

# Measurement of the viscosity of chalcogenide glasses by a parallel plate technique

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The parallel plate technique of viscosity measurement in the range  $10^6$  to  $10^{8.5}$  P has been successfully applied to chalcogenide glasses. It offers a simple and quick alternative to traditional techniques such as fibre elongation.

## 1. Introduction

It has been shown that glasses from the Ge-As-Se [1] and Ge-As-Se-Te [2] systems are suitable as passive bulk optical component materials for 3 to  $5\ \mu\text{m}$  and 8 to  $12\ \mu\text{m}$  applications. Certain of these glasses (Texas Instruments, TI1173 Ge<sub>28</sub> Sb<sub>12</sub> Se<sub>60</sub> and TI20 Ge<sub>33</sub> As<sub>12</sub> Se<sub>55</sub>) have been produced on a commercial scale and used for correcting chromatic aberration in 8 to  $12\ \mu\text{m}$  germanium lenses. Recently Barr and Stroud Ltd\* have offered a chalcogenide glass type 1 and Jener Glaswerk Schott U. Gen.† have offered glass IRG 100 with similar optical properties to the TI1 173 and TI20. From the published data on absorption coefficients in the Ge-As-Se [3], Ge-Sb-Se [4] and Ge-As-Se-Te [2] glass systems, it is clear that the absorption coefficients between 8 and  $12\ \mu\text{m}$  are sufficiently low to allow these materials to be used for short length fibre optic applications such as image transfer through faceplates or coherent fibre bundles. A knowledge of the viscosities of these glasses is necessary to allow proper choice of core and cladding materials. In making viscosity measurements on oxide glasses, the glass transition temperature,  $T_g$ , gives a fixed viscosity point of  $10^{13.3}$  P [5] and the fibre elongation technique is usually used to give the Littleton softening point of  $10^{7.6}$  P. However, chalcogenide glasses are unsuitable for flame working into fibres in a normal laboratory environment and would necessitate specialized fibre drawing in an inert gas electric muffle furnace. It has been shown that a parallel

plate viscometer method can be successfully applied to oxide glasses in the range  $10^5$  to  $10^9$  P for specimens 6 mm diameter and 2.5 to 5 mm thick [6]. Thus it was decided to test the applicability of this method of viscosity measurement to chalcogenide glasses since the specimen sizes and equipment already available were ideally suited to this technique.

## 2. Glass preparation, measurements and calibration

### 2.1. Glass preparation

The glasses were synthesized from the elements inside sealed evacuated silica tubes at  $970^\circ\text{C}$  in a rocking rotation furnace [7]. They were air quenched and after differential thermal analysis (DTA) were annealed before being cut and polished. For viscosity measurements samples between 4 and 5 mm diameter and 2 mm thickness were core drilled from the bulk glass and the cylindrical ends were polished flat and parallel within  $\pm 0.001$  cm.

### 2.2. Measurements

A Du Pont 900 thermal analyser console, a differential scanning calorimeter cell, and a thermomechanical analyser were employed in this work. The differential scanning calorimeter was used to measure  $T_g$  (viscosity =  $10^{13.3}$  P) as previously described [8] while the thermomechanical analyser (TMA) was used to measure viscosity. Each chalcogenide glass sample was sandwiched between two plane parallel silica glass plates 1 mm thick

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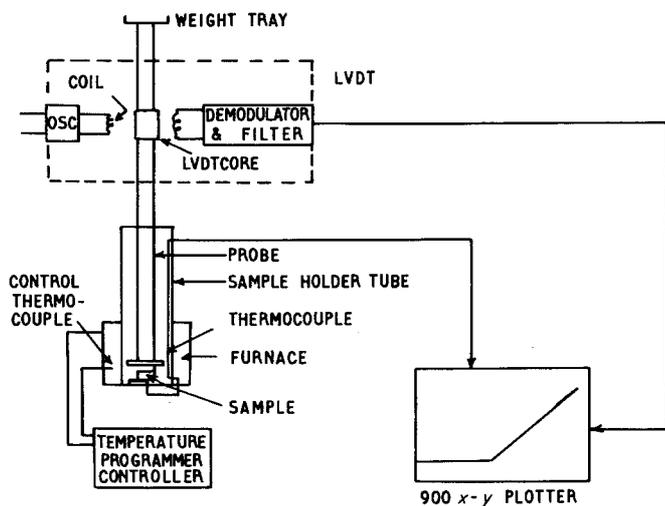


