

Differential scanning calorimetry studies of $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 4, 6, 8$ and 10) glasses

N B MAHARAJAN[†], N S SAXENA*, DEEPIKA BHANDARI, MOUSA M IMRAN and D D PAUDYAL[†]

Department of Physics, University of Rajasthan, Jaipur 302 004, India

[†]Central Department of Physics, Tribhuvan University, Kirtipur, Kathmandu, Nepal

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Abstract. Results of differential scanning calorimetry (DSC) studies of $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 4, 6, 8$ and 10) glasses have been reported and discussed in this paper. The results have been analyzed on the basis of structural relaxation equation, Matusita's equation and modified Kissinger's equation. The activation energies of structural relaxation lie in between 226 and 593 kJ/mol. The crystallization growth is found to be one-dimensional for all compositions. The activation energies of crystallization are found to be 100–136 kJ/mol by Matusita's equation while 102–139 kJ/mol by modified Kissinger's equation. The Hruby number (indicator of ease of glass forming and higher stability) is the highest for $\text{Se}_{85}\text{Te}_9\text{Pb}_6$ glass while S factor (indicator of resistance to devitrification) is highest for $\text{Se}_{85}\text{Te}_7\text{Pb}_8$ glass at all heating rates in our experiment. Further the highest resistance to devitrification has the highest value of structural activation energy and the activation energy of crystallization is maximum for the most stable glass by both Matusita's equation and the modified Kissinger's equation.

Keywords. Stability; devitrification; activation energy; dimension of growth.

1. Introduction

Study on chalcogenide glasses received attention due to their unique properties that are not shown by others (Elliot 1990). The current interest on the chalcogenide glasses is on X-ray imaging and photonics (Rowlands and Kasap 1997). To the best of our knowledge, very few attempts have been made to the study of chalcogenide glasses with one of the element as Pb. It may be due to the fact that lead is the last element in radioactive series, which is most stable, or lead is one with which it is most difficult to form a glass. The charge reversal from p -type to n -type in Ge–Se–Pb system (Toghe *et al* 1987) is observed in spite of the usual p -type charge carrier in the chalcogenide glasses. Charge reversal (Bhatia *et al* 1986) is also found in Ge–Se–Bi system. However, no serious attempt has been made to study the different kinetic parameters and their correlation with the thermal stability of the glass. In view of this an effort has been made to determine the activation energy of structural relaxation and crystallization using relaxation equation, Matusita equation and Kissinger's equation for non-isothermal reaction in the case of $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ (with $x = 4, 6, 8$ and

10) glasses. Also a correlation is established between the stability and resistance to devitrification of the glasses at different compositions with the above studied kinetic parameters.

2. Experimental

Bulk glasses in the $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 4, 6, 8$ and 10) were prepared by melt quenching technique. Appropriate atomic weight percentage of the elements (99.999% purity) was kept in cleaned quartz ampoules and sealed at vacuum of 10^{-6} torr. The sealed quartz ampoules were kept in a furnace where the temperature was raised through 4 to 5 K/min up to 800 K. The ampoules were then kept at that temperature for 12 h with rocking at an interval of around 10 min. After the said time the ampoules were taken out from the furnace and quenched in ice cold water. About 10–15 mg of the powder samples were taken and subjected to the differential scanning calorimetry at different heating rates. The DSC equipment was calibrated prior to the measurement using high purity elements such as Pb, Sn and In, with known melting enthalpies and melting points. The temperature precision of the instrument was ± 0.1 K with an average standard error of 1 K in the measured value.

*Author for correspondence

3. Results and discussion

Figure 1 shows the typical DSC thermograms of $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 4, 6, 8$ and 10) glasses at the heating rate of 20 K/min. The endothermic peak of glass transition and the exothermic peak of crystallization have been clearly observed in the figure. The glass transition temperature, T_g , and the on-set crystallization temperature, T_c , are defined as the intersection of the two linear portions of the transition elbows of the glass transition region and the crystallization, respectively (Cahn *et al* 1991).

The characteristic temperatures of the glass such as the glass transition temperature, on-set crystallization temperature, peak temperature of crystallization, T_{cp} , and the melting point, T_m , are the factors that determine its stability and resistance to devitrification. The most commonly used definition of the stability is $T_c - T_g$, which is frequently referred to as draw fibre.

