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A Study of Glass Transition Kinetics of $\text{Te}_{15}(\text{Se}_{100-x}\text{Sb}_x)_{85}$ Amorphous Alloys using Differential Thermal Analysis

Kameshwar Kumar

Maharaja Lakshman Sen Memorial College, Sundernagar, H.P, India

ABSTRACT: A study of glass transition kinetics of $\text{Te}_{15}(\text{Se}_{100-x}\text{Sb}_x)_{85}$ amorphous semiconductors ($x = 0, 1, 2, 3$ and 4 at. %) has been reported in this communication. The samples were prepared by quenching the melt process. 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 thermo grams have been analysed for glass transition temperature (T_g). The Glass transition temperature increases with increase in heating rate (β) and with increase in Sb content (x). T_g has also been found using covalent bond approach (CBA) theoretically. The experimental and theoretical values of T_g both increases with Sb addition. The activation energy of glass transition (E_g) has been calculated using the Kissinger and Moynihan approaches. The activation energy of glass transition has been found to increase with Sb content. E_g values calculated using different methods are in good agreement with each other.

KEYWORDS: differential thermal analysis, phase transition, activation energy of glass transition, coordination number.

I. INTRODUCTION

Amorphous alloys have great importance because of their technological applications like electrical switching [1]. Pure amorphous Se shows property of reversible phase transition [2-3]. Pure Se has short lifetime, low photo sensitivity and low thermal stability. Se has long polymeric chains and eight member rings [4]. These chains and rings are broken by adding Te making Se-Te alloys important because of advantages like higher photo sensitivity, lesser aging effects, higher crystallization temperature and greater hardness [5]. Se-Te has limited reversibility, low glass transition and crystallization temperatures [6]. These problems can be overcome by adding third element to Se-Te host. Further the properties of Se-Te binary alloys can be varied by adding a third element like Bi, Sb, Cd and In etc. 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 [7-8]. It also produces compositional and configurational disorder in the system.

We have chosen Sb as the third element because it produces remarkable changes in the thermal and optical properties of the Se-Te amorphous glasses [9-10]. Sb addition causes a p to n transition in conductivity [11-12]. The Sb addition also increases the glass transition temperature indicating the hardening of Se-Te host. The study of kinetics of glass transition of ternary amorphous semiconductors can be carried out using isothermal and non-isothermal methods [13-14]. Non isothermal DTA study has been used for the glass transition kinetics of the samples because it is rapid and precise in manner [15].

In the present work the effect of Sb addition on the glass transition kinetics of $\text{Te}_{15}(\text{Se}_{100-x}\text{Sb}_x)_{85}$ ($x = 0, 1, 2, 3, 4$ at.%) amorphous alloys have been studied using DTA. The glass transition temperature (T_g) is recorded as a function of

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heating rate (β) and Sb content (x) from the DTA thermo grams. The activation energy of glass transition has been calculated using different approaches.

II. EXPERIMENTAL DETAILS

Amorphous bulk alloys of $\text{Te}_{15}(\text{Se}_{100-x}\text{Sb}_x)_{85}$ ($x = 0, 1, 2, 3$ and 4 at%) were prepared by the melt quenching technique. The constituent elements 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^{-6} mPa. 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 glass transition temperature T_g .

