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KINETIC STUDIES OF BULK $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 AND 8) SEMICONDUCTING GLASSES

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Abstract

Results of phase transformations, enthalpy released and specific heat of $Ge_{22}Se_{78-x}Bi_x$(x=0, 4 and 8) chalcogenide glasses, using differential scanning calorimetry (DSC), under non-isothermal condition have been reported and discussed. The glass transition temperature, T_g, is found to increase with an average coordination number and heating rates. Following Gibbs–Dimarzio equation, the calculated values of T_g (i.e. 462.7, 469.7 and 484.4 K) and the experimental values (i.e. 463.1, 467.3 and 484.5 K) increase with Bi concentration. Both values of T_g, at a heating rate of 5 K min^{-1}, are found to be in good agreement. The glass transition activation energy increases i.e. 102±2, 109±3 and 115±8 kJ mol^{-1} with Bi concentration. The demand for thermal stability has been ensured through the temperature difference T_c–T_g and the enthalpy released during the crystallization process. Below T_g, specific heat has been observed to be temperature independent but highly compositional dependent. The growth kinetic has been investigated using the Kissinger, Ozawa, Matusita and modified JMA equations. Results indicate that the crystallization ability is enhanced, the activation energy of crystallization increases with increasing the Bi content and the crystal growth of these glasses occur in 3 dimensions.

Keywords: activation energy, crystal growth, glass transition temperature, specific heat, thermal stability

Introduction

Germanium chalcogenide glassy alloys belong to an interesting and unique class of amorphous materials and have wide technical applications in electronic and optoelectronic devices. The structural model describing GeSe glasses is based upon the Ge atoms of coordination four and Se atoms of coordination two [1]. When about 33 at% of Ge are incorporated to Se, linear chains or rings of Se are bridged by the tetrahedral bonds of Ge forming the basic structural unit of GeSe glasses [2]. According to Phillips [3] the molecular structure of melt-quenched GeSe glasses is much more ordered than would be expected from a continuous random network model. The glassy alloy is described by small chemically ordered clusters viz. $(Se)_n$ chains and $(GeSe_{1/2})_4$ cor-

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ner-sharing tetrahedral in Se rich GeSe glass, whereas in Ge-rich compositions (≈40 at% of Ge) ethane-like structural units $(GeSe_{1/2})_6$ dominate [4].

Amorphous chalcogenide glasses prepared by melt-quenching generally behave as *p*-type semiconductors as evidenced by thermopower measurements [5]. A change from *p*-type conduction for *n*-type by doping, unlike crystalline semiconductors, could hardly take place. The addition of Bi or Pb [6, 7] at a certain atomic percentage into germanium based chalcogenide glasses causes the reversal of the conduction type. This has been attributed [8] to the pining of Fermi level towards the conduction band due to the upset of equilibrium between negatively, D^-, and positively, D^+, charged defects states. The most stable bismuth chalcogenide glasses have been found [5] to contain 20–30 at% of Ge and less than 20% of Bi. The electrical conductivity gradually increases with Bi content [8] and in the vicinity of 7–9 at% of Bi it increases abruptly by many order of magnitude changing from *p*-type to *n*-type semiconductor [9]. Investigation of the temperature dependence of conductivity [10] at low and high percentage of Bi indicates that at ≤4 at% of Bi no transitions observed in the conductivity. At higher percentages a transition in conductivity has been observed in the region of 25–35 kbar pressure. Furthermore, at lower percentage of Bi, it is found [11] that the optical band gap decreases rapidly whereas, for higher Bi concentrations only little change in the optical gap was observed.

The amorphous state is essentially a metastable one; therefore it inherently possesses the possibility of transforming into a more stable crystalline state. The most promising properties of chalcogenide glasses have been found to deteriorate drastically during crystallization. Understanding the micromechanism of crystallization to impede or control crystallization is, therefore, a prerequisite for most of the applications, as stability against crystallization determines their effective working limits. The present paper is addressed to this aspect of the problem. In this regard, a set of parameters from the thermoanalytical experiments that completely describe the kinetics of transformation and thermal properties of $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) glasses are obtained. Variation of the glass transition temperature as a function of heating rate and coordination number is discussed. Besides, activation energy of both phases, specific heat and thermal stability have also been investigated.

Experimental

Glassy alloys of $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) are prepared by a quenching technique. High purity (99.999%) materials were weighed according to their atomic percentage and were sealed in quartz ampoules (length 5 cm and internal diameter 8 mm) with a vacuum of 10^{-5} torr. The sealed ampoules are kept inside the furnace where the temperature was raised to 950°C at the rate of 3 to 4 K min^{-1}. The ampoules are frequently rocked for 10 h at the maximum temperatures to make the melt homogeneous. Taking the ampoules out of the furnace and blowing room temperature air does quenching by an air blower.

The thermal behaviour of three samples of the system has been investigated using a Rigaku DSC Model 8230B. The temperature precision of this equipment is

±0.1 K with an average standard error of about 1 K in the measured values. DSC runs have been taken at four different heating rates i.e.. 5, 7, 10 and 12 K min^{-1} on accurately weighed samples taken in aluminum pans. The temperature range covered in DSC was from room temperature to 723 K. The DSC equipment was calibrated prior to the measurement, using high purity standards Pb, Sn and In with well known melting points. The results obtained for the standard materials were with in 3% of the values given in literature [12]. The instrument constant of this DSC, as measured, is 1.5. For the sake of accuracy four measurements were conducted for each heating rate and each specimen under identical conditions. Throughout this paper the experimental data points are taken as the average values of the four supposedly identical measurements. Best-fit method is used for plotting experimental data points.

