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GLASS FORMING TENDENCIES OF CHALCOGENIDES
OF THE SYSTEM $(As_2Se_3)_{1-x} : (Tl_2Se)_x$ *

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ABSTRACT

In this paper glass forming capabilities of chalcogenide glasses based on As_2Se_3 with Tl_2Se concentrations are discussed. The studies were made using the differential thermal analysis (DTA) technique. These studies show that the glass forming tendency of As_2Se_3 decreases as the concentrations of Tl_2Se molecules are increased. Also these studies show that with addition of Tl_2Se , the glass transition temperature T_g of As_2Se_3 decreases, suggesting a tendency for weaker bonding and hence less stability of Tl-rich compositions.

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For the last two decades or so there has been a wide spread interest in amorphous semiconductors, partly due to a desire to confront fresh problems and partly due to an increasing awareness of their potential applications which range far beyond the optical and structural uses of the silica glasses (1,2). The chalcogenide glasses based on Se have attracted particular attention. The optical and electrical properties of these new materials have been studied extensively. Also a great deal of efforts have been made to understand the structural properties of these solids.

Structural changes affect the electrical behaviour of the compounds, lack of knowledge about these changes may lead to misinterpretation of experimental results, particularly when these studies are extended beyond the softening temperatures. In the present paper, information about such changes in As_2Se_3 and its compounds with Tl_2Se , is presented by investigating their differential thermal analysis (DTA) characteristics. The DTA-studies of these glasses were performed upto about 50 C° above their softening points. In the case of As_2Se_3 , similar studies are reported by Liang et al (3), whereas in the case of the other two compositions, to the author's knowledge, no such information is available.

2. EXPERIMENTAL

The glasses used in this study were synthesized by the conventional method of heating the constituents (all of 99.999% purity) in evacuated silica glass ampules. These ampules were

sealed off after being evacuated to 2×10^{-6} torr and degassed for about 20 hours to ensure a complete degassing of the atmospheric constituents. The ampules were heated to high temperatures above the melting temperature of the highest melting constituent. To ensure a thorough mixing of the constituents, the ampules during heating were shaken well several times. Quenching was carried out in ice cooled water. The glasses thus prepared were completely amorphous. Amorphous state of the glass was checked by examining their X-ray diffraction patterns.

Present investigations were carried out using equipment built in this laboratory. In this set-up the specimens were heated in air at normal atmospheric pressure conditions. Chromel-alumel thermocouples were used. Because of the interaction of these glasses with copper, copper-constantan thermocouples were avoided. The thermocouple was so mounted that it did not touch the specimen holder and its output was recorded using an Hewlett-packard chart recorder model hp 7100. Al_2O_3 (M.P. 2070 K) was used as the reference material. The amount of the sample used was, approximately 0.5 gm. The specimens used were in the form of fine powder ($\sim 5 \mu m$ grain size). The set-up was sensitive enough to detect temperature difference signals as small as $10^{-6} V$ corresponding to $\Delta T \sim 2 \times 10^{-5} V$.

3. RESULTS AND DISCUSSION

In the differential thermal analysis technique the sample is heated at the same rate as an inert reference sample and the temperature difference (ΔT) between these two samples

is plotted against the temperature of the glass. Second order transformations (viz, changes in specific heat, thermal expansivity (etc.) produce vertical displacement of the otherwise horizontal ΔT curve (base line). The range of temperature over which this transition takes place is called the glass transition or glass transformation temperature T_g . The magnitude of this endothermic effect is sensitive to the thermal history of the glass (4). A glass slowly cooled yields a larger area under the endothermic peak (a quantity proportional to the energy which is absorbed by the relaxation of glass structure) than one rapidly chilled (5). As the glass is heated through this temperature T_g , enough vibrational energy is present to help relaxation of glass structure and to break some of the weaker (highly strained) bonds, thus introducing some degrees of freedom into the system. These additional degrees of freedom result in an increase in the heat capacity.

