THE PRODUCTION AND TRANSMISSION CHARACTERISTICS
OF LOW-LOSS OPTICAL FIBRE WAVEGUIDES

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THE PRODUCTION AND TRANSMISSION CHARACTERISTICS OF LOW-LOSS OPTICAL FIBRE WAVEGUIDES

by David Neil Payne

A study is made of both the manufacture and the characteristics of low-loss cladded optical fibres for use in the telecommunications network. A description is given of the evolution of the fibre drawing technology and of the development of several types of low-loss fibre. These include fibres having core materials composed of commercially-available compound glasses, a specially-produced high-purity lead glass, an organic liquid and a vapour-deposited phosphosilicate glass. Attenuation figures range from 150dB/km to 1dB/km respectively.

The propagation characteristics of the fibres are considered and it is shown that partial excitation of multimode step-index waveguides is both advantageous and practicable. Particular emphasis is placed on an investigation of the effect on pulse dispersion of preferential mode filtering and mode conversion.

The thesis includes three new measurement techniques for the characterisation of optical fibres. The first is a method for the determination of the material dispersion in phosphosilicate glass over a wide wavelength range. Resulting from the measurement it is shown that a wavelength region exists in phosphosilicate fibres where the material dispersion is zero and the loss is small. It is suggested that operation at this wavelength would be preferable to that currently envisaged for optical communications.

The second is a means for evaluating the waveguide parameters of a single-mode fibre. The method relies on observations of the far-field radiation pattern and permits the simultaneous measurement of both core diameter and refractive-index difference.
The third is a near-field scanning technique for assessment of the profile of graded-index fibres. The near-field intensity distribution of the fibre is plotted and a correction applied to yield the refractive index profile. A study of leaky modes in graded-index fibres furnishes the required correction.
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It is inconceivable that the work would have even started without the help of Mr. R. Came, of the mechanical workshop. He has the uncanny ability to convert my half-formed ideas and an incomprehensible sketch into a precision-dowelled, stainless-steel distillation of my requirement. His scorn at subsequent modifications has convinced me of the wisdom of clear experimental planning.

Mrs. Jan Ditchfield has contributed both to the thesis and to the publications by her painstaking preparation of the manuscripts. There have been times when her assistance has stopped only just short of actually writing the text. In addition, her wrath has taught me that two drafts of a manuscript are sufficient, even for the most meticulous of authors.

Lastly, I would like to acknowledge the substantial assistance of my wife, Linda, in the completion of the thesis. Her departure for the U.S.A. for four months and the vacuum this has created has finally persuaded me to write this long-overdue dissertation.
Notes on the text:

i) References are numbered consecutively and listed at the end of each chapter.

ii) Relevant publications are bound at the end of each chapter. As an aid to the reader the appropriate publication number is given in brackets after the title of the subsection in which it is introduced. Publications within each chapter are numbered consecutively and are preceded by the letter P and the chapter number.

iii) A publications index giving the thesis numbering may be found after the conclusions.

iv) Figures are given at the end of each chapter.

v) Page numbering is confined to the text only. The page numbers found on the publications are those of the source journal, and should be ignored.
INTRODUCTION
Fibre optical communications and the allied field of optical electronics is expected to have a technological impact similar to those of the transistor and, more recently, the integrated circuit. The work reported in this thesis charts the progress of the new technology, from shortly after its speculative inception with the classic paper of Kao and Hockham to its present prominence. The publications which are included in the text cover the period August 1971 to August 1976, a period which has seen the growth of published work from an unsteady trickle to an overwhelming avalanche. The present work, therefore, has both a scientific and a historical interest in that it traces the emergence of what is undoubtedly one of the major technologies of the 1970's.

If it is not too immodest a claim, the work presented here has played a not inconsiderable part in the advancement of fibre communications. Milestones which may be found in the text, but which are particularly worthy of recall are:-

1) The first demonstration of precision fibre drawing and the achievement of fibre losses similar to those of the bulk glass (1970).

2) The development of a novel, low-loss liquid-core fibre based on a high-loss, compound-glass cladding filled with hexachloro-buta-1,3-diene. The fibre for some time claimed the lowest loss recorded and remains the lowest loss liquid-core fibre ever produced (1972).

3) The realisation that partial excitation can lead to high bandwidth in multimode step-index fibre waveguides. The first theory of pulse dispersion in multimode fibres was evolved to describe the effect (1972).

4) The observation and characterisation of 'microbending' in optical fibres. The effect is now recognised as having critical importance in the cabling of optical fibres (1972).

5) The first public demonstration by the British Broadcasting Corporation of a live colour television programme transmitted over 1.25km of liquid-core optical fibre. The quality of the signal broadcast and received throughout the United Kingdom was indistinguishable from a normal transmission (January 1973).
6) The development of the homogeneous chemical vapour deposition technique for fibre production. This was accompanied by the discovery of a new material, phosphosilicate glass, for the fabrication of ultra-low-loss, silica-based waveguides. The technique of fibre fabrication has subsequently been adopted worldwide, while the phosphosilicate material has since been used with outstanding success by both Japanese and American laboratories (1974).