Results and discussion

A typical DSC curves at the heating rate of 7 K min^{-1} of $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) glasses is shown in Fig. 1. Figure 2 shows the DSC curves of $Ge_{22}Se_{70}Bi_8$ glass at four different heating rates. The characteristic phenomena (endothermic and exothermic peaks) are evident in the DSC curves in the temperature range of the investigation. From the analysis point of view, the DSC curve is divided into two parts, the first one corresponds to the glass transition region which appears as an endothermic reaction and the other part is related to the crystallization process indicated by exothermic reaction in the DSC curve. The glass transition temperature T_g, and the onset crystallization temperature T_c, have been defined as temperatures corresponding to the intersection of two linear portions adjoining the transition elbow of the DSC trace in the

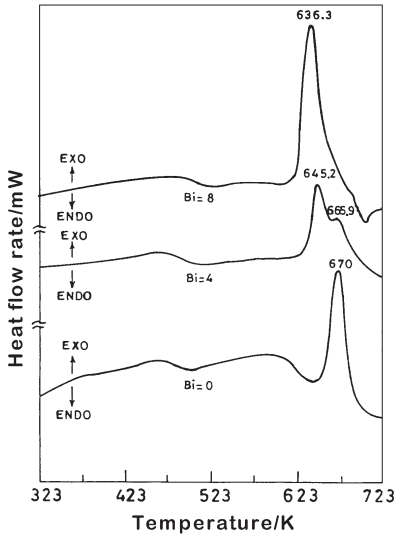

Fig. 1 Non-isothermal DSC curves of $Ge_{22}Se_{78-x}Bi_x$ (x=0 , 4 and 8) at a heating rate of 7 K min^{-1}

endothermic and exothermic directions, respectively. In the glassy region a small inflexion due to the glass transition is detected in the DSC curves of the samples under consideration. A similar inflexion in the glassy region of GeSe and GeSBi glasses has been observed [13, 14].

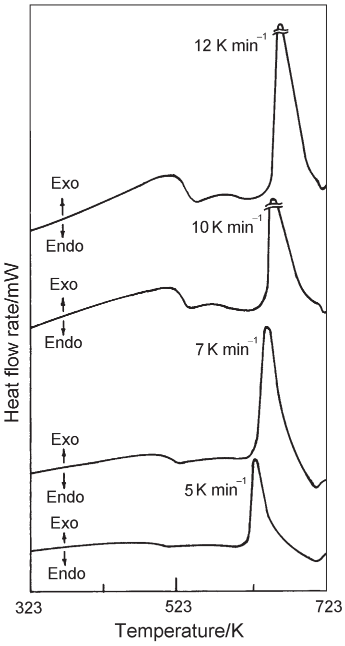

Fig. 2 Non-isothermal DSC curves of $Ge_{22}Se_{70}Bi_8$ glass at four different heating rates

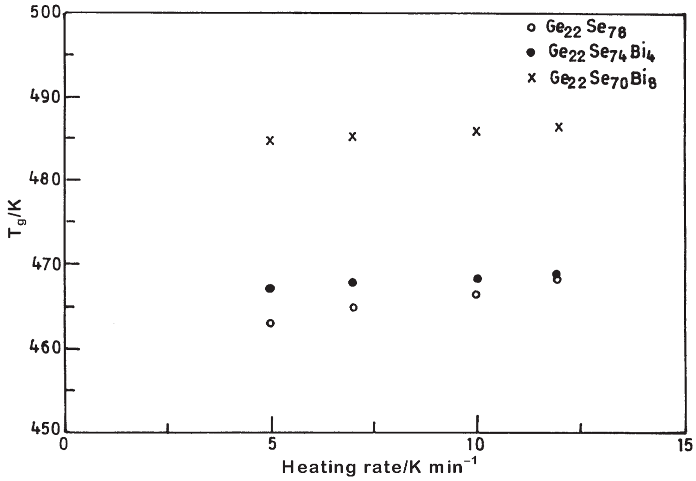

Fig. 3 Variation of glass transition temperature with heating rate and Bi concentration

It is observed that T_g increases with the increase of Bi concentration and varies linearly with the heating rate as shown in Fig. 3. An abrupt increase in T_g has been observed when x=8 for all the heating rates. Further, it can also be seen that the onset crystallization temperature, T_c increases with the increase of heating rate whereas it shows a decreasing trend with the increase of Bi content in the glassy $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8).