The glass transition is not a precisely defined temperature. To start with the glass transition is not sharp but occurs over a range of temperature. T_g is sensitive to the total thermal history of the glass i.e. to rate of cooling from the liquid as well as to subsequent heat treatment in the neighbourhood of T_g (6). T_g is also known as the softening temperature since the viscosity of the glass drops perceptibly at this point. The temperature at which viscosity of the glass falls to $\sim 10^{13}$ poise, is also taken as the measure of T_g (6,7).

As the glass is heated above T_g , in a DTA-experiment, one may observe an exotherm for the crystallization of the sample

and on still further heating another endotherm for the melting point T_m of the glass. In some cases one observes only one endotherm at T_g and the glass gradually becomes liquid without showing any other transition (8).

The start of the transition (peak) represents the onset of the reaction. The peak maximum represents the temperature at which the reaction (ΔT) is maximum and the end of the peak at which the quasi steady state ($\Delta T = 0$) is re-established, the completion of the reaction (8).

In the present studies, the start of the endothermic peak was taken as the measure of glass transition temperature T_g . To read this temperature from DTA curves, a method of tangents similar to Hruby (9) and Abraham et al (10) was employed. The accuracy in the measurements was $\pm 3^\circ\text{C}$. These results were recorded at a sensitivity scale of $0.1^\circ\text{C}/\text{cm}$ for ΔT .

I. As_2Se_3

The DTA characteristics of this glass were noted upto 523 K. Heating rates in the range of $8^\circ\text{C}/\text{min}$ to $16^\circ\text{C}/\text{min}$ were tried. At high heating rates, the baseline did not remain straight, therefore, comparatively low heating rates ($\approx 8-9^\circ\text{C}/\text{min}$) were preferred.

Figure 1 illustrates the DTA-curves of this glass. Curve (a) was obtained by heating the specimen up to about 523 K at $8.5^\circ\text{C}/\text{min}$ heating rate. In this temperature range, it shows only one endothermic peak. Allowing the sample to cool down slowly ($\approx 4^\circ\text{C}/\text{min}$), no transition was observed, and the specimen transferred from the liquid to the amorphous solid state (curve b). On reheating, the endothermic transition as obtained during the

first heating cycle, was repeated approximately at the same position (curve c).

The average value of T_g obtained from these studies was 451 K. The maximum value of the ΔT was found to be, approximately 0.3°C . The maximum area under the endothermic peak for this glass was found to be approximately 10 ± 1 joules/gm.

II. $(\text{As}_2\text{Se}_3)_3 : \text{Tl}_2\text{Se}$

The DTA characteristics of this chalcogenide glass were studied upto about 473 K. In this temperature range, the studies show only one endothermic peak. Figure 2 shows the DTA curves of this chalcogenide. Curve (a) was obtained by heating the specimen at $8.5^\circ\text{C}/\text{min}$ heating rate. On cooling, this glass, similarly to As_2Se_3 became an amorphous solid without undergoing any phase transition. This is shown in curve (b) which is the DTA trace of $(\text{As}_2\text{Se}_3)_3 : \text{Tl}_2\text{Se}$ while cooling down from 473 K to the room temperature at about $4^\circ\text{C}/\text{min}$ cooling rate. The reheating of the specimen resulted in a curve with similar details as curve (a). Average value of T_g as obtained from these studies was 403 K. The maximum area under the endothermic peak for this composition was measured to be approximately 8 ± 1 joules/gm.

III. TlAsSe_2

DTA studies of this glass were made upto 433 K. This glass also shows only one endothermic transition representing the glass transition region. Figure 3 illustrates the DTA-curves of this glass. Curve (a) was obtained during first heating cycle of the charge at $8.5^\circ\text{C}/\text{min}$ heating rate. On cooling, no phase transition was observed and the charge transferred from the liquid to

the amorphous solid state (curve b). On re-heating the specimen, the above mentioned transition was repeated. This is shown in curve (c).

