

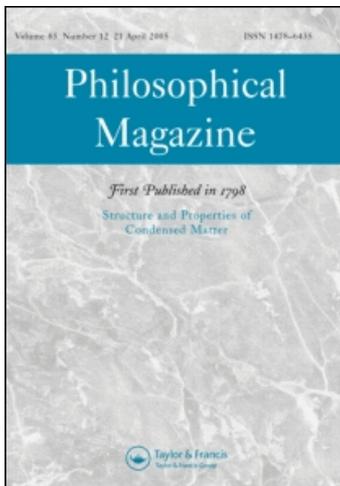
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Calorimetric study of $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ glassy alloys using differential thermal analysis

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A calorimetric study of $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ glassy alloys ($x = 0, 1, 2, 3$ and 4 at. %) is reported. Differential thermal analysis (DTA) was performed at heating rates of 10, 15, 20 and 25 K/min. The spectra were used to determine the glass transition temperature, T_g , the crystallisation temperature, T_c and the melting temperature, T_m . All these parameters shift to higher values with increasing heating rate, β . The glass transition temperature and the melting temperature increase, and the crystallisation temperature decreases, with increase in the Bi content, x . The activation energy of the glass transition, E_g , was evaluated using the Moynihan and Kissinger methods. The activation energy of crystallisation, E_c , was calculated using modified Kissinger and Matusita approaches. The thermal stability of these glasses has been studied and found to decrease with increase in Bi content. The results obtained are explained on the basis of a chemically ordered network model and an average coordination number.

Keywords: differential thermal analysis; glass transition temperature; activation energy; chalcogenide glass

1. Introduction

Amorphous semiconductors containing elements of Group VI of the Periodic Table are known as chalcogenide glasses. These glasses have applications in optics, optoelectronics, holography and as IR lenses [1]. Amorphous Se in its pure form is useful in applications like switching, memory and xerography [2,3] but it has disadvantages due to its low photosensitivity, low crystalline temperature and short lifetime. Addition of Te to Se produces higher photosensitivity, slower ageing effects, higher crystallisation temperature and greater hardness [4,5]. Te addition initially retards crystallisation but at higher contents this trend is reversed. The properties of binary alloys can be varied by adding a third element from Group IV or V of the Periodic Table so that the new materials can be tailor-made for specific purposes. The glass transition temperature and the glass forming ability of the Se–Te matrix

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can be increased by adding a third element [6–8], which also produces compositional and configurational disorder in the system.

In the present study, Bi was chosen as the third element because it produces remarkable changes in the thermal and optical properties of the Se–Te chalcogenide glasses. Bi addition causes a p-to-n transition in the conductivity [9–12]. Bi addition also increases the glass transition temperature, indicating a hardening of the Se–Te host. Applications based on the amorphous to crystalline photo-induced phase transition and vice versa require understanding of the glass-forming tendency and crystallisation kinetics. Crystallisation kinetics has been studied by various workers [13–15]. Non-isothermal differential thermal analysis (DTA) study has been used for this purpose. In DTA, the glass transition is exhibited by an endothermic peak and crystallisation by an exothermic peak due to a change in the specific heat of the sample.

In the present work, the effect of Bi addition on the crystallisation kinetics of $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) glassy alloys was studied using DTA. Characteristic temperatures, such as the glass transition temperature, T_g , and the crystallisation temperature, T_c , were recorded as a function of the heating rate, β , and the Bi content, x . The activation energies of the glass transition and crystallisation were calculated using different approaches. The glass-forming ability has also been calculated using Hruby's number, K_{gt} , and reduced transition temperature, T_{rg} .