The slight increase in T_g at 4 at% of Bi and the abrupt increase at 8 at% of Bi can be explained as follows. According to Bhatia *et al.* [10] at this percentage of Bi, it enters into the chain forming Bi–Se bonds. This substitution is not expected to affect drastically either the structure or the overall cohesion of the alloys. The addition of Bi is at the expense of Se concentration, which enters into the $(Se)_n$ chains connecting the tetrahedral units and may also cross-link the chain. This cross-linking by the addition of Bi further strengthens the bond structure and therefore accounts for the increase of T_g with the increase of Bi content [13]. At higher percentage of Bi, the dopant atoms enter into the tetrahedral units $(GeSe_{1/2})_4$ and induce a modification in the host semiconductor which moves the Fermi level towards the conduction band making it *n*-type semiconductor. This addition of Bi at this percentage relatively increases the Ge concentration with respect to Se and hence Ge–Bi bonds are favoured instead of Se–Bi bonds [4, 8, 10]. As the number of covalent bonds per atom for Ge is four and two for Se, the increased Bi–Ge bonds are expected to produce a more compact structure [4]. This type of structural modification may account for the sharp increase of T_g as observed in $Ge_{22}Se_{70}Bi_8$. A similar increase in T_g has also been observed in Ge based chalcogenide glass doped with Bi in the range of $0 \le x \le 15$ [13]. This aspect has further been dealt with based on the fact that T_g shows a very good correlation with the average coordination number $<r>$; T_g increases with increase of $<r>$ over the entire glass forming range chalcogen [15]. Following modified Gibbs–Dimarzio [16] equation, T_g is written as

$$T_g = \frac{T_0}{1-\beta(<r>-2)} \tag{1}$$

where β is constant and varies from 0.75–0.6 for binary and ternary, respectively; T_0 is the glass transition temperature of the non-cross-linked parent chain and taken 310 and 333 K, respectively.

The average coordination number of the $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) glasses has been calculated. The average coordination number of $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) along with the corresponding glass transition temperatures at all heating rates are listed in Table 1. Bi atoms show a variable coordination number and several mechanisms involving positively charged Bi having threefold [5] and fourfold coordination [11], as well as negatively charged Bi having twofold [2] and sixfold [11] coordination have been proposed. Nevertheless, photo-emission experiments [17] on amorphous Bi_2Se_3 films have indicated that the Bi atoms are positively charged and the coordination number would be 3. Besides, X-ray absorption fine structure measurements, on a series of GeSeBi glasses, as carried out by Elliot and Steel [18] indicate that Bi atoms are positively charged and the coordination number is three. In the present study the coordination number of Bi has been taken three for the calculation of the average coordination number of GeSeBi in the composition range of study. The calculated values of T_g, using Eq. (1) are listed in Table 1. These values are found to be in good agreement with experimental values, which are given in Table 1, at a heating rate of 5 K min^{-1}.

Table 1 Calculated parameters in the glassy region of $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) glasses

Alloy	$<r>$	T_g/K heating rate/K min^{-1}				T_g/K using Eq. (1) 5 K min^{-1}	E_t/kJ mol^{-1}
		5	7	10	12		
$Ge_{22}Se_{78}$	2.44	463.1	465.8	466.6	468.5	462.7	102±2
$Ge_{22}Se_{74}Bi_4$	2.48	467.3	467.9	468.2	469.5	469.7	109±3
$Ge_{22}Se_{70}Bi_8$	2.52	484.5	485	485.7	487.6	484.4	115±8

The dependence of T_g on the heating rate has been studied using three different formulations. The first one corresponds to the empirical relation of the form $T_g=A+B\ln(\alpha)$, where A and B are constants for a given glass composition [19]. It is found that this equation holds good for the studied samples. Figure 4 shows the validity of this equation for $Ge_{22}Se_{70}Bi_8$ as an example. From this figure the value of A and B can be obtained. The value of A indicates the glass transition temperature for the heating rate of 1 K min^{-1} and the value of B indicates the temperature which is 0.693 times the glass transition temperature when the sample is scanned at a heating rate of 10 K min^{-1} in the DSC. The values of A and B for all compositions are listed in Table 2.

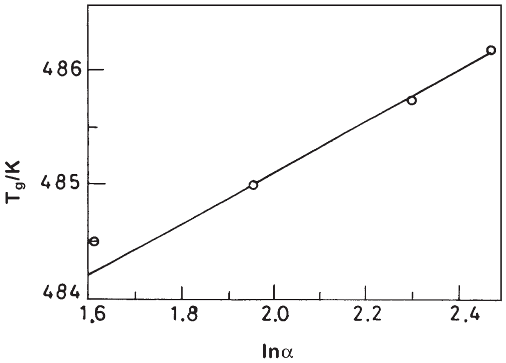

Fig. 4 Variation of T_g with lnα for $Ge_{22}Se_{70}Bi_8$ chalcogenide glass

It has been shown in Fig. 3 that the glass transition temperature varies linearly with the heating rate and this variation may be described by the empirical [20] relation; $T_g=T_0'+S\alpha$, where T_0' is the glass transition temperature at zero heating rate, normally depicted as ideal glass transition temperature. S is the rate of change of T_g with heating rate α, and comes out to be constant. The constant S is also related to the relaxation time τ, through $\tau\alpha=S$. Theoretically, T_g is defined as the temperature, at which the relaxation time τ, becomes equal to the experimental time of observation $\tau_{obs.}$ At the same time T_g varies inversely as the relaxation time. With the increase of the heating rate [20] τ_{obs} decreases and hence T_g increases.