The average value of the glass transition temperature T_g of this glass as obtained from these studies was 366 K. The maximum area under the endothermic peak was measured to be, approximately 6.5 ± 1 Joules/gm.

4. GLASS FORMING TENDENCY

The glass-forming tendency of these materials was calculated on the basis of Kautzman's ^{crit} criterion (11). According to Kautzman's model the criterion for good glass-forming ability is given by

$$G_{rg} \geq \frac{2}{3}$$

G_{rg} being the reduced temperature of transformation and is written as

$$G_{rg} = T_g/T_m$$

where T_g is the glass transition temperature and T_m the melting point of the glass, in degree Kelvin.

Demovskii et al (12) as well as Roland et al (13) have reported the phase diagrams for this system of glasses. The melting points of the glasses under present studies as obtained from Roland et al's (13) results are listed in Table 1 along with their glass forming abilities. Also listed are the values of T_g obtained from the X-ray crystallization method.

This study has shown that among the glasses of the family

Table 1.

Glass Transition Temperature T_g and Glass Forming Ability G_{rg} of Chalcogenide Glasses of the Family $(As_2Se_3)_{1-x} : (Tl_2Se)_x$

Glass Composition	x	$T_g \pm 3$ K (D.T.A.)	$T_g \pm 5$ K (X-ray)	T_m K (Roland et al (1974))	G_{rg}
As_2Se_3	0	451	453	645	0.72
$(As_2Se_3)_3:Tl_2Se$	0.25	403	408	573	0.70
$TlAsSe_2$	0.50	366	378	545	0.67

$(As_2Se_3)_{1-x} : (Tl_2Se)_x$, As_2Se_3 has the highest glass transition temperature and the strongest glass-forming ability, the addition of Tl_2Se lowering both the T_g and glass-forming ability of this glass, resulting in ternary compounds of slightly weaker glass-forming tendencies. This leads to the conclusion that Tl_2Se atoms hasten the crystallization kinetics of the resultant glass. This has been found indeed in this laboratory during the investigation of crystallization kinetics of these glasses.

These investigations suggest a gradual drop of G_{rg} with Tl_2Se concentrations x. We may speculate that addition of Tl_2Se content higher than 50 at % in As_2Se_3 will probably result in compounds whose glass-forming abilities lie below the critical limit ($G_{rg} = 2/3$) set by the Kautzman's criterion. Thus such compounds, when vitrified by the normal methods of vitrification (air quenching, etc) should not form good glasses i.e. they will not vitrify completely. This is in agreement with the findings.

of Flaschen et al (14) and Kolomiets et al (15). These authors, have reported that in the As-Tl-Se system of glasses compositions having concentrations of Tl-atoms, approximately higher than 50 at % do not form good glasses when quenched by normal methods and need higher cooling rates (200°C/min or higher) to do so.

Also these results show that T_g decreased with increasing Tl_2Se content in As_2Se_3 . This suggests a tendency for weaker bonding and hence less stability in Tl-rich compositions. This is indeed found.

For As_2Se_3 , our value of T_g (451 K) is in good agreement with that reported by Plasck et al (16; $T_g = 453$ K), Demovskii (17; $T_g = 450$ K), Schnaus et al (18; $T_g = 448$ K). But compared with that reported by Liang et al (3; $T_g = 465$ K) our value of T_g is about 15°C less.

The value of the area under the endothermic peak at T_g for As_2Se_3 as obtained in the present investigations is in agreement with that reported by Kuriyama et al (19). These authors from their DSC measurements on the As-Se system of glasses have reported the area under the endothermic peak at T_g to be of the order of 8.5 Joules/gm for slowly cooled As_2Se_3 specimens.

In the case of the other two compositions included in these investigations, to the author's knowledge, no such information is available therefore, no comparison can be made.

