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Thermal characterization of glassy $Se_{70}Te_{20}M_{10}$ using DSC technique

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Differential scanning calorimetry (DSC) has been employed to study the phase transformation in glassy $Se_{70}Te_{20}M_{10}$ ($M = Ag$, Cd, Sb) to understand the glass forming tendency (GFT) and rate of crystallization. The difference (T_c–T_g) (indicator of GFT and thermal stability) has been determined by DSC thermograms for each sample. The values of T_c and T_g are found to depend on GFT. The rate constant K (indicator of rate of amorphous to crystalline phase transformation) has been evaluated using method of Augis and Bennett. The parameter K is also found to be related with (T_c–T_g).

1. Introduction

Phase change (PC) optical recording based on marking of micron-sized spots on a data storage disk using a laser beam is an area with on going research activity. In this recording, spots of a crystalline material are melted momentarily by short laser pulses for recording and the recorded marks are erased through annealing process during which long laser pulses heat the amorphous spots to return in to crystalline phase. The laser induced amorphous to crystalline (a-c) and crystalline to amorphous (c-a) phase changes have been observed in different chalcogenide glasses by various workers [1–11].

In PC technology, the laser pulse duration used to write and erase is usually several hundred nanoseconds. Hence, the a-c and c-a phase transformations in PC recording layer material should be very fast so that erasing and recording are possible in such a time scale. For this reason, the study of both types of phase changes is very important for the development of some new chalcogenide glasses as better PC recording materials. This can be done by the determination of two important parameters: glass forming tendency (GFT) and the rate of crystallization. GFT of a glassy alloy is related to the ease by which melt can be cooled with the avoidance of crystal formation. On the other hand, the rate of crystallization represents the divitrification of glassy alloy through the nucleation and growth process. The origin of GFT and the rate of crystallization is, therefore, a subject of great interest.

The present paper reports the thermal characterization of ternary $Se_{70}Te_{20}M_{10}$ alloys for optical memory application in terms of GFT and rate of crystallization. The effect of metallic additives (Ag, Cd, Sb) on GFT in $Se_{70}Te_{20}M_{10}$ systems is explained with the help of chemically ordered network model (CONM) and Pauling's concept of electronegativity. The rate of crystallization is explained in terms of thermal stability.

2. Experimental

Glassy alloys of $Se_{80}Te_{20}$ and $Se_{70}Te_{20}M_{10}$ ($M = Ag$, Cd, Sb) were prepared by quenching technique. High purity materials (5 N pure) were weighed according to their atomic percentages and were sealed in quartz ampoules under the vacuum of 10^{-5} Torr. Each ampoule was kept inside the furnace at an appropriate temperature (where the temperature was raised at a rate of 3–4°C/min). The ampoules were rocked frequently for 10 h at the maximum temperature to make the melt homogeneous. Quenching was done in ice water and the glassy nature of alloys was checked by X-ray diffraction technique.

The glasses, thus prepared, were ground to make fine powder for DSC studies. 10 to 20 mg of each sample was heated at a constant heating rate and the changes in heat flow with respect to an empty pan were measured. Four heating rates (5, 10, 15 and 20°C/min) were chosen in the present study. Measurements were made under almost identical conditions so that a comparison of activation energy of crystallization E_C could be made.

3. Results and discussions

3.1. Glass transition temperature and glass forming tendency

Fig. 1 shows a DSC thermogram for glassy $Se_{70}Te_{20}Cd_{10}$ at different heating rates. Similar thermograms have been obtained for other glassy alloys. From these thermograms, glass transition temperature T_g has been determined for each alloy at all the four heating rates. Theoretical values of T_g for these alloys have also been evaluated using Gibbs Dimarzio equation [12]

$$T_g = T_o/[1 - \gamma(\langle Z \rangle - 2)] \qquad (1)$$

where T_o is the value of glass transition temperature of the non-cross linked binary alloy and $\langle Z \rangle$ represents