Table 2 The values of A and B along with the kinetic parameters under non-isothermal condition of $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) glasses

Alloy	A/	B/	E_c/kJ mol^{-1}				m
	K		Eq. (7)	Eq. (8)	Eq. (9)	Eq. (10)	
$Ge_{22}Se_{78}$	459±1	5±2	69±4	89±4	65±2	73±3	2.7±0.1
$Ge_{22}Se_{74}Bi_4$	464±1	8±1	79±2	102±3	79±1	83±4	2.6±0.2
$Ge_{22}Se_{70}Bi_8$	480±1	6±2	87±5	110±6	86±3	106±3	2.9±0.1

The third approach to the study of the dependence of T_g on the heating rate is the Kissinger formulation [21] for the evaluation of the glass transition activation energy, E_t. In spite of the fact that the Kissinger equation is basically for the determination of the activation energy for crystallization process, it has been shown [22, 25] that the same equation can be used for the evaluation of E_t, and may be written as

$$\ln\frac{T_{pg}^2}{\alpha}=\frac{E_t}{RT_{pg}}+\text{const.} \tag{2}$$

where T_{pg} is the peak temperature in the endothermic direction of DSC curve.

Figure 5 shows the plot of $\ln(T_{pg}^2/\alpha)$ as a function of $1/T_{pg}$ for $Ge_{22}Se_{70}Bi_8$. The slope of the resulting straight line gives the activation energy, E_t. The values of E_t for all the compositions are given in Table 1. The glass transition activation energy is the

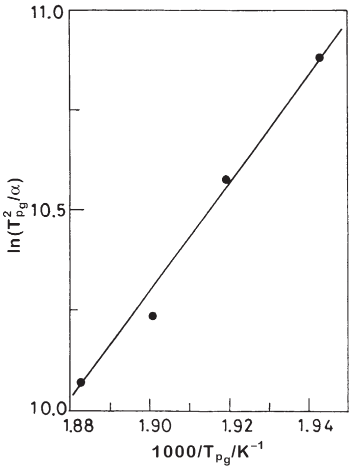

Fig. 5 A plot of $\ln(T_{pg}^2/\alpha)$ *vs.* $1000/T_{pg}$ for $Ge_{22}Se_{70}Bi_8$ chalcogenide glass

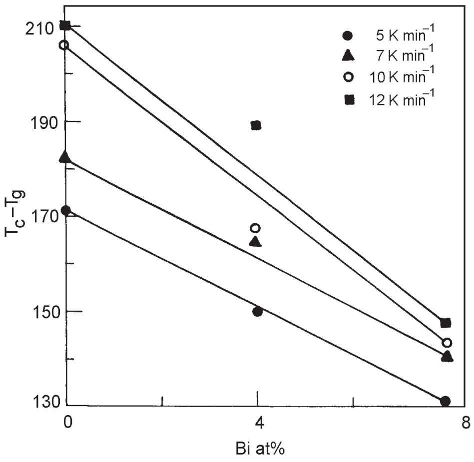

Fig. 6 A plot of T_c–T_g as a function of Bi concentrations at all heating rates

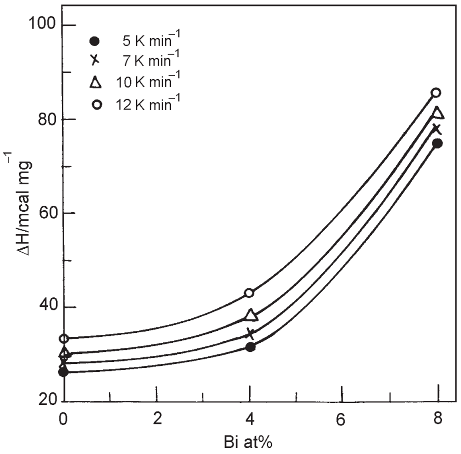

Fig. 7 A plot of enthalpy released as a function of Bi concentration at all heating rates

amount of energy that is absorbed by a group of atoms in the glassy region so a jump from one metastable state to another is possible [26]. In other words, the activation energy is involved in the molecular motions and rearrangements of the atoms around the glass transition temperature [27]. When the sample is reheated in the DSC furnace, the atoms undergo infrequent transitions between the local potential minima separated by different energy barriers in the configuration space where each local minimum represents a different structure. The most stable local minimum in the glassy region has lower internal energy. Accordingly, the atoms in a glass having minimum activation energy has higher probability to jump to the metastable (or local minimum) state of lower internal energy and hence is the most stable [26]. Therefore, one can argue that the addition of Bi reduces the stability of the glasses under investigation.

Although the glass transition temperature increases slightly with the heating rate, it has been discussed to use three different approaches. It is well-known [26, 27] that the dependence of T_g in chalcogenide glasses is interpreted in terms of thermal relaxation phenomena. In such kinetic interpretation, the enthalpy at a particular temperature and time of the glassy system relaxes towards an equilibrium value. The knowledge of the relaxation enthalpy is essential to understand its structure and properties. The relaxation equations describing such processes involve the glass transition activation energy, $E_{t,}$ and the relaxation time, τ. Utilizing the foregoing equations these two parameters are easily obtained.

From technological application points of view, the glass should be thermally stable with temperature and time during use. The kinetic resistance to crystallization is higher for larger difference between T_c and T_g. The difference T_c–T_g, which is an indication [28] of the thermal stability of glasses, decreases rapidly as Bi contents increase in these glasses as shown in Fig. 6 for all heating rates. The glass, thus, shows an increased tendency towards crystallization and, therefore, it becomes more difficult to prepare glasses with higher percentage of Bi. It has been reported [28] that the enthalpy ΔH_c released during crystallization process is associated with the stability of glasses i.e. glasses with the lowest value of T_c–T_g will have maximum value of ΔH_c. The experimental determination of the enthalpy released ΔH_c during the crystallization process has been made by measuring the area under the exothermic peak and converted it into unit of millicalorie through the use of the instrument constant [29] using the formula

$$\Delta H_c = \frac{KA}{M} \tag{3}$$

where K is the instrument constant which is found to be 1.5; A is the area under the crystallization peak and M is the mass of the sample.

