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Calorimetric studies and thermal stability of $(Se_{80}Te_{20})_{100-x}Ge_x$ (x = 0, 2, 4 and 6) chalcogenide glasses by thermal analysis

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The crystallization kinetics and thermal stability of the $(Se_{80}Te_{20})_{100-x}Ge_x$ (x = 0, 2, 4 and 6) glassy alloys are made at different heating rates (10, 15, 20 and 25 ^oC/min) under non-isothermal conditions using simultaneous thermal analysis (TG/DTA). Well defined endothermic and exothermic peaks are obtained at glass transition (T_g) and crystallization temperatures (T_c). From the dependence of the glass transition temperature on the heating rate (β), the activation energy of glass transition (E_t) has been calculated on the basis of Kissinger model. It has been found that the T_g and E_t increases with the increasing Ge content in Se-Te glassy alloy. The thermal stability of the studied glasses has been evaluated using various thermal stability criteria ((T_c - T_g), thermal stability parameter (S), Hruby parameter (H_r) and reduced glass transition temperature (T_{rg})), based on the characteristic temperatures such as the glass transition temperature, the crystallization temperature and the melting temperature (T_m).

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1. Introduction

Crystallization studies of chalcogenide glasses are important in determining the transport mechanism, thermal stability and practical applications. The non-isothermal method has been used for the determination of the thermal stability of the amorphous alloys in the investigation of the processes of the nucleation and growth that occur during transformation of the metastable phases in the glassy alloys as it is heated. These techniques provide valuable information on such parameters, as the glass transition temperature (T_g), the crystallization temperature (T_c) and the activation energy (E_t), over a wide range of temperature [1-5]. Our present research work is concentrated on calorimetric studies of $(Se_{80}Te_{20})_{100-x}Ge_x$ (x =0, 2, 4 and 6) chalcogenide glasses by using differential thermal analysis with different continues heating rates. In the present system we use Se, because of its wide commercial applications. It exhibits [6] a unique property of reversible transformation. The seleinde glasses are easy to form and it is possible to vary the composition of the various components over a wide range. However, pure selenium has short life-time and low sensitivity. This problem can be overcome by alloying Se with some impurity atoms (Ge, Te, S, Bi, Sb and As, etc.) which gives high sensitivity and high crystallization temperature and smaller aging effects [7-10]. Primary region to add Te, as it improves the long wave transmission of the glass. In fact glasses are very stable against crystallization [11]. The properties of chalcogenide semiconductors are usually affected by the addition of third element. Here we choose Ge as an additive to Se-Te binary alloy because; Ge serves to increase the chemical and thermal durability of the glass. In the Ge–Se–Te system, germanium is known to contribute to long-term room temperature stability and selenium is considered as interesting material due to its wide commercial importance [12]. In the present study, a considerable shift in the glass transition temperature (T_g) towards higher temperature is observed. This characteristics shift of T_g with heating rate can be used to extract the activation energy of the glass transition from glassy to supercooled phase. Crystallization kinetics of chalcogenide glasses are always connected with the concept of activation energy. This activation energy in glass crystallization phenomenon is associated with the nucleation and growth processes that dominate the divitrification of most glassy solids [13]. The stability of glass forming systems against crystallization is often reported in terms of temperature interval between the T_g and T_c detected during heating a glassy sample at a study rate [14-15]. Other stability parameter viz. Hruby Parameter (H_r), Thermal Stability Parameter (S) and Reduced Glass Transition Temperature (T_{rg}) have been evaluated for the present glassy alloys.

2. Experimental procedure

Glassy alloys of $(Se_{80}Te_{20})_{100-x}Ge_x$ (x = 0, 2, 4, 6) were prepared by the melt quenching technique. The exact proportion of high purity (99.99%) elements with their atomic percentage were weighed and sealed in an evacuated (10^{-5}Torr) quartz ampoule. Then each ampoule was kept inside the furnace at 1000°C temperature for about 12 hr. During heating all the ampoules were constantly rocked, this was done to obtain the homogeneous glassy alloys. After rocking for about 12hr, the obtained melt were cooled rapidly by removing them from the furnace and dropping them to ice-cooled water rapidly. The ingots of the samples were then taken out by breaking the quartz ampoules. The amorphous nature of the alloys in general was ascertained through X-ray diffraction pattern of the samples using X-Pert PRO, as no prominent peak was observed in the spectra as shown in the Fig. 1. Similar results are obtained for other samples.

