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DIFFERENTIAL SCANNING CALORIMETRY OF SEMICONDUCTING As–Se GLASSES CONTAINING Sb

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The compositional dependence of the glass transition temperature (T_g), and the temperature of the maximum rate of crystallization (T_p) of As–Se glasses containing Sb has been measured using non-isothermal DSC. The variation of these characteristic temperatures is found useful in interpreting the structural changes in As–Sb–Se glasses. The role of Sb in these glasses and its effect on the crystallization characteristics is analyzed.

A great deal of attention has been given to chalcogenide glasses in recent years. Their established or possible applications related to switching, electrophotography, electronic and optical memory and holography have been acknowledged [1–3].

Myers and Berkes [4, 5] have shown that chalcogenide glasses in the As–Sb–Se and As–Bi–Se system can be heat treated to form glass-ceramics with a morphology consisting of crystalline Sb_2Se_3 or Bi_2Se_3 uniformly dispersed in a glassy matrix. Varistor-like behaviour in partially crystallized $As_{.15}Sb_{.05}Se_{0.8}$, $As_{0.2}Sb_{0.1}Se_{0.7}$, and $As_{.25}Sb_{.15}Se_{0.6}$ glass-ceramic composites observed recently [6], may be of considerable practical interest.

In this paper the compositional dependence of the characteristic glass transition temperature (T_g), and the maximum rate of crystallization or peak temperature (T_p) of amorphous As–Sb–Se are discussed. These data provide insight into the structural variations and energetics of the glass bonding network. The composition of the residual glass in the heat treated glasses to form glass-ceramics are also deduced from the T_g of the residual glass (T_{gr}) because of it's strong influence on the electrical properties [6]. The effect of Sb on the crystallization process is analyzed and crystallization parameters are determined from the T_g dependence of the DSC heating rate (β).

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Experimental

Twenty gram batches of the desired compositions (Table 1) were compounded from optical grade As_2Se_3, 99.99% Se and 99.99% Sb, and sealed in evacuated silica ampules. Glasses were melted for 24 h at 800° in a rocking furnace and homogenized at 600° by rocking at a rate of 1 cycle/min. The melts were quenched in an oil bath to a temperature $\approx$5–10° below the glass transition temperature (T_g) and annealed for 15 min. After annealing, the glass samples were transferred to an oven to induce crystallization. Heat treatment consisted of a nucleation step at 15° above T_g for 15 min, and crystallization at temperatures 25–85° above T_g for 1, 2 or 3 h.

During all thermal analysis the sample chamber was purged with dry N_2. The samples consisted of approximately 25 mg of glass or glass-ceramic powder in crimped (but not hermetically sealed) aluminium sample pans. The reference holder always contained an empty Al pan. To determine the T_g, the fraction crystallized (f_r) upon heat treatment, T_p and T_{gr}; samples were scanned at a rate of 10 deg/min. For dynamic (non-isothermal) experiments, glass samples were heated from 400 K to 650 K at scan rates of 5, 10, 20 and 40 deg/min.

Table 1 a) Variation of T_g in the system As–Sb–Se (present study)

Group	Composition	T_g, °C
I	$As_{0.4}Sb_{0.0}Se_{0.6}$	184
	$As_{0.35}Sb_{0.05}Se_{0.6}$	185
	$As_{0.3}Sb_{0.1}Se_{0.6}$	186
	$^*As_{0.25}Sb_{0.15}Se_{0.6}$	187
	$As_{0.2}Sb_{0.2}Se_{0.6}$	Crystallized
II	$As_{0.3}Sb_{0.0}Se_{0.7}$	129
	$As_{0.25}Sb_{0.05}Se_{0.7}$	131
	$^*As_{0.2}Sb_{0.1}Se_{0.7}$	133
	$As_{0.15}Sb_{0.15}Se_{0.7}$	Crystallized
III	$As_{0.2}Sb_{0.0}Se_{0.8}$	95
	$^*As_{0.15}Sb_{0.05}Se_{0.8}$	87
	$As_{0.1}Sb_{0.1}Se_{0.8}$	Crystallized

b) Variation of T_g peak in the system $(1-x)As_2Se_3 \cdot xSb_2Se_3$ [7]