The values of ΔH_c at all heating rates are plotted as a function of Bi content in Fig. 7. It is seen that ΔH_c keeps on increasing with Bi content. From Figs 6 and 7 it can be noted that for x=0 the difference of T_c–T_g and the enthalpy released are maximum and minimum respectively in the $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) glasses. This gives further support to our earlier arguments regarding the enhancement of the crystallization ability (i.e. reduction of the stability) as Bi is doped it to Ge–Se binary.

The measurement of the specific heat is regarded as one of the methods for the characterization of a material as a glassy substance. At T_g, an abrupt change in specific heat is the characteristic thermodynamic feature of all the glassy materials [30]. From the DSC heating data the specific heat of experimental samples has been determined using the following formula [31].

$$C_p = \left(\frac{m_r \Delta_s}{m_s \Delta_r}\right) C_r \tag{4}$$

where m_r is the mass of the reference material, m_s that of the sample, Δ_S and Δ_r are the shift for sample and reference materials with respect to base line, respectively. C_r is the specific heat of the reference material (white sapphire) which was taken from the standard literature [12].

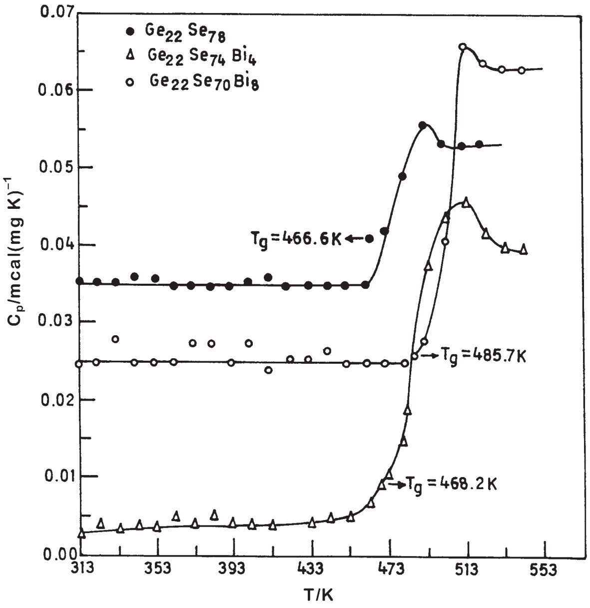

Fig. 8 Variation of specific heat of $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) glasses at a heating rate 10 K min^{-1}

The variation of C_p with temperature, for $Ge_{22}Se_{78-x}Bi$ (x=0, 4 and 8) glasses, at a heating rate of 10 K min^{-1} is shown in Fig. 8. It is quite clear from the figure that, except for a sudden jump in C_p at T_g, it is weakly temperature dependent. However, after attaining a maximum value, C_p becomes stable above T_g, which is slightly higher than its stable value below T_g. Besides, C_p is found to be highly composition dependent at all temperatures. Specific heat of $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) is found to decrease as Bi impurity increases from x=0 to 4. For x=8, the specific heat is found to increase as compared to x= 4 but keeps below the value obtained for x=0 up to glass transition temperature, T_g. Moreover at T_g and higher temperature C_p values are higher than that of x=0 i.e. $Ge_{22}Se_{78}$. The decrease in the value of C_p of $Ge_{22}Se_{74}Bi_4$ (with introduction of Bi) as compared to $Ge_{22}Se_{78}$ is due to defects that the system possesses depending upon the concentration of Bi which also accounts for the increase of C_p again in $Ge_{22}Se_{70}Bi_8$ as compared to $Ge_{22}Se_{74}Bi_4$. Bhatia *et al.* [10] investigated the presence of defects at low and high percentage of Bi. According to them, since the electronegativity of Se(2.4) is greater than that of Bi(2), a shift of electron density from Bi to Se is expected to occur. It indicates that Bi atoms are positively charged.

The addition of Bi into $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) in smaller concentration (<4) leads to [10] the formation of $P_4^+(C_4)$ and $C_1^-(P_1)$ charged defects. Here 'P' stands for pnictide (Bi belongs to this category), C stands for chalcogen, and the superscript and subscript are the charge state and atomic coordination, respectively. Therefore positive and negative defects are centered at Bi and Se respectively. Since GeSeBi glasses at low Bi content exhibit *p*-type conduction, the addition of Bi into the system merely converts defects without changing the position of the Fermi level. At higher Bi concentration, the dopant introduces network modification, as a result of which positive correlation energy defects like $C_3^+(T_3)$ that are already present in the parent GeSe glass are converted, upon doping, into T^- (C_3) thus shifting the Fermi level towards the conduction band [10, 13]. This shift in the Fermi level causes a change in the physical properties of the glass [6, 10, 11, 13, 17].

