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THE STUDY OF PHYSICAL PARAMETERS OF SeZnSb CHALCOGENIDE GLASSES

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The crystallization kinetics of $Se_{90-x} Zn_{10}Sb_x$ (x = 0, 2, 4, 6) alloys have been studied at heating rate (10 K/min) using Differential Scanning Calorimetric (DSC) technique. The effect on the physical properties of $Se_{90-x} Zn_{10}Sb_x$ (x = 0, 2, 4, 6) chalcogenide glasses with the variation in antimony content has been studied theoretically. Our results indicate the dependence of glass transition temperature Tg, atomic percentage of Se with variation in average coordination number Z. The glass transition temperature is calculated by Tichy-Ticha, Lankhorst and Sreeram approaches.

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1. Introduction

The intense studies have developed to understand the nature of glass transition phenomena particularly in chalcogenides glasses due to their specific application in technologies such as optoelectronic, optical (infrared fibers, planar guides, lenses, photo-detectors), and memory switching devices [1,4].Understanding the glass transition kinetics of Se-based glassy alloys is of great importance to know its thermal stability and finally to determine the useful range of operating temperatures for a specific technological application before the crystallization takes place. The glass transition temperature Tg, is generally defined as the inflection point of the rising curve of specific heat as a function of temperature. The value of glass Temperature Tg transition directly depends on the methods of fabrication of glass. Different methods have been performed to understand the relationships between microscopic structures and the glass transition. In this paper we completed study of physical properties [5] such as coordination number, mean bond energy and thermal stability are investigated for SeZnSb system alloys with different Sb contents, each one with different compositions. The effect of antimony addition is discussed; the theoretical values of glass transition temperature are compared to experimental results.

2. Experimental

Bulk sample of the $Se_{90-x} Zn_{10}Sb_x$ (x = 0, 2, 4, 6) were prepared by the melt quenching technique. High purity materials (99.999%) were weighted according to their atomic percentages and were sealed in quartz ampoules under the vacuum of 10^{-5}Torr. The sealed ampoules are kept inside the furnace where the temperature was raised to 800˚C for 10 hand quenched in ice water.The amorphicity of the sample is checked by X-ray diffraction, the thermograms were recorded using a Setaram DSC92 at heating rate 10 K/min.

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3. Result and discussion

3.1 Thermal stability and the ability of glass formation

The DSC curves of glassy alloys Se_{90-x} $Zn_{10}Sb_x$ (x = 0, 2, 4, 6) were recorded at different heating rate 10°C/min is shown in Figure 1**.** The values of the glass transition temperature T_g, the onset-of-crystallization temperature T_c, the peak crystallization temperature T_p and the onset-of-melting temperature T_m for all composition of the glassy materials at a heating rate of 10 K/min are given in table 1respectively. For a good glass, the value of reduced glass transition temperature T_g/T_m is approximately around 0.67 [6,8].The average value of reduced glass transition temperature T_{gr} of all compositions is 0.67 showing in the table 1, it clear that with the increase in content of Sb the glass transition decrease in Se_{90-x} $Zn_{10}Sb_x$ the same effect observed in [9,10].However the value of crystallization temperature increase with Sb content increase can be explain in the terms of the crystallization ability of the glasses.

Table.1. Values of glass temperature T_g, crystallization temperature Tc , the peck temperature T_p and reduced glass temperature T_{gr}at rate 10 K/min.

Sample	T_g(K)	T_c(K)	T_P(K)	T_m(K)	T_{gr}
$Se_{90}Zn_{10}$	331	381	420	491	0.674
$Se_{88}Zn_{10}Sb_2$	329	401	423	491	0.669
$Se_{86}Zn_{10}Sb_4$	327	408	424	492	0.665
$Se_{84}Zn_{10}Sb_6$	325	429	448	492	0.662

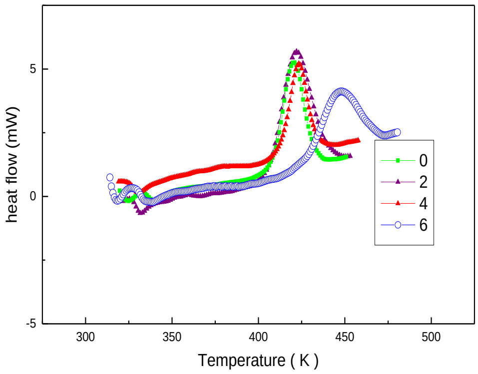


Fig.1.DSC thermograms of Se_{90-x} $Zn_{10}Sb_x$ (x = 0, 2, 4, 6) glassy system at a heating rate 10 K/min.

