Non-isothermal crystallization of As, Se₃ glass

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Abstract. The results of non-isothermal crystallization studies performed at different heating rates on batches of As_2Se_3 glasses prepared from melts at 400°C, 600°C and 800°C are reported. The peak temperature of crystallization T_c the enthalpy of crystallization ΔH, and the activation energy for crystallization E_c are independent of the melt temperature used in the preparation. Bulk nucleation with three-dimensional growth of crystals is indicated for As_2Se_3. The values of ΔH_c and E_c are found to be respectively 23.3 ± 0.9 cal/g and 36.5 ± 0.9 kcal/mol for As_2Se_3.

Keywords. As_2Se_3 glass; non-isothermal crystallization; activation energy for crystal growth.

1. Introduction

The As_2Se_3 glass prepared from the congruently melting compound As_2Se_3 is one of the widely characterized chalcogenide glasses, the characterization encompassing its optical, thermal, electrical and other physical properties. It is easily prepared in bulk form by cooling (generally by quenching in cold water) the melt; the melt temperature employed in various investigations ranges from 500°C to 850°C (Henderson and Ast 1984; El Fouly and Edmond 1974; Thornburg and Johnson 1975; Moynihan *et al* 1975).

The crystallization behaviour of this glass has been studied under isothermal conditions using density and electrical conductivity measurements (Myuller and Shkolnikov 1966), x-ray methods (Majid *et al* 1974) and thermal analysis (Henderson and Ast 1984). In a preliminary non-isothermal study using DTA (El Fouly and Edmond 1974), it was observed that As_2Se_3 glasses quenched from melts at 600°C did not show any crystallization peak. However, in a later DSC study (Thornburg and Johnson 1975) on samples quenched from 600°C, crystallization exotherm was present, suggesting that the observed variance probably results from other differences in sample preparation. In order to see if there is difference in crystallization behaviour of samples quenched from melts at different temperatures, studies were made on glasses prepared from melts at 400°C, 600°C and 800°C; the results of this study are reported in this communication.

2. Experimental

Bulk glasses of As_2Se_3 were prepared by homogenization (10 g per batch) of 99.999% pure **As** and **Se** (obtained from Koch Light Co., U.K.) in appropriate atomic per cent proportions in quartz ampoules sealed in a vacuum of better than 10^{-3} torr. Homogenization was carried out under continuous agitation for 24 hr at the end of

which the ampoule was quenched in cold water. Three batches of samples with melts at 400°C, 600°C and 800°C were prepared for the study.

The thermal analysis runs were carried out using a Perkin-Elmer DSC–2 differential scanning calorimeter after performing the temperature and energy calibration of the instrument using high purity tin, indium and lead supplied with the instrument. Powdered samples (typically 60 mg) were taken in crimped aluminium pans and all the measurements were referenced to an empty aluminium pan. High purity dry nitrogen was used as the purge gas.

The crystallization exotherm sets in around 540 K to 570 K depending upon the heating rate employed. All the samples were first heated in situ from *300* K to 520 K at 40 K/min and the crystallization exotherm was then recorded from 520K onwards at the various desired heating rates starting from 0.31 K/min. The temperature of onset of crystallization increases with increasing heating rate. Therefore, the measurements could not be extended for heating rates higher than 5 K/min because, for heating rates higher than this, the melting endotherm used to set in before the completion of the crystallization exotherm. Measurements were carried out on freshly prepared and annealed (for an hour around the glass transition temperature T_g, namely, at 450 K) samples which were quenched from melts at 400°C, 600°C and 800°C.

As indicated schematically elsewhere (Sudha Mahadevan *et al* 1986) the peak temperature of crystallization was obtained as the temperature corresponding to the intersection of the two linear portions adjoining the peak. The crystallization enthalpy ΔH_c was obtained by multiplying the area of the exotherm *(A)* by the calibration constant *C*. The value of C was deduced by measuring the total area of the complete melting endotherm of high purity tin and indium and using the well-known enthalpy of melting of these standard materials. The fraction **x** crystallized at any temperature T is given by $x = A_T/A$, where A is the total area of the exotherm between temperature T_1 where crystallization just begins and T_2 where the crystallization is completed; A, is the area between T_1 and T. The area measurements were made using an Autotrol AD-380 graphic system.