The plot of T_g vs Pb at wt.% is shown in figure 2. From the figure it is observed that T_g decreases with the increase of Pb in the Se-Te-Pb system. The decrease of T_g with the increase of Pb content in the Se-Te-Pb system can be explained on the basis of structural change due to the introduction of Pb atoms in the Se-Te system.

In the glassy Se, about 40% of the atoms have ring structure and 60% of the atoms are bounded as polymeric

chains. Tellurium enters as co-polymeric chain and tends to reduce the number of Se_8 member rings. Simultaneously, it increases the number of Se and Te atoms in the chain structure (Predeep *et al* 1996a). The addition of Pb atoms in Se-Te makes bonds with Se and Te separately with bond energy of Se-Pb ($= 72.4$ kcal/mol) and Te-Pb ($= 60$ kcal/mol). The bond energies of Se-Se ($= 79.5$ kcal/mol) while that of Se-Te is ($= 64$ kcal/mol) (David 1977). The introduction of Pb in Se-Te system reduces the effective bond energy of $[(\text{Se-Se}) + (\text{Se-Te}) - ((\text{Se-Pb}) + (\text{Te-Pb}))] = 11.1$ kcal/mol. Hence increase of Pb at.% in the Se-Te system causes the decrease of T_g in the system. A similar decreasing trend has also been shown (figure 3) by T_c as the atomic wt.% of Pb increases in the Se-Te-Pb system.

The thermal stability parameter, Hruby number H_R , (Jha 1979) is defined as the ratio of $T_c - T_g$ and $T_m - T_c$ and is given by

$$H_R = T_c - T_g / T_m - T_c, \quad (1)$$

where T_m is the melting temperature.

The S parameter

$$S = (T_c - T_g) (T_{cp} - T_c) / T_g, \quad (2)$$

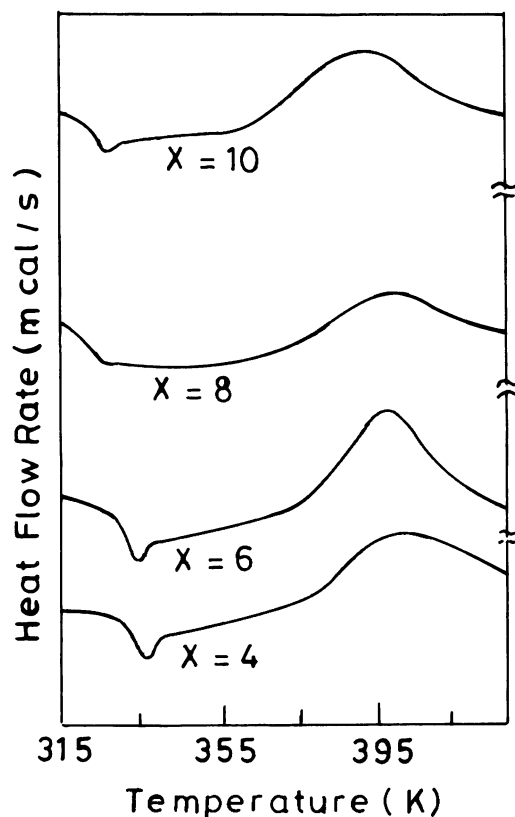


Figure 1. DSC thermograms of $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 4, 6, 8$ and 10) glasses at the heating rate of 20 K/min.