The kinetics of crystallization as a function of composition has been studied to aid our understanding of transformation that are encountered in the samples under consideration. The most successful and applicable theoretical model for crystallization studies is the one suggested by Johnson–Mehl–Avrami [32–35] (JMA). According to this model, the fraction, *X*, of precursor that has been transformed into the product phase is given by

$$X=1-\exp(-Kt^{n}) \tag{5}$$

where, *n* is the Avrami exponent and reflects the details of crystal growth. *K* is the effective overall reaction rate, which actually reflects the rate of crystallization [36], and usually assigned an Arrhenian temperature dependence,

$$K=K_0\exp\left(-\frac{E}{RT}\right) \tag{6}$$

Here K_0, the frequency factor, indicates the number of attempts to overcome the energy barrier. *E* is the activation energy. In a heterogeneous reaction, such as crystallization, activation energy is superimposed of more than one activation energy [37], basically growths and nucleation activation energies.

The JMA equation has been developed to study the kinetics of phase transformations involving nucleation and growth processes. However, if a transformation consisting of nucleation and growth occurs non-isothermally, it can still be described by the JMA equation the following conditions are satisfied [38, 39]. Firstly, all nucleation should occur at the early stages of the process, secondly, the nucleation is random and, finally, if the growth rate depends on instantaneous temperature and not on time. In this case the transformation will have an identical form at all temperatures. According to Cahn [40], for isokinetic reactions, the instantaneous rate of transformation is a unique function of the extent of transformation, *x*, and the absolute temperature, *T*, and is entirely independent of prior thermal history.

The temperature dependence associated with the JMA transformation rate equation assumed that in glass forming systems *K* could demonstrate a single Arrhenian behaviour given by Eq. (6). Since it is extremely doubtful whether both the nucle-

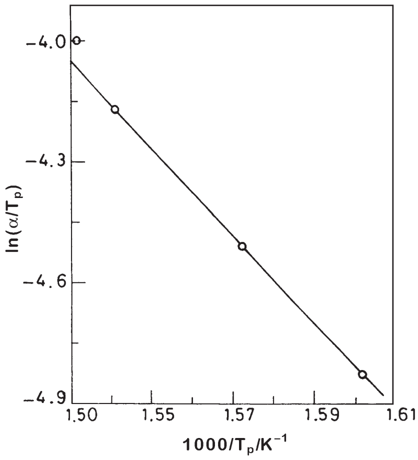

Fig. 9 A plot of $\ln(\alpha/T_{\mathrm{p}})$ *vs.* $1000/T_{\mathrm{p}}$ for $Ge_{22}Se_{70}Bi_8$ chalcogenide glass

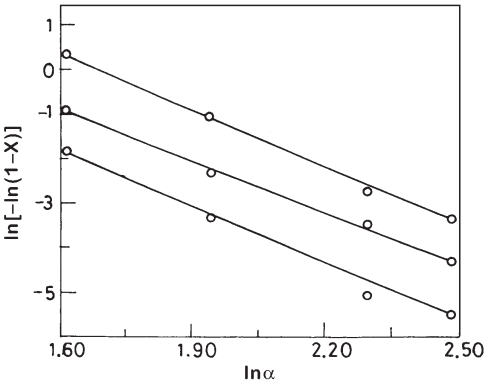

Fig. 10 A plot of $\ln[-\ln(1-X)]$ as a function of $\ln(\alpha)$ at three different temperatures for $Ge_{22}Se_{70}Bi_8$ chalcogenide glass

ation rate and the crystal growth rate [38] will have the same temperature dependence during the observable non-isothermal crystallization process. This restricts the temperature range of the possible experiments to temperature regimes where the growth rate is dominated by the molecular mobility in the liquid phase (i.e. K depends only on the growth rate and not on the nucleation rate). Specially, this temperature regime refers to the low temperature side of the peaked growth rate curve [41]. Thus, in order to experimentally obtain the simplified temperature dependence for K given by Eq. (6) in glass forming liquids, scans from low to high temperatures must be used which allow the melt to fully crystallize at temperatures which are dominated by the low temperature growth behaviour.

Extending the use of the JMA equation to interpret the dynamic heating (non-isothermal) data is controversial since the analysis requires time differentiation

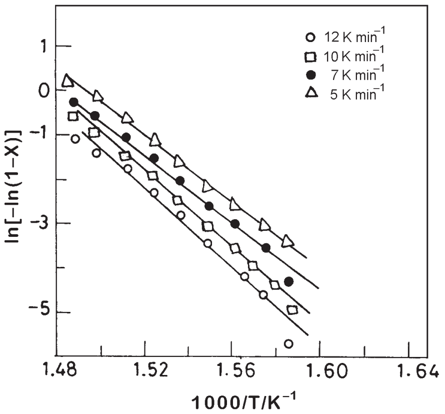

Fig. 11 A plot of ln[–ln(1–*X*)] *vs.* 1000/*T*, at different heating rates, of $Ge_{22}Se_{70}Bi_8$ chalcogenide glass

of the JMA equation with the implicit assumption that the process parameters are independent of time [42, 43]. Following White and Crane [44] the non-isothermal equation obtained from JMA, equation is given by

$$\ln\frac{\alpha}{T_p}=\text{const.}-\frac{E}{nRT_p} \tag{7}$$

where, T_p is the temperature at which the crystallization attains its maximum value and considered to be the peak temperature of the exothermic reaction in DSC curves.