Figure 1 Schematic diagram of the viscosity measurement apparatus.

and 10 mm diameter in the base of the TMA as shown in Fig. 1. A thermocouple was placed next to the sample and a 3 mm diameter silica probe assembly with a weight pan at its upper extremity was lowered into contact with the centre of the top silica plate. Appropriate weights were then placed on the weight pan. A moveable core differential transformer as shown in Fig. 1 provided d.c. output proportional to the linear displacement of the core (LVDT) attached to the probe rod. A self-contained oscillator supplied a.c. input to the primary windings. The position of the core and hence the probe rod determined the voltage induced in the transformer secondary windings, two of which were connected in series opposition. The resultant rectified output was a d.c. voltage (proportional to the core displacement from the electrical centre) which was applied directly to the y-axis of the 900 thermal analyser. The thermocouple next to the sample provided an output which after compensation was applied to the x-axis of the recorder. Thus a record of probe movement or sample compression was obtained as a function of temperature and, in addition, the chart was marked manually at two minute intervals over the temperature range where measurements were to be made in order to provide a record of time. Four experimental determinations on individual samples were made on each glass composition at a heating rate of  $5^{\circ}\text{C min}^{-1}$  in an argon atmosphere. Two determinations were made with a load of 2 g on the sample probe pan in the range  $10^6$  to  $10^7$  P and two determinations were made with a load of 10 g on the probe pan in the range  $10^{7.5}$  to  $10^{8.5}$  P. The dimensions of each sample

were measured with a micrometer at the beginning and end of each determination. The precision of temperature measurement was  $\pm 2.0^{\circ}\text{C}$  and that of  $\log_{10}\eta$  was  $\pm 0.04$ .

### 2.3. Calibration

The TMA was calibrated by making measurements on a standard viscosity reference glass No. 711 from the National Bureau of Standards, USA. The sample preparation and measurement were as detailed in Sections 2.1 and 2.2 except that sapphire plates were used instead of silica ones to avoid corrosion by the glass. The viscosity range used for calibration and obtained with a 2 g load in the probe pan was  $10^6$  to  $10^8$  P. The Fulcher equation for glass 711 was given as

$$\log_{10}\eta = -1.621 + (4254.649/T^{\circ}\text{C} - 152.1) \quad (1)$$

with a standard error of  $\log_{10}\eta$  of 0.035. When the results were calculated according to method given in Section 3 it was found necessary to apply a correction factor of  $\times 1.04$  to obtain the values calculated from the above Fulcher equation. This correction factor was applied to the results which will be discussed in Section 4.

### 3. Theory and calculations

An equation for calculating viscosity by the parallel plate method was derived by Dienes and Klemm [9] but required that the specimen radius be at least 10 times the thickness. Gent [10] extended the theoretical treatment to include specimens of any thickness and the following is valid for a wide range of thickness/radius combinations.