7) A proposal to shift the operational wavelength for a fibre communication system from the present-day 0.9 µm, to 1.3 µm. With the discovery of the phosphosilicate fibre came the demonstration of both the advantages in terms of channel bandwidth and the technical feasibility of the change. The impact of this radical proposal has yet to be fully felt, but existing work on phosphosilicate fibres in other laboratories confirms that a major change of emphasis may well result in the near future (1975).

8) The discovery of three techniques for the characterisation of step-index, graded-index and single-mode fibres. These enable the determination of
   i) the chromatic dispersion of the waveguide material over a wide wavelength range;
   ii) the refractive-index profile of graded-index fibres from a near-field scan;
   iii) the simultaneous measurement of the propagation parameters of a single-mode fibre from a single observation of the far-field intensity distribution.

The thesis is divided into three Sections, covering fibre fabrication, optical propagation studies and graded-index fibres. Although there is considerable overlap between the Sections, the work within each is presented in chronological order. The Sections are inter-related in that the first Section details the manufacture of a particular fibre, while the remaining two are concerned with its evaluation.

Section I describes fibre fabrication. It begins with the production of fibres having a loss of 1 dB per metre and traces the progress to the present day attenuation figure of 1 dB per kilometre. In order of attenuation, the investigation covers (a) fibres made from commercial compound glasses, (b) fibres made from
high-purity preforms provided by Sheffield University, (c) liquid-core fibres and (d) phosphosilicate fibres made by homogeneous chemical vapour deposition.

Section II is devoted to an investigation of the propagation characteristics of the various fibres described in Section I. A simple ray model is developed to account for the observed dependence of pulse dispersion on launching conditions. Comparison with experiment reveals good agreement for all but the lowest-order modes. Departures from the simple theory caused by mode coupling and differential modal attenuation are investigated, leading to a theory modified to include the latter effect. A comprehensive study of mode coupling follows, culminating in the development of a method for measuring the degree of coupling which exists in a step-index waveguide. It is shown that the intrinsic mode scattering present in our fibres is negligible; the small amount normally found is induced by external stress. The Section ends with a description of the most recent work on single-mode fibres.

Finally, Section III describes a simple and rapid method for determining the refractive-index profile of an optical fibre by observation of the near-field intensity distribution. It is shown that in many cases the presence of tunnelling leaky modes is unavoidable and that these cause an error in the measurement. A study of leaky modes shows that their existence accounts for several other inconsistencies previously encountered in measurements on graded-index fibres. A correction factor is developed which permits accurate observations to be made.

The thesis consists of both explanatory text and published papers. The text is intended to provide a review of the published work and to relate it to more recent results. The appropriate publications are collected at the end of each chapter and it is suggested that they are read in conjunction with the text, rather than after it.

References
SECTION I

FIBRE PRODUCTION
CHAPTER 1

THE DEVELOPMENT OF A FIBRE-FABRICATION FACILITY

1.1 The Fibre-Drawing Machine (P1.2, P3.5)

In early 1968, at the commencement of the work to be described, very little expertise was available in optical fibre production, much less in production of optical fibres for communications purposes. As in most budding technologies, the manufacturing process was shrouded in mystery, and was generally thought to be an art rather than a science. Thus it was accepted that optical glasses which were known to have bulk losses of around 1000dB/km would inevitably give an attenuation of 1000dB/km when pulled into a cladded-glass lightguide. It was clear, therefore, that if optical-fibre communication was to become a reality a careful, investigative study of the fibre drawing process would be necessary in order to determine the origin of this, so-called, 'excess loss'. It is instructive to note that despite the almost unbelievable attenuation figure of 0.47dB/km\(^1\) now achieved in communication lightguides, the attenuation of commercially-available fibre bundles has remained almost unchanged at 1dB/km; this loss is apparently acceptable for most simple 'light pipe' applications.

The initial objective, therefore, was to design and construct a precision fibre-drawing machine specifically for research into the fibre fabrication process. Additional work was initiated\(^2\) to determine the losses of commercially-available bulk glasses, and it was hoped eventually to produce fibres of a similar attenuation, that is in the region of 100dB/km. Although it was accepted that this figure was too high for optical communications to be a viable proposition, it was clear that its achievement would provide impetus for the development of glass of higher purity. In retrospect the objective of 100dB/km appears trivial, however the excitement generated by our eventual achievement of first 400dB/km and then 150dB/km is an indication of the magnitude of the task at that time.

Faced with a total lack of expertise in both glass technology and fibre optics, it was decided that the only logical design strategy for the fibre-drawing machine was one of precision. For example, the accuracy that would be required for the fibre pulling
speed was unknown, so it was decided to make it as constant as could reasonably be achieved. This policy was followed for all major components of the machine and some care was taken to ensure stability and vibration-free operation. The rod and tube method of manufacture was chosen after some consideration of the alternative concentric crucible method. The decision was made on the basis of cost, simplicity and versatility. The concentric crucible approach whereby molten glass is drawn from two coaxial nozzles has several attractions, not least of which is its continuous production capability; however the merits of our decision will become apparent in the chapter on silica-based fibres. A brief description of the machine follows.