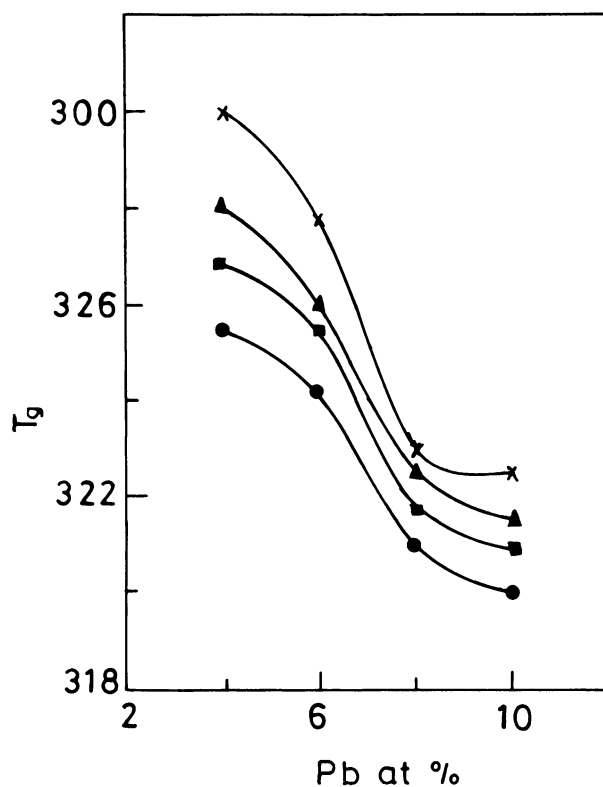


Figure 2. Plot of T_g vs Pb at. wt% for $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 4, 6, 8$ and 10) glasses at the heating rate of (●) 5 K/min, (■) 10 K/min, (▲) 15 K/min and (×) 20 K/min.

reflects the resistance to devitrification after formation of the glass. Higher value of $(T_c - T_g)$ delays nucleation and the small value of $(T_m - T_c)$ retards the growth process of the nucleated crystals. The Hruby number thus combines the nucleation and the growth aspects of the crystallization process. On the other hand $T_{cp} - T_c$ is related to the rate of devitrification transformation of the glassy phases.

Values of different characteristic temperatures, Hruby number and S -parameters obtained at the heating rate of 20 K/min are shown in table 1. The values of H_R at other heating rates are also calculated. The variations of H_R with the compositions at the different heating rates are shown in figure 4. From the figure it is observed that the highest value of Hruby number is around $x = 6$ and there-

fore in the neighbourhood of this composition the glass could be taken as the most stable.

Similarly, the values of S factor at the other heating rates are also calculated. The variations of S factor with the composition, at the different heating rates are shown in figure 5. It is observed from the figure that the highest value of S is around just below $x = 8$.

Figure 6 shows the typical DSC thermograms at the heating rates of 5, 10, 15 and 20 K/min for $Se_{85}Te_5Pb_{10}$. It is evident from the figure that the glass transition temperature and the peak temperature of crystallization shift to the higher temperature side as the heating rate is increased from 5 to 20 K/min. Similar results are also obtained in all other glasses used in the present study. The heating rate dependence of glass transition temperature in chalcogenide glass is explained in terms of the thermal relaxation phenomena. Structural relaxation is kinetically embedded with the rearrangement of the temperatures dependent structure of liquid and it is accompanied by the change in the macroscopic properties such as enthalpy, H , volume, V , and the refractive index, n (Ma 1992). The time scale for the structural relaxation is highly dependent both on the temperature and on the instantaneous structure itself. In this kinetic interpretation the enthalpy at a particular temperature and time, $H(T, t)$, of the glassy system after an instantaneous isobaric

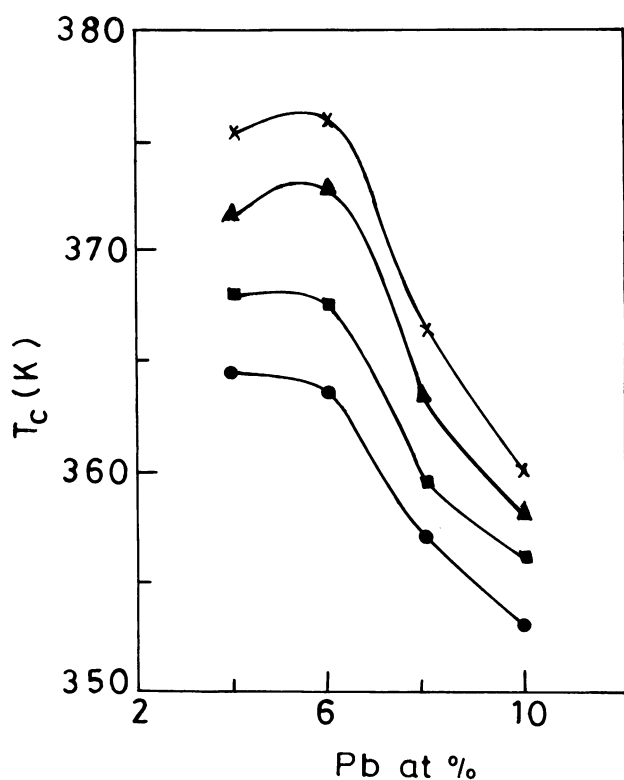


Figure 3. Plot of T_c vs Pb at. wt.% for $Se_{85}Te_{15-x}Pb_x$ ($x = 4, 6, 8$ and 10) glasses at the heating rate of (●) 5 K/min, (■) 10 K/min, (▲) 15 K/min and (×) 20 K/min.

