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Effects of thermal history on crystal size distributions and scattering in fluoride glass fibres

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The rates of nucleation and growth of crystals in ZBLAN glass have been analysed and differences have been found between previously reported models. These differences are most acute in the case of crystal nucleation rates. It is shown that, depending on which model is selected, the predicted stability of the glass is dramatically altered. The lowest stability predictions appear to have been based upon the most reliable data. The more reliable nucleation and growth models are used in a computer simulation which predicts crystal size distributions for any chosen thermal cycle. The thermal cycles arising from preform casting and fibre drawing are considered, and the resulting distributions are presented. Signal losses due to scattering of between 0.1 and 10 dB/km at wavelength 2.55 μm are predicted for long optical fibres, assuming that the nucleation and growth models are accurate. The predicted loss is sensitive to the time and temperature of the fibre drawing process, and is shown to be lower for a fast hot draw than for a slower cooler draw.

1. Introduction

ZBLAN (ZrF_4–BaF_2–LaF_3–AlF_3–NaF) glass offers the promise of optical fibres that are stable under normal environmental conditions, and whose signal loss is of the order of 0.01 dB/km for light of wavelength 2.55 μm. To date this promise has not been realised and losses in the range 1–100 dB/km are typical. This discrepancy is apparently due to imperfections in the experimental glasses that have been developed so far. Crystallisation of the glass during preform casting and fibre drawing has been identified as a major source of scattering losses in the fibres. This paper begins by assessing previous work on crystal nucleation and growth in ZBLAN glasses, and points out some discrepancies. One of the principal difficulties in measuring nucleation rates is to determine whether nuclei are formed by the solidifying material (homogeneous nucleation), or whether they are present as impurities in the melt prior to solidification (heterogeneous nucleation).

In the current study, crystal size distributions have been calculated as a function of thermal history. Many authors use size distributions as an intermediate step in calculating a fibre loss expressed in dB/km. However, the size distributions are interesting in their own right, since they offer an insight into the statistics of fibre loss as well as a means of calculating a total loss. For this reason, size distributions that have been predicted for particular thermal histories are presented here.

2. Crystal nucleation and growth

In recent years, two groups of researchers have published papers which address the mathematics of crystal nucleation and growth in ZBLAN glasses. These are Schneider and Staudt of Siemens AG [1], and Lu et al. of the Naval Research laboratory (NRL) [2]. Both groups represent the crystal nucleation rate, I, as

$$I = a_0 T \exp\left(\frac{-a_1}{T-a_3}\right) \exp\left(\frac{-a_2}{T(T-a_4)^2}\right), \qquad (1)$$

where T is absolute temperature and a_0, a_1, a_2, a_3, a_4 are constants whose values are chosen so as to give the best fit to experimental data. The NRL workers omit the constant a_3, or in other

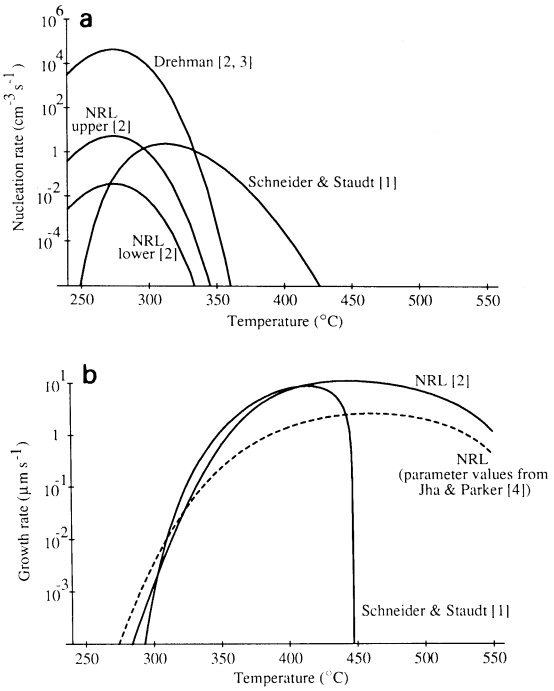

Fig. 1. (a) Crystal nucleation rate as a function of temperature. (b) Crystal growth rate as a function of temperature.

words they assume $a_3 = 0$. Their paper includes three curves corresponding to the data of Drehman [3], and upper and lower limits for their own experimental data. These curves, together with that of Schneider and Staudt, are reproduced in fig. 1(a). The parameters used are given in table 1.