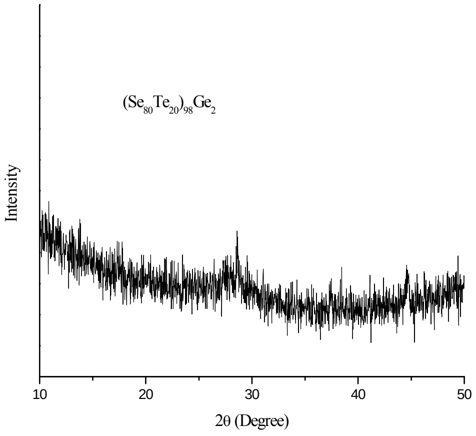

Fig. 1. XRD pattern for $(Se_{80}Te_{20})_{98}Ge_2$ glassy alloy.

SHIMADZU DTG-60, simultaneous TG/DTA module is used to measure the caloric manifestation of the phase transformation and to study the crystallization kinetics under non-isothermal conditions. The TG/DTA scans are taken at four heating rate (10, 15, 20, 25 °Cmin^{-1}) for the four different composition in the micro alumina pans under dry nitrogen gas. The masses of the samples varied between10 and 30 mg.

3. Results and discussion

3.1 Thermal Characterization

Thermal analysis is measurement of physical and chemical properties as a function of temperature. Thermo gravimetric analysis (TGA), records the change in the weight of sample and the differential thermal analysis (DTA), measures the nature of chemical change (exothermic and endothermic). Figure 2 shows the DTA thermogram of glassy $Se_{80}Te_{20}$ and $(Se_{80}Te_{20})_{98}Ge_2$ alloys at heating rate of 15 °C/min. It can be seen from the figure that glass transition temperature (T_g) and crystallization temperature T_c shifts toward higher temperature with increase of Ge content in Se-Te glassy alloy. Similar DTA scans are obtained at other heating rate for the entire samples in present study. All the samples show a single glass transition temperature and a single crystallization peak. The loss in mass over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability. From the perusal of TG curve for glassy $Se_{80}Te_{20}$ alloy (Figure 3), it is clear that there is no mass loss in the sample over the entire temperature range. Similar TG curves are obtained for the other glassy alloys.

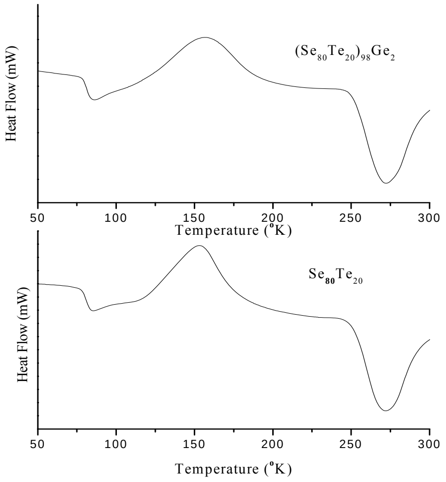

Fig. 2. DTA thermogram for $Se_{80}Te_{20}$ and $(Se_{80}Te_{20})_{98}Ge_2$ glassy alloys at heating rate of 15 °C /min.

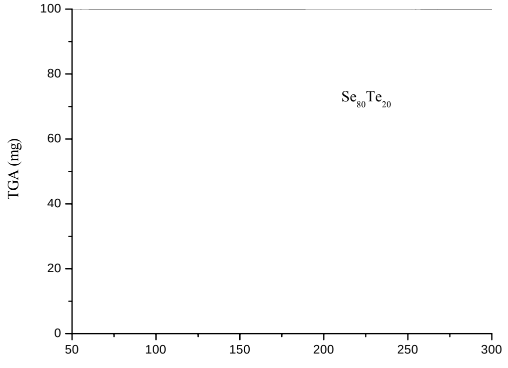

Fig. 3. TGA analysis of $Se_{80}Te_{20}$ glassy alloy at heating rate of 10°C /min.