Table 1. Values of different characteristic temperatures, Hruby number and S parameter for $Se_{85}Te_{15-x}Pb_x$ ($x = 4, 6, 8$ and 10) glasses at the heating rate of 20 K/min.

| Composition | T_g (K) | $T_c - T_g$ (K) | T_p (K) | H_R | S (K) |
|----------------------|-----------|-----------------|-----------|-------|---------|
| $Se_{85}Te_{11}Pb_4$ | 330.0 | 45.3 | 396.0 | 0.35 | 2.84 |
| $Se_{85}Te_9Pb_6$ | 327.8 | 47.2 | 395.8 | 0.37 | 2.87 |
| $Se_{85}Te_7Pb_8$ | 323.0 | 43.4 | 396.0 | 0.33 | 3.98 |
| $Se_{85}Te_5Pb_{10}$ | 322.5 | 37.5 | 390.0 | 0.27 | 3.49 |

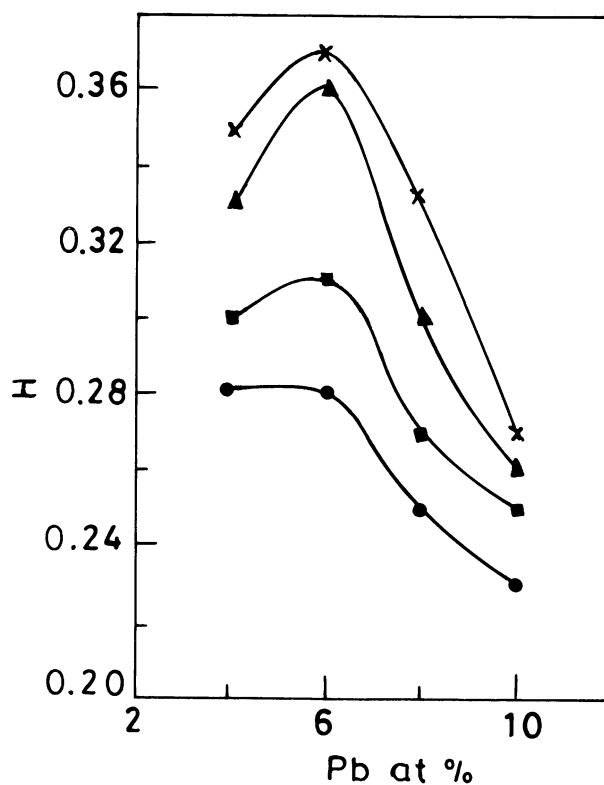


Figure 4. Plot of H_R vs Pb at. wt.% for $Se_{85}Te_{15-x}Pb_x$ ($x = 4, 6, 8$ and 10) glasses at the heating rate of (●) 5 K/min, (■) 10 K/min, (▲) 15 K/min and (×) 20 K/min.

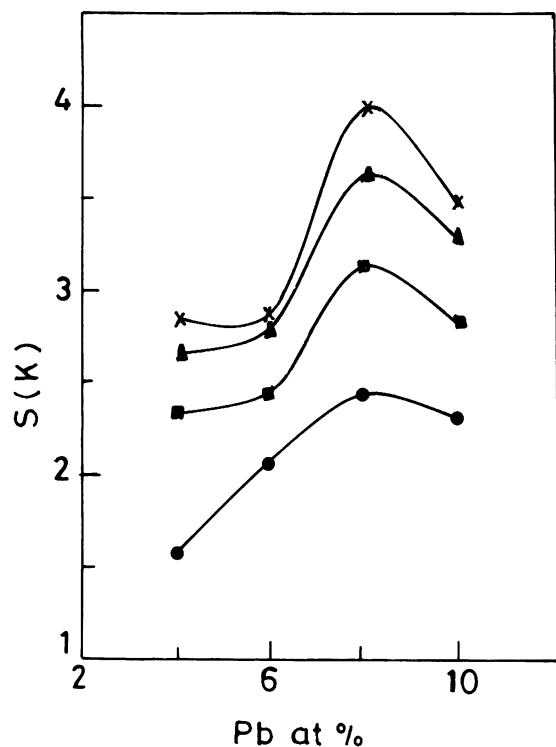


Figure 5. Plot of S parameter vs Pb at. wt.% for $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 4, 6, 8$ and 10) glasses at the heating rate of (●) 5 K/min, (■) 10 K/min, (▲) 15 K/min and (×) 20 K/min.