As shown in Fig.1.1, the machine consists of two vertical bars to which all units are clamped, enabling removal or adjustment of any unit. The cleaned and concentrically-assembled rod and tube are clamped in a gimbaled chuck which, together with the centering iris diaphragm at the top of the furnace, allows for slight bends in the preform. The assembly is mounted on a crosshead and smoothly lowered into the furnace at a predetermined rate by a vertically-mounted lead screw. The feed rate is adjustable both by means of a system of belts and pulleys, and by an electronic speed controller. The glass softens within the furnace and tapers into a filament whose diameter is a function of the ratio of the preform feed rate to the fibre-drawing speed. The fibre passes over a graphite guide onto an accurately-machined speed-controlled aluminium drum at the base of the machine. The drum is traversed slowly sideways to ensure that the fibre is wound in a mono-layer, one layer having a length of \( \sim 3 \) km. The pulling speed is variable between 0 and 10 metres per second. Means is provided to electronically lock the pulling speed and feed rate together, thereby causing the rates to vary in a predetermined ratio and the fibre diameter to remain substantially unchanged as the pulling speed is increased. The stability of both speeds is better than 0.1%.

It was appreciated from the outset that the degree of fluctuation in fibre diameter would be largely determined by the accuracy with which the furnace temperature could be controlled. The furnace construction is sketched in Fig.1.5. The design was chosen to have a low thermal inertia to allow rapid temperature changes to be made. The heating element is based on a spiral-
cut alumina tube into which a multi-tapped platinum wire element is cemented. Each of the taps is brought out to a terminal board so that experiments can be made to determine the optimum length of the hot zone. Other novel features are the use of iris diaphragms at both input and output ends of the furnace, as well as a thermocouple whose position may be adjusted within the hot zone so as to monitor and control a given region of the softened preform. The upper iris diaphragm has the dual role of centering the preform within the furnace and of excluding convection air currents. The presence of turbulent air flow through the furnace was found to be a major cause of fibre diameter fluctuations.

Further details of the fibre-drawing machine may be found in publication P1.2 and P3.5. A measure of the success of the design may be gained by noting that both machine and furnace are today operating substantially unchanged from the original concept. The versatility of the machine has been shown by the production of various fibres including liquid-core, single-material and silica-based waveguides. The latter has required the addition of a graphite furnace (publication P3.1) in order to achieve the necessary pulling temperature of 2000°C. The design of this furnace has drawn heavily on the experience gained with the earlier experimental furnace.

A further indication of the performance of the machine is given by the adoption of the design by two major industrial concerns, one in the United Kingdom and one in North America. Moreover, it is gratifying to have been consulted by long-established glass manufacturers on the production of precision glass fibres for use in mechanical engineering.

1.2 Fibres Produced from Optical Glasses (P1.1, P1.2)

After the construction of the fibre-drawing machine, a systematic investigation was made of the origins of the high fibre losses which had been previously observed. It had now been established\(^2\) that the lowest-loss commercial glasses available were Schott F7, a lead-based optical glass, for the core and Chance-Pilkington ME1 tubing for the cladding. Fortunately, this combination proved compatible both thermally and mechanically, and so it was used exclusively. A scanning-electron micrograph of a typical fibre is shown in Fig.1.2.
Publications P1.1 and P1.2 at the end of this chapter give details of the results obtained. We were able to show that the high losses associated with commercial fibres were largely a result of core/cladding interface imperfections and that with care a loss of 300dB/km could be routinely achieved. This was brought about by:-

a) Elimination of impurities on the surfaces of both rod and tube by a cleaning procedure which involved degreasing and hydrofluoric acid etching, followed by vapour drying in isopropyl alcohol.

b) Degassing of the surfaces at high temperature so as to avoid interfacial bubble inclusions.

c) The evolution of a novel technique which allowed fire-polishing of the surfaces before they fused. This was accomplished by using a loose-fitting 5mm F7 rod centered within a 12mm bore ME1 tube. The core and cladding then taper separately and fusion between the two glasses is delayed to a point where the preform has virtually attenuated into a fibre. Both surfaces are then smoothed by viscous flow induced by surface-tension forces.

The final elimination of the excess fibre loss was achieved by heat treatment of the fibre, as described in detail in the following publications P1.1 and P1.2 (note that the captions to figs 2 and 3 are reversed in P1.1). After extensive trials had failed to reduce the fibre loss below 300dB/km, it was reasoned that the only remaining possibility lay in the difference in thermal history of the core glass in bulk and in fibre form. The exact mechanism involved in the dramatic reduction to 150dB/km which followed is not fully understood, although a tentative explanation is given in the publications. It is interesting to observe however that recently it has been further recognised that the properties of a glass in its chilled fibre state may be radically different from those in its annealed bulk condition.

1.3 Fibres Produced from High-purity Compound Glass (P1.2)

We had succeeded in developing a fibre-drawing technique which did not result in an increase in attenuation over that observed in the bulk glass. This was put to the test when preforms of high-purity glass became available from the University of Sheffield. The preforms were in the form of a high-lead-content core glass sheathed with a borosilicate composition. The glasses
were chosen to provide a large refractive index difference and thus a high numerical aperture. The drawing of these preforms into fibre proved a severe test of the fibre drawing machine capabilities as they were of small diameter (approximately 2mm), were often far from straight, and had a low softening point. However 500 metres of good quality fibre were obtained from each preform, and a typical attenuation result is given in Fig.1.4.