2. Experimental details

Glassy alloys of $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) were prepared by melt quenching. Se, Te and Bi of high purity (99.999%) were weighed according to their atomic percentages and sealed in quartz ampoules evacuated to 10^{-3} Pa. The sealed ampoules were kept inside a vertical furnace where the temperature was raised up to 1073 K at a heating rate of 3–4 K/min. The ampoules were heated at the highest temperature for 12 h, during which time the ampoules were frequently rocked to make the melt homogenous. After quenching in ice cold water, the samples were obtained by breaking the ampoules. The amorphous nature of the glasses was confirmed by the absence of any prominent peaks in their X-ray diffraction profiles (see Figure 1). The glasses were ground into fine powder for DTA studies. The thermal behaviour of the samples was recorded using a 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 obtain the characteristic temperatures T_g , T_c and T_m .

3. Results

The DTA curves of $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ for $x=3$ at. % (as reference) at different heating rates of 10, 15, 20 and 25 K/min are shown in Figure 2. In DTA, the glass transition appears as an endothermic peak or a shift in the base line due to change in the specific heat as the glassy system relaxes quickly due to a decrease in viscosity. The position of the peak represents the strength of the glassy structure.

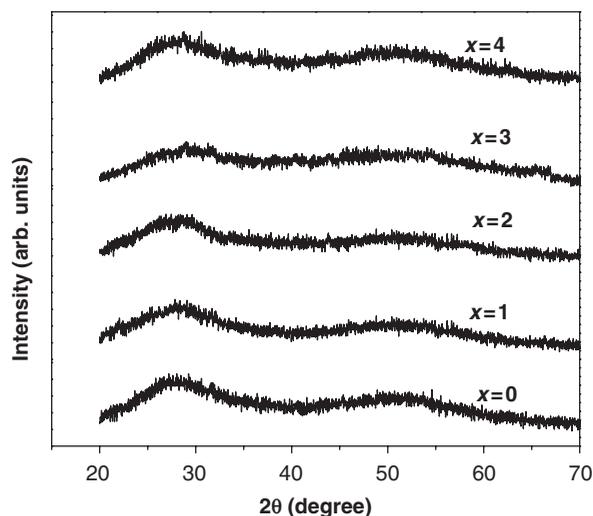


Figure 1. X-ray diffraction profiles of $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) glassy alloys.

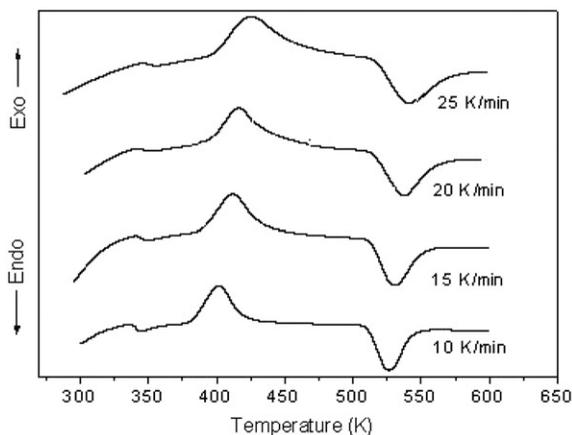


Figure 2. DTA thermograms for $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ glassy alloys for $x=3$ at. % at heating rates of 10, 15, 20, 25 K/min.

Figure 3 shows the DTA thermograms for $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) at a heating rate of 10 K/min. It is clear from the figure that the glass transition temperature, T_g , and the melting temperature, T_m , both increase and the crystallisation temperature, T_c , decreases with increase in Bi content.

The characteristic temperatures T_g , T_c and T_m were recorded from the DTA data and are listed in Table 1 for different heating rates, β . It can be seen that T_g increases with heating rate and obeys the empirical relation [16]