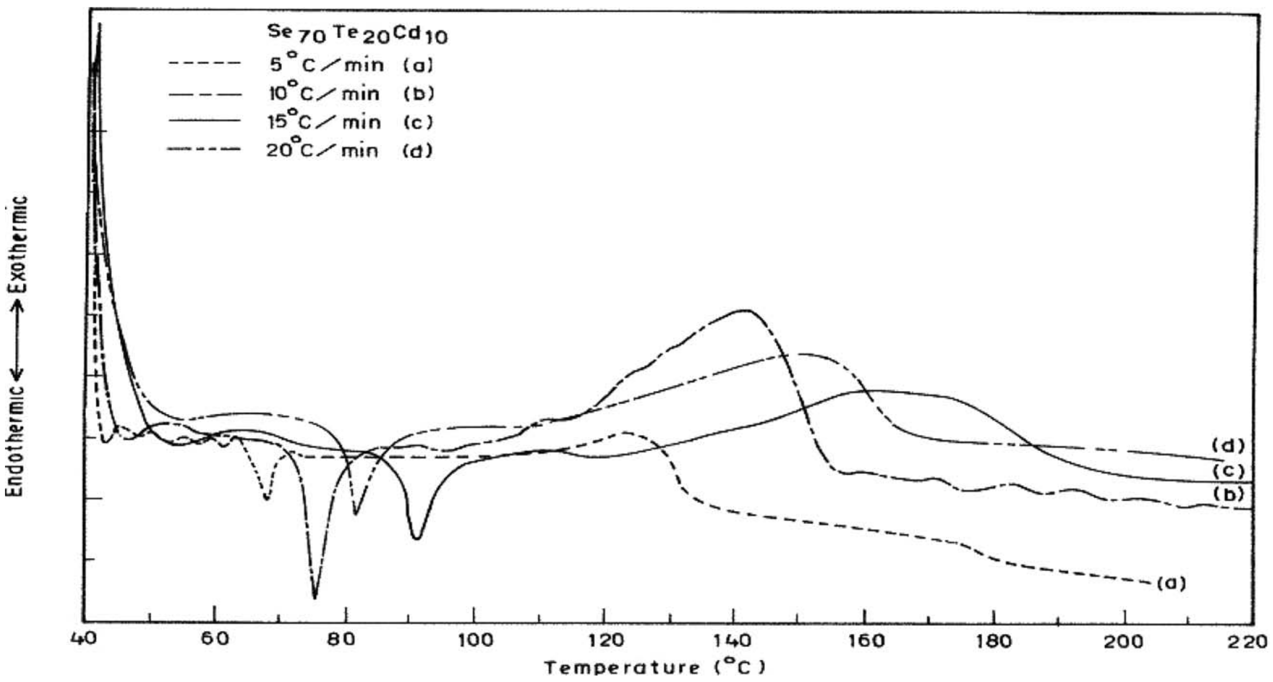

Figure 1 DSC Thermograms for $Se_{70}Te_{20}Cd_{10}$ alloy at different heating rates.

the average co-ordination number of ternary alloys. The values of $\langle Z\rangle$ for ternary alloys $Se_{70}Te_{20}M_{10}$ are evaluated by the formula

$$\langle Z\rangle = [Z_{Se.}(70) + Z_{Te.}(20) + Z_{M.}(10)]/100 \qquad (2)$$

where Z_{Se}, Z_{Te} and Z_M are the co-ordination numbers of Se, Te and metallic additive M (M = Ag, Cd, Sb) respectively in $Se_{70}Te_{20}M_{10}$ systems. In Equation 1, γ is an arbitrary constant whose value is evaluated for each ternary alloy by substituting the values of T_g and T_o at a known heating rate (here 5°C/min) and the value of $\langle Z\rangle$ in Equation 1. The values of T_o at the other three heating rates used in the present work are given in Table IA. The experimental values of T_g obtained from DSC scans and its theoretical values evaluated from Equation 1 for each ternary alloy are given in Table IB at the other three heating rates. An excellent agreement has been observed between the experimental and theoretical values of T_g for the alloys at the three heating rates. The experimental and theoretical values of T_g are plotted against the heating rate β in Fig. 2.

TABLE IA Glass transition temperature (T_o) of glassy $Se_{80}Te_{20}$ (non-cross linked) at different heating rates

β (°C/min)	10	15	20
T_o (°C)	68.02	69.31	71.12

TABLE IB Experimental and theoretical values of T_g for ternary alloys

	$Se_{70}Te_{20}Ag_{10}$		$Se_{70}Te_{20}Cd_{10}$		$Se_{70}Te_{20}Sb_{10}$	
β (°C/min)	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
10	64.50	64.17	72.30	72.36	78.37	79.09
15	67.30	65.38	75.88	73.73	80.61	80.50
20	67.60	67.09	76.92	75.66	82.04	82.69

The glass transition temperature T_g represents the strength or rigidity of the glass structure in chalcogenide glasses. Hence T_g affords valuable information on the thermal stability of glassy state [13, 14] but T_g alone does not give any information on the GFT [15]. However, it has been found that the difference of T_c and T_g is a strong indication of both the thermal stability and GFT [16]. The higher the values of (T_c–T_g), the greater is the GFT. The values of T_c and (T_c–T_g) at all heating rates are given in Table II. It is interesting to note that the values of (T_c–T_g) are maximum for ternary alloy $Se_{70}Te_{20}Cd_{10}$ at all the four heating rates. This shows maximum thermal stability and GFT in case of Cd additive.