n	peak T_g, °C
0	198
0.1	199
0.2	200
0.3	200
0.4	201.5

Experimental results and discussion

The glass transition

Figure 1 shows a typical DSC trace for pure Se and defines T_g and T_p. The variation of T_g as one varies the composition from stoichiometry ($As_{0.4}Se_{0.6}$) to a Se-rich composition (Group I →II →III) is tabulated in Table 1 (a) and shows a monotonic decrease. Systematic addition of Sb in the three groups resulted in a wide range of glasses showing an increase in T_g with increasing Sb within a group. The limits of Sb in each group (asterisk sign in Table 1(a)) decrease as one deviates from stoichiometry (Group I) towards a Se-rich composition (Group III). The small variation of T_g with increasing Sb content within a group is similar to that observed by Das et al. [7] who made glasses from melts in the system $(1-x)\,\mathrm{As_2Se_3}\cdot x\mathrm{Sb_2}Se_3$ ($x = 0-0.4$). Their data is illustrated in Table 1(b) for comparison.

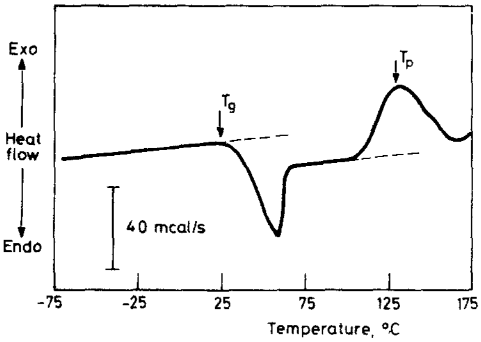

Fig. 1 Typical DSC trace of pure Se

The variation of T_g with composition in the system As–Se in quite systematic, showing a maximum around $As_{0.4}Se_{0.6}$. The primary covalent bond energies of As–Se, Se–Se, and As–As are 52, 49, and 46 K cal mol^{-1}, respectively [8]. Only As–Se bonds are present in stoichiometric $As_{0.4}Se_{0.6}$ and as one departs from stoichiometry to Se- or As-rich compositions, formation of relatively weaker but primary covalent Se–Se and As–As bonds result in order to form a fully covalent network. Although the average bond energy correlates well with the T_g, the phenomenon of the glass transition is, however, much more complex. The bonds which account for the cohesion into the condensed state are much stronger than those responsible for the rigidity of amorphous material. It has been suggested that weaker secondary bonds (As–As, Se–Se or As–Se) other than primary covalent bonds are broken or excited at the glass transition and this is the basis of a bond-lattice model [9].

Diffraction studies suggest that glasses with As_2Se_x ($x > 3$) composition have the layer structure but with increasing Se, Se exists as $(Se)_x$ chains between As and As, and when x is between 8–10; both chain and ring type forms co-exist [10]. A change in the structure of As_2Se_x glasses from $x = 3$ to $x = 10$ is associated with a decrease in T_g, indicating the role of As in glassy Se as a cross-linking or branching additive and is consistant with our results. A small increase in T_g with increased Sb within a group may be due to increased interaction (bonding) between layers i.e., stronger Sb–Se bonds [11].

The results in Table 1(a) also indicate that the limit of Sb incorporated by replacement of As within a group, without the glass crystallizing, decreases with decreasing As/Se ratio. The role of As in glassy Se as a cross-linking or branching additive, results in a viscosity increase and retardation of reorientation necessary for crystallization. Its optimum effect is realized in stoichiometric $As_{0.4}Se_{0.6}$. Myers' [5] work suggests that increasing Sb content in As–Se system results in phase separation and crystallization of a primary Sb_2Se_3 phase. Platakis et al. [12] conclude that in the system $(1-x)\ As_2Se_3 \cdot xSb_2Se_3$, enhanced crystallization is observed due to the lowering of the melt's viscosity with increasing Sb content. Lowering of viscosity is associated with increased mobility of constituent atoms. Therefore, stoichiometric $As_{0.4}Se_{0.6}$ can accommodate a higher Sb content in place of As to form a homogeneous glass. As the As/Se ratio decreases or the branching additive decreases (Group I →II →III), there is a corresponding decrease in the maximum incorporation of Sb.

