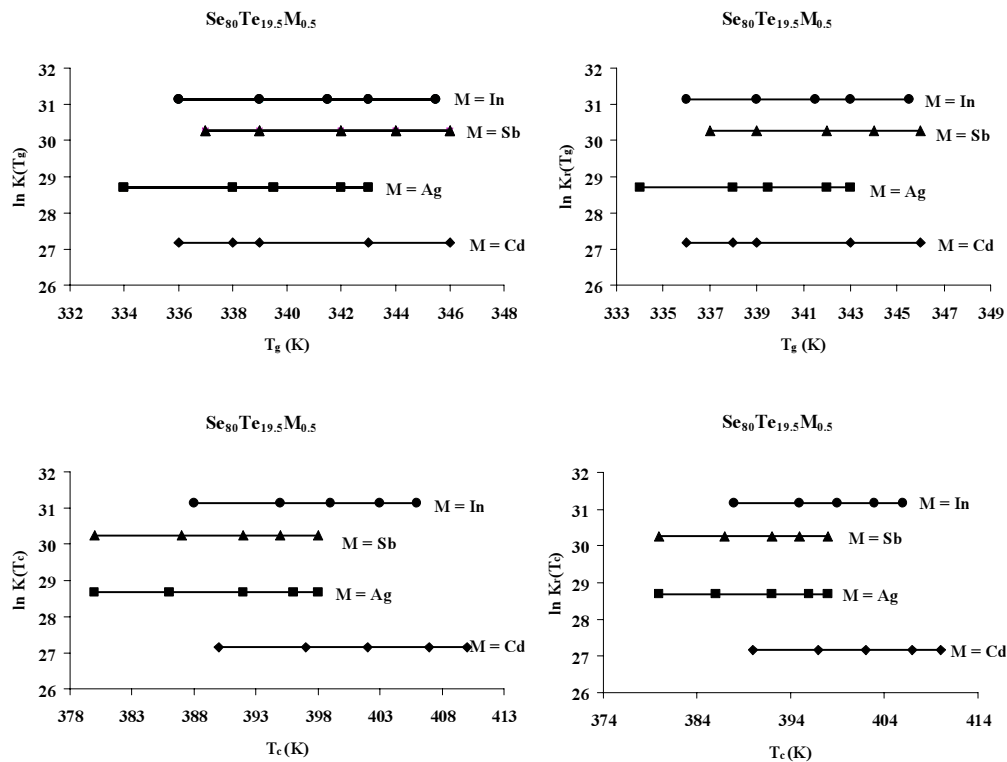


Fig. 5. Plots of  $\ln K$  vs.  $T$  for various glassy alloys using different criteria.

The Hruby number ( $H_r$ ), the strong indicator of GFT, is evaluated by characteristic temperatures of the various glassy alloys. The thermal stability parameter  $S$  for these glassy alloys and the stability criteria based on Arrhenius dependence of rate constant  $K$  are also calculated. In present work, the significant variation has been found in the GFT and thermal stability even at low concentration of the additives. The results show that the stability criteria based on Arrhenius dependence of rate constant  $K$  agrees with  $S$  criterion.

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