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VISCOSITY MEASUREMENTS ON INFRARED TRANSMITTING GLASSES

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ABSTRACT

The technique of parallel plate rheometry has been used to study the viscosity-temperature characteristics of candidate glasses for use in infrared transmitting optical fibres.

INTRODUCTION

A number of candidate materials are being considered for the fabrication of low-loss optical fibres operating in the 2 - 5 μm wavelength range (ref.1). These include glasses based on oxide, halide and chalcogenide compositions. Measurement of the viscosity-temperature characteristics of such materials is essential for determining their suitability for drawing into high quality fibre from preform rods. In particular, information is required on the sensitivity of viscosity to small temperature variations during the drawing process, the compatibility of the materials chosen for the core and cladding structure of the optical fibre, and the possible effects of crystallisation processes.

EXPERIMENTAL

The technique of parallel plate rheometry (ref.2,3) involves following the deformation of a cylindrical sample under an applied load, whilst it is subjected to a chosen temperature programme. A Dupont 1090 Thermal Analyser with a Model 943 TMA cell is used for this work. The glass samples are of cylindrical geometry, cut from annealed cast rods and then polished. They are sandwiched between carefully aligned, rigid 10 mm diameter plates, normally made from silicon carbide to minimise corrosion effects. The silica probe is lowered until it just touches the top plate and then loaded with suitable weights. Temperature, deformation and deformation rate data are stored in the 1090, then transferred to a microcomputer (Apple IIe) for calculation of viscosity-temperature curves. Data sampling is normally performed at a rate of 1 sec/point, with subsequent averaging in the computer to give viscosity data points every 10 sec, this latter procedure only becoming important to reduce noise when deformation rates are very small. A Hooke's Law correction to the applied load is performed to counteract the effect of the spring supporting the silica probe.

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The equation used for calculating viscosity is that due to Gent (ref.4):

$$\eta = \frac{2\pi Mgh^5}{3V\,(dh/dt)\,(2\pi h^3 + V)} \qquad (1)$$

where η (poise) is viscosity, Mg (g cm sec^{-2}) the applied force including that due to the upper plate, h (cm) the instantaneous sample thickness , V (cm^3) the sample volume, and dh/dt (cm/sec) the deformation rate.

The viscosity range accessible in any one experiment is dependent on sample dimensions, applied load and heating rate, but by careful choice of these parameters measurements may be made in the viscosity range $10^{4.5}$ - 10^9 poise, which conveniently covers the region of the fibre drawing viscosity (about $10^{5.5}$ poise). In the current work the sample diameter was normally 6 mm, the initial sample thickness in the range 2 to 5 mm, the applied load in the range 1 to 100g and the heating rate normally 10 deg/min. Experiments were terminated when the extent of deformation indicated the sample diameter to be approaching 10 mm. After cooling, the final sample thickness was checked by micrometer, absence of chemical attack at the sample/plate interface was confirmed visually, and the sample was examined microscopically for the appearance of crystallisation.

CALIBRATION

For calibration purposes an NBS standard viscosity lead silicate glass SRM 711 was used. Experiments were performed under a variety of loads, and results of three of these are shown in Fig. 1, together with the NBS standard data. Each experiment provided good quality data over a different viscosity range. The low temperature deviations from the NBS data seem to be characteristic of the technique, similar behaviour having been observed in all measurements undertaken. Deviations are also observed at the high temperature end of the experimental curves. In all cases the deviations correspond to experimental conditions where the deformation rate was small. To obtain the highest quality data, therefore, a composite is required of viscosity curves obtained under different loading conditions. In this way, for SRM 711, a good fit to the NBS data was obtained in the range 10^6 - $10^{8.5}$ poise.

VISCOSITY OF I.R GLASSES

The slope of the experimental viscosity-temperature curve for a given glass composition is of fundamental importance in determining fibre drawing characteristics. First, it indicates the extent of the working range of the glass; second, it reveals the degree of temperature control required to draw high-quality dimensionally-stable fibre; and third, the data may be used to aid design of appropriate temperature profiles in the drawing furnace. In general, the candidate materials for 2 - 5 μm transmission show higher sensitivity to small temperature fluctuations, and thus present greater problems, than the

silica-based compositions used in the current generation of optical fibres.

We have measured the viscosities of a large number of glasses based on GeO_2, TeO_2 and ZrF_4 - BaF_2. Fig. 2 shows schematically the behaviour of typical tellurite (showing the onset of crystallisation) and fluoride compositions, together with that of some representative compositions in the binary antimony germanate system. This type of reciprocal temperature plot (when the data is extrapolated to the fixed viscosity point of $10^{13.3}$ poise at T_g) shows the non-Arrhenius behaviour of many of these glass compositions. In all cases the data is better fitted to an empirical Fulcher equation of the form $\log_{10} \eta = A + \frac{B}{T - T_o}$. Nevertheless, apparent activation energies for viscous flow may be calculated, and provide valuable data for comparison with results of kinetic studies of crystal growth in glasses, particularly in helping to elucidate mechanisms (eg. refs 5, 6). For diffusion-controlled crystal growth, the higher the activation energy for viscous flow, the higher will be the tendency for devitrification. For example, the activation energy for the fluoride glass in Figure 2 is about 600 kJ/mol whereas that for SRM 711 is about 300 kJ/mol.