The non-isothermal activation E/n has been interpreted as the activation energy for the rate limiting step for growth at the interface during crystallization as interatomic diffusion [38]. The average value of E/n of the four supposedly identical measurements for $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) glasses have been deduced from the slope of the plots of $\ln(\alpha/T_p)$ as a function of $1/T_p$ using best fit method. Figure 9 depicts the plots of the experimental data points of $\ln(\alpha/T_p)$ *vs.* $1/T_p$ for $Ge_{22}Se_{70}Bi_8$ glass. The values of E/n, and their uncertainties for all the glasses in the mentioned ternary are listed in Table 2.

For the determination of the Avrami exponent and activation energy of crystallization, Matusita *et al.* [45] have suggested an equation which is applicable for non-isothermal crystallization and is given by

$$\ln[-\ln(1-X)]=-n\ln(\alpha)-1.052\frac{mE_c}{RT}+\text{const.} \tag{8}$$

In Eq. (8), X, is the volume of the fraction crystallized at any temperature, n and m are constants related to the crystallization mechanism. For as-quenched glasses containing no preexisting nuclei $n=m+1$, where as for a glass containing a sufficiently large number of nuclei $n=m$ [45]. The value of n and hence m can be obtained by plotting ln[–ln(1–x)] as a function of ln(α) at a specific temperature. Figure 10 shows the plot for $Ge_{22}Se_{70}Bi_8$ glass at three different temperatures. A small variation in the values of n is observed. Therefore the average of all the n values for all temperatures were used as the n value for the sample. The average value of n, as evaluated from the slope of the plots at the three temperatures, comes out to 3.9(=4). Since our samples are as quenched, the value of m is 3 indicating bulk nucleation with three-dimensional growth occurs in these glasses. The values of m, along with their uncertainties, for all compositions are listed in Table 2.

In order to evaluate the activation energy of crystallization from Matusita equation the slope of the plot of $\ln[-\ln(1-x)]$ *vs.* $1/T$ at different heating rates (as shown in Fig. 11 for $Ge_{22}Se_{70}Bi_8$) are computed. It is observed that the plots are linear over a wide temperature range. At a higher temperature range, a break in linearity is seen at all heating rates. This is due to the saturation of the nucleation sites at the final stage of crystallization [46, 47] or due to the restriction [48] of crystal growth by small size of the particles. To analyse the data and to evaluate E_c, we confined ourselves to the linear regions of these plots. The activation energies and their uncertainties at all compositions, as calculated from the slope of these plots, are listed in Table 2.

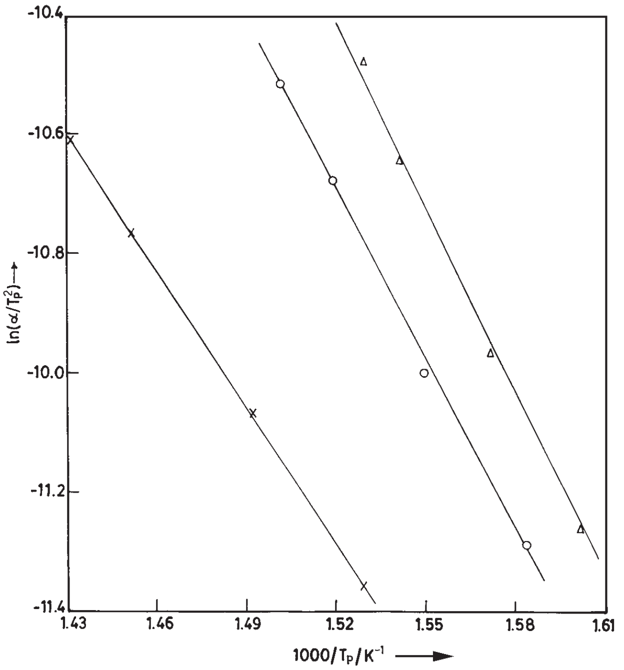

Fig. 12 A plot of $\ln(\alpha/T_p^2)$ *vs.* $1000/T_p$ for $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) glasses

The activation energy of crystallization E_c has also been evaluated using peak shift method of Kissinger [21]. This method involves the use of the equation

$$\ln\frac{\alpha}{T_p^2}=-\frac{E_c}{RT_p}+\text{const.} \tag{9}$$

where T_p is the temperature of the crystallization peak.

The activation energies for the three compositions in the mentioned system have been determined from the slope of the plot of $\ln(\alpha/T_p^2)$ *vs.* $1/T_p$ as shown in Fig. 12. The values of E_c, and their uncertainties, for three compositions are given in Table 2.

Ozawa [49] suggested another method for the evaluation of the crystallization activation energy from the variation of the onset-crystallization temperature, T_c with the heating rate. This method involves the use of the following equation,

$$\ln\alpha=-\frac{E_c}{RT_c}+\text{const.} \tag{10}$$

The plot of $\ln\alpha$ as a function of $1/T_c$ yields a straight line, the slope of which gives the activation energy E_c. Figure 13 shows the plot for $Ge_{22}Se_{70}Bi_8$ glass. The values of E_c with their uncertainties for all the compositions are given in Table 2.

In analyzing the crystallization data in DSC experiments, the Kissinger method is the most commonly used one. This equation was developed for a simple first order reaction. Kissinger showed that for first order reactions a linear dependence is obtained between α/T_p^2 and $1/T_p$. It is reported [50] that Kissinger method can be applied to any reaction, the kinetics of which are described by $dx/dt=g(x)h(T)$; ($g(x)$ and $h(T)$ can be formulated since x and T are function of time). Application of this method to crystallization process without modification does not yield the same dependence as suggested by Kissinger. However, it has been suggested [51] that the error involved in the activation energy determined by Kissinger equation is lower than 5% provided $E/(RT)>10$.