III. RESULTS

A. Glass transition temperature and activation energy of glass transition:

Fig.1 shows X-ray diffractograms for $\text{Te}_{15}(\text{Se}_{100-x}\text{Sb}_x)_{85}$ ($x=2$ at%) system. The amorphous nature is confirmed as there is no sharp peak in the X-ray diffraction spectra (XRD). The other samples also do not show any sharp peak in their XRD spectra. The DTA graphs of $\text{Te}_{15}(\text{Se}_{100-x}\text{Sb}_x)_{85}$ for $x = 3$ at.% at different heating rates of 10, 15, 20 and 25 K/min are shown in fig. 2. It is clear from the figure that glass transition temperature (T_g) increases with increase in heating rate. The T_g is also found to increase with Sb content. The increase in the value of glass transition temperature (T_g) with increase in Sb content can be explained to some extent with the help of chemically ordered network model (CONM), according to which the formation of heteropolar bonds is favoured over the homopolar bonds. When Sb is added, it is expected to form bonds with Se because the bond energy of Sb-Se (183.84 kJ/mol) is greater than bond energy of Sb-Te (159.55 kJ/mol) resulting in decrease of Se-Se bonds (184 kJ/mol) [16]. This explains the increase in T_g with increase in Sb content due to formation of large number of heteropolar Sb-Se bonds and decrease in homopolar Se-Se and Te-Te bonds. The increase in T_g can also be explained partly on the basis of the average coordination number $\langle r \rangle$ given by [17]

$$\langle r \rangle = \frac{a(CN_{Te}) + b(CN_{Se}) + c(CN_{Sb})}{a + b + c} \quad (1)$$

Where a, b and c are the at. % of Te, Se and Sb respectively and $CN_{Te} = 2$, $CN_{Se} = 2$ and $CN_{Sb} = 3$ are their respective coordination numbers. On increasing Sb content the average coordination number increases therefore the glass transition temperature also increases.

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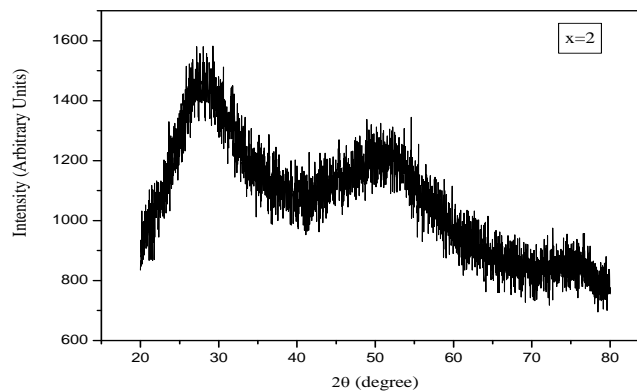


Fig. 1 X-ray diffraction spectra of $Te_{15}(Se_{100-x}Sb_x)_{85}$ ($x=2$ at.%) amorphous alloys.

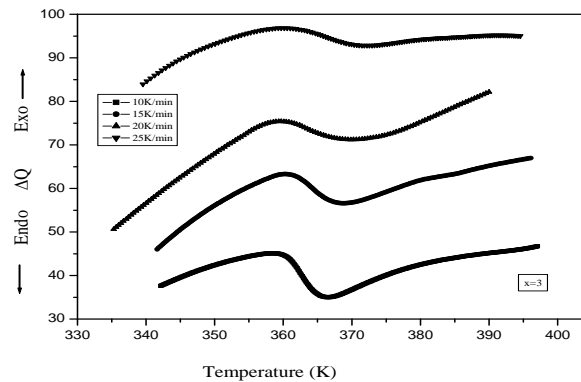


Fig. 2 DTA thermo grams for $Te_{15}(Se_{100-x}Sb_x)_{85}$ amorphous alloys for ($x = 3$ at.%) at heating rates of 10, 15, 20, 25 K/min. The glass transition temperature T_g was recorded from the DTA data and is listed in table1 for different heating rates. It has been observed that T_g increases with heating rate and obeys the empirical relation [19]

$$T_g = A + B \ln \beta \quad (2)$$

where A and B are constants. The increase in T_g with the heating rate is explained on the fact that when the heating rate increases the system does not get sufficient time for nucleation and crystallization. The increase in T_g also results in increase in activation energy of glass transition and is in good agreement with Cofmenero et. al [18].