Table 2 provides the heat-treatment schedule for samples which are of considerable practical (electronic device) interest [6, 11] and corresponds to limits of Sb incorporated in Group I, II and III (asterisk sign in Table 1(a)). The fraction crystallized (f_r; a value of 1.0 corresponds to 60–70 volume percent crystallinity and is determined by scanning electron microscopy and dielectric relaxation studies), and T_g of the glass and T_{gr} of the glass-ceramic of composition A, B and C are shown in Table III. The T_{gr} of the glass-ceramic is lower compared to the parent glass. The composition corresponding to these values of T_{gr} was obtained from the

Table 2 Glass compositions, glass transition temperatures and corresponding heat-treatment schedule

Glass	Composition	T_g, °C	Heat treatment schedule
A	$As_{.15}Sb_{0.5}Se_{0.8}$	97	112°, 15 min. 172°, 180 min.
B	$As_{0.2}Sb_{0.1}Se_{0.7}$	133	148°, 15 min. 207°, 180 min.
C	$As_{.25}Sb_{.15}Se_{0.6}$	187	202°, 15 min. 237°, 120 min.

data of Borisova [13], and is given in the last column of Table 3. One may conclude that the residual glass has become Se-rich when compared to its parent glass, i.e. depleted of Sb (also determined by energy dispersive spectrometry) and As (forming solid solution in Sb_2Se_3) [11]. The effect of the residual Se-rich glass on the electrical characteristics is noteworthy [6, 11].

Table 3 Fraction crystallized and T_g for glass and glass-ceramic

Glass	T_g, °C	f_r	T_{gr}, °C	Composition (residual glass) [13]
A	97	0.99	81	$AsSe_{5.0}$
B	133	0.99	94	$AsSe_{3.5}$
C	187	0.99	148	$AsSe_{1.6}$

Evaluation of kinetic parameters

A number of methods have been developed to analyze solid state transformations from non-isothermal studies. The method derived by Kissinger [14] to determine the kinetics of crystallization has been used on chalcogenide systems by several workers [15, 16]. For a reaction following first order kinetics, the rate of crystallization may be expressed as:

$$\frac{df}{dt} = K(1-f) \tag{1}$$

where f is the fraction crystallized, K is a rate constant given by Arrhenius relation:

$$K = A\exp\left[-\frac{E}{RT}\right] \tag{2}$$

where E is the activation energy for crystallization, A is the frequency factor, R is the gas constant, and T is the temperature in degrees Kelvin. At T_p, the reaction rate is maximum and we have:

$$d^2f/dt^2 = 0 \tag{3}$$

or

$$A\exp\left|-\frac{E}{RT_p}\right] = E\beta/RT_p^2 \tag{4}$$

where β is the heating rate.

Using the experimental data given in Table 4, ln β/T_p^2 was plotted versus $1/T_p$ to investigate the effect of substituting Sb for As. The data did not fit the equation, however, they indicated a decrease in the temperature of the crytallization peak

Table 4 Crystallization data in the system As–Sb–Se

Composition	Heating rate, β, deg/min	T_p, K	$\log \beta$	$1000/T_p$, K^{-1}
$As_{0.25}Sb_{0.15}Se_{0.6}$	5	542	0.7	1.85
	10	549	1.0	1.82
	20	561	1.3	1.78
	40	572	1.6	1.75
$As_{0.3}Sb_{0.1}Se_{0.6}$	5	595	0.7	1.68
	10	604	1.0	1.66
	20	620	1.3	1.61
	40	638	1.6	1.57

with increasing Sb (lowering of viscosity) at a constant heating rate. This effect has been observed by Myers and coworkers who studied the phase equilibria in the system As_2Se_3–Sb_2Se_3. Pure As_2Se_3 crystal grew very slowly, whereas at a composition of 20 m/o Sb_2Se_3, a radical effect on viscosity was observed and the glass devitrified rapidly with the formation of As_2Se_3 crystals in a single stage heat treatment process [4]. In the present investigation, Sb_2Se_3 nucleii formed in the first stage of the heat-treatment process and then crystallized into a solid solution of Sb_2Se_3–As_2Se_3 in the second stage [11].

The heterogeneous process of nucleation and crystallization can be described by the Johnson–Mehl–Avrami (JMA) equation [17, 18]:

$$-\ln(1-f) = (Kt)^n \qquad (5)$$

where f is the volume fraction transformed at time t, n is a reaction mechanism parameter and K follows Eq. (2). Here the activation energy, E, represents the overall barrier to nucleation and crystallization.