Hruby [11,12] has introduced a parameter H_r as an indicator of the glass forming ability (GFA) using thermal stability $\Delta T = T_C - T_g$is given by:

$$H_r = \frac{\Delta T}{T_m - T_C} \tag{1}$$

H_r reflects the resistance to devitrification after formation of glass. If $H_r < 0.1$, the glass is usually difficult to prepare and the glass is good formed if $H_r \geq 0.4$[13,14]. The values of H_r of different composition are listed in Table 2. It is found that the values of H_r increase with increasing Sb content. It means that the thermal stability increases with increasing the Sb content in $Se_{90-x}Zn_{10}Sb_x$ alloy system. The same effect of antimony observed in chalcogenide glass [15], Saad and Poulain [16] obtained two other criteria, H' and S criterion

$$H' = \frac{\Delta T}{T_g} \text{ and } \qquad S = (T_P - T_C)H' \tag{2}$$

The glass forming tendency Kg can be describe by the following formula [15],

$$K_g = \frac{T_C - T_g}{T_m - T_g} \tag{3}$$

From Table 2 it is remarkable that values of H' and S obtained for all the sample increase with increase of antimony content but highest value of Kg corresponds to $Se_{84}Zn_{10}Sb_6$ composition and the lowers one corresponds to $Se_{90}Zn_{10}$.

Table. 2 Values of thermal parameters ΔT ,H_r, H', S and K_g at rate 10 K/min of $Se_{90-x}Zn_{10}Sb_x$ (x = 0, 2, 4, 6).

Sample	ΔT(K)	H_r	H'	S(K)	K_g
$Se_{90}Zn_{10}$	50	0.455	0.151	5.893	0.313
$Se_{88}Zn_{10}Sb_2$	72	0.800	0.219	4.814	0.444
$Se_{86}Zn_{10}Sb_4$	81	0.964	0.248	3.963	0.491
$Se_{84}Zn_{10}Sb_6$	104	1.650	0.320	6.080	0.623

The structural changes in Se-Zn glassy alloy with Sb concentration may be explained on the basis of coordination number of the system. For the glassy $Se_{90-x}Zn_{10}Sb_x$ (x= 0, 2, 4, and 6) alloys, the average coordination number $<r>$can be calculated using the formula

$$\langle r \rangle = \frac{\alpha N_{Se} + \beta N_{Zn} + \gamma N_{Sb}}{100} \tag{4}$$

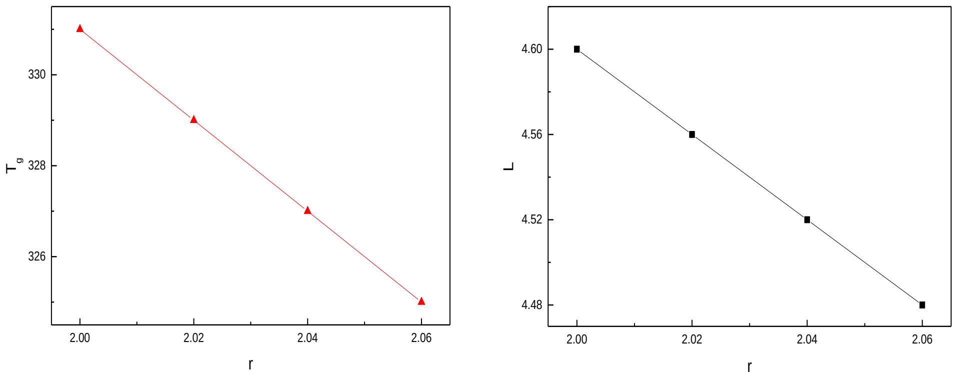
whereα, β and γ are atomic fractions of Se, Zn and Sb respectively and $N_{Se} = 2, N_{Sb} = 3, N_{Zn} = 2$are their respective coordination numbers [9,17]. The calculated values of the average coordination number are given in Table 3, where it is seen that $\langle r \rangle$increases for with increasing Sb content. The calculated value of coordination numbers $\langle r \rangle$ lie in the range $2.00 \le r \le 2.06$. The glasses with a low average coordination number ($r < 2.4$). The glass transition decreases linearly with increase in coordination number as seen in Fig. 2 a.