The dependence of T_g on the heating rate β has been discussed on the basis of two approaches reported in the literature. The first empirical relationship has originally been suggested by Lasocka [16] and has the form:

$$T_g = A + B Log\beta \tag{1}$$

Where A and B are the constants. The value of A indicates the glass transition temperature for the heating rate of 1K/min., while B is related with the cooling rate of melt [16]. Plots of $Log\,\beta$ vs T_g are shown in the Figure 4. It is found that equation holds good for our samples. The values of A and B for different compositions are given in the Table 1. The values of B are found to be different for these compositions, indicating that Se-Te-Ge alloy undergoes structural changes for different Ge concentration.

Table 1. Calculated values of constants A and B, and activation energy (E_t) by Kissinger method for ($Se_{80}Te_{20})_{100-x}Ge_x$ (x = 0, 2, 4 and 6) glassy alloys.

Composition	A (K)	B (K)	E_t (Kj/mol)
$Se_{80}Te_{20}$	335.85	4.92	142.83
$(Se_{80}Te_{20})_{98}Ge_2$	340.96	5.50	166.13
$(Se_{80}Te_{20})_{96}Ge_4$	341.31	5.61	181.41
$(Se_{80}Te_{20})_{94}Ge_6$	341.31	5.80	192.64

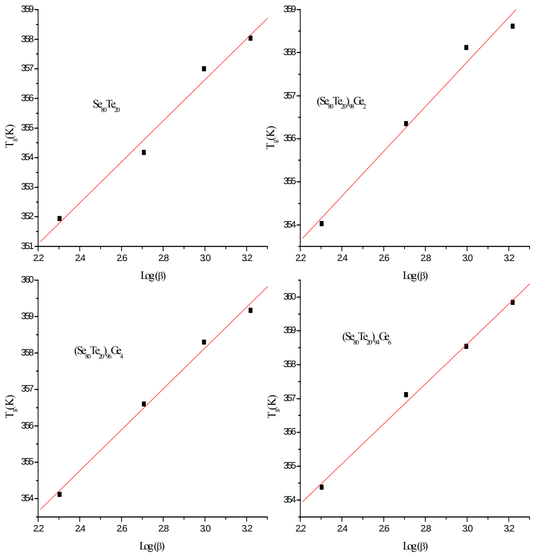

Fig. 4. Plots of Log (β) vs glass transition temperature (T_g K) for ($Se_{80}Te_{20})_{100-x}Ge_x$ (x = 0, 2, 4 and 6) glasses.

The glass transition region has been studied in terms of variation of glass transition temperature with composition and heating rate. In addition to this, activation energy of glass transition region has also been evaluated by using the Kissinger equation [17]. In spite of the fact that Kissinger equation is basically for the determination of the activation energy for crystallization process, it has been shown [18] that the same equation can be used for evaluation of the glass transition activation energy, and may be written as.

$$\ln\left(\frac{\beta}{T_g^{\,2}}\right) = -\frac{E_t}{RT_g} + cons\tan t \qquad (2)$$

The value of E_t is evaluated from the slope of the plots of $\ln\left(\frac{\beta}{T_g^{\,2}}\right)$ vs $\frac{10^3}{T_g}$ for different compositions. The plots are shown in the Fig. 5 at heating rate of 15 °C/min and the values are given in the table 1. The glass transition activation energy is the amount of energy that is possessed by the group of atoms in the glassy region so that a jump from one metastable state to another state is possible [19]. In other words, the activation energy is involved in the molecular motion and rearrangement of atoms around the glass transition temperature [20]. Form the table 1, it is clear that activation energy increases with the increase of Ge content in Se-Te glassy alloy. The increase in E_t is due to the increase in T_g (increasing the rigidity) with increasing Ge content. This result is in good agreement as reported by Y. Calventus and co workers [21]. The glass transition temperature is known to depend on several independent parameters such as the average coordination number [22-23]. The increase in the glass transition temperature which is accompanied by an increase in the coordination number can be ascribed to the increase of the rigidity (strength) of the system with increasing the Ge content [24]. The variation of T_g with the composition is shown in the figure 6. It is observed from the figure that there is an increase in the T_g with the addition of Ge content in the Se-Te glassy alloy. The variation of T_g with composition suggests that addition of Ge leads to an increase in the length of Se-Te chains [25-27].