Unfortunately heat treatment of those fibres did not produce as dramatic a reduction in attenuation as had been experienced with the F7/Me1 combination. Nevertheless, at the culmination of the cooperative programme a very acceptable loss figure of 35dB/km had been achieved at a wavelength of 850nm, as shown in Fig.1.4. The insistence on a high fibre numerical aperture by the contractors supporting the work without doubt prevented further improvements in the fibre attenuation. A high numerical aperture (0.68) requires a core glass having a large refractive index. High-lead content (40m/o) glasses must be used and these have increased intrinsic absorption and scattering losses. It may be observed that present-day ultra-low-loss fibres all have a numerical aperture lower than 0.2. The attenuation of 35dB/km represents the lowest reported for a fibre having so high a numerical aperture.

1.4 Discussion

The value of the precision fibre drawing machine and the techniques learned in these early experiments cannot be overstated. They form the groundwork on which all our subsequent activities in fibre technology have been based. The equipment has been extensively used in the later development of both liquid-core and silica fibres. Furthermore, the understanding of the surface smoothing which occurs during fibre drawing and the fundamental stability of the fibre drawing process led to a greater insight into the accompanying work on optical propagation. It is, after all, the viscous nature of softened glass and the ease with which it can be drawn into a smooth fibre devoid of all rapid variations along its length which is the raison d'être of optical communications. Fortunately an early paper\textsuperscript{7} which implied that fibre attenuation would be limited by the existence of such imperfections did not prove too discouraging!

Although not described here, the construction of the fibre-drawing machine was accompanied by the development of measurement
techniques for the determination of fibre spectral attenuation, numerical aperture, diameter and scatter loss.

References


FIG. 1.1  THE FIBRE DRAWING MACHINE
FIG. 1.2 Broken end of ME1/F7 fibre
Diameter 95 μm
FIG. 1.3 THE PLATINUM-WOUND FURNACE
FIG. 1.4 Spectral attenuation of fibre drawn from preforms supplied by Sheffield University
RELAXATION PROCESSES IN GLASSES
AS SHOWN BY OPTICAL ATTENUATION EXPERIMENTS

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Some optical attenuation experiments on both bulk glasses and cladded glass fibres (fibre optics) are described. They reveal the presence of relaxation processes in the glass in its transformation range.

The basic loss mechanisms giving rise to optical attenuation in glasses are not yet completely understood, but their basic features are well accounted for. In recent years, great strides have been made in the development of low-loss glasses. The result is the availability of glasses of exceptional purity (less than 1 ppm impurities). The resulting contribution to glass science can be very significant in the near future, quite apart from the immediate applications in optical communication systems.

Normal commercial glasses have attenuation losses of greater than 10 000 dB/km within the visible spectrum [1]. As a point of reference, 200 dB/km is approximately equivalent to a 1% transmission loss in a 25 cm length specimen. This type of high-loss glass, when used as the cladding, contributes only a small amount to the total loss of multimode fibre optics. For example ME1 glass (Chance Pilkington) used as a cladding contributes 1–20 dB/km to the fibre loss, in spite of having a bulk attenuation of 3000 dB/km. Imperfections such as bubbles and foreign particles, even in small amounts, produce very large losses. For instance 1 ppm of platinum particles with 1 μm size gives a loss of 900 dB/km. Consequently, such imperfections must be reduced to a very low level, in the cladding glass and particularly in the glass core. Inhomogeneity in the boundary between the cladding and the core, and bending of the fibre can contribute an attenuation of about 1–2 dB/km. The major limiting sources of attenuation loss are therefore scattering by the glass and absorption by impurities. Measurement of the angular distribution and the wavelength dependence shows that the scattering is close to Rayleigh in form. For example in both Schott F-7 bulk glass and fibres drawn with an F7 core and Chance–Pilkington cladding, the scattered light [2] has a $\lambda^{-n}$ dependence (where $n = 4.1$ for fibre and 4.4 for the

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bulk glass), with the bulk glass having the lower loss. Because of the strong wavelength dependence the scattering loss is high at the ultraviolet wavelengths but falls rapidly through the visible region to a level of only a few dB/km in the near infrared at 0.9 μm which is the wavelength of interest for optical communications. The Rayleigh scattering loss is a function of the glass composition, but it is in the order of less than 40 dB/km at wavelengths greater than 600 nm. Lead glasses have a slightly higher Rayleigh scattering loss than soda-lime silicates, and fused silica has the lowest Rayleigh scattering loss. By and large, the absorption loss due to impurities assumes the predominant portion of the total optical attenuation loss except in the best available silica. As a rule of thumb, impurity contribution to the loss is very roughly 10 dB/km per 1 ppm but depends very much on the type and oxidation state of the impurity. Consequently, the elimination of impurities from the glass is a prerequisite for achieving low attenuation loss.

