Estimation of T_g for Se-Te-Sb System using Modified Gibbs-DiMarzio Law

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***Abstract*—In the present paper, glass transition temperature for Se-Te-Sb system is estimated using modified Gibbs-DiMarzio law. The bulk alloys of $Se_{80-x}Te_{20}Sb_x$ (x = 1, 2, 4, 6 and 10) are prepared by using melt quenching technique. X-ray diffraction pattern of various samples indicate the amorphous nature of the investigated samples. The glass transition temperature (T_g) for investigated glasses are obtained via differential scanning calorimetery (DSC) technique at the heating rate of 10°C/min. Experimental results have been compared with the theoretical value of T_g obtained from modified Gibbs-DiMarzio law.**

Keywords*—Chalcogenide glasses, DSC, Glass transition temperature

I. INTRODUCTION

Glass transition temperature is one of the most interesting parameter in materials science and engineering. When a chalcogenide glass is reheated at a constant heating rate in the DSC experiment, the sample undergoes structural changes and crystallizes. The glass transition is exhibited as an endothermic peak in DSC. In chalcogenide glasses, an endothermic peak may also be observed due to fast change in enthalpy when the glassy system relaxes quickly due to a decrease in viscosity at the transition temperature. Therefore, DSC technique is useful in the study of thermal relaxation of glasses [1-7].

A lot of attention has been devoted to the characterization and improvement of the properties of chalcogenide glasses, especially for those materials which are used in the switching memories. The kinetics of glass transition phenomenon is an important field in the study of chalcogenide alloys. Glasses exhibiting no exothermic crystallization peak above the glass transition temperature (T_g) show a threshold switching and glasses show crystallization above T_g exhibiting memory type switching [3].

Mostly Se based chalcogenide materials are preferred due to its commercial use and technological applications. Moreover, its device applications like switching, memory and xerography etc made it attractive. But the pure Se has short life time and low sensitivity although it is characterized by high viscosity. The problem can be overcome by alloying Se with some impurities such as Te, Ge etc which in turns gives high sensitivity, greater hardness, high crystallization temperature (T_p) and small ageing effects as compared to pure Se glass. The Se-Te alloys are found to be useful from the technological point of view if these alloys are thermally stable with time and temperature during use. However, thermal instability leading to crystallization is found to be one of the drawbacks of these alloys. Hence, attempts have been made to improve the stability of Se-Te binary alloys by the addition of third element. The insertion of an impurity such as Sn, In etc in Se-Te binary alloy at the cost of Se is of interest owing to the advantages like glass transition temperature which in turns gives thermally more stable effects as compared to host Se-Te alloy [4-7]. It is observed that the addition of the third element helps in getting cross linked structure thus increasing glass transition temperature of the binary alloy.

The kinetics of glass transition phenomenon has vital importance in the study of chalcogenide glassy alloys. There is no quantitative equation for the T_g as a function heating rate either in a form generalized for all materials or even for any single material with in a wide range of heating rate. In the present study, T_g has been estimated for ternary $Se_{80-x}Te_{20}Sb_x$ (x =1, 2, 4, 6 and 10) bulk glassy alloys theoretically using an empirical relationship by modifying the Gibbs- DiMarzio equation for glass transition [1]. The results so obtained have been compared with experimental values of T_g at the heating rate of 10°C/min to see the effect of using modified Gibbs-DiMarzio law in the determination of glass transition temperature.

II. EXPERIMENT DETAILS

Bulk glassy alloys of $Se_{80-x}Te_{20}Sb_x$ (x = 1, 2, 4, 6 and 10) are prepared by using melt quenching technique. 5N pure materials are weighted according to their atomic percentages and sealed in the quartz ampoules (length = 5 cm, diameter = 12 mm) under a vacuum of 2×10^{-5} mbar. The ampoules have been kept inside the furnace where the temperature is raised to 1000°C at a rate of 3-4°C/min. During heating, the ampoules are rocked constantly to make the melt homogenous. After rocking for about 12 hours, the obtained melts are cooled rapidly by removing the furnace and dropping into ice-cooled water very rapidly to prevent crystallization. The ingots of the samples are then taken out by breaking the quartz ampoules.

X-ray diffraction pattern verified the amorphous nature of glassy alloys. Fig. 1 shows the XRD pattern for ternary $Se_{79}Te_{20}Sb_1$ bulk alloy and absence of any prominent peak in the spectrum confirmed the amorphous nature of the investigated chalcogenide alloy. Similar XRD patterns have been observed for the other investigated samples (not shown here).