Table. 3 coordination number r ,number of constraints$N_{co}$and lone pair electrons L of $Se_{90-x}Zn_{10}Sb_x$ (x = 0, 2, 4, 6) .

Sample	⟨r⟩	N_{bs}	N_{bb}	N_{co}	floppy	V	L
$Se_{90}Zn_{10}$	2.00	1	1.000	2	0.333	6.600	4.600
$Se_{88}Zn_{10}Sb_2$	2.02	1.04	1.010	2.05	0.317	6.580	4.560
$Se_{86}Zn_{10}Sb_4$	2.04	1.08	1.020	2.10	0.300	6.560	4.520
$Se_{84}Zn_{10}Sb_6$	2.06	1.12	1.030	2.15	0.283	6.540	4.480

According to Phillips [18] constraints theory, in the glasses having the highest stability, the number of topological constraints N_{co} evaluated for an atom is equal to the number of the flexibility, namely the spatial dimension$N_d = 3$. In chalcogenide system the number of the bond stretching constraints are given by $N_{bs} = \frac{r}{2}$, bond bending constraints are $N_{bb} = 2r - 3$ and average number of constraints

$$N_{co} = N_{bs} + N_{bb} \tag{5}$$



a) *b)*

Fig. 2a)-Variation of glass transition temperature Tgas function ofcoordination number r,
b) Variation oflone pair electrons L as function ofcoordination number r for $Se_{90\text{-}x}Zn_{10}Sb_x$ *(x = 0, 2, 4, 6).*

Thorpe [19,20] has pointed out that under coordinated networks would possess a finite fraction of zero frequency normal vibrational modes, floppy modes. The fraction, *f* of zero frequency modes is given as

$$f = 2 - \frac{5}{6}\langle r\rangle \tag{6}$$

The value of *f* approaches zero when <*r*> approaches the critical value of 2.4. Networks with <*r*> < 2.4 are polymeric glasses The calculated values of N_{bs} , N_{bb} , N_{co}, and *f* of glassy $Se_{90\text{-}x}$ $Zn_{10}Sb_x$ system are shown in Table 3.

The number of lone pair electrons in a chalcogenide glass system can be calculated by using the relation[21]

$$L = V - \langle r\rangle \tag{7}$$

where L and V are the lone pair electrons and valence electrons, respectively. The number of lone pair electrons obtained by using equation (7) is listed in Table 3. A graphical representation of L and coordination number r is given in Fig. 2b. It is evident from the Fig. 3 that with the increase in the Sb concentration, the both of average coordination number and number of the constraints N_{co} increase, hence average number of the lone pair decrease.

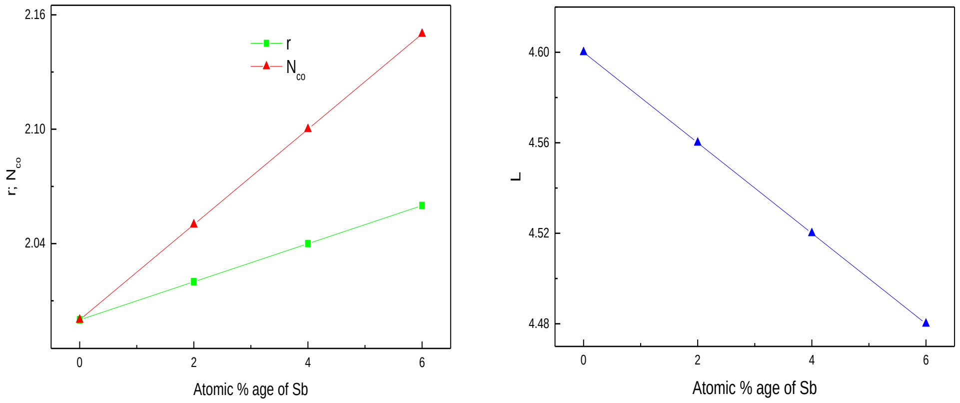


Fig. 3. Variation of coordination number r , number of constraints N_{co} lone pair electrons as function of Antimony Sb for $Se_{90-x}Zn_{10}Sb_x$ (x = 0, 2, 4, 6)

3.2 Mean bond energy and glass transition temperature

The Parameter R deviation of stoichiometry is expressed by the ratio of covalent bonding possibilities of chalcogen atom to that of non-chalcogen atom. For glassy $Se_{90-x}Zn_{10}Sb_x$ ($0 \leq x \leq 6$) alloys, the quantity R is

$$R = \frac{\alpha N_{Se}}{\beta N_{Zn} + \gamma N_{Sb}} \tag{8}$$

The chalcogenide systems can be organized into three different categories. The threshold at R=1 (the point of existence of only heteropolar bonds) marks the minimum selenium content at which a chemically ordered network is possible without metal–metal bond formation. For R>1, the system is chalcogen rich and for R<1, the system is chalcogen poor [22, 23]. From the table 4, it is clear that our system is chalcogen rich and turning towards less chalcogen rich with the increase in content of Sb in the system.