$$T_g = A + B \ln \beta, \quad (1)$$

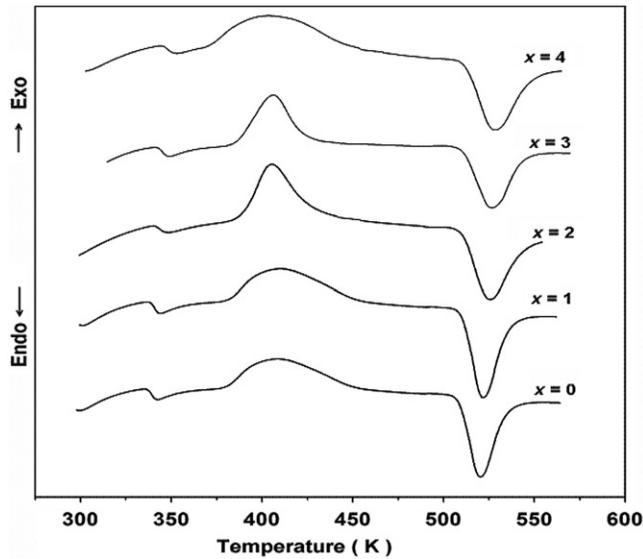


Figure 3. DTA thermograms for $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ glassy alloys for $x = 0, 1, 2, 3, 4$ at. % at a heating rate of 10 K/min.

Table 1. Values of T_g , T_c , T_m , $(T_c - T_g)$, $(T_m - T_c)$, K_{gl} and T_{rg} for $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x = 0, 1, 2, 3$ and 4 at. %) glassy alloys at heating rates of 10, 15, 20 and 25 K/min.

Composition	β (K/min)	T_g (K)	T_c (K)	T_m (K)	$T_c - T_g$ (K)	$T_m - T_c$ (K)	K_{gl}	T_{rg}
$\text{Te}_{15}(\text{Se}_{100})_{85}$	10	341.15	407.66	520.42	66.51	112.76	0.589	0.655
	15	344.15	418.31	527.42	74.16	109.11	0.679	0.653
	20	347.71	423.82	530.13	76.11	106.31	0.715	0.656
	25	349.95	430.22	530.72	80.27	100.52	0.798	0.659
$\text{Te}_{15}(\text{Se}_{99}\text{Bi}_1)_{85}$	10	342.11	404.61	521.91	62.50	117.30	0.533	0.655
	15	345.09	415.00	529.16	69.91	114.16	0.612	0.652
	20	348.36	420.91	532.13	72.55	111.22	0.652	0.654
$\text{Te}_{15}(\text{Se}_{98}\text{Bi}_2)_{85}$	25	350.37	427.28	532.48	76.91	105.20	0.731	0.658
	10	343.17	403.51	522.00	60.34	118.49	0.509	0.657
	15	346.05	413.95	530.81	67.90	116.86	0.581	0.652
$\text{Te}_{15}(\text{Se}_{97}\text{Bi}_3)_{85}$	20	349.22	419.99	533.97	70.77	113.98	0.621	0.654
	25	351.11	427.18	536.15	76.07	108.97	0.698	0.654
	10	344.19	401.47	526.31	57.28	124.84	0.459	0.653
	15	346.97	411.97	530.01	65.00	118.04	0.551	0.654
$\text{Te}_{15}(\text{Se}_{96}\text{Bi}_4)_{85}$	20	350.03	420.16	537.75	70.13	117.59	0.596	0.651
	25	351.81	425.36	541.69	73.55	116.33	0.632	0.649
	10	345.10	399.10	527.96	54.00	128.86	0.419	0.653
	15	347.77	409.46	532.00	61.69	122.54	0.503	0.653
$\text{Te}_{15}(\text{Se}_{96}\text{Bi}_4)_{85}$	20	350.73	419.01	542.74	68.28	123.73	0.551	0.646
	25	352.38	423.86	543.07	71.48	119.21	0.599	0.648

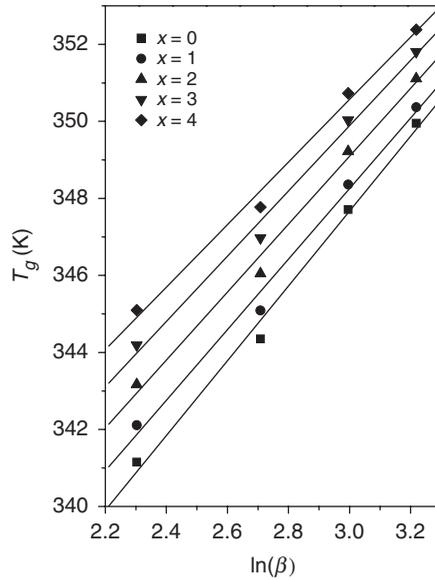


Figure 4. Variation of T_g with $\ln(\beta)$ for $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) glassy alloys.