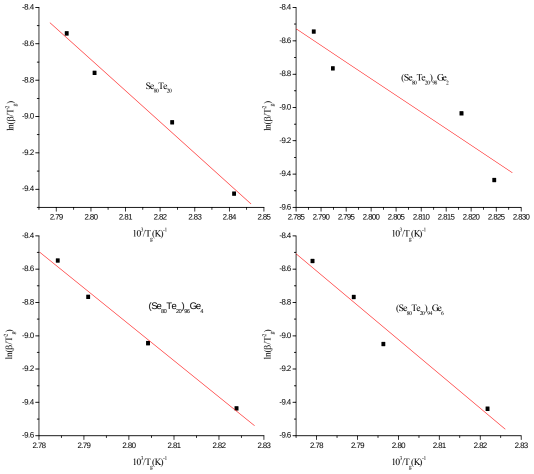

Fig . 5. Plots of $\ln\left(\frac{\beta}{T_g^{\,2}}\right)$ *vs* $\frac{10^3}{T_g}$ *for ($Se_{80}Te_{20})_{100-x}Ge_x$ (x = 0, 2, 4 and 6) glasses.*

3.2 Thermal stability and glass forming tendency

In non-isothermal study, the stability of the glasses is usually in terms of two independent factors; the first stability criterion was introduced by Dietzel [28], $\Delta T = (T_c - T_g)$ and the other is the heat content of the samples i.e. enthalpy. The thermal stability and glass forming tendency (GFT) plays an important role in determining the utility of chalcogenide alloys as recording material due to the fact that PCO recording and erasing techniques are based on the laser induced thermal amorphization and crystallization of chalcogenide glasses. Therefore thermal stability and GFT is a subject of great interest [29-32]. The thermal stability and crystallization of Se-Te and Se-Te-Ge alloys were studied by differential thermal analysis (DTA). To assess the level of stability of the glassy materials in the above mentioned system are based on characteristic temperatures, obtained by heating of the samples in non-isothermal regime, such as the glass transition temperature (T_g), the crystallization temperature (T_c) and the melting temperature (T_m) and values are given in Table 2. The kinetic resistance to crystallization is given by the difference between T_c and T_g, the larger the difference, the higher the resistance. Therefore, the temperature difference T_c-T_g is a good indication of thermal stability, because the greater the difference, the more the delay in the nucleation process.

Table 2. DTA result for $(Se_{80}Te_{20})_{100-x}Ge_x$ (x = 0, 2, 4 and 6) at the heating rate of 10 °C/min.

Composition	Glass Transition Temperature T_g (K)	Onset Crystallization Temperature T_c (K)	Melting Temperature T_m (K)
$Se_{80}Te_{20}$	351.94	411.47	541.59
$(Se_{80}Te_{20})_{98}Ge_2$	354.03	412.13	540.68
$(Se_{80}Te_{20})_{96}Ge_4$	354.12	413.20	538.45
$(Se_{80}Te_{20})_{94}Ge_6$	354.38	414.52	532.92

The thermal stability parameter, *S*, proposed by Saad and Poulin [33], reflect the resistance to divitrification after the formation of the glass.

$$S = (T_c - T_o)(T_c - T_g)/T_g \tag{3}$$

In Equation 3, the term (T_c-T_g) is related to the rate of divitrification transformation of the glass phase. The higher values of term (T_c-T_g) delay the nucleation process. The values of S are given in the Table 3 for the present investigated alloys. The crystallization temperature (T_c) is another important factor, which is the strong indicator of thermal stability. With the addition of Ge content, the glassy matrix becomes heavily cross linked and steric hindrance increases. The Se-Se bonds (1.91 eV) will be replaced by Se-Ge bonds, which have higher bond energy (2.12 eV). Hence the cohesive energy of the system increases with addition of Ge content [24]. Thus substantiating the increase in thermal stability of present glassy alloys.