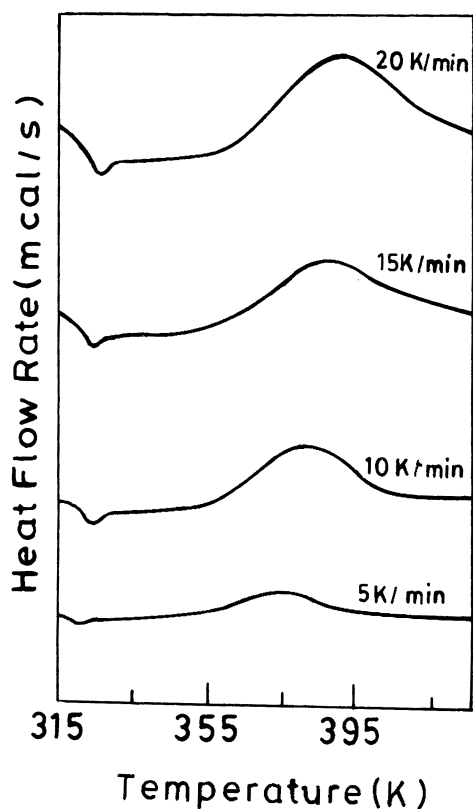


Figure 6. DSC thermograms of $\text{Se}_{85}\text{Te}_5\text{Pb}_{10}$ at the heating rates of 5, 10, 15 and 20 K/min.

change in temperature relaxes isothermally towards a new equilibrium value $H_c(T)$. The relaxation equation can be written in the following form (Moynihan *et al* 1974)

$$(dH/dt)_T = -(H-H_c)/t, \quad (3)$$

where t is the temperature dependent structural relaxation time and is given by the following relation (Agarwal *et al* 1991)

$$t = t_0 \exp(\Delta E_t/RT) \exp(-c(H-H_c)), \quad (4)$$

where t_0 and c are constants and ΔE_t the activation energy of the relaxation time. From (3) and (4) it can be shown that

$$d \ln b / d(1/T_g) = -\Delta E_t/R. \quad (5)$$

It is clear from (5) that the plot of $\ln b$ vs $1/T_g$ should be a straight line and the activation energy involved in the molecular motions and rearrangement around T_g can be calculated from the slope of the plot. Figure 7 shows the plot of $\ln b$ vs $1000/T_g$ for various compositions in Se-Te-Pb systems. In the present case such curves are found to be straight lines. Full line in the figure is the best fit of the experimental data. The values of structural relaxation activation energies (ΔE_t) are calculated from the slope of these curves and are plotted in figure 8. From the figure it is observed that $x = 8$ has highest activation energy of structural relaxation.

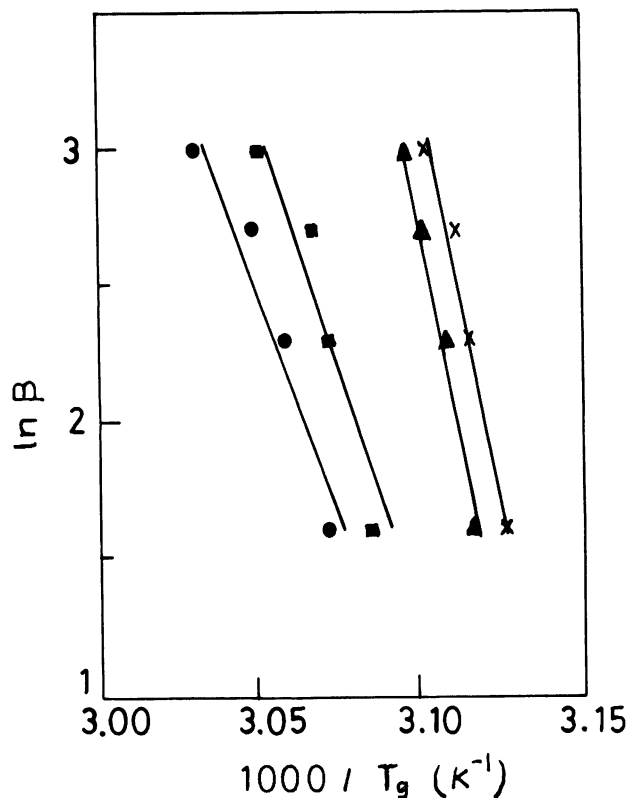


Figure 7. Plot of $\ln b$ vs $1000/T_g$ for (●) $\text{Se}_{85}\text{Te}_{11}\text{Pb}_4$, (■) $\text{Se}_{85}\text{Te}_9\text{Pb}_6$, (▲) $\text{Se}_{85}\text{Te}_7\text{Pb}_8$ and (×) $\text{Se}_{85}\text{Te}_5\text{Pb}_{10}$ glasses.