To calculate E and n for Li_2O—$2SiO_2$ composition, an equation was derived to account for the T_p dependence of β. The method proposed was based on two assumptions [19]:

$$\text{(a)} \Delta T = C_1\, \mathrm{d}f/\mathrm{d}t \qquad (6)$$

and

$$\text{(b)}\ t = C_1\, 1/\beta \qquad (7)$$

where ΔT is the temperature differential in DTA (or the ordinate in DSC), t is the time of heating, β is the heating rate, and C_1, C_2 are constants. Using the JMA equation, the two final equations derived were:

$$\log \Delta T = -n\,E/4.57\ T + C_3 \qquad (8)$$

and

$$\log \beta = -E/4.57\ T_p + C_4 \tag{9}$$

where C_3 and C_4 are constants.

Using the data of Table 4 and 5; $\log \beta$ versus $1/T_p$ and $\log \Delta T$ versus $1/T$ were plotted, from the slopes of which; n and W were determined.

Henderson [20] summarizes the values of n found under different transformation conditions. A magnitude of 2.1 and 2.3 (Table 5) implies a diffusion controlled process with a decreasing nucleation rate.

Table 5 Data and results of crystallization in the system As–Sb–Se

Composition	ΔT (ordinate)	T, K	$\log \Delta T$	$1000/T$, K^{-1}	β, deg/min
$As_{0.25}Sb_{0.15}Se_{0.6}$	0.2	528	−0.699	1.89	10
	0.875	535	−0.058	1.87	
	2.075	540	−0.317	1.85	
	3.4	545	0.5314	1.83	
$As_{0.3}Sb_{0.1}Se_{0.6}$	0.2	579.5	−0.699	1.73	10
	0.55	585	−0.26	1.71	
	1.05	590	0.021	1.69	
	1.508	595	0.178	1.68	
	1.85	600	0.267	1.67	

	n	E, kcal/mol	
$As_{0.25}Sb_{0.15}Se_{0.6}$	2.3	41.4	Present study
$As_{0.3}Sb_{0.1}Se_{0.6}$	2.1	35.4	Present study
$As_{0.4}Se_{0.6}$		31.2 [12]	
$As_{0.4}Se_{0.6}$		28.6 [15]	

A monotonic decrease of E with decreasing Sb is consistent with values reported in the literature [12, 15]. Furthermore, the activation energy of viscous flow of pure As_2Se_3, which is believed to be relevant to the devitrification process was found to be 37 K cal mol^{-1}. Although increase of Sb content leads to an increase in activation energy, the frequency factor increases by several orders of magnitude. Similar effects have been observed [15, 21] on the system Cd–Ge–Sb–As, where Ge replaced Sb and effected an increase in the activation energy and increase of the frequency factor over several decades, thereby increasing the net crystallization rate.

Conclusion

The compositional dependence of T_g and T_p was useful in interpreting the structural changes in As–Sb–Se glasses. A decrease in T_g and the limit of Sb incorporation ($Sb_{0.15} \rightarrow Sb_{0.1} \rightarrow Sb_{0.05}$) was observed as one varied the composition from stoichiometry (Group I) to a Se-rich composition (Group III). Replacement of As by Sb indicated a lowering of viscosity and a strong influence on the crystallization characteristics. Sb effected an increase in the activation energy and the frequency factor, thereby increasing the net crystallization rate.

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Zusammenfassung — Die Abhängigkeit der Glasumwandlungstemperatur (T_g) und der Temperatur bei maximaler Kristallisationsgeschwindigkeit (T_p) von der Zusammensetzung von Sb enthaltenden As–Se-Gläsern wurde mittels nicht-isothermer DSC bestimmt. Veränderungen dieser charakteristischen Temperaturen haben sich als nützlich zur Interpretation der strukturellen Veränderungen in As–Sb–Se-Gläsern erwiesen. Die Rolle des Sb in diesen Gläsern und dessen Wirkung auf die Kristallisationskenndaten wird untersucht.

Резюме — Методом неизотермической ДСК измерены температуры расстекловывания (T_g) и температуры максимальной скорости кристаллизации (T_p) стекол As–Se–Sb в зависимости от их состава. Установлено, что изменения этих характеристических температур являются полезными при интерпретации структурных изменений стекол. Проанализирована роль сурьмы в стеклах и ее влияние на характеристики кристаллизации.