3. Results and discussion

The results of the present study are summarized in table I and figures 1–3. The values of T_p listed (table 1) for all the six batches of samples are representative values obtained for a single run at the various heating rates specified. In order to assess the spread in the value of T_p (for any given heating rate), measurements were carried out on four samples from the same batch. A spread of ± 0·7% in T_p was obtained giving a standard deviation of 4. Similar measurements on four samples of another batch gave the same spread and standard deviation values. The data of table 1 indicate that T_p does not depend on the melt temperature used in the preparation because the spread in the T_p values of samples from batches with different melt temperatures is of the same magnitude as that obtained for different samples of the same batch. Also shown in table 1 are the *AH,* values, which indicate that to within experimental errors ΔH_c is independent of the heating rate employed, a result observed in other chalcogenide glass systems also, namely, As-Sb-Se (Sudha Mahadevan *et al* 1986) and As-Ge-Te (Sugi *et al* 1971). Further ΔH_c **is** also found to be independent of the

Table 1. Data of T_p(K) and ΔH_c(cal/g) of As₂Se₃.

| Sample details	Heating rate (K/min)					
	0·31	0·62	1·25	2·5	5·0	
Quenched from	560·3	572.4	584·9	599·9	619·0	T_p
400 C, fresh	22·9 ·	22·9	23.7	24·3	23·6	ΔH_c
-do-, annealed	561·0	575.0	588·6	605·5	622.0	T_p
1 hr at T_g	23.3	23·9	24.1	24·1	—	ΔH_c
Quenched lrom	555·2	569.4	584·6	5095	6155	T_p
600 C. fresh	22.9	24·2	23·7	22.5	23·9	ΔH_c
-do-, annealed	554·4	568·9	583·2	599·0	613·0	T_p
1 hr at T_g	22·6	23.2	24·0	24·2	228	ΔH_c
Quenched from	553·1	566·5	5825	597·5	614.0	T_p
800 C. fresh	22.5 ·	238	24.2	23·9	24.1	ΔH_c
-do-, annealed	559·1	571.1	584.6	601·0	618.0	T_p
1 hr at T_g	22·7	23·0	22·7	23·8	23·3	ΔH_c
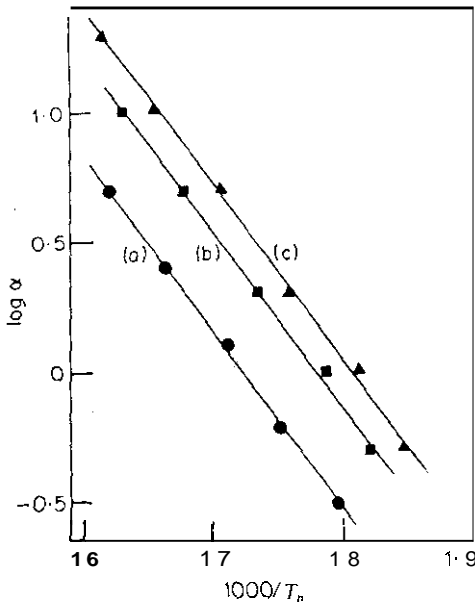
Figure 1. *Logr* vs $1/T_p$ for As₂Se₃ (line a); The solid circle denotes the mean value obtained lor all the batches (table 1) at each ol the heating rates; lines (b) and (c) denote the data from literature (Thornburg and Johnson 1975) on lresh and aged samples.

melt temperature used in the preparation and on the annealing treatment given to the samples; ΔH_c was found to have a value of $23·3 \pm 0·9$ cal/g (table 1).