In the last two years, the lowest attenuation losses in glasses have been decreased from a level of 200 dB/km to a level of 20 dB/km [3]. In the particular case of doped silica fibres attenuations as low as 4 dB/km have been achieved [4]. Thus new standards of purity of glass and silica are attainable and thus the new data on optical attenuation in glasses are relevant to all glass scientists.

At the University of Southampton, techniques and equipment have been developed for investigations of optical scattering [2, 5] and optical absorption loss [6, 7]. Extensive measurements have been made on bulk glass specimens [8] (up to 30 cm length) and on cladded glass fibres [9] (up to 1 km length). In the following, several sets of experimental data, pertaining to the effect of heat treatment, are described which allow comparisons between bulk glass specimens and cladded glass fibres and which are very illuminating. The fibres were drawn using the rod-and-tube technique in an equipment [9] having a high degree of control over the furnace temperature and the pulling speed. The resulting dimensional accuracy is such that the overall diameter [10] varies by less than 1 μm in several hundred metres.

In fig. 1, optical attenuation loss curves, for the wavelength range 0.5 to 1.0 μm, of Schott F-7 bulk glass first in the form of a redrawn sample as supplied, and then after heat treatment, are presented. The heat treatment consisted of holding the glass specimen for 4 h at 450°C and cooling it to room temperature over a period of 12 h. This heat treatment produced an overall lowering of the attenuation loss by the amount of 60 dB/km. In fig. 2 [9], optical attenuation loss curves of cladded glass fibre (Schott F-7 glass core with ME-1 cladding) are presented. In this case the heat treatment consisted of a constant temperature soak at 460°C for 2½ h followed by a natural furnace cool at the rate of 60°C/h. Again, the heat treatment reduced the attenuation loss over the whole wavelength range by a uniform amount of 150 dB/km. Moreover, in fig. 2, the attenuation loss curve of an annealed bulk F-7 glass rod is also shown and is in close agreement with that of the heat-treated fibre. This seems to indicate that it is possible to make fibres with the same loss as that of the starting glass, using the rod-and-tube technique. These data show that relaxation processes occur in the glass during the heat treatment process.
Fig. 1. Total optical attenuation loss as a function of wavelength for Schott F-7 glass rods before and after heat treatment. Each curve is the average of three separate measurements on a double-beam spectrophotometer with repolishing of end surfaces to avoid errors due to differing end losses (after Dakin and Gambling [10]).

Experiments have also been conducted on cladded glass fibres and the attenuation loss was measured during the heat treatment. Detailed discussion of these experiments will be reported in a future publication [11]. A representative curve is presented here in fig. 3. The cladded glass fibre used consisted of an 80 μm diameter special lead glass core with a borosilicate glass cladding, supplied by the University of Sheffield. The data were taken at a wavelength of 600 nm where the attenuation loss of the cladded fibre prior to heat treatment was 220 dB/km. The furnace temperature was maintained at 340°C. The cladded fibre, having a total length of 20.7 m
Fig. 2. Optical attenuation losses as a function of wavelength for a cladded glass fibre before and after heat treatment. The core was Schott F-7 glass and the cladding was Chance-Pilkington ME-1 glass (after Payne and Gambling [11]). A curve for bulk F-7 glass is also included.

Fig. 3. The change in optical attenuation loss at 600 nm as a function of soaking time at 340°C for a 20.7 m length, cladded glass fibre. Core and cladding glasses are from special melts supplied by the University of Sheffield (after Payne and Gambling [11]).
was wound on a 11 cm diameter pyrex pipe, and 90% of the fibre length was placed inside the furnace. The time duration of the heat treatment was counted from the time of its insertion into the furnace. The curve in fig. 3 can be divided into three segments. The first segment is the result of the rise in temperature which always increased the attenuation loss. The second segment is the result of heat treatment which decreased the loss. The combination of these two effects produces the first maximum in the attenuation loss. Because such combinations are complex in nature, the increase in attenuation loss at the maximum does not have a simple functional temperature dependence. However, higher heat-treating temperatures produce greater increases in attenuation loss. An independent experiment with the same clad glass fibre produced a decrease of 16 dB/km when it was placed in liquid N₂ bath, while heating to 340°C produced an increase of 40 dB/km [11]. Referring again to the experiment described by fig. 3, when the attenuation loss value appeared to reach a plateau in the second segment, the fibre was taken out of the furnace. Its attenuation loss in this third segment is the result of cooling, which always decreased the attenuation loss.

The amount of decrease in attenuation loss through cooling was of the same order of magnitude as the amount of increase through heating, but they have no direct correlation. All the heat treatment experiments were conducted thus far only on clad glass fibres after their being formed in the fibre-pulling apparatus. Experiments have been done to establish whether or not these heat treatment effects are repeatable, and these show that the second section of the curve is not reversible.

Analysis of a number of heat-treatment curves such as that shown in fig. 3 reveals that none of the time segments can be fitted to any simple exponential function or diffusional type of $t^{1/2}$ functional dependence. Each segment appears to be complex in nature, and can only be fitted by superposition of functions. With cognisance of the lack of physical reality for the ‘relaxation time’ $\tau$ given in the fitted exponential functions, as indicated in the preceding paper by Douglas [12], it is nevertheless interesting to mention that the ‘relaxation time’ $\tau$ values, obtained from curves such as fig. 3, were of the order of the order of 100 sec. Such values are considerably shorter than the usual relaxation times for this temperature range.