In choosing glass compositions for use in optical fibres, the properties of major importance are the transparency at the desired wavelength and the scattering properties of the material. In choosing the compositions for core and cladding the prime concern becomes the ability to tailor refractive index to provide the light-guiding property of the optical fibre. At the same time, the two compositions must be compatible in terms of their thermal expansion and viscosity characteristics. Figure 3 shows the effect on viscosity of additions of 10 cat% of third oxides, which might be considered as potential refractive index modifiers, to a binary germanate base glass containing 48 cat% Sb.

CRYSTALLISATION STUDIES

The crystallisation of glasses is usually studied using DSC measurements. In general there is good correspondence between observations made by both DSC and viscosity studies. The measurement of viscosity, however, seems very sensitive to the early stages of crystallisation and to small volume effects difficult to detect by DSC. Figure 4 shows an experimental viscosity curve for a fluoride glass of complex composition, based on ZrF_4 - BaF_2 with additions of La, Al, Pb and Li fluorides, taken through the onset of crystallisation. The anomalous feature in the region 315 - 330°C, prior to the onset of gross crystallisation, has been identified by microscopy as due to surface crystallisation of a finely acicular phase. The proximity of the onset of this event to the fibre drawing temperature, as well as the steepness of the viscosity curve, illustrates well the problems associated with drawing high quality fibre from this type of material, and the constraints imposed on the drawing conditions.

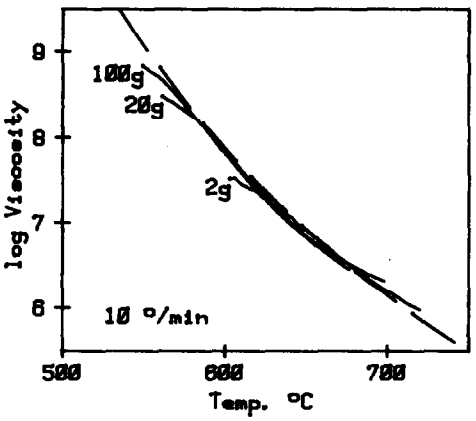

Fig. 1. Experimental viscosity curves for SRM 711, and NBS reference data (dashed curve).

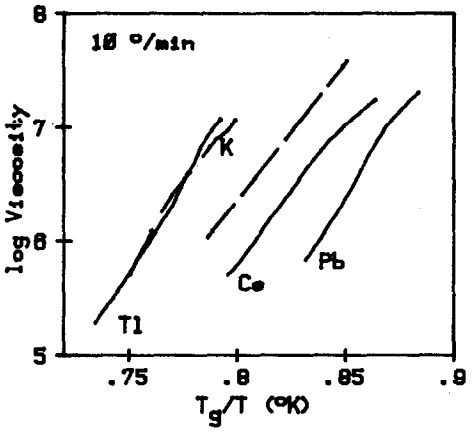

Fig. 3. Effect of addition of 10 cat% of a third oxide on the viscosity of a binary Sb germanate glass (dashed).

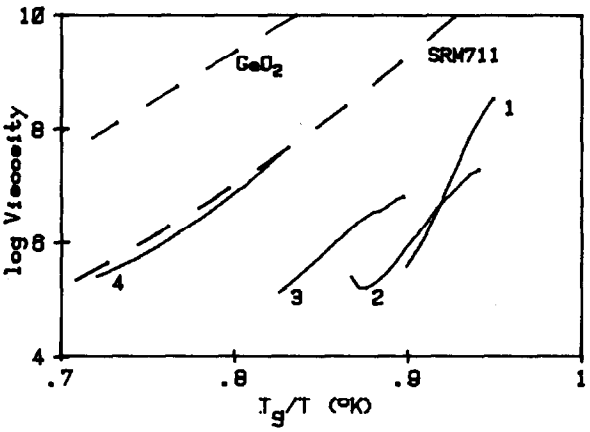

Fig. 2. Comparison of viscosities of
1) fluoride 2) tellurite 3) 80 cat% Sb-GeO_2
4) 37 cat% Sb-GeO_2 glass compositions.

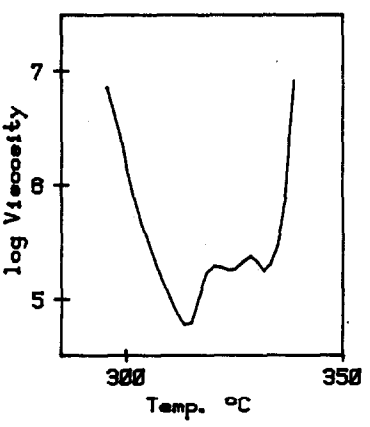

Fig. 4. Viscosity behaviour of ZrF_4 - BaF_2 based glass; 2g load; 10 deg/min.

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