Based on the chemical bond approach,the bonds are formed in strict sequence decreasing their bond energy until all the valences of the atoms are saturated [24]. According to the Pauling relationships [21, 25] the covalent bond energy $E_{A\text{-}B}$ between atoms A and B is

$$E_{A-B} = (E_{A-A} - E_{B-B})^{1/2} + 30(\chi_A - \chi_B)^2 \tag{9}$$

where $E_{A–A}$ and $E_{B–B}$ are the single-bond energies andχ_A and χ_B are the electronegativities of atoms A and B, The bond energy of the homopolar bonds Se-Se, Zn-Zn, and Sb-Sb used here are 44.04 Kcal/mol, 35.80 Kcal/mol, 30.22 Kcal/mol and the electronegativity value for Se, Zn and Sb are 2.55, 1.65, 2 and 2.05 respectively [10].the calculated values of Se–Sb, Se-Zn and Sb–Zn bonds are 43.98 kcal/mol, 64.00 kcal/mol and 37.69 kcal/mol respectively.

The mean bond energy *E* is an important parameter in chalcogenide glasses which determine many properties of material. It depends upon the factors like average coordination number,

Table. 4 Parameter R ,mean bond energy E, heat of atomization and glass transition temperature of $Se_{90-x}Zn_{10}Sb_x$ (x = 0, 2, 4, 6) .

Sample	R	Pr	Dc	Ec	Em	E(eV/atom)	$T_{gLankhrot}$	Hs(KJ/mol)	T_{gTichy}
$Se_{90}Zn_{10}$	9.00	0.20	2.77	0.55	1.53	2.081	367.31	217.5	268.20
$Se_{88}Zn_{10}Sb_2$	6.77	0.26	2.57	0.67	1.42	2.086	368.58	218.2	270.60
$Se_{86}Zn_{10}Sb_4$	5.38	0.36	2.45	0.78	1.31	2.094	371.33	218.9	273.06
$Se_{84}Zn_{10}Sb_6$	4.42	0.38	2.36	0.90	1.20	2.102	373.66	219.6	275.42

degree of cross-linking, type of bond and bond energy in a system. For chalcogenide rich system the mean bond energy can be calculated by correlation proposed by Tichy and Ticha [22, 23]. The overall mean bond energy of the systemis given by

$$\langle E \rangle = E_{cl} + E_{rm} \tag{10}$$

whereE_{cl} is the overall contribution towards bond energy arising from the average cross-linking per atom is given a

$$E_{cl} = P_r \, . D_{hb} \tag{11}$$

Here is the degree of cross linking and is given as P_r

$$P_r = \frac{\beta N_{Zn} + \gamma N_{Sb}}{\beta + \gamma} \tag{12}$$

$D_{hb}$is the average heteropolar bond energy and is given by

$$D_{hb} = \frac{\beta N_{Zn} E_{Se-Zn} + \gamma N_{Sb} E_{Se-Sb}}{\beta N_{Zn} + \gamma N_{Sb}} \tag{13}$$

$E_{rm}$is the average bond energy per atom of the remaining matrix *i.e.* contribution from weaker bonds that remains after the strong bonds have been maximised .$E_{rm}$is given by

$$E_{rm} = \frac{2(0.5r - P_r)}{r} \tag{14}$$

An impressive correlation of mean bond energy with glass transition temperature Tg was illustrated by the relation given by Tichy and Ticha [22, 23] where Tg is in Kelvin and E is in eV/atom.