There are several factors which play a significant role in determining the ease of glass formation. Since chalcogenide glasses are amorphous in nature, they form a disordered and matastable structure. Due to lack of translational symmetry, their properties (thermal stability, GFT etc.) strongly depend upon the character and concentration of chemical bonds, which hold the atoms together in glassy network. Hence, here we have focused on this important factor, i.e., chemical bonding to explain our result regarding GFT.

TABLE II Values of T_c and (T_c–T_g) for ternary alloys at different heating rates

	$Se_{70}Te_{20}Ag_{10}$		$Se_{70}Te_{20}Cd_{10}$		$Se_{70}Te_{20}Sb_{10}$	
β (°C/min)	T_c	T_c–T_g	T_c	T_c–T_g	T_c	T_c–T_g
5	103.30	43.30	125.60	57.91	87.62	12.99
10	109.70	45.20	130.00	57.70	92.00	13.63
15	115.30	48.00	136.47	60.59	95.00	14.39
20	118.40	50.80	139.23	62.31	100.00	17.96

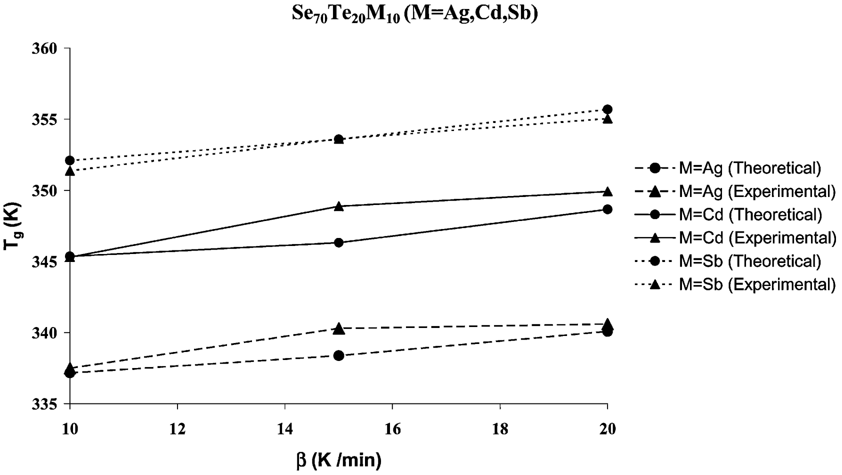

Figure 2 Plot of experimental and theoretical values of T_g vs. heating rate β.

The values of (T_c–T_g) have been found to be increasing in the order Sb $<$ Ag $<$ Cd in ternary alloys $Se_{70}Te_{20}M_{10}$. This sequence can be explained to some extant with the help of CONM. According to CONM, the formation of hetropolar bonds is favored over homopolar bonds in glassy alloys. In Se—Te—M system, the various bonds involved are Se—Se, Te—Te, Se—Te, M—Se, M—Te etc. The strength of Se—Se bond is greater than that of Te—Te bonds. The electronegativity of Se is also greater than that of Te. Thus according to Pauling [17, 18], M—Se bonds are found stronger than M—Te bonds. Hence, the metallic additives (Ag, Cd, Sb) are expected to combine preferably with Se as suggested by Shukla *et al.* [19] also in glassy alloys $Se_{80}Te_{10}M_{10}$ using X-ray spectroscopy.

The bond energies of Se—M bonds (M = Ag, Cd, Sb) increase in the order Cd $<$ Ag $<$ Sb [20] (see Table III). Thus, the cross linking of metallic additives with Se in Se—Te chains and Se—Te mixed rings probably takes place easily in the sequence Cd $>$ Ag $>$ Sb. The ease of glass formation is, therefore, expected to be associated with ease of bond formation of foreign atoms (Ag, Cd, Sb) with Se. This is found true in the present case as the value of (T_c–T_g), indicating the ease of glass formation, increases with decrease in strength of Se—M bonds. The plot of (T_c–T_g) vs. strength of Se—M bonds is shown in Fig. 3.