The glasses thus prepared are ground to make fine powder for DSC studies. The thermal behavior of the glasses is investigated using DSC. Approximately, 3-5 mg of sample in powder form is encapsulated in standard aluminum pan and heated at 10°C/min. The values of glass transition temperature are determined by using the microprocessor of the thermal analyzer.

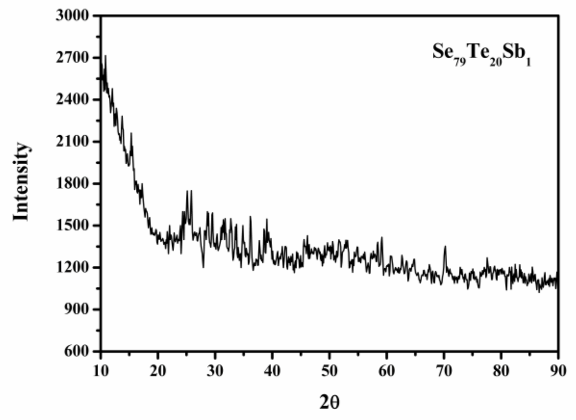

Fig. 1. XRD pattern for ternary chalcogenide $Se_{79}Te_{20}Sb_1$ bulk sample.

III. RESULTS AND DISCUSSION

Typical DSC thermograms for glassy $Se_{80-x}Te_{20}Sb_x$ (x = 1, 2, 4, 6 and 10) bulk alloys obtained at a constant heating rate of 10°C/min displaying characteristics glass transition temperature as endothermic peak is shown in Fig. 2-6. The well defined endothermic peaks are observed at T_g indicates that the investigated alloys are exist in single phase. It is observed that T_g shifts to a higher value with the increase in Sb content at the cost of Se. The experimental values of T_g obtained at a heating rate 10°C/min for investigated glassy alloys are also given in Table1.

The non-isothermal DSC technique has been widely used in the literature [1-8] for the study of glass transition kinetics. This technique is particularly important because of the fact that it is easy to carry out, requires little sample preparation, quite sensitive and independent of sample geometry. Therefore, we have employed the non-isothermal DSC technique in the present study.

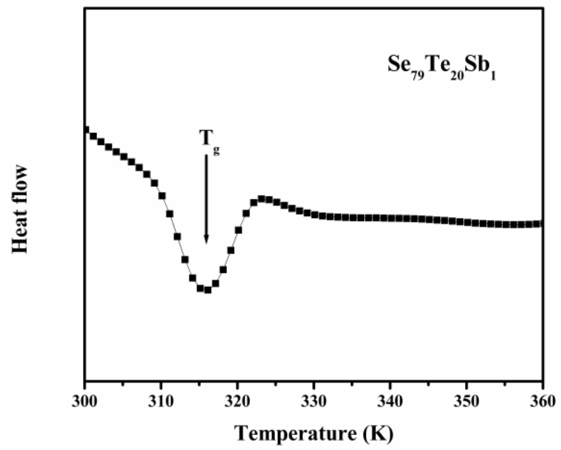

Fig. 2. DSC endothermic curve obtained along glass transition temperature for $Se_{79}Te_{20}Sb_1$ bulk sample.

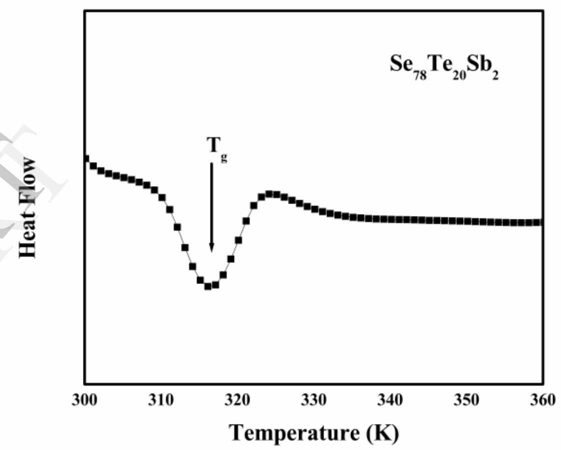

Fig. 3. DSC endothermic curve obtained along glass transition temperature for $Se_{78}Te_{20}Sb_2$ bulk sample.