The crystallization mechanism of amorphous materials is controlled by nucleation and growth process, which can be characterized by the activation energy and dimensionality of the growth process. According to Matusita, the fraction crystallized, X , the non-isothermal crystallization (Matusita *et al* 1984) is given by

$$\ln[-\ln(1-x)] = -n \ln a - 1.052 m E_c / RT + \text{const}, \quad (6)$$

where n and m are constants that depend on the nucleation and growth mechanism. E_c is the activation energy of crystallization. The plot of $\ln[-\ln(1-x)]$ vs $1/T$ gives a straight line and the slope of the curve gives the activation energy. A typical plot of $\ln[-\ln(1-x)]$ vs $1/T$ for $Se_{85}Te_5Pb_{10}$ glass at the heating rates of 5, 10, 15 and 20 K/min is shown in figure 9. From the slope of the curves the activation energy is calculated. The activation energies calculated for all the compositions are reported in table 2.

To determine the value of n , the plot between $\ln[-\ln(1-x)]$ vs $\ln a$ has been made. The typical plot of $Se_{85}Te_5Pb_{10}$ at temperatures 367.7 K, 374.5 K, 381.7 K and 389.1 K is shown in figure 10. The values of n thus obtained from the slope of all the curves and for all compositions lie between 1.1 and 1.5 and are given in table 2 (column 3). For as-quenched glass, the constant m is taken to be $m = n - 1$. Here it is to be noted that if the value of n is less than 2 then the value of m will be 1

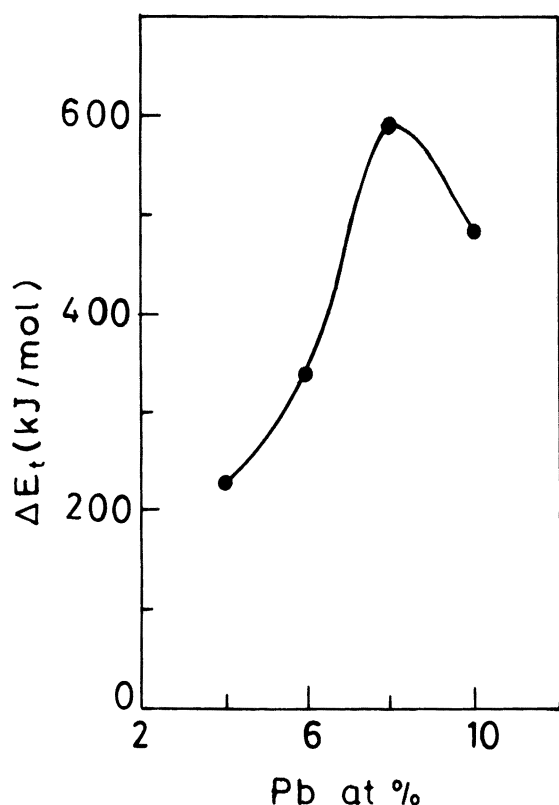


Figure 8. Activation energies due to structural relaxation for $Se_{85}Te_{15-x}Pb_x$ ($x = 4, 6, 8$ and 10) glasses.

(Mehera *et al* 1991). Hence the value of m in Se-Te-Pb system is 1 for all the compositions, which indicates one-dimensional crystal growth in all compositions for Se-Te-Pb glasses.