The two groups have used different models for calculating the crystal growth rate, K. Schneider and Staudt have followed classical theory in order to derive the equation

$$K = b_0(b_1 - T)\exp\left(\frac{-b_2}{T - b_3}\right), \tag{2}$$

where b_0, b_1, b_2, b_3 are experimentally derived constants with the values given in table 2.

Table 2
Parameters used in eq. (2) to calculate the crystal growth rate

	b_0 (μm s^{-1} K^{-1})	b_1 (K)	b_2 (K)	b_3 (K)
Schneider and Staudt	40.08	720	847.9	518.6 [a]

[a] Altered from the published value of 530 K in order to obtain graphs similar to those in ref. [1].

The NRL workers assumed the growth to be controlled by interface kinetics. Using the Cohen–Grest viscosity equation, and by relating diffusion coefficient to viscosity through the Stokes–Einstein relation, they derived the following expression for the growth rate:

$$K = PT(T_m - T)\left[1 - \exp\left(\frac{\Delta S(T - T_m)}{RT}\right)\right] \times \exp\left(\frac{-2G}{\left(T - J + \left[(T-J)^2 + (4MT)\right]^{1/2}\right)}\right). \tag{3}$$

The differences between the two models are displayed in fig. 1(b), which also shows the effect of re-plotting eq. (3) using values for parameters G, J and M taken from the work of Jha and Parker [4]. Values for P, $\Delta S/R$ and T_m were

Table 1
Parameters used in eq. (1) to calculate the crystal nucleation rate

	a_0 (cm^{-3} s^{-1} K^{-1})	a_1 (K)	a_2 (K^3)	a_3 (K)	a_4 (K)
Schneider and Staudt	2.2×10^{55}	1317	3.659×10^{10}	483.2	1307
Drehman	e^{270}	1.05×10^5	3.7×10^9	0	850 [a]
NRL upper	e^{261}	1.05×10^5	3.7×10^9	0	850 [a]
NRL lower	e^{256}	1.05×10^5	3.7×10^9	0	850 [a]

[a] No value was quoted, so 850 K was chosen in order to obtain graphs similar to those in ref. [2].

assumed to be the same. The parameter values are summarised in table 3.

3. Computational method

Given nucleation and growth rates, it is possible to derive isothermal temperature–time–transformation (TTT) curves which relate the time and temperature required to produce specific volume fractions, W, of crystals. This is achieved through the Avrami equation, which relates W to nucleation rate, I, growth rate, K, and time, t:

$$W = 1 - \exp\left(\frac{-\pi}{3} K^3 I t^4\right). \quad (4)$$

The NRL nucleation curves represent upper and lower limits on highly scattered data, and alternative curves (such as Schneider and Staudt's) could also be fitted to their data. On the other hand, Schneider and Staudt's data fit their models well. For this reason, the statistical distributions derived in this paper are based upon Schneider and Staudt's models of nucleation and growth.

Using Schneider and Staudt's expressions for the nucleation and growth of crystals, a computer model has been built which calculates the expected distribution of particle sizes for any particular thermal history. The temperature patterns that are considered here represent typical thermal histories seen in the preparation of ZBLAN optical fibres.

First, we consider the thermal history of a glass preform. Molten glass at 600 °C is poured into a cylindrical brass mould of diameter 8 mm, which is held at 260 °C. It is assumed that the glass cools exponentially. In our model, the cooling 'half life' (time to cool from 600 °C to 430 °C) is assumed to be 10 s. This cooling rate has been experimentally determined for a location 2 mm from the side of the mould. Having cooled to within 1 °C of 260 °C, the glass is then annealed at 260 °C for 2 h.