It is well known (Thornburg and Johnson 1975; Kissinger 1956: Chcn 1978; Yinnon and Uhlman 1983; Frahn 1983; Cadergren and Backstrom 1980; Matusita and Sikka 1979; MacFarlane 1984; Matusita and Sikka 1980 Morotta *et al* 1983) that $\log a$ vs $1/T_p$ data is linear for most glasses and the slope of this plot is related to the activation energy for crystallization. Figure 1 shows the $\log \alpha$ vs $1/T_p$ data for the samples studied presently. Also shown in figure 1 are the T_p data from literature
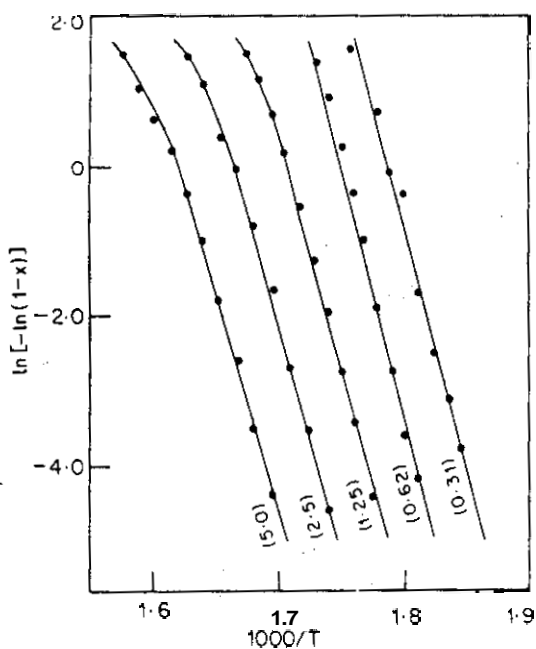
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Figure 2. $\ln[-\ln(1-x)]$ vs $1000/T$ lor As_2Se_3 samples at various heating rates (K/min) indicated in parentheses.
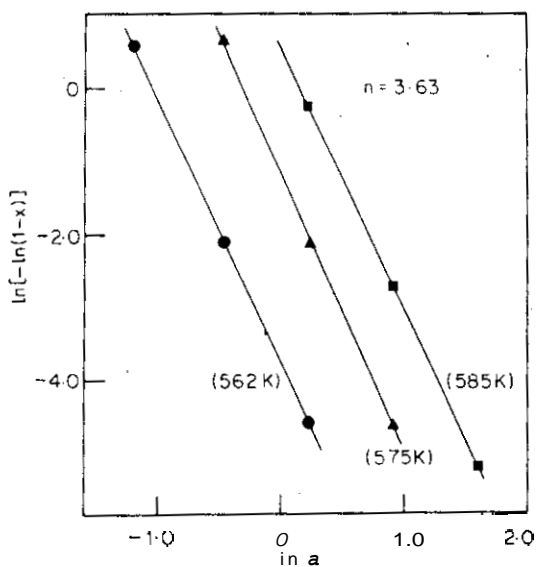

Figure 3. $\ln[-\ln(1-x)]$ vs $\ln\alpha$ lor As_2Se_3 at three different temperatures.

(Thornburg and Johnson 1975) for fresh samples quenched from melt at 600°C, (figure 1, line b) and for the same samples after ageing them at room temperature for 800 days (figure 1, line c); with this ageing, a reduction of about **2%** in T_p is seen. The present values of T_p for any given heating rate are systematically about **5%** higher

than the data of figure 1, line b. The present study shows that melt temperature does not affect the T_p values and the reason for the observed difference in T_p is attributable to other differences in preparation conditions which are yet to be identified. The present results further indicate that annealing for about an hour at T_g does not affect the values of T_p. These results are in accordance with other observations which conclude (Henderson and Ast 1984; Myuller and Shkolnikov 1966; Majid *et al* 1974) that **no** appreciable rearrangements or reorganisations of the atomic structure would occur in this short annealing period around T_g.

Though the values of T_p at any heating rate (figure 1, line a) are systematically slightly higher than that of figure 1, line b, the slope of the $\log \alpha$ vs $1/T_p$ data and the crystallization enthalpy agree with each other. This result is in accordance with the result reported for fresh and aged samples of $As_2 Se_3$ (Thornburg and Johnson 1975); while the T_p values of the samples aged for 800 days are about 2% lower than that of fresh samples, the slope of the $\log a$ vs $1/T_p$ line and the value of **AH,** are unaffected.