To compare some crystallization parameters obtained by Matusita model, the modified Kissinger's equation (Predeep *et al* 1996b)

$$\ln(a^n/T_{cp}^2) = -1.052 m E_c / RT_{cp} + \text{const}, \quad (7)$$

has also been employed, where T_{cp} is the peak temperature of crystallization, E_c the activation energy of crystallization and a the heating rate. The plot of $\ln(a^n/T_{cp}^2)$

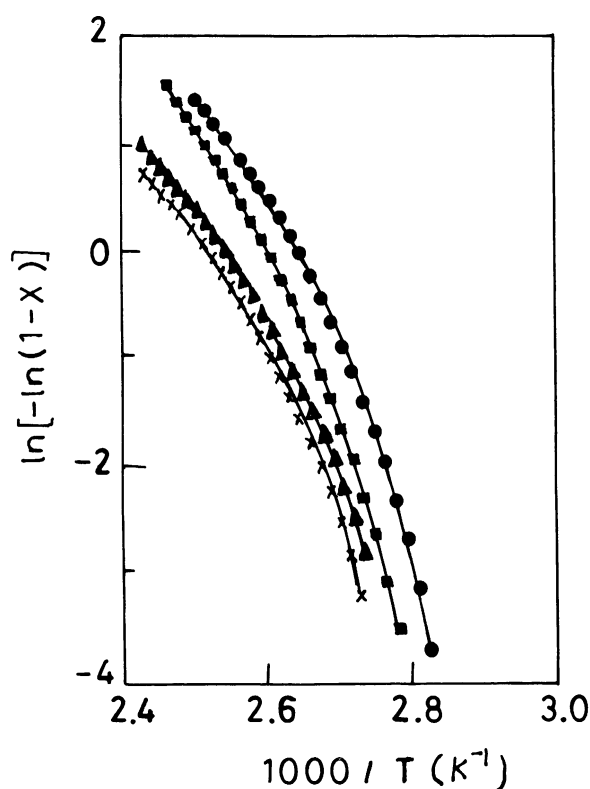


Figure 9. Plot of $\ln[-\ln(1-x)]$ vs $1000/T$ for $x = 10$ at the heating rate of (\bullet) 5 K/min, (\blacksquare) 10 K/min, (\blacktriangle) 15 K/min and (\times) 20 K/min.

Table 2. Activation energies (kJ/mol) of crystallization from Matusita's and modified Kissinger's equation and parameters n and m as obtained from Matusita's equation.

| Composition | Activation energies (E_c) | | | |
|----------------------|-------------------------------|-----|-----|-----------------------------|
| | Matusita's method | | | Modified Kissinger's method |
| | E_c | n | m | E_c |
| $Se_{85}Te_{11}Pb_4$ | 100 | 1.2 | 1 | 102 |
| $Se_{85}Te_9Pb_6$ | 136 | 1.4 | 1 | 139 |
| $Se_{85}Te_7Pb_8$ | 111 | 1.5 | 1 | 133 |
| $Se_{85}Te_5Pb_{10}$ | 107 | 1.1 | 1 | 114 |

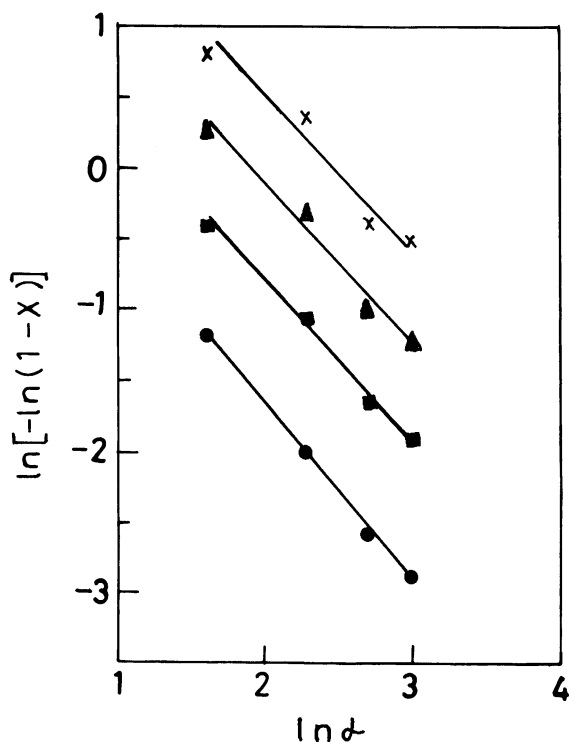


Figure 10. Plot of $\ln[-\ln(1-x)]$ vs $\ln a$ for $\text{Se}_{85}\text{Te}_7\text{Pb}_8$ glasses at the temperature of (●) 367.7 K, (■) 374.5 K, (▲) 381.7 K and (×) 389.1 K.