3.2. Crystallization temperature and rate of crystallization

The crystallization temperature T_c in ternary alloys $Se_{70}Te_{20}M_{10}$ (M = Ag, Cd, Sb) has been found to be increasing in the order $(T_c)_{Sb} < (T_c)_{Ag} < (T_c)_{Cd}$. It is evident from Table II that T_c is following the same increasing trend as is for (T_c–T_g) for different glassy alloys at all the heating rates. This indicates that higher the GFT, higher the crystallization temperature.

TABLE III Bond energies of Se—M bonds (M = Ag, Cd, Sb)

Additive element	Bond energy with Se (eV)
Silver (Ag)	1.86
Cadmium (Cd)	1.13
Antimony (Sb)	2.60

In chalcogenide glasses, the rate of crystallization is related [21] to the rate constant K, which is expressed by Arrhenius equation

$$K = K_o \cdot \exp[-E_c/(RT)] \qquad (3)$$

where E_c is the activation energy of crystallization, K_o the pre-exponential factor and R the universal gas constant. In Equation 3, E_c and K_o are assumed to be practically independent of the temperature (at least in the temperature interval accessible in the calorimetric measurements). The T_c and E_c in terms of heating rate β, can be expressed by the equation

$$\ln \beta/T_c = -E_c/(RT_c) + \ln K_o \qquad (4)$$

The above equation is derived by Augis and Bennett [22] from the classical JMA model [23–25]. Equation 4 has been used by various workers [26–28]. Their results show that E_c values obtained by Equation 4 are in good agreement with the E_c values obtained by well known Kissinger's relation [29] and relation of Matusita and Sakka [30, 31]. We have therefore used the method of Augis and Bennett (Equation 4) to evaluate activation energy of crystallization E_c. This method has an extra advantage that the intercept of ln β/T_c vs. $1/T_c$ gives the value of pre-exponential factor K_o of Arrhenius equation.

The plot of ln β/T_c vs. $1000/T_c$ for ternary alloy $Se_{70}Te_{20}Cd_{10}$ is shown in Fig. 4. Similar curves were obtained in other glassy alloys also. The values of E_c and ln K_o for each alloy are given in Table IVA. Knowing the values of E_c and ln K_o, the values of rate constant have been determined by Equation 3. The values of ln K at different temperatures in the crystallization region are given in Table IVB for each ternary alloy.

The values of ln K at different temperatures have been found to be decreasing in the sequence $(\ln K)_{Sb} > (\ln K)_{Ag} > (\ln K)_{Cd}$ which indicates that the rate of crystallization is more in case of Sb additive. It is interesting to note that thermal stability (T_c–T_g) is also lowest in this case. Hence one can conclude that the rate of crystallization is related to thermal stability in the present glasses.

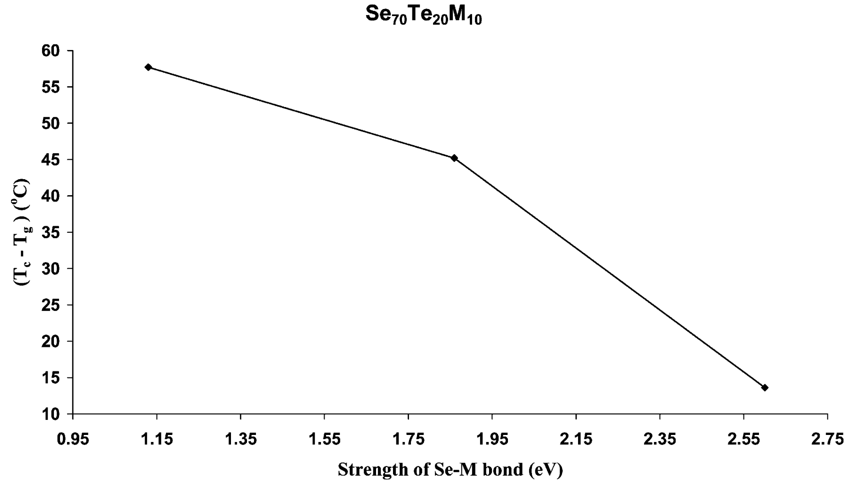

Figure 3 Plot of (T_c–T_g) vs. strength of Se—M bonds.