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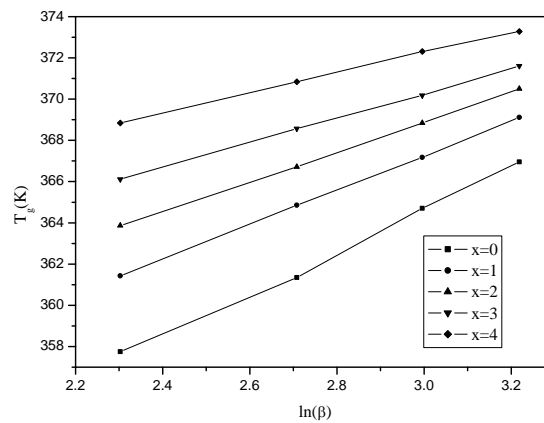


Fig. 3 Plots of T_g vs $\ln(\beta)$ for $\text{Te}_{15}(\text{Se}_{100-x}\text{Sb}_x)_{85}$ ($x = 0, 1, 2, 3$ and 4 at.%) amorphous alloys.

Fig. 3 shows the variation of T_g with $\ln(\beta)$ for the glassy alloys. T_g is further found to increase with increase in Sb content. Glass transition and structural relaxation theory developed by Moynihan and others [20-22] was used to analyse the kinetics of glass transition from the heating rate dependence of glass transition temperature. The activation energy of glass transition (E_g) has been calculated using Moynihan theory. The dependence of T_g on heating rate is given by [21-22]

$$\frac{d(\ln \beta)}{d(1/T_g)} = -\frac{E_g}{R} \quad (3)$$

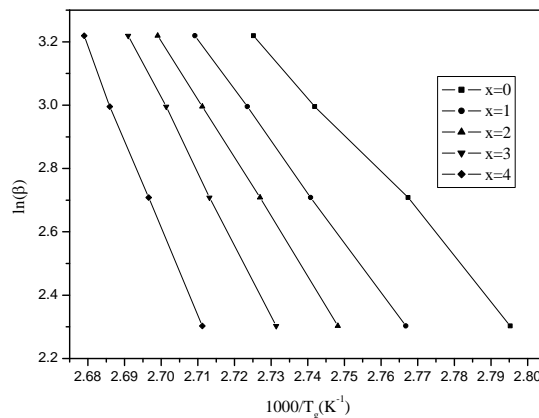


Fig. 4 Plots of $\ln(\beta)$ vs $1000/T_g$ for $\text{Te}_{15}(\text{Se}_{100-x}\text{Sb}_x)_{85}$ ($x = 0, 1, 2, 3$ and 4 at.%) amorphous alloys.

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where R is gas constant.

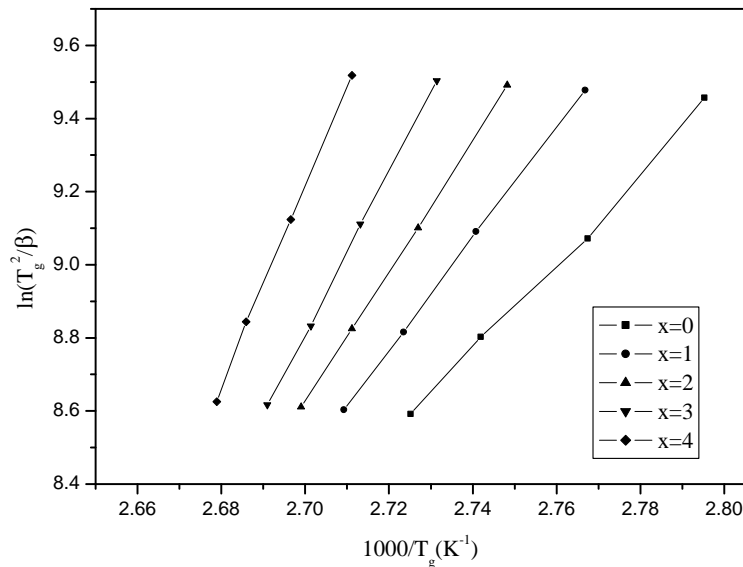


Fig. 5 Plots of $\ln(T_g^2/\beta)$ vs $1000/T_g$ for $\text{Te}_{15}(\text{Se}_{100-x}\text{Sb}_x)_{85}$ ($x = 0, 1, 2, 3$ and 4 at.%) amorphous alloys.