where A and B are constants. A represents the value of T_g for a heating rate of 1 K/min, whereas B is related to the cooling rate of the melt and to the response of configurational changes in the glass formation region. Different values of B indicate that the system has undergone structural changes with different Bi compositions.

Figure 4 shows the variation of T_g with $\ln(\beta)$ for the glassy alloys. T_g is found to increase with the Bi content. The structural relaxation theory developed by Moynihan and others [17–19] was used to analyse the kinetics of the glass transition from its heating rate dependence. The activation energy of the glass transition E_g has been calculated using Moynihan's theory. The dependence of T_g on heating rate is given by [18,19];

$$\frac{d(\ln \beta)}{d(1/T_g)} = -\frac{E_g}{R}, \quad (2)$$

where R is the gas constant. The plot of $\ln(\beta)$ vs. $1000/T_g$ is a straight line, as shown in Figure 5 and the activation energy of the glass transition was calculated from the slope of this plot. The activation energy was found to increase with Bi content.

The activation energy of the glass transition was also calculated from the Kissinger equation [20]:

$$\ln\left(\frac{T_g^2}{\beta}\right) + \text{const.} = \frac{E_g}{RT_g}, \quad (3)$$

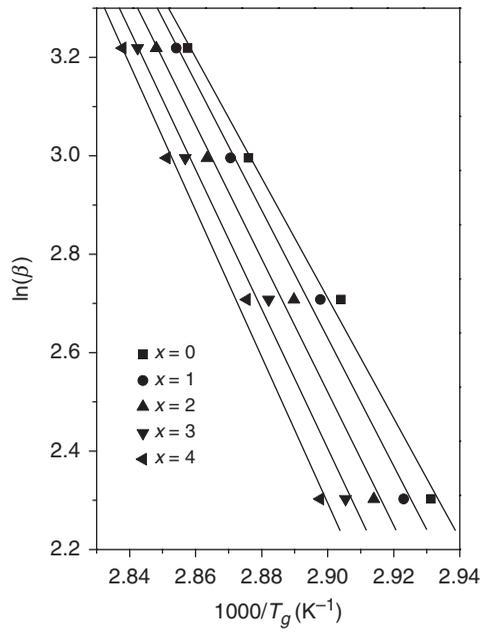


Figure 5. Plot of $\ln(\beta)$ vs. $1000/T_g$ for $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) glassy alloys.

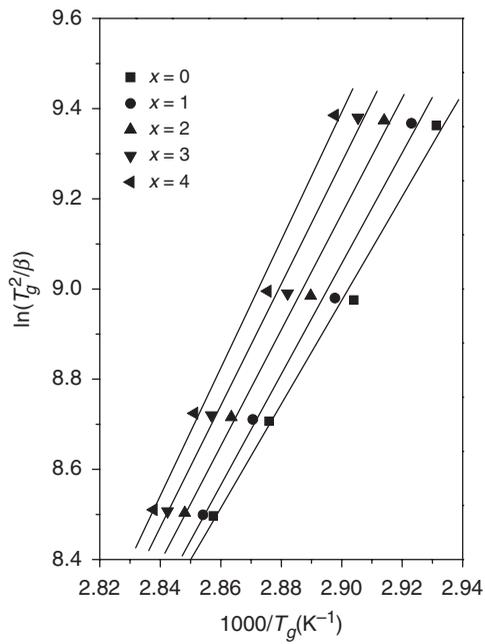


Figure 6. Plot of $\ln(T_g^2/\beta)$ vs. $1000/T_g$ for $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) glassy alloys.