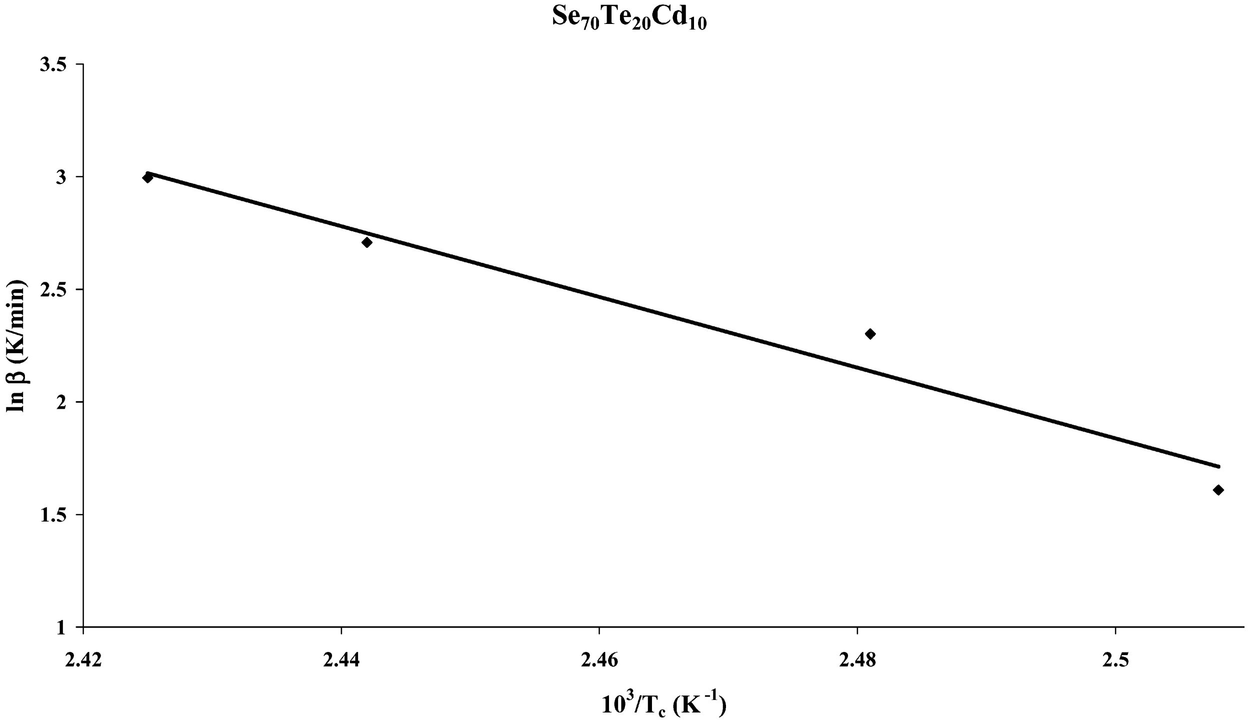

Figure 4 Plot of ln β/T_c vs. $1000/T_c$ for $Se_{70}Te_{20}Cd_{10}$ alloy.

TABLE IVA The values of E_c and ln K_o for ternary alloys using method of Augis and Bennett

Sample	E_c (eV)	ln K_o
$Se_{70}Te_{20}Ag_{10}$	1.106	29.813
$Se_{70}Te_{20}Cd_{10}$	1.319	34.084
$Se_{70}Te_{20}Sb_{10}$	1.263	36.453

TABLE IVB The values of ln K for ternary alloys at different temperatures

	ln K					
Sample	70°C	80°C	90°C	100°C	110°C	120°C
$Se_{70}Te_{20}Ag_{10}$	−7.57	−6.51	−5.51	−4.56	−3.66	−2.81
$Se_{70}Te_{20}Cd_{10}$	−10.49	−9.23	−8.04	−6.91	−5.84	−4.82
$Se_{70}Te_{20}Sb_{10}$	−6.23	−5.02	−3.88	−2.80	−1.77	0.80

4. Conclusion

The calorimetric measurements have been performed in binary $Se_{80}Te_{20}$ and ternary $Se_{70}Te_{20}M_{10}$ (M = Ag, Cd, Sb) alloys using DSC technique. It has been found that (T_c–T_g) increases with decrease in the bond energy of metallic additives (Ag, Cd, Sb) with Se. This shows that ease of glass formation is related to ease of Se—M bond formation in the present study.

The T_c values in ternary alloys increase in the order $(T_c)_{Sb} < (T_c)_{Ag} < (T_c)_{Cd}$ at each heating rate. This increasing sequence of T_c is explained in terms of increasing sequence of (T_c–T_g). This shows that increase in GFT is related to the increase in crystallization temperature.

Activation energy of crystallization and the crystallization rate constant have been calculated from the heating rate dependence of T_c. The rate constant is found to depend on (T_c–T_g). It is observed that the rate of crystallization is more in case of Sb additive where thermal stability is found to be small.

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