The crystallization data obtained presently were further analyzed using a procedure suggested for non-isothermal crystallisation (Matusita *et al 1984);* this method has been successfully applied for crystallization studied on As-Sb-Se glasses (Sudha Mahadevan *er al* 1986). Referring to these papers (Matusita *er al* 1984; Matusita and Sakka 1980; Sudha Mahadevan *et al* 1986) for details of analysis and discussion, the method will be briefly outlined here and the results for $As_2 Se_3$ presented.

For non-isothermal crystallization (Matusita *et al* 1984), the fraction x of crystals precipitated in **a** glass heated at a uniform rate α is related to the activation energy E_c through the relation

$$\ln[-\ln(1-x)] = -n\ln\alpha - 1 \cdot 052\, mE_c / RT + constant,$$

where m and n are numerical constants having values between 1 and 4 depending on the morphology (whether it is surface or bulk crystallization and whether the crystal growth is predominantly one-, two- or three-dimensional); values of m and n for various conditions *are* listed (Matusita and Sakka 1980; Matusita *et al* 1984). When nuclei formed during the heating at constant rate are dominant, n is equal to $m + 1$ and when nuclei formed during any heat treatment prior to the thermal analysis run are dominant, n is equal to *m.*

Figure 2 shows the $\ln[-\ln(1-x)]$ vs $1/T$ data at various heating rates for one of the batches **of** $As_2 Se_3$ studied ptesently. The slope of this line (average value of the data at five heating rates, figure 2) gives a value of $112\,kcal/mol$ for mE_c. To infer the value of m, the dimensionality of the growth, $\ln[-\ln(1-x)]$ was plotted as **a** function of $\ln\alpha$ at fixed temperatures. Figure 3 shows such a data for three temperatures, which gives an average value of $3 \cdot 63$ for the slope n. The break in the $\ln[-\ln(1-x)]$ vs $1/T$ data (figure 2) for large crystallized fractions for some heating ,rates has been reported and discussed for several other glass systems (Sudha Mahadevan *er al* 1986; Colemenero and Barandiaran 1978; Speyer and Risbud 1983; Shelestak *et al* 1978; Duhaj *et al* 1976; Burton and Ray 1971).

Similar analysis on other batches of $As_2 Se_3$ gave mE_c values in the range of 112 to 118 kcal/mol; n had values between 3.63 and 3.78 thereby giving a value of 3 for *m* (Matusita et *al* 1984). These values of n and *m* indicate that bulk nucleation with three-dimensional growth is likely in $As_2 Se_3$, a result similar to that obtained for

$As_2Se_3 - Sb_2Se_3$ glasses (Sudha Mahadevan *et al* 1986). The value of E_c is found to be 36.5 ± 0.9 kcal/mol.

It **is** also indicated (Illekova 1984) that in crystallization studies using non-isothermal **DSC** experiments, the activation energy obtained pertains to the activation energy for crystal growth. In non-isothermal measurements, generally due to a rapid temperature rise and big differences in the latent heats **of** nucleation and growth, the crystallization exotherm characterizes the growth of the crystalline phase from the amorphous matrix; the nucleation' is more or less calorimetrically unobservable at temperatures below the crystallization exotherm or it takes place very rapidly immediately after overheating of the material, which results in the deformed beginning of the measured exotherm (Illekova 1984). Direct measurements of the activation energy for crystal growth in As_2Se_3 using electron microscopy technique (Henderson and Ast 1984) give a value of 36.8 kcal/mol. The value of 36.4 kcal/mol obtained by the present non-isothermal DSC measurements agrees well with this value.

4. Summary and conclusions

Using the DSC technique, non-isothermal crystallization has been studied at various heating **rates** on batches of As_2Se_3 glass prepared from melts at $400°C$, *600°C* and $800°C$. The **peak** temperature of crystallization, the enthalpy of crystallization and the activation energy for crystallization are found to be independent of the melt temperature used in the preparation.

The crystallization data have been analyzed using a method suggested for non-isothermal crystallization. The results indicate bulk nucleation with three-dimensional growth of crystals for As_2Se_3. The crystallization enthalpy ΔH_c is found to be 23.3 ± 0.9 cal/g for As_2Se_3. **A** value of 36.5 ± 0.9 kcal/mol is obtained for the activation energy for crystallization in As_2Se_3. This value agrees well with the activation energy for crystal growth obtained by direct measurement using electron microscopy technique.

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