Second, we consider a typical thermal cycle for casting a preform, annealing, and then drawing into a fibre. The cycle now contains an additional section, corresponding to the fibre drawing. Using the geometry of the neck down, Rosman [5] calculated the change in viscosity of the glass during his draw, and showed that log(viscosity) decreased linearly with time, reaching a minimum viscosity of $10^{6.5}$ P. The Cohen–Grest model, with parameters determined by Jha and Parker [4], shows that log(viscosity) is approximately linear against temperature in the range 260–330 °C. Thus, it was concluded that a typical thermal cycle for fibre drawing comprises a linear increase in temperature from the annealing temperature (260 °C) to a maximum of 317.4 °C after 8 min. Since tension is proportional to both viscosity and draw speed, other drawing conditions were derived by varying time and temperature while maintaining constant tension.

The computer simulation has been implemented by taking a large set of small time segments. For each time segment, the number of nuclei produced is calculated, with temperature being determined according to the chosen thermal cycle. The accumulated growth of the nuclei is then calculated for each remaining time segment. For example, if the thermal cycle runs from time t_0 to t_1, a nucleus formed at time t_i grows in each of the time segments between t_i and t_1.

Table 3
Parameters used in eq. (3) to calculate the crystal growth rate

	P ($\mu m\ s^{-1}\ K^{-2}$)	$\Delta S/R$	T_m (K)	G (K)	J (K)	M (K)
NRL	6×10^{-4} [a]	5	850 [b]	110	632	1.2
Jha and Parker	same	same	same	388.7	588.3	3.6

[a] Altered from the published value of 0.42 $\mu m^3\ s^{-1}\ K^{-2}$ in order to obtain graphs similar to those in ref. [2].
[b] No value was quoted, so 850 K was chosen in order to obtain graphs similar to those in ref. [2].

4. Results

Given the four alternative models of nucleation (fig. 1(a)), and three alternative models for crystal growth (fig. 1(b)), we have twelve ways in which the TTT curves might be derived. Each of these combinations has been plotted, and a large discrepancy was found between TTT curves derived using Schneider and Staudt's model of nucleation and those using any of the NRL nucleation models. The biggest discrepancy occurred when the 'NRL lower' parameters were used, and the smallest discrepancy when Drehman's parameters were used.

Figure 2 shows TTT curves derived from Schneider and Staudt's nucleation and growth models, and those derived from the 'NRL upper' model of nucleation with the NRL growth model. A comparison of these two families of curves is particularly informative since the nucleation rate and growth rate vary over a similar range. This similarity suggests that the differences between the two families of TTT curves have arisen from the reduced degree of overlap of the nucleation and growth curves in the case of the NRL model. Crystallisation is dramatically retarded in the NRL model, in accord with their conclusion that ZBLAN glasses are inherently more stable than previously thought. Their model shows crystallisation to be most rapid at around 330 °C, compared with 370 °C in Schneider and Staudt's model.

Figure 3 shows the crystal size distributions that are predicted from Schneider and Staudt's models of nucleation and growth. The ordinate

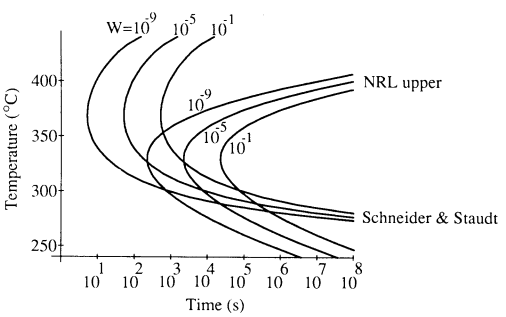

Fig. 2. Isothermal TTT curves.

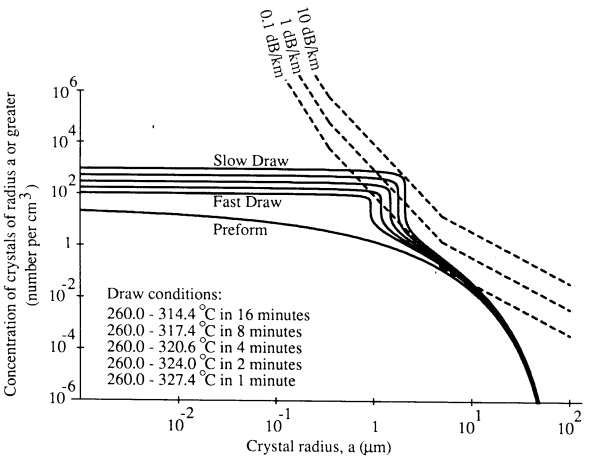

Fig. 3. Predicted crystal size distributions.

axis of the distributions shows the number of crystals per unit volume whose size is *at least* that of the corresponding abscissa value. This representation overcomes the difficulties associated with representing size distributions with a logarithmic size axis.