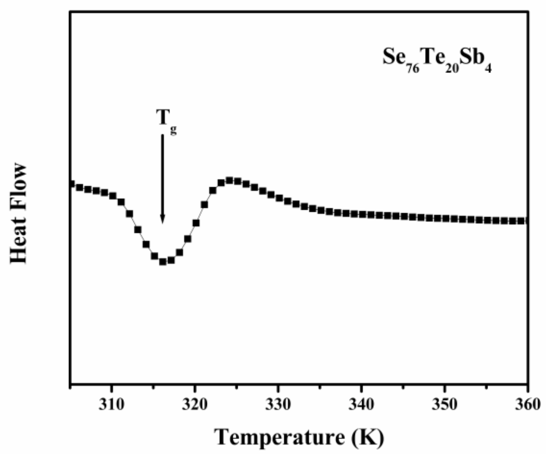

Fig. 4. DSC endothermic curve obtained along glass transition temperature for $Se_{76}Te_{20}Sb_4$ bulk sample.

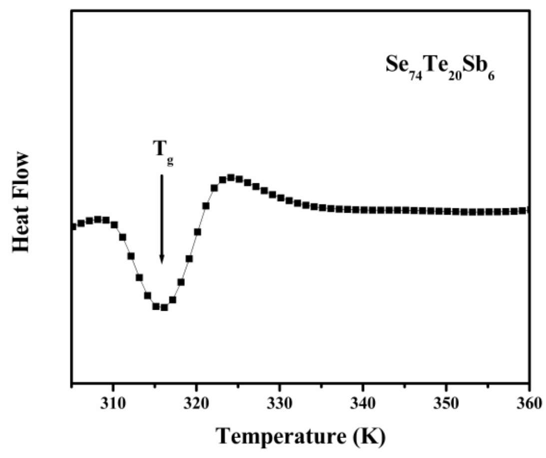

Fig. 5. DSC endothermic curve obtained along glass transition temperature for $Se_{74}Te_{20}Sb_6$ bulk sample.

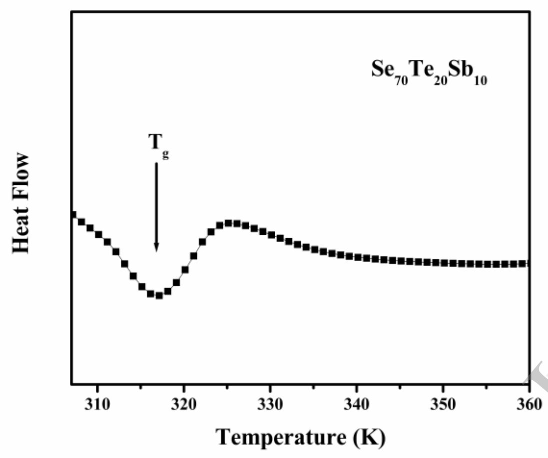

Fig. 6. DSC endothermic curve obtained along glass transition temperature for $Se_{70}Te_{20}Sb_{10}$ bulk sample.

The glass transition temperature for Se-Te-Sb glassy alloys is predicted by using modified Gibbs-DiMarzio law [1, 8]:

$$T_g = T_o / (1 - \beta (< r > - 2)) \quad (1)$$

where T_o is the glass transition temperature of the chain like glass (T_o of selenium = 316 K) and $< r >$ is the average co-ordination number [2]. In [1] Sreeram *et al.* started their investigation of multi-component chalcogenide systems from pure vitreous selenium, β is a system dependent parameter and is given by:

$$1/\beta = \sum (m_i - 2) \ln [m_i /2] \quad (2)$$

Here the value of β can be computed if the co-ordination number m_i of the involved atoms are known. In Se-Te-Sb system, the calculated value of β is 2.47. It is obvious from the Table 1 that the obtained values from the modified Gibbs-DiMarzio law are not in accord with the experimental value obtained from DSC scans.

TABLE I. EXPERIMENTAL AND THEORETICAL (GIBBS-DIMARZIO LAW) VALUES OF GLASS TRANSITION TEMPERATURE (K) FOR X = 1, 2, 4, 6 AND 10.

Composition	Experimental (10°C /min)	Gibbs-DiMarzio law
$Se_{79}Te_{20}Sb_1$	315.61	324.00
$Se_{78}Te_{20}Sb_2$	316.33	332.42
$Se_{76}Te_{20}Sb_4$	316.53	350.64
$Se_{74}Te_{20}Sb_6$	315.60	370.98
$Se_{70}Te_{20}Sb_{10}$	316.82	419.65

IV. CONCLUSIONS

In the present study, the glass transition temperature T_g have been determined for ternary $Se_{80-x}Te_{20}Sb_x$ (x = 1, 2, 4, 6 and 10) alloys theoretically using an empirical relationship i.e. modified Gibbs-DiMarzio law. Theoretically deduced values has been compared with experimental values of T_g obtained at the heating rate of 10°C/min and it is found that the theoretical results obtained by modified Gibbs- DiMarzio law are not in accordance with the experimental results.

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