Fusion temperatures of SiO_2–P_2O_5 binary glasses

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Experimental measurements of fusion temperatures against glass composition for binary phosphosilicate glasses, as used in optical fibres, were made. The glasses were prepared in layers within a silica tube by chemical vapour deposition. Using a model based on the fraction of P–O to Si–O bonds and the known viscosity of vitreous silica and glassy P_2O_5, theoretical calculations of fusion temperatures were made and compared with experiment. Good agreement was obtained. The model was also applied to the fusion temperatures of binary SiO_2–GeO_2 and SiO_2–B_2O_3 glasses, and agreement with qualitative experimental measurement was found. Viscosity–temperature data for glasses in these three systems may also be calculated from the same model.

The phosphosilicate glass core fibre[1] is one of the silica based structures currently used in fibre optic communications. In cross section such a fibre consists of an outer silica cladding and an inner core of binary phosphosilicate glass, P_2O_5 being added to the silica in order to obtain the necessary increase in refractive index of the core glass above that of the silica cladding. The amount of P_2O_5 that can be added to the silica is limited to about 25 mol% by expansion coefficient mismatch, and for this particular phosphosilicate glass composition a maximum refractive increase of ~0·9% above that of silica is obtained.

Usually such fibres are fabricated by a modified chemical vapour deposition technique.[2] $SiCl_4$ and $POCl_3$ are vaporised, diluted with excess oxygen, and passed through a silica tube which is traversed by a short hot zone within which simultaneous oxidation and fusion of the chlorides occur to produce a layer of glass typically 10–15 μm thick. The hot zone temperature must be sufficiently high to satisfy two requirements; firstly, it must be above about 1000°C so that the oxidation reactions to form P_2O_5 and SiO_2 can proceed and, secondly, the dense dispersion of glass particles formed by the oxidation must be fused onto the tube walls to give a clear vitreous layer. Any particles left in the glassy layer as a result of incomplete fusion can produce very high optical losses in the subsequent fibre by acting as scatter centres. The exact fusion temperature depends on the glass composition of the layer.

This paper reports experimental measurements of fusion temperature against composition for binary phosphosilicate glasses as used in optical fibres. By using the known viscosity of silica[3] and P_2O_5[4] and a bonding fraction as the composition variable,[5] theoretical calculations are made and compared with experimental results.

Theory

For simple glass forming oxides the viscosity, η, fits an Arrhenius type equation over wide ranges of temperature:

$$\eta = \eta_0 \exp\left(\frac{Q}{RT}\right) \tag{1}$$

where Q and η_0 are the activation energy and pre-exponential factor, respectively.[6] For vitreous silica Hofmaier & Urbain[7] have measured Q = 123 kcal mole^{-1} and $\eta_0 = 5{\cdot}75 \times 10^{-7}$ P over the temperature range 1600 to 2500°C. For vitreous P_2O_5, Cormia *et al.*[4] found that Q = 41·5 kcal mole^{-1} and $\eta_0 = 1{\cdot}18 \times 10^{-4}$ P over the temperature range 545 to 655°C.

For a binary glass such as $xSiO_2$, $1P_2O_5$ it is assumed that the viscosity may still be expressed by Equation (1). As the viscous flow of a glass at elevated temperatures is associated with the breaking of the cation–oxygen bonds, it seems likely that the activation energy of a binary glass is related to the activation energies of its end members by a relationship

$$Q(u) = Q(p) + u[Q(s) - Q(p)] \tag{2}$$

where, for phosphosilicate glass, $Q(p)$ and $Q(s)$ are the activation energies of P_2O_5 and silica respectively and u is the fractional content of Si–O and P–O bonds, given by

$$u = \frac{x}{x+2} \tag{3}$$

since both P_2O_5 and SiO_2 are four coordinated.[6]

For the range of compositions considered here, up to 25 mol% P_2O_5, $1 \geqslant u \geqslant 0{\cdot}8$ so that the binary glass still closely resembles silica and consequently η_0 for the binary glass is made independent of composition and given the silica value of $5{\cdot}75 \times 10^{-7}$ P.