Table 2. Values of $\langle r \rangle$, E_g , E_c , n , m and CE for $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) glassy alloys.

x	$\langle r \rangle$	E_g (kJ/mol) (Moynihan)	E_g (kJ/mol) (Kissinger)	E_c (kJ/mol) (mod. Kissinger)	n	m	E_c (kJ/mol) (Matusita)	CE (kJ/mol)
0	2.15	101.45	95.71	53.13	1.39	1	75.15	180.37
1	2.16	107.91	102.15	51.92	1.33	1	74.63	180.12
2	2.17	112.67	106.90	49.50	1.35	1	71.52	179.86
3	2.18	117.87	112.06	46.90	1.24	1	68.39	179.61
4	2.19	123.57	117.79	43.81	1.17	1	67.78	179.07

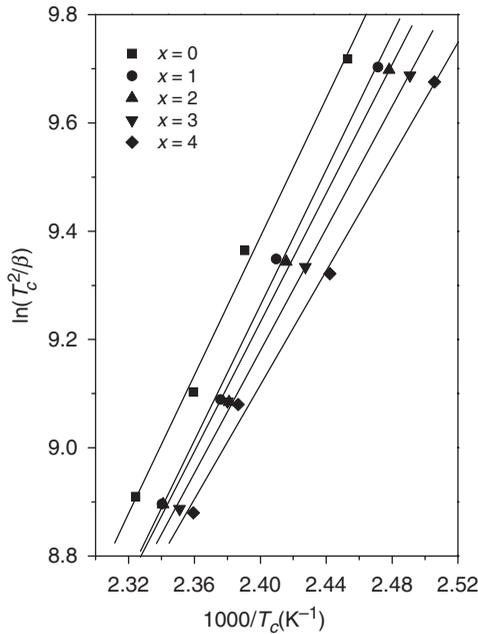


Figure 7. Plot of $\ln(T_c^2/\beta)$ vs. $1000/T_c$ for $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) glassy alloys.

from the slopes of plots of $\ln(T_g^2/\beta)$ vs. $1000/T_g$ (Figure 6). The calculated values of E_g are reported in Table 2. The activation energies calculated from both approaches are comparable and increase with Bi content x .

The activation energy of crystallisation was calculated from the variation of the peak crystallisation temperature, T_c , with heating rate using the modified Kissinger's equation [21,22]:

$$\ln\left(\frac{T_c^2}{\beta}\right) + \text{const.} = \frac{E_c}{RT_c} \tag{4}$$

The graph of $\ln(T_c^2/\beta)$ vs. $1000/T_c$ is shown in Figure 7. The slope of this graph gives the value of the activation energy of crystallisation, E_c .

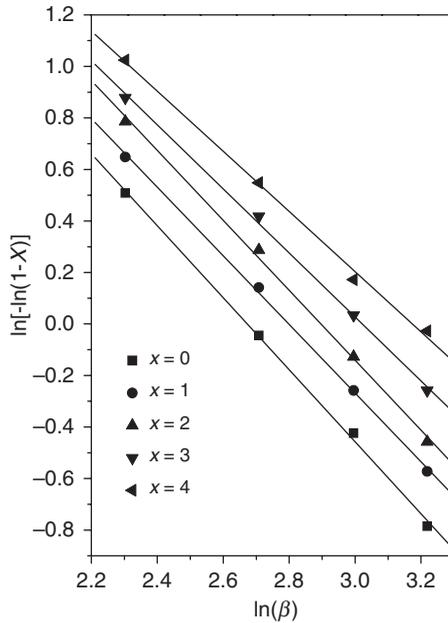


Figure 8. Plot of $\ln[-\ln(1-X)]$ vs. $\ln(\beta)$ for $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) glassy alloys.