In summary, this paper shows how optical attenuation loss data can give an interesting insight into the fundamental properties of glass and the use of fibres enables extinction coefficients to be measured which are too small to be measured in bulk glass. In particular, heat treatment data of the type shown here provide an interesting method of studying relaxation processes in glass.

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References

The preparation of multimode glass- and liquid-core optical fibres

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A preform technique for drawing cladded-glass and hollow fibres suitable for application to optical communications is described. The parameters which need to be controlled are discussed and the preparation of the preforms is described. The resulting fibres have a high geometric uniformity and a probe beam remains largely at the same angle to the axis after more than $10^4$ reflections at the core/cladding interface. Fibre attenuations of 150, 60 and 5.8 dB km$^{-1}$ have been obtained with commercial glasses, preforms made from a special melt at Sheffield University [5], and a commercial liquid, respectively. The fibre drawing process does not appear to introduce any additional impurities and heat treatment has produced a significant reduction of transmission loss in glass fibres.

1. Introduction
The techniques for making fibres for optical communications can be divided into two broad classifications, namely those involving drawing directly from a melt and those in which the draw takes place from solid material in the form of a preform. The classical melt-type process is the concentric-crucible technique in which the inner crucible container is fed with the core glass and the outer one with cladding material. The method has the advantage of obviating the need for machining or polishing of the starting materials and thus avoids the possible introduction of impurities which could result from these processes. In addition, preforms for single-mode fibres are difficult to prepare. On the other hand instabilities can occur if care is not taken and the melt levels in the crucibles should ideally be kept reasonably constant. Thus the rate of introduction of new material must be well controlled and this is sometimes done by feeding in from preforms, thus depriving the method of one of its potential advantages. There is also the problem of avoiding the introduction of impurities from the crucible, particularly as the interface surfaces flow over both sides of the inner orifice. The technique is even more difficult to apply to silica fibres and tubes due to the high temperature involved and the necessity to avoid most transition metal impurities since these can give rise to a high transmission loss in the wavelength region of interest.

The preform methods include the rod-and-tube and early Selcloc [1] techniques and drawing from composite rods which themselves can be drawn directly from a two-layer melt. The two latter techniques involve fairly straightforward fibre-pulling which is discussed below but the rod-and-tube combination also involves machining or
re-drawing the two glasses into suitable shapes and sizes. Such operations can, in principle, introduce additional impurities over and above those already present in the bulk starting glasses but in practice any such contamination can be removed by suitable cleaning and etching. The length of fibre which can be drawn in one continuous length is limited by the length and diameter of the preform thereby resulting in a batch process. However, several kilometres of 100 μm fibre can be obtained from a preform 50 cm long and 1 cm diameter and this is likely to be adequate in practice. The advantages of the rod-and-tube method are its great versatility in allowing a wide range of fibre diameters and glass compositions to be used and the high degree of precision which can be achieved. It is more difficult to apply to single-mode fibres than to multimode ones because of the necessity to drill (and clean) long narrow holes in the tube material. The particular method to be used depends on the type of fibre to be produced, such as single-mode, multimode, graded index or liquid-core, and on the glass or glasses available. In this article the rod-and-tube method is discussed in detail and the results obtained are described.

2. Fibre-drawing machine
The method of making cladded fibres is to mount the rod-and-tube preform vertically in a gimballed chuck (to allow for slight bends in the tube) and to lower it slowly into a small resistance-heated furnace. The temperature is accurately controlled and is set at a value where both glass viscosities are below 10² poise. The fibre is drawn from the lower end of the furnace and is taken up on a precision-made aluminium winding drum of 1.3 m circumference having a smooth cylindrical surface accurately concentric with its axis of rotation. As the drum rotates it is traversed sideways so that the free drop of fibre remains vertical and lengths of several kilometres are wound in a single layer at speeds of several metres per second.

The equilibrium fibre diameter is determined only by the ratio of the preform feed rate to the fibre pulling speed. In order to maintain a fixed diameter over the full range of pulling speeds an electrical control circuit is used automatically to keep the ratio constant. The maximum pulling speed is governed by the glass viscosity, and therefore by the furnace temperature, since the fibre will obviously break when the tension becomes too high. In practice a careful selection of furnace temperature has to be made in order to achieve good fibre quality and a reasonable pulling speed. Changes or fluctuations in pulling speed and furnace temperature cause transient excursions from the equilibrium diameter (as set by the ratio of preform speed to drum speed). Unwanted fluctuations can be eliminated by suitable furnace design and accurate control. In our case the furnace temperature is constant to 0.1°C and the pulling speed to better than 0.1%.

A wide range of fibres has been produced limited only by the maximum furnace temperature of 1500°C and the availability of suitable preforms. Fibres with overall diameters between 20 and 500 μm, and core diameters between 0.5 and 450 μm, have been made using mainly Schott F7 glass as core material. The range of cladding materials has included Pilkington PWL84 and ME1, Pyrex, soda glass and Schott LF5. The machine has also been used to redraw F7 rod for making preforms. The overall diameter is monitored continuously by projecting a shadow of the fibre on a slit and
measuring the amount of transmitted light. Over lengths of a few hundred metres the
diameter varies by less than 1 μm and is generally due to taper in the preform. A typical
150 μm fibre taper is ± 2 μm over 1 km and could easily be corrected for during pulling,
if necessary, by introducing a control system to vary the ratio of drum to preform speed.
The circularity and concentricity of core and cladding are also excellent.