5. Discussion

The size distributions show that for typical thermal histories, it is reasonable to expect to find a few hundred crystals per cm^3 of size greater than 1 μm in a drawn fibre. If Schneider and Staudt's data are assumed to have been gathered for homogeneous nucleation, then such particles are an inevitable result of the processing of the glass, and are not necessarily caused by impurities. The effects of particles on scattering losses in optical fibres can be estimated using the expressions provided by Hattori et al. [6]:

$$\text{loss (dB km}^{-1}) = k_1 c(a^6/\lambda^4) \quad \text{for small } a; \quad (5)$$

$$\text{loss (dB km}^{-1}) = k_2 c(a^4/\lambda^2)$$

$$\text{for intermediate } a; \quad (6)$$

$$\text{loss (dB km}^{-1}) = k_3 c a^2, \quad \text{for large } a, \quad (7)$$

where k_1, k_2, k_3 are constants for a particular glass, a is crystal size (μm), c is crystal concentration (cm^{-3}) and λ is the wavelength (μm) of the

light. Assuming that the crystals are ZrF_4 and that the ratio of refractive index of the crystals to that of the glass is 1.052 [6], the following values were derived for the constants: $k_1 = 0.364$; $k_2 = 6.86 \times 10^{-3}$; $k_3 = 2.7 \times 10^{-2}$.

Using equations (5)–(7) contours of equal scattering loss have been superimposed on the crystal size distributions. Where a contour just touches the step of a distribution, the contour provides an estimate of the anticipated fibre loss. For the drawing conditions considered, fibre losses of between 0.1 and 10 dB/km are predicted. Crystals of intermediate size are the dominant scatterers (eq. (6)), except in the lowest loss fibre, where larger crystals (which are present in the preform) become dominant. Alterations to the time and temperature of drawing alter the step of the distribution curve for the fibre, thereby substantially changing the predicted losses. The predicted losses are lowest for a fast hot draw and highest for a slow cooler draw. The losses are greater than those anticipated by Lu et al. [2]. However, there are several differences between our calculations and theirs. First, the work presented here was based on Schneider and Staudt's models rather than NRL's. Second, we assume exponential cooling of the melt, whereas Lu et al. assume linear cooling. Finally, Lu et al. have not introduced the effects of fibre drawing, although we have shown that the predicted fibre losses are critically dependent on the drawing process.

6. Conclusions

It has been shown that there are substantial discrepancies between previously published models of crystal nucleation and growth in ZBLAN glasses. These discrepancies may be due to unknown amounts of impurities, which give rise to heterogeneous nucleation. The small temperature range over which the processes of nucleation and growth overlap according to the NRL models has led the NRL workers to predict a high degree of stability for these glasses. However, the models of Schneider and Staudt are based upon less scattered data and therefore we have used these models to predict crystal size distributions. We consider the size distributions to be interesting in their own right, since they offer an insight into the statistics of fibre losses. Crystal size distributions, and therefore fibre losses, have been shown to be sensitive to thermal processing. This sensitivity is particularly apparent during the drawing process. Consequently, close control of the temperature and time of fibre drawing is likely to be critical to the future production of low loss fibres. A fast hot draw has been shown to produce lower scattering losses than a slower cooler draw.

For the drawing conditions considered here, it is shown that a minimum signal loss in the range 0.1–10 dB/km at wavelength 2.55 μm is predicted. These figures coincide with the best experimental fibres that have been produced to date (see, for example, refs. [7,8]), but a proper comparison requires precise details of the thermal histories of the experimental fibres. Discrepancies between predicted and experimentally determined losses can occur either because of the effects of heterogeneous nucleation on Schneider and Staudt's model, or because of its effects on experimental fibres. A further consideration is that the current paper predicts the loss per km for a long fibre, whereas measured losses are often quoted for selected fibre lengths of 200 m or less. As the most significant scattering particles number only a few hundred per cm^3 (or fewer when large crystals dominate), selectively testing short lengths of fibre may show misleadingly low loss measurements.

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