The activation energy of crystallisation was also calculated from the Matusita relation [23]

$$\ln[-\ln(1-X)] = -n \ln \beta - 1.052 \frac{mE_c}{RT} + \text{const.}, \quad (5)$$

where X is the volume fraction of crystalline material precipitated in the glass, E_c is the activation energy of crystallisation and R is the gas constant. X at a particular temperature is given by A_T/A , where A is the total area under the exothermic peak and A_T is the area under the exotherm between the onset temperature of crystallisation and the particular temperature; n and m are constants depending on the nucleation mechanism and the morphology of growth. The slope of a $\ln[-\ln(1-X)]$ vs. $\ln(\beta)$ graph (Figure 8) gives the value of n . The mean value of n for the system is found to be 1.299. It has been shown that value of n may be 4, 3, 2 or 1 depending on the type of nucleation and growth. For as-quenched glasses containing no nuclei, the constant m is taken to be $m=n-1$ and $m=n$ for glasses containing a large number of nuclei. The value of m is 1 for all compositions, indicating one-dimensional growth [24,25]. The slope of a graph of $\ln[-\ln(1-X)]$ vs. $1000/T$ (Figure 9) gives the activation energy of crystallisation, E_c . The values of E_c calculated using the modified Kissinger's equation and Matusita's equation are reported in Table 2. The values of E_c calculated from either method decreases with increasing Bi content.

In glassy alloys, the glass-forming tendency (GFT) is related to the ease with which the melt can be cooled with avoidance of crystal formation. The difference

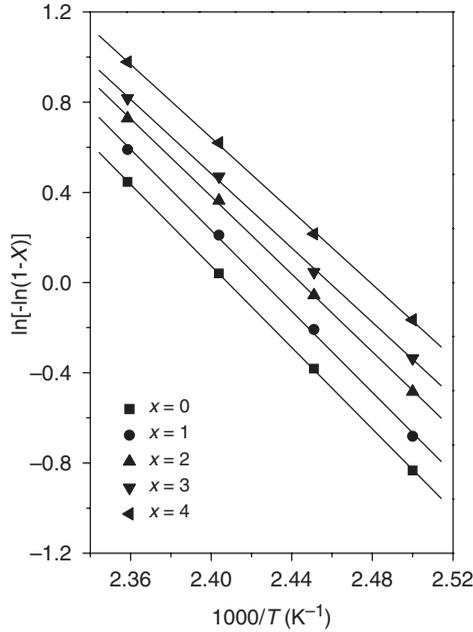


Figure 9. Plot of $\ln[-\ln(1-X)]$ vs. $1000/T$ for $\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) glassy alloys.

of T_c and T_g is a strong indication of glass-forming tendency and the higher the value of $(T_c - T_g)$ the greater is the glass-forming tendency. The GFT can be estimated from Hruby's parameter [26]:

$$K_{gl} = \frac{T_c - T_g}{T_m - T_c}. \quad (6)$$

The ease of glass formation is determined by calculating the reduced glass transition temperature, T_{rg} , given by [27];

$$T_{rg} = \frac{T_g}{T_m}. \quad (7)$$

The calculated values of T_{rg} obey the two-thirds rule, which states that $T_g/T_m = 2/3$. This holds well for the studied compositions. The values of K_{gl} and T_{rg} for different compositions are reported in Table 1.

4. Discussion

The increase in the value of the glass transition temperature, T_g , with increase in Bi content can be explained to some extent with the concept of the chemically ordered network model (CONM) according to which the formation of heteropolar bonds is favoured over that of homopolar bonds. When Bi is added, it is expected to form

bonds with Se because the bond energy of Bi–Se (175.6 kJ/mol) is greater than bond energy of Bi–Te (121.2 kJ/mol) resulting in a decrease in the number of Se–Se bonds (184 kJ/mol) [8]. This explains the increase in T_g with increase in Bi content due to formation of large numbers of heteropolar Bi–Se bonds and a decrease in the concentration of 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 $\langle r \rangle$ [28], given by

$$\langle r \rangle = \frac{2X_{\text{Se}} + 2X_{\text{Te}} + 3X_{\text{Bi}}}{100}, \quad (8)$$

where X_{Se} , X_{Te} and X_{Bi} are the atomic percentages of Se, Te and Bi, respectively. On increasing the Bi content the average coordination number increases and therefore the glass transition temperature also increases. The increase in T_g with heating rate is explained by the fact that when the heating rate increases, the system does not have sufficient time for nucleation and crystallisation to occur. The increase in T_g also results in an increase in the activation energy of the glass transition and is in good agreement with the report of Cofmenero and Barandiaran [29].