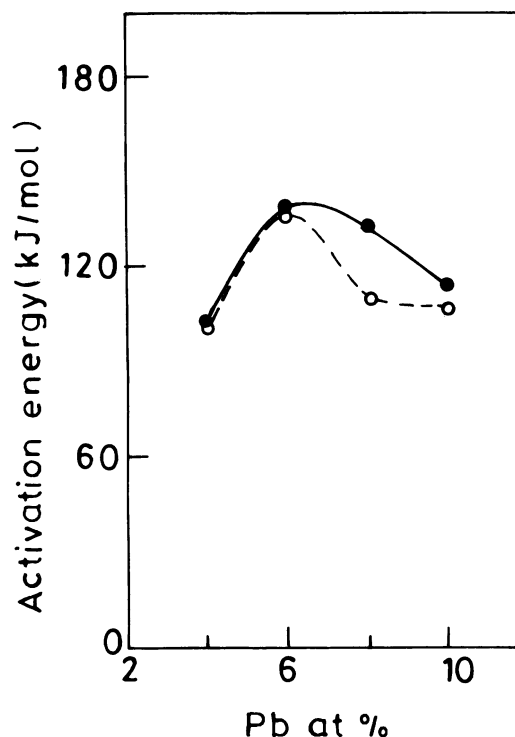


Figure 12. Activation energy vs Pb at. wt.% as obtained from Matusita's (○) and modified Kissinger's equation (●).

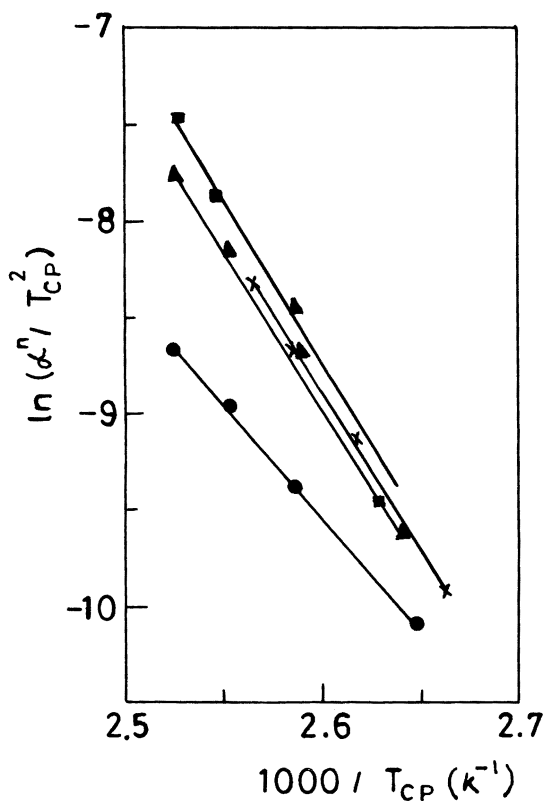


Figure 11. Plot of $\ln(a^n/T_{cp}^2)$ vs $1000/T_{cp}$ for (●) $\text{Se}_{85}\text{Te}_{11}\text{Pb}_4$, (■) $\text{Se}_{85}\text{Te}_9\text{Pb}_6$, (▲) $\text{Se}_{85}\text{Te}_7\text{Pb}_8$ and (×) $\text{Se}_{85}\text{Te}_5\text{Pb}_{10}$ glasses.

versus $1000/T_{cp}$ is a straight line as shown in figure 11 for $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 4, 6, 8$ and 10) glasses. The slope of the curves gives the value of E_c , which has been reported in table 2.

The values of activation energies obtained by Matusita's model and modified Kissinger's model are quite close and their trends of variation with composition are nearly similar. The differences in the E_c values are within average of experimental error. The plot of activation energy obtained by Matusita's and modified Kissinger's methods are shown in figure 12. A comparison of two curves in figure 12 reveals that the most stable glass $\text{Se}_{85}\text{Te}_9\text{Pb}_6$ has the highest activation energies as calculated from both Matusita's and modified Kissinger's equations.

4. Conclusion

The study of Se-Te-Pb system shows that the most easiest glass former is $\text{Se}_{85}\text{Te}_9\text{Pb}_6$ and it is also most stable.

Decrease of T_g and T_c on the further addition of Pb at wt.% in the Se-Te-Pb system is due to decrease of effective bond energy of the system.

It has also been concluded that in this glassy system the growth of crystal is one-dimensional.

Highest value of crystallization activation energies for $\text{Se}_{85}\text{Te}_9\text{Pb}_6$ system is suggestive of the fact that this specific composition of glass is highly thermal stable.

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