During deposition the fusion temperature of the binary glass layer, T_f, is also assumed to be equivalent to the softening point of the glass, T_s, where $\eta = 10^{7{\cdot}6}$ P

by definition. Thus, for a given binary glass composition, $Q(u)$ can be found through Equations (2) and (3) and, by setting $\eta = 10^{7.6}$ P and $Q = Q(u)$ in Equation (1), a theoretical calculation of T_f can be made.

Experimental

Using the deposition system described by Gambling *et al.*[2] a number of phosphosilicate glass layers were deposited inside a 13 mm o/d by 11 mm i/d by 100 cm long Heralux (Heraeus Quartzschemelze GmbH) fused silica tube. For each layer the P_2O_5 concentration was increased in 2 mol% steps, starting with pure silica and finishing with 18 mol% P_2O_5, thus depositing 10 layers. A silicon carbide resistance furnace, which could be set to ± 5 degC was used to provide a hot zone 4 cm long which was translated along the tube at a rate of ~ 4 cm/min. At this speed the tube and furnace were nearly in thermal equilibrium, and thermocouple measurements indicated that the interior wall temperature of the tube was only slightly lower than the set temperature of the furnace.

Starting with a temperature higher than the expected fusion temperature of a layer with a particular composition, the furnace temperature was gradually reduced during translation until fusion of the layer was observed to have stopped. For the compositions examined, the transition between a clear glassy layer and on amorphous powdery layer was fairly sharp and thus the fusion temperature could be found to within ± 20 degC.

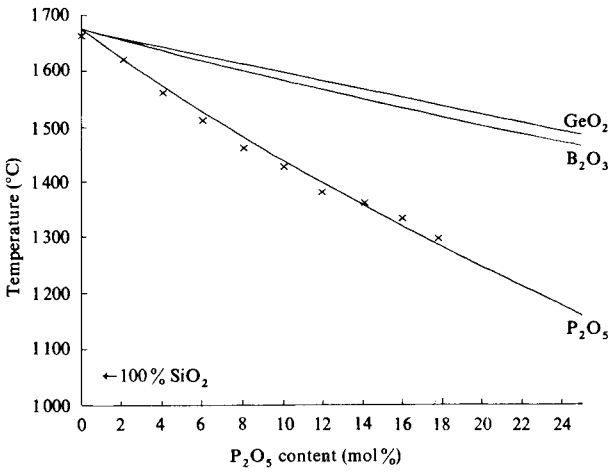

Figure 1. *Fusion temperature as a function of composition for P_2O_5–SiO_2, B_2O_3–SiO_2, and GeO_2–SiO_2 binary glasses*

× measured values
— theoretical calculations

Results

Figure 1 shows the experimental measurements of the variation of fusion temperature with composition and the theoretical results calculated by the method outlined above. The measured fusion temperature of pure silica, 1660 °C, is in excellent agreement with that of 1670 °C calculated from the silica viscosity data of Hofmaier & Urbain.[7] In general the measured fusion temperatures of the binary SiO_2–P_2O_5 glasses are also in close agreement with those obtained from the theoretical model.

Conclusions

In view of the good agreement between theory and measurements for SiO_2–P_2O_5 glasses, the method should be applicable to the other two common binary silica based glass systems used in fibre fabrication, SiO_2–B_2O_3 and SiO_2–GeO_2, and calculated results for these are also shown in Figure 1. The variation of fusion temperature with composition for SiO_2–GeO_2 was calculated using $Q(g) = 75$ kcal mole^{-1} from Kurkjian & Douglas.[8] For boric oxide, however, $Q(b)$ shows large changes with temperature, and the highest value of 83 kcal mole^{-1} [6] found in the literature was taken as being appropriate.

Although no quantitative measurements have been made on SiO_2–B_2O_3 and SiO_2–GeO_2 glasses, qualitative measurements made during the fabrication of fibres support the theoretical conclusion that phosphosilicate glasses are easier to fuse.

Finally the theoretical model can be made to yield viscosity–temperature data for those three systems, although experimental verification is outside the aim of the research programme which is primarily concerned with fabricating optical fibres for communications.

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