During the pulling process it is possible for the more volatile of the glass components
to be evaporated in the hot zone of the furnace and to condense on the cooler glass
higher up in the preform. This sometimes shows up as a white deposit on the boule
remaining at the end of the pull. The interface is the part most badly affected by this
volatilization which results in a higher fibre attenuation. Care must therefore be taken
not to pull at too high a temperature which can also cause interdiffusion between the two
glasses. The amount of diffusion in our case is less than 1 μm as shown by the electron
micrograph in Fig. 1.

Degradation of the fibre can also arise due to devitrification but this can be minimized
by operating at a low temperature and designing the temperature profile so that the
fibre is cooled rapidly on leaving the hot zone.

Hollow fibres for the production of liquid-core fibres, require only a hollow tube
preform and in this case, for a given furnace temperature, there is a minimum pulling
speed below which the hole size falls to zero and a solid fibre results. Above this speed,
which depends on a number of factors including type of glass and dimensions of
preforms, the area of the fibre bore increases linearly with speed giving a gradually
increasing ratio of bore to overall diameter. This ratio is an important parameter and
can be optimized for minimum filling time as described in Appendix 1.
3. Preparation of preforms

Originally it was thought that in order to obtain a good interface between core and cladding which was smooth and free of scattering it would be necessary for the rod and inner tube surfaces to be highly polished. It seemed to the authors that this would be a very difficult condition to meet without introducing impurities at the interface. In fact the opposite approach has been taken of primarily ensuring cleanliness and, contrary to general belief, the surface finish of the preform interface is not important as each irregularity is smoothed by surface-tension-induced viscous flow and stretched by \( \sim 10^4 \) during the drawing process. By delaying the point of closure between core and cladding the surface tension smoothing effect may be increased resulting in an improved interface. For this reason and for ease of cleaning, as well as to avoid introducing scratches when making up the preform, a large gap is left between rod and tube. A suitable cleaning process has been evolved with various stages of detergent, solvent and acid soaks. This is followed by careful drying and baking to remove adsorbed gases. A similar process is carried out with tube preforms.

4. Results

4.1. Cladded-glass multimode fibres

We have pulled two main types of cladded fibre, namely those made from (i) commercially-available glass materials and (ii) preforms drawn from a special glass melt and supplied by the University of Sheffield [5]. In the former case a range of combinations has been investigated and the most interesting results have been obtained with F7 core glass and ME1 cladding. We have reduced the attenuation with this combination to 150 dB km\(^{-1}\) which is the lowest yet reported for commercially-available materials and we believe it to be limited by losses in the F7 starting material.

It is thought that this improvement has been brought about by paying attention to the following three factors in particular. Firstly, the high degree of stability in the drawing process and the prevention of gross defects such as air bubbles, has reduced scattering, particularly in the interface, to a very low level. Measurements have shown [2] that the total fibre scattering loss is less than 8 dB km\(^{-1}\) at 0.9 \(\mu\)m and is comparable with that in the bulk glass. Secondly, adequate cleaning has greatly reduced the amount of interface contamination. Thirdly, by drawing at a low temperature, volatilization of glass components and diffusion of impurities between core and cladding, and from the interface, has been minimized.

An attenuation curve for a fibre with a core of F7 is given in Fig. 2 and shows the typical characteristic of a broad minimum from 0.75 \(\mu\)m to longer wavelengths and a rise towards shorter wavelengths. Superimposed on this general shape are two peaks, a strong broad one centred at about 0.64 \(\mu\)m and a smaller one at 0.97 \(\mu\)m. The former is attributed to chromium ion impurity and the latter to the OH radical. Other common impurities which can be troublesome in glass are copper, iron, nickel, manganese and platinum and it is likely that a mixture of these, and others, gives rise to the broad minimum in the curves. The rise at short wavelengths may be due to the u.v. absorption edge arising from transitions associated with the Pb\(^{2+}\) ions in this lead-based glass, although a similar effect can be produced by Fe\(^{3+}\) ions. Using a Perkin-Elmer, type
The preparation of multimode glass- and liquid-core optical fibres

![Graph showing attenuation vs wavelength for F7 multimode fibre and bulk F7 glass.](image)

**Figure 2** Comparison of attenuation of F7 multimode fibre with that of bulk F7 glass. Curves (a), (b) and (c) are for the fibre with heat treatment at 460°C for (a) 0 h, (b) 2.5 h, (c) 8.5 h while the dashed curve is for bulk F7 glass.