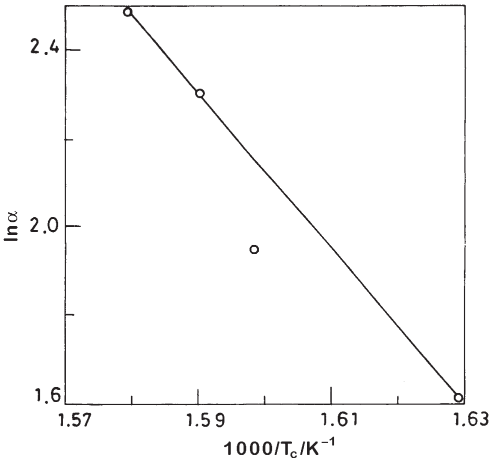

Fig. 13 A plot of ln(α) as a function of $1000/T_c$ for $Ge_{22}Se_{70}Bi_8$ chalcogenide glass

To simplify the mathematical equations involved in the integration of the rate of transformation, Ozawa realized that the fraction transformed, x_p, at the peak in the transformation rate, dx/dt, is constant, independently of the scan rate α. It is shown that [22] approximately 63% of the transformation occurred at the peak in dx/dt. Therefore, according to Yinnon and Uhlmann [50] if the fraction x_p at the peak of the exotherm is constant, the temperature involved in Ozawa equation is the onset crystallization temperature, T_c, or the peak temperature of crystallization T_p. This will also amplify the errors in the calculated activation energy from Eq. (10).

Matusita *et al*. [45] have suggested that the Kissinger and Ozawa equations cannot be applied directly to the crystallization of amorphous materials and therefore the physical meaning of the activation energies thus obtained are obscure because the crystallization is advanced not by the n^{th} order reaction but by the nucleation and growth process. Indeed they succeeded in obtaining an equation (Eq. 8) to analyze the non-isothermal crystallization kinetics on the basis of nucleation and growth process. This equation involved the crystallization mechanism such as bulk crystallization or surface crystallization and therefore a meaningful activation energy is obtained. In this equation $n=m+1$ for as-quenched glass containing no nuclei and $n=m$ for a glass containing a sufficiently large number of nuclei. Also, m=3, 2, 1 for three, two and one-dimensional growth, respectively. They have also shown that under certain conditions, the so-called Ozawa and Kissinger equations can be deduced from Eq. (8).

The observed difference in the value of E_c evaluated by different formulations may be attributed to the different approximations that have been adopted while arriving at the final equation of the various formalisms. Besides, the variability of the location of temperature measuring thermocouple (i.e. the location of the sample and heat source) may introduce an error on the temperature axis of a thermoanalytical curve. In addition, the temperature and pressure gradients in the sample (resulting from heat effect e.g. heating rate) vary randomly and such random variations have predominant effects on kinetic parameters. Since the activation energy in the above equations has been deduced from the variation of the heating rate and temperature hence variation in the value of E_c is expected to occur in the light of the reasons mentioned above. However, a similar variation in the activation energy calculated by using various formalisms in other chalcogenide glasses has also been observed [28, 52]. It may be mentioned that the activation energy obtained from Matusita equation is more accurate than those obtained from other methods. This is due to the fact that the activation energy in this method has been derived from the variation of the temperature that scans the whole curves starting from the beginning of the crystallization process till approximately its end. Besides, it allows the determination of the dimensionality of growth and the crystallization mechanism involved in amorphous materials.

The values of the activation energy obtained through different equation have been found to increase in general with the increase of Bi content. Since the activation energy is an indication of the speed of crystallization [28] therefore, one can argue that $Ge_{22}Se_{70}Bi_8$ has the maximum rate of crystallization. This result agrees fairly well with that reported [2, 13] by others, in which the addition of Bi enhances the crystallization ability.

This increase in the activation energy may be explained by considering the structural change in the sample due to the addition of Bi. As mentioned earlier the addition of Bi would considerably modify the host amorphous network. At lower percentage of Bi, it dissolved in Se chains [2] and makes bonds with Se. As Bi concentration is increased, some kind of atomic arrangements are developed [10] and Bi favours the formation of bonds with Ge. Such arrangements lead to an increase in the chain length and a decrease in the mobility of molecular species and hence much energy is required to complete the disorder-order transformations.

Conclusions

A systematic study of $Ge_{22}Se_{78-x}Bi_x$ (x=0, 4 and 8) chalcogenide glasses has been carried out and we conclude the following:

Drastic increase in the glass transition temperature, enthalpy released and specific heat at 8 at% of Bi, a vicinity in which the reversal of the conduction type takes place and the electrical conductivity in these glasses also increases drastically, shows that some kind of structural modifications have taken place around this composition.

The factors that determine thermal stability of glasses, i.e. the temperature difference T_c-T_g and the enthalpy released ΔH_c, indicate that the formation of GeSeBi glasses with higher percentage of Bi is not favoured. Furthermore, results of glass transition activation energy of the mentioned glasses and in the composition range of the investigation support the above arguments.

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