The decrease in activation energy of crystallisation with increase in Bi content can be explained on the basis of bond energies. The bond energies, $D(\text{AB})$, for heteropolar bonds have been calculated using the relation [30]

$$D(\text{AB}) = [D(\text{AA})D(\text{BB})]^{1/2} + 30(\chi_{\text{A}} - \chi_{\text{B}})^2, \quad (9)$$

where $D(\text{AA})$ and $D(\text{BB})$ are the energies of the homopolar bonds and χ_{A} and χ_{B} are the electronegativities of the atoms involved. The types of bonds expected to occur in the system are Se–Te ($D = 184.7$ kcal/mol), Se–Bi ($D = 175.6$ kJ/mol) and Se–Se ($D = 184$ kJ/mol). Knowing the bond energies, the cohesive energy (CE) can be calculated using the equation [31]

$$\text{CE} = \sum \frac{C_i D_i}{100}, \quad (10)$$

where C_i and D_i are, respectively, the number of bonds expected and the energies of the corresponding bonds. The cohesive energy has been found to decrease with increase in Bi content [32]. The decrease in cohesive energy means a lower bonding strength, which leads to a decrease in the temperature of crystallisation and hence the activation energy of crystallisation.

The decrease in thermal stability with increase in Bi content has been explained on the basis of formal theory of transformation kinetics. Surinach et al. [33] and Hu and Jiang [34] introduced the kinetic parameter

$$K(T_g) = K_0 \exp(-E_c/RT_g). \quad (11)$$

The smaller value of $K(T_g)$ implies a better glass forming ability [35–37]. In our system, the value of $K(T_g)$ increases with increase in Bi content meaning the glass-forming ability decreases.

5. Conclusions

The glass transition temperature, crystallisation temperature and melting temperature have been found to increase with the heating rate for

$\text{Te}_{15}(\text{Se}_{100-x}\text{Bi}_x)_{85}$ ($x=0, 1, 2, 3$ and 4 at. %) glasses. The glass transition temperature and the melting temperature increase, whereas the crystallisation temperature decreases with Bi addition for the system. The activation energy for the glass transition has been calculated from the heating rate dependence of T_g using the Moynihan and Kissinger approaches. The values calculated using both methods are in good agreement with each other and are found to increase with the Bi content. The activation energy of crystallisation calculated using the modified Kissinger and Matusita approaches decreases with an increase in the Bi content. Using Hruby's parameter, it is found that glasses with lower Bi content are easier to form in comparison to those with higher Bi content.