![Graph showing attenuation of F2 glass over the wavelength range 0.34 to 0.56 μm.](image)

**Figure 3** Attenuation of F2 glass over the wavelength range 0.34 to 0.56 μm.

EPS-3T, spectrophotometer the measurements have been extended to a wavelength of 0.34 μm with a sample of Schott F2 glass, which is very similar to F7, as shown in Fig. 3. This result agrees closely with that obtained by Stroud [3] for a glass of composition Na₂O·SiO₂·2PbO and who claims that the short wavelength absorption is characteristic of the glass and not of impurities. Further, a similar rise is present in the Sheffield University glass which has been produced under pure conditions [5] and has a very low iron content.

As well as impurities the thermal history of a fibre can have an important influence on the attenuation as indicated in Fig. 2. The upper curve shows that when first drawn a particular fibre had a minimum attenuation of 300 dB km⁻¹ but after soaking for 2.5 h at a temperature of 460°C the attenuation fell to 150 dB km⁻¹. What is interesting is that more or less the same drop in attenuation of 150 dB km⁻¹ occurred over the
Figure 4 Change of attenuation at 0.8 μm for an F7 core fibre at a temperature of 460°C. The dashed curve is for a Sheffield University [5] fibre at 390°C and the time scale has been expanded by a factor of 10, i.e. the total time occupied by the dashed curve is 35 min.

The entire spectral range of 0.5 to 1.1 μm. Further heat treatment for another 6 h caused an increase in attenuation. Also shown in Fig. 2 is an absorption curve for the best sample of bulk F7 glass rod measured in these laboratories by J. P. Dakin [6], which coincides very closely with the best fibre curve.

Two conclusions can be drawn from this result. Firstly that it is possible to draw fibre with the same attenuation as the bulk glass from which it is made, implying in turn that the interface between core and cladding is good and that there is little diffusion of the lossy (in our case) cladding into the core. Secondly, since heat treatment does not affect the general shape, but mainly the level, of the attenuation curves that the similar variation in the corresponding curves for different samples of F7 glass* may be, in part, due to varying thermal histories. If this is so then it may be possible to obtain lower loss glass by more careful thermal processing.

We have investigated this effect further by monitoring continuously the attenuation of various fibres while they were undergoing treatment and a typical result is shown in Fig. 4. This shows that when a particular fibre with an F7 core was put in a furnace at 460°C the attenuation, measured at a wavelength of 0.8 μm, first increased by 30 dB km\(^{-1}\) over a period of 5 min, then fell by 100 dB km\(^{-1}\) over a further 30 min. The attenuation remained constant for a further hour or so and then gradually increased over a period of 6 h by 100 dB km\(^{-1}\). When, after a total period of 8 h, the test was terminated, the attenuation fell by 40 dB km\(^{-1}\). Experiments with a range of temperatures, times and fibres have shown that the initial increase in attenuation is reversible and corresponds to that recovered when the fibre is removed from the furnace. The intermediate change is irreversible and comprises initially a fall in attenuation followed by a subsequent rise. Obviously in order to obtain a minimum final fibre attenuation it is necessary to monitor the change in loss and to remove the fibre from the furnace after the appropriate interval. This has been done for the fibre represented by the dashed curve in Fig. 4.

*The fibre and bulk glass attenuations were measured by quite different techniques.
which again shows all the features described above but in this case the fibre was removed from the furnace before any appreciable permanent degradation was allowed to occur.

The three effects involved, namely the reversible increase in loss, the irreversible decrease and the irreversible increase in loss can be commented on as follows. The initial, relatively rapid and reversible, increase may be attributed simply to the change in temperature of the fibre which causes a broadening, and an increase in intensity, of the absorption bands of the impurity ions [4]. This will cause an increase in attenuation if the u.v. and infra-red bands are broadened towards the visible and also if the 'background' loss is due to a mixture of impurities. The reverse effect has been observed by cooling the fibre to liquid nitrogen temperature. The time constant of the process is simply related to the thermal mass of the fibre.

The irreversible decrease in fibre attenuation is superimposed on the reversible change and has a time constant which is strongly dependent on the temperature. It probably results from a stabilization of the glass structure to a form corresponding to a lower temperature than that frozen in by rapid fibre cooling (to a lower fictive temperature). Two effects may occur, namely a change in the ionic environment in the glass and a change in the oxidation state of an impurity ion. A well-known illustration of the first effect is that the colour of glass may be changed by heating [4]. The colour change can often be frozen in by quench cooling when the apparent high-temperature environment, as seen by the impurity ion, is preserved. The high-temperature structure can then be released by annealing and this could well be happening when the fibres are heat treated. The second effect, namely a change in oxidation state, may result from the high-temperature equilibrium ratio of two oxidation states of an impurity ion being frozen in by rapid cooling and relaxing to a lower temperature equilibrium during annealing.

The irreversible increase in attenuation appears to be due to some other mechanism such as diffusion of impurities from the cladding, phase separation or devitrification, etc. Again the time constant is strongly dependent on temperature and, in particular, at a sufficiently low annealing temperature the effect is absent, i.e. the heat treatment can be continued indefinitely after maximum improvement has been obtained without such degradation occurring. A careful choice of annealing temperature is therefore necessary.

The second type of preform we have used has been supplied by H. Rawson and B. Scott of the Department of Glass Technology, University of Sheffield. They avoid the

![Figure 5 Attenuation of fibre made from Sheffield University glass [5]. The lower curve was obtained after heat treatment.