TABLE I

Composition	$\log_{10}\eta/T^\circ\text{C}$										Fulcher equation
1. Ge30 As13 Se57	13.3/342	8.2/431	7.8/440	7.4/454	6.9/468	6.5/477	6.2/486	6.0/495	—	—	$\log_{10}\eta = -4.71 + 4070/(T^\circ\text{C} - 116.13)$
2. Ge30 As13 Se47 Te10	13.3/308	8.2/395	8.0/400	7.3/419	6.8/433	6.4/441	6.1/449	5.9/460	5.8/464	5.8/464	$\log_{10}\eta = -5.91 + 4627/(T^\circ\text{C} - 67.49)$
3. Ge30 As13 Se37 Te20	13.3/285	8.4/363	8.2/368	7.5/381	6.8/395	6.4/404	6.0/414	5.7/423	5.6/428	5.6/428	$\log_{10}\eta = -9.74 + 6466/(T^\circ\text{C} - 5.06)$
4. Ge30 As13 Se27 Te30	13.3/262	8.3/330	7.8/340	7.4/349	6.7/363	—	6.3/372	5.9/381	5.6/390	5.6/390	$\log_{10}\eta = -8.19 + 4868/(T^\circ\text{C} - 35.52)$
5. As40 Se60	13.3/178	8.4/236	8.2/241	7.5/256	7.0/266	6.5/276	—	6.0/285	5.8/290	5.8/290	$\log_{10}\eta = -4.44 + 2764/(T^\circ\text{C} - 22.25)$
6. Ge28 Sb12 Se60	13.3/277	8.1/339	7.9/343	7.3/352	6.9/361	6.4/371	—	5.9/380	5.7/389	5.7/389	$\log_{10}\eta = -4.97 + 2824/(T^\circ\text{C} - 122.41)$

$$\eta = \frac{2\pi Mgh^5}{3V dh/dt(2\pi h^3 + V)}, \quad (2)$$

where  $\eta$  is the viscosity (P),  $M$  is the applied load (g),  $g$  is the gravity acceleration ( $980 \text{ cm sec}^{-2}$ ),  $t$  is the time (sec),  $V$  is the specimen volume ( $\text{cm}^3$ ) and  $h$  is the specimen thickness at time,  $t$  (cm). Equation 1 was used to calculate the viscosity. The load,  $M$ , includes the weight of all parts of the TMA resting on the specimen, the upper silica plate and any weight in the probe pan. The volume,  $V$ , was calculated from the initial dimensions of the cylindrical specimen measured with a micrometer. The thickness,  $h$ , was determined from the initial and final specimen thicknesses and the chart recorder deflection at the time of measurement. The rate of deformation,  $dh/dt$ , at any time was measured from the slope of a line drawn tangentially to the recorder trace at that time.

#### 4. Results and discussion

Glasses from the Ge-As-Se-Te system offer a suitably wide range of thermal and optical properties to be considered as good candidates for fibre optic applications [2]. Four glasses from this system were chosen for measurement together with one glass from the Ge-As-Se [11] system and one glass from the Ge-Sb-Se [12] system whose viscosity were in the range  $10^{11}$  to  $10^{12}$  P and which have previously been reported. The experimental results obtained for these glasses are given in Table I together with the constants for the Fulcher equation calculated from the plotted data. The temperature calculated from the equations of Table I at which glasses As40 Se60 and Ge28 Sb12 Se60 attain viscosities of  $10^{11}$  and  $10^{12}$  P are given in Table II. In this table values obtained from the literature measured by reference techniques are shown in parenthesis. It is seen that these values agree to within  $12^\circ \text{C}$  (or approximately one order of magnitude in viscosity) which is reasonable considering the

TABLE II Temperatures at which As40 Se60 and Ge28 Sb12 Se60 attain viscosities of  $10^{11}$  and  $10^{12}$  P

Composition	$10^{11}$ P	$10^{12}$ P
As40 Se60	$190^\circ \text{C}$ ( $178^\circ \text{C}$ )	$201^\circ \text{C}$ ( $193^\circ \text{C}$ )
Ge28 Sb12 Se60	$299^\circ \text{C}$ ( $302^\circ \text{C}$ )	$288^\circ \text{C}$ ( $283^\circ \text{C}$ )

likely errors involved when employing reference techniques. The precision obtained during the present work was sufficient to allow the use of the parallel plate technique to determine self consistent sets of data on a series of chalcogenide glasses for experimental purposes. This technique offers a simple and quick alternative mode of measurement to traditional techniques such as fibre elongation.

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