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FIGURE CAPTIONS

Fig.1: DTA traces of vitreous As_2Se_3 :

- a) heating at $8.5^\circ\text{C}/\text{min}$.
- b) cooling
- c) re-heating

Fig.2: DTA traces of vitreous $(\text{As}_2\text{Se}_3)_3 : \text{Tl}_2\text{Se}$:

- a) heating at $8.5^\circ\text{C}/\text{min}$
- b) cooling
- c) re-heating

Fig.3: DTA traces of vitreous TlAsSe_2 :

- a) heating at $8.5^\circ\text{C}/\text{min}$
- b) cooling
- c) re-heating

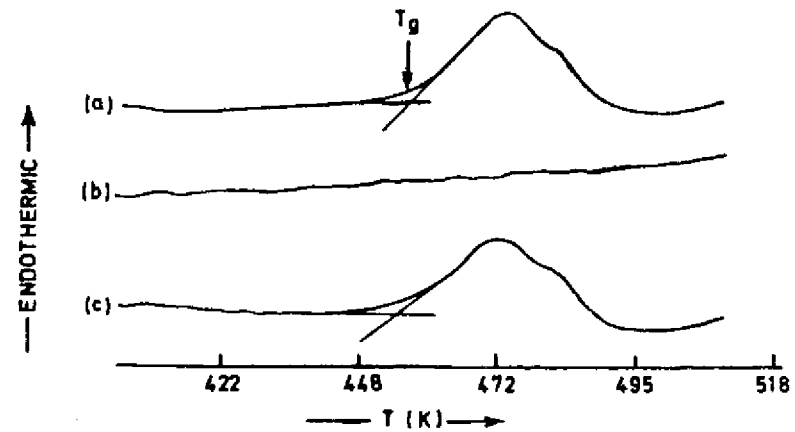


Fig.1

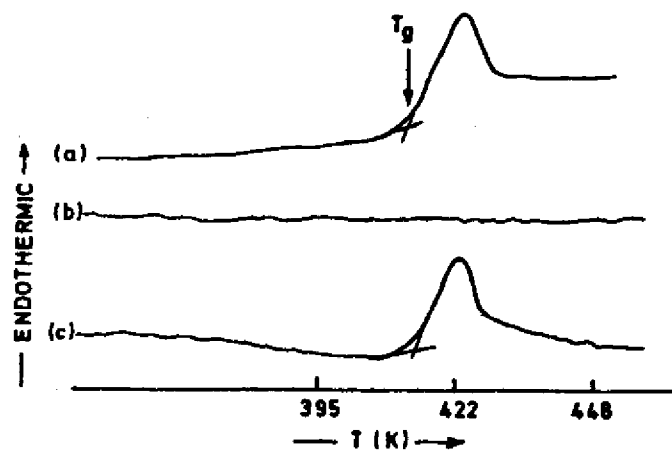


Fig. 2

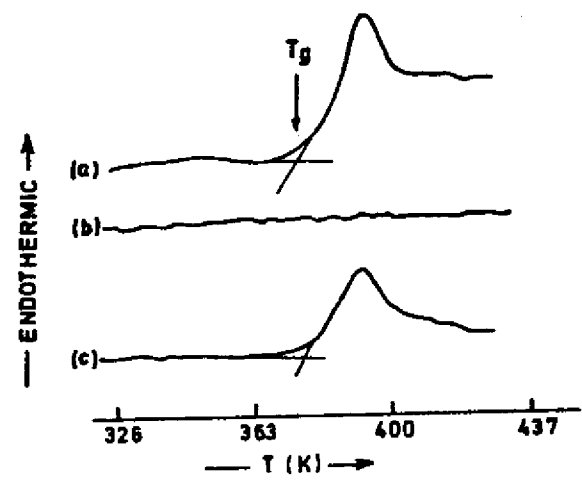


Fig. 3