The plots of $\ln(\beta)$ vs $1000/T_g$ for all the samples are a straight line and are shown in Fig. 4. The activation energy of glass transition is calculated from the slope of these plots. The activation energy is found to increase with Sb content. The activation energy of glass transition is also calculated from the Kissinger's equation [23]

$$\ln\left(\frac{T_g^2}{\beta}\right) + \text{constt.} = \frac{E_g}{RT_g} \quad (4)$$

The activation energy of glass transition was calculated from slope of $\ln(T_g^2/\beta)$ vs $1000/T_g$ plots. The calculated values of E_g are reported in table 1. The activation energy of glass transition is found to increase with Sb content (x) in both approaches. The activation energy calculated from both the approaches is comparable which means that either of the two approaches can be used to calculate the activation energy of glass transition.

TABLE 1 Values of $\langle r \rangle$, E_g (kJ/mol) (Moynihan), E_g (kJ/mol) (Kissinger), theoretical (T_g) and T_g from DTA for $\text{Te}_{15}(\text{Se}_{100-x}\text{Sb}_x)_{85}$ ($x = 0, 1, 2, 3$ and 4 at.%) glassy alloys at the heating rate of 10, 15, 20 and 25 K/min.

x	$\langle r \rangle$	T_g (K) 10K/min	T_g (K) 15K/min	T_g (K) 20K/min	T_g (K) 25K/min	E_g (kJ/mol) (Moynihan)	E_g (kJ/mol) (Kissinger)	T_g (K) (Theoretical)
0	2.000	357.75	361.35	364.71	366.95	107.25	101.26	298.6
1	2.008	361.43	364.86	367.17	369.11	132.77	126.71	300.1
2	2.017	363.87	366.71	368.84	370.5	154.81	148.65	301.4
3	2.025	366.11	368.57	370.18	371.61	189.64	183.49	303.2
4	2.034	368.84	370.84	372.31	373.28	234.21	228.05	304.2

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B.Theoretical glass transition temperature and mean bond energy:

The glass transition temperature (T_g) is that characteristic temperature below which the glassy system freezes into a structure which cannot change into another structure and is related to the magnitude of the cohesive forces in the system. Thus T_g is assumed to be proportional to system parameter which strongly depends on cohesive forces in the system. One such parameter is mean bond energy $\langle E \rangle$. Tichy and Ticha [24] illustrated an impressive relation of T_g with $\langle E \rangle$ in the form

$$T_g = 311[\langle E \rangle - 0.9] \quad (5)$$

$\langle E \rangle$ is sum of mean bond energy per atom due to strong heteropolar bonds (E_c) and average bond energy per atom of remaining matrix, the weak homopolar bonds (E_{rm}). The bond energies of heteropolar bonds calculated from Pauling relation are quite different from bond energies of weak homopolar bonds so chemically ordered networks are expected. Based on chemical bond ordering model the mean bond energy is given by

$$\langle E \rangle = E_c + E_{rm} \quad (6)$$

For Se rich glass system, the values of E_c and E_{rm} are given in [25]

$$E_c = 2aE_{Se-Te} + 3cE_{Se-Sb} \quad (7)$$

$$E_{rm} = \frac{2b - 2a - 3c}{\langle r \rangle} E_{Se-Se} \quad (8)$$

where a, b and c are at. % of Te, Se and Sb respectively. The theoretically calculated glass transition temperature is reported in table 1.

IV. CONCLUSION

The glass transition temperature has been found to increase with heating rate and with Sb addition to Se-Te host. The activation energy of glass transition has been found to increase with Sb addition in both Kissinger and Moynihan approaches. The theoretically calculated glass transition temperature is also found to increase with Sb addition. The activation energy calculated from both the approaches is comparable with each other.

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