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References

- [1] V. Trnovcova, I. Furar and D. Lezal, *J. Non-Cryst. Solid* 353 (2007) p.1311.
- [2] J. Vazquez, D. Garcia-G. Barreda, P.L. Lopez-Aleman, P. Villares and R. Jimenez-Garay, *J. Non-Cryst. Solid* 142 (2004) p.345.
- [3] G. Singh, J. Sharma, A. Thakur, N. Goyal, S.S.S. Saini and S.K. Tripathi, *J. Optoelectron. Adv. Mater.* 7 (2005) p.2069.
- [4] M.A. Majeed Khan, M. Zulfequar and M. Husain, *J. Opt. Mater.* 22 (2003) p.21.
- [5] P. Sharma and S.C. Katyal, *Phys. B Condens. Matter* 403 (2008) p.3667.
- [6] N. Mehta, S.K. Agrahari and A. Kumar, *Phys. Scripta* 74 (2006) p.579.
- [7] N. Suri, K.S. Bindra, P. Kumar, M.S. Kamboj and R. Thangaraj, *J. Ovonic Res.* 2 (2006) p.111.
- [8] M. Saxena and P.K. Bhatnagar, *Bull. Mater. Sci.* 26 (2006) p.547.
- [9] N. Tohge, T. Minami and M. Tanaka, *J. Non-Cryst. Solid* 59–60 (1983) p.1015.
- [10] N. Tohge, Y. Yamamoto, T. Minami and M. Tanaka, *J. Appl. Phys. Lett.* 34 (1979) p.640.
- [11] P. Nagels, L. Tichey, A. Tiska and H. Ticha, *J. Non-Cryst. Solid* 59–60 (1983) p.999.
- [12] P. Nagels, M. Rotti and W. Vikhrov, *J. Phys.* 42 (1981) p.907.
- [13] N. Mehta, M. Zulfequar and A. Kumar, *J. Optoelectron. Adv. Mater.* 6 (2004) p.441.
- [14] S. Sahay and S.K. Krishnan, *Phys. B Condens. Matter* 348 (2004) p.310.
- [15] A.H. Moharram, A.A. Abu-Shely, A.S. Abu El-Oyoun and Sultan, *Phys. B Condens. Matter* 324 (2002) p.344.
- [16] S. Mahadevan, A. Giridhar and A.K. Singh, *J. Non-Cryst. Solid* 88 (1986) p.11.
- [17] S.O. Kasap and C. Juhag, *J. Mater. Sci.* 24 (1986) p.1329.
- [18] J.P. Larmagnac, J. Grenet and P. Michon, *J. Non-Cryst. Solid* 45 (1981) p.157.
- [19] C.T. Mohynihan, A.J. Easteal, J. Wilder and J. Tucker, *J. Phys. Chem.* 78 (1974) p.2673.
- [20] H.E. Kissinger, *J. Res. Mater. Bur. Stand.* 57 (1956) p.217.
- [21] K. Matusita and S. Saka, *Phys. Chem. Glasses* 20 (1979) p.81.
- [22] D.R. Macfarlane, M. Maecki and M. Maulain, *J. Non-Cryst. Solid* 64 (1984) p.351.
- [23] K. Matusita, T. Komatsu and R. Yokata, *J. Mater. Sci.* 19 (1984) p.291.

- [24] K.A. Aly, A.A. Othman and A.M. Abousehly, *J. Alloy Comp.* 467 (2009) p.417.
- [25] A. Dahshan, K.A. Aly and M.T. Dessouky, *Phil. Mag.* 88 (2008) p.2399.
- [26] A. Hruby, *Czech. J. Phys. B* 22 (1972) p.1187.
- [27] W. Kauzmann, *Chem. Rev.* 43 (1948) p.219.
- [28] J.J. Tauc, in *The Optical Properties of Solids*, F. Abeles, ed., North Holland, Amsterdam, 1970, p.227.
- [29] J. Cofmenero and J.M. Barandiaran, *J. Non-Cryst. Solid* 30 (1979) p.263.
- [30] A.F. Yoffe and A.R. Regel, *Progr. Semicond.* 4 (1960) p.239.
- [31] J. Bicerano and S.R. Ovshinsky, *J. Non-Cryst. Solid* 74 (1985) p.75.
- [32] K. Kumar, P. Sharma, S.C. Katyal and N. Thakur; submitted.
- [33] S. Surinach, M.D. Baro, M.T. Clavaguera-Mora and N. Clavaguera, *J. Mater. Sci.* 19 (1984) p.3005.
- [34] L. Hu and Z. Jiang, *J. Chin. Ceram. Soc.* 18 (1990) p.315.
- [35] J. Vazquez, P.L. Lopez-Aleman, P. Villares and R. Jimenez-Garay, *J. Alloy Comp.* 354 (2003) p.153.
- [36] E.R. Shaaban, M.T. Dessouky and A.M. Abousehly, *Phil. Mag.* 88 (2008) p.1099.
- [37] E.R. Shaaban, *Phys. B Condens. Matter* 373 (2006) p.211.