IJP A

Calorimetric measurements on Te-Bi-Se glasses with variation in Se content

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Abstract . The alloys of Te-Bi-Se glass system, obtained by rapid quenching technique, have been characterized by calorimetric measurements and differential thermal analysis for different heating rates. In the present work, a systematic investigation of crystallization kinetics of Te-Bi-Se glass system is carried out for the composition range in which amorphous alloys with a large glass forming ability in Se-based systems, the glass transition temperature T_g and the peak temperature T_p at different heating rates have been studied with the increase in Se content. With the increase in heating rates, T_g and T_p are found to increase. This analysis helps in finding the suitability of an alloy to be used in phase transition optical memories/switches. Thermal stability of these glasses is found in good command to form the glasses with ease.

Keywords : Glass transition, thermal stability, Se-based glass

PACS Nos. . 61.43 Fs, 65.60.+a, 81.70 Pg

1. Introduction

The growing interest in the chalcogenide glasses is partly because of their interesting electrical and optical properties, and hence their wide technological applications. The electrical properties are influenced by the structural effects associated with thermal effects and can be related to thermally induced transitions. In chalcogenide glass systems, the glasses which exhibit no exothermic crystallization reaction above the glass transition temperature T_g, could possibly be used in threshold switching systems whereas glasses exhibiting an endothermic crystallization reaction above T_g, show a memory type of switching [1,2]. Memory switches come from the boundaries of glass-forming regions where glasses are more prone to crystallization. Among amorphous chalcogenide alloys, selenium-based melt are characterized by a high viscosity [3,4]. Recently, various workers have reported the use of these materials for reversible optical recording by amorphous to crystalline phase change [5]. The appearance of metallic amorphous alloys, with extremely large glass forming ability comparable to oxide glasses, enables the production of bulk

amorphous alloys by a conventional casting process with low cooling rates. Selenium-based glasses have been extensively studied as regards their optical properties [6,7]. In Se, each atom needs two neighbours to satisfy the valence requirements. This can be achieved either by the formation of small molecules Se_8 or linear polymeric chain S_n. Selenium can melt without appreciable change within these structural units, the required random arrangement of atoms being obtained by the breaking of the weak bonding between units, and by increased flexibility of the chains which accompanies this. A rearrangement into a crystal structure on cooling is a difficult step, and a glass is easily formed. Glassy Selenium does crystallize after moderate heating, presumably because of the thermal dissociation of a few Se bonds. Amorphous Selenium is believed to consist predominantly of a mixture of two structural species, long helical chains and eight member rings, held to each other by weak forces perhaps of the Van der Waal type. Strong covalent bonds exist between the atoms in the chains and rings. The relative proportions of the two species, as well as the length of the chains, is expected to depend on the condition of preparation, which can be either by melt quenching or by vacuum evaporation. Addition of tellurium Te, has a catalytic effect on

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the crystallization of selenium. The presence of Te in Se chains probably favours their thermal dissociation, the Se-Te bond being weaker than the Se-Se bond. This makes crystallization easier, by facilitating the close packing of a new Se chains to form a nucleation center. When Te is incorporated, an enhanced interaction between the chains is probably conducive to crystallization [8].

However, through a careful analysis of the DTA curve, one can find the glass transition temperature. The studies of crystalline kinetics of a glass upon heating can be performed in several different ways. In the isothermal method, the sample is brought quickly to a temperature above the glass transition temperature T_g, and the heat evolved during the crystallization process at a constant temperature is recorded as a function of time. In the non-isothermal method, the sample is heated at a fixed rate (β) and the heat evolved is recorded as a function of temperature or time [9]. For phase change optical switching systems, it is important to optimize various parameters like, the glass transition temperature T_g, the crystallization temperature T_c, the peak temperature T_p, and the melting temperature T_m by varying the composition and heating rate [10]. The crystallization studies are carried out under non-isothermal conditions with samples heated at several uniform rates. From the heating rate (β) dependence of the glass transition temperature T_g and both the onset temperature of crystallisation T_c and the crytallization peak temperature T_p, can be evaluated [11, 12]. The thermal stability of Te-Bi-Se glass system and the dependence of the glass transition temperature (T_g) and the peak temperature (T_p) on the composition and heating rate have been studied in the present work.

2. Experimental procedures

For the preparation of Te-Bi-Se glasses, high purity elements (99.999 %) in appropriate atomic percentage were weighed in to quartz ampoules. The ampoule was sealed off in a vacuum of 10^{-5} torr. Then the ampoules were held inside a furnace whose temperature has been raised to 900° C at a rate of 3–4° C/min for 24 hours and rotated frequently to ensure homogenization of the melt. The ampoules were then rapidly quenched in ice-water mixture. Then the quenched samples were removed from the ampoules by dissolving the ampoules separately in a mixture of HF + H_2O_2 for about 20 hours. The calorimetric thermograms of various compositions of the samples were obtained with a DTA Calorimeter in the temperature range 50-700°C at various heating rates (10-20°C/min).

3. Results and discussion

The aim of this study was to present the alloy system and composition range in which amorphous alloys with a large glass forming ability formed in Se-based systems. The compositional dependence of the reduced glass temperature T_g/T_m, which is one of the dominant factors for glass formation, is also examined

for few samples. DTA curves for Se at 42% for different heating rates, ranging from 10 K/min to 20 K/min have been shown in Figure 1.
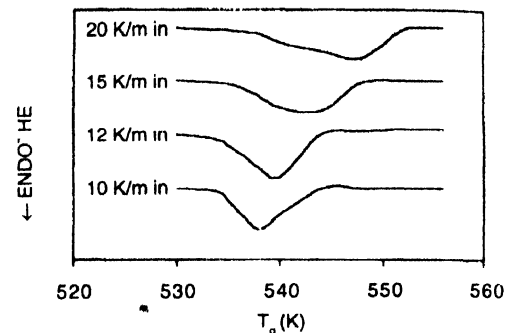

Figure 1. DTA curves for Se at 42% for different heating rates

In the present Te-Bi-Se glass system, the values of glass transition temperature T_g and the peak temperature T_p were found to increase with the increase in heating rates from 10 K/min to 20 K/min. This may be attributed to the fact that when heating rate is high, the system doesn't get sufficient time for nucleation and crystallization. The variations of T_g as a function of Se content in the Te-Bi-Se system has been shown in Figure 2 which shows that the value of T_g increases by about 24 K with the increase in Se content from 36% to 57%, as well as heating rates
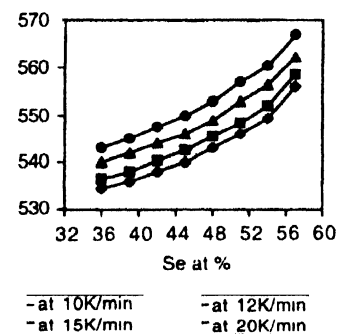

Figure 2. Variation of T_g as a function of Se content at different heating rates

The glass transition temperature T_g represents the strength or rigidity of glass structure. This drastic change in T_g is expected when the concentration of selenium is increased and that of
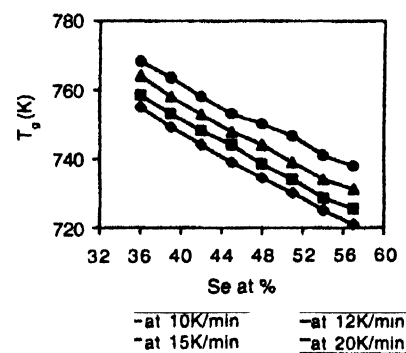

Figure 3. Variation of T_p as a function of Se content at different heating rates.

tellurium is decreased [13]. Figure 3 shows the decrease in the values of T_p with the increase in Se content, from 36% to 57%.

A simple theoretical relationship between T_g and T_m is used [13,14] to determine the values of T_g/T_m. The values so obtained obey the 'two-third rule' which states that

$$T_g/T_m = 2/3.$$ (1)

Figure 4 plots the ratio of T_g/T_m versus Se content. It is evident from the figure that the 'two-third rule' holds fairly well in Te-Bi-Se glass system. The values of T_g/T_m are found to vary from 0.628 to 0.644 with the variation of Se content from 42% to 57%.
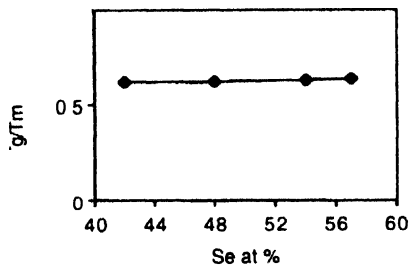

Figure 4. Variation of ratio of T_g/T_m with Se content.

The kinetic resistance to crystallization is higher for larger differences between T_c and T_g. The difference between T_c and T_g, which is an indication of thermal stability of the glasses, decreases rapidly with the increase in Se content for any given heating rate and the behaviour is similar at other heating rates.

Outside the glass-forming region, the melts are metallic; the bonding is such that the atoms are mobile and rearrangement to a crystalline state on cooling is favoured. Near the borderline of the glass-forming region, the melts have a high conductivity but the temperature dependence is that of a semiconductor. Thus, the bonding is more localized and rearrangement to a crystalline state in impeded. Mild heating however, can crystallize Glass samples in this range. According to the theory on the homogeneous nucleation and growth of a crystalline phase from a liquidus phase, the nucleation rate decreases with an increase of interfacial energy between liquid and solid phases and viscosity [15]. Similarly, the growth rate is also dominated by viscosity. The large values of T_g/T_m and ΔT_c for the present amorphous alloys imply that the viscosity increases steeply with decreasing temperature. The crystallization process indicates that the crytallization requires the redistribution of the constituent elements over a long-range scale, which is thought to be a significant barrier for the phase transition to a crystalline phase. The glass forming ability for the present amorphous alloys may be achieved by increasing the viscosity through the variation of composition.

For a given uniform heating rate, the glasses show a single glass transition endothermic peak and a single exothermic crystallization peak. The single endothermic glass transition peak

indicates the homogeneity of the glass. For a memory/switching material, the thermal stability and ease of glass formation are of crucial importance. The value of (T_c-T_g) is found to decrease with increase in Se concentration. The value of (T_c-T_g) is also found to increase with the increase in heating rates from 10K/min to 20K/min.

This indicates a decrease in thermal stability of glass [8, 16] with an increase in selenium concentration in the Te-Bi-Se glass system. The glass forming ability can be calculated using the following relations [17, 18]

$$K_{gl} = \frac{T_c - T_g}{T_m - T_c}$$ (2)

The values of K_{gl} are found to decrease from 0.749 to 0.480 with an increase in Se content from 42% to 57%. Figure 5 shows the variation of K_{gl} with Se content. It is noticed that the glasses with lower Se content are easy to form compared to those with higher Se content.
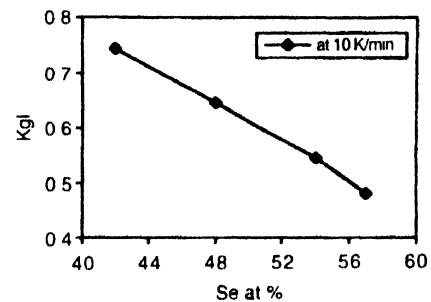

Figure 5. Variation of K_{gl} with Se content

4. Conclusions

In the present work, a systematic investigation of crystallization kinetics of Te-Bi-Se glass system reveal that there is a heating rate dependence of T_g and T_c. Drastic changes in T_g cannot be expected by increase in Se content, which results in iso-structural units of nearly same bond strength. The slight increase in T_g observed is probably due to the increase in mean molecular weight of the glasses with increasing Se content. The glass transition temperature T_g increases slightly with the variation of Se content from 42% to 57%. Thermal stability of these glasses is also found in good command to form the glasses with ease. The values of K_{gl} are found to decrease with an increase in Se content. It is seen that the glasses with lower Se content are easy to form compared to those with higher Se content. It is also concluded that the Te-Bi-Se system shows a reduced tendency towards glass formation at higher Se concentration.

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