Table 3. Calculated values of (T_c-T_g), Thermal Stability Parameter S (K), T_{rg} and Hruby Parameter (H_r) for $(Se_{80}Te_{20})_{100-x}Ge_x$(x = 0, 2, 4 and 6) at the heating rate 15 °C /min.

Composition	(T_c-T_g)	Thermal Stability Parameter *S* (*K*)	T_{rg}	Hruby Parameter (H_r)
$Se_{80}Te_{20}$	66.20	7.32	0.65	0.53
$(Se_{80}Te_{20})_{98}Ge_2$	68.06	7.11	0.65	0.56
$(Se_{80}Te_{20})_{96}Ge_4$	66.82	6.96	0.65	0.56
$(Se_{80}Te_{20})_{94}Ge_6$	67.02	6.79	0.66	0.59

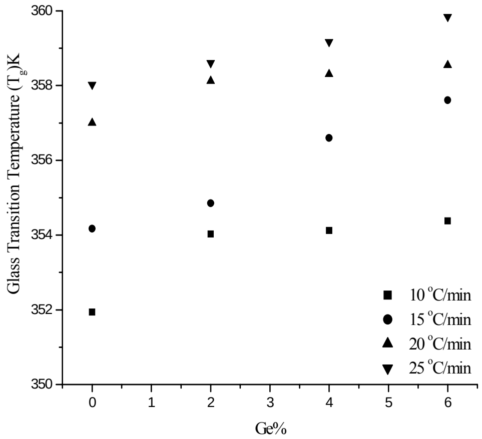

Fig. 6. Composition dependence of glass transition temperature T_g at different heating rate.

The glass forming tendency (GFT) has been related to several parameters, such as the crystal growth rate and nucleation rate of the material. The best known parameter was proposed by Turnbull, and is known as the reduced glass transition temperature. It is given by $T_{rg} = \dfrac{T_g}{T_m}$ [34, 35]. The values so obtained obey the 'two-third rule', (Table 3)

$$T_{rg} = \frac{T_g}{T_m} = \frac{2}{3} \tag{4}$$

From the table it is evident that 'two-third rule' holds well in the present Se-Te-Ge glass system. The obtained values are found to be nearly equal to 0.66 for different Ge concentration at each heating rate. Another parameter which is a strong indicator of GFT, introduced by Hruby (H_r) that combines both nucleation and growth aspects of phase transformation is given by [36]

$$H_r = \frac{(T_c - T_g)}{(T_m - T_c)} \tag{5}$$

where T_m is the melting temperature. Hruby parameter stresses the fact that the probability of obtaining the glass increases as the supercooling interval, T_m-T_c decreases and its stability increases with the difference T_c-T_g. If $H_r \leq 0.1$ the glass is usually difficult to prepare. Good glass former have values of $H_r \geq 0.4$. From the table 3 it is clear that glass forming ability is good for Ge added Se-Te glassy alloys.

4. Conclusion

In the present research work, a systematic investigation on the thermal stability and crystallization studies of $(Se_{80}Te_{20})_{100-x}Ge_x$ (x = 0, 2, 4 and 6) glassy alloys has been performed using non-isothermal method at four different heating rates. It is found that the glass transition temperature increases with increase in Ge content indicating a crosslinkings of Se-Te chains with the addition of Ge. The observed heating dependence of T_g was used to evaluate E_t by Kissinger's equation. The value of E_t is found to be increase with the addition of Ge and is correlated with the increase of coordination number and glass transition temperature. Stability parameters so calculated for Ge added Se-Te glassy alloys shows a good glass forming tendency.

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