$$T_g = 311(\langle E \rangle - 0.9) \tag{15}$$

The variation of mean bond energy E and glass transition temperature Tgwith Sb content and heat of atomization are tabulated in Table 4.Lankhorst [10] has introduced a model to estimate the glass transition temperature based on enthalpy of atomization. This method is useful for development of phase change materials for rewritable optical recording. According to this model glass transition temperature is related to heat of atomization by an empirical relation given as

$$T_g = 3.44 H_s - 480 \tag{16}$$

whereTg is in Kelvin and Hs is in KJ/mol. Heat of atomization or the enthalpy of atomization is the enthalpy change that is required for total separation of all atoms in a chemical compound such that the compound bonds are broken and component atoms are reduced to individual atoms. The average heat of atomization Hs for a compound $Se_\alpha Zn_\beta Sb_\gamma$ is considered as a direct measure of the cohesive energy and thus average bond strength,as the formula[26]:

$$H_s = \frac{\alpha H_s^{Se} + \beta H_s^{Zn} + \gamma H_s^{Sb}}{\alpha + \beta + \gamma} \tag{17}$$

where α, β, and $\gamma$are the atomic percentages of Se, Zn and Sb. Heat of atomization (*Hs*) value for Se, Zn and Sb are 227 KJ/mol, 132 KJ/mol and 262 KJ/molrespectively. The value of heat of atomization for Se_{90-x} Zn_{10} Sb_x (x= *0, 2, 4, and 6)*chalcogenide glass are calculated and are enlisted in Table 4.The compositional variations of glass transition temperature studied by TichyTicha and Lankhorst approaches are shown in Figure 4.The variations of glass transition temperature Tg with coordination number r in chalcogenide glasses was proposed by Sreeram et al [27] according to the Gibbs DiMarzio modified relationship [28]:

$$T_g = \frac{T_{g0}}{1 - \beta(r-2)} \tag{18}$$

where T_{g0} is the glass transition temperature of the linear polymer and β a system parameter included between $0<\beta<1$. The stochastic origin of the Gibbs DiMarzio modified equation, M. Micoulaut et al [29] allows proposing a topological origin, for the constant β according to the relationship:

$$\beta^{-1} = \sum_{i=1}^{M-1} (r_i - 2)\ ln\left(\frac{r_i}{2}\right) \tag{19}$$

The linear relation between the $Tg/Tg_0$and Sb content is shown in Fig. 4. I the theoretical values of glass transition for $Se_{90-x}\ Zn_{10}\ Sb_x$ (x= *0, 2, 4, and 6)*chalcogenide glass using different models are different from the experimental values.

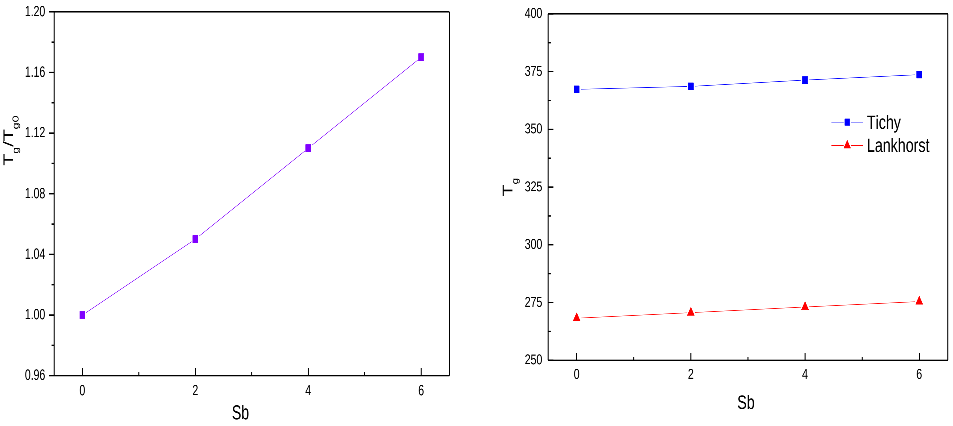


Fig.4. Variation of glass transition Temperature Tg as function of Antimony Sb.

4. Conclusions

Thermal stability of the glassy system SeZnSb has been studied with different compositions using the characteristic temperatures. Our results indicate the role of number of coordination on glass transition temperature; It has been found that lone pair electrons (L) and deviation of stoichiometry R decrease with increasing content of Sb.

The mean bond energy is calculated using the covalent bond approach and the glass transition temperature was deduced theoretically using a suitable relation and compared to experiment. The glass seems to have high value of glass transition temperature as per theoretical calculations and is monotonically decreasing with increasing Sb content because increasing concentration of Sb reduces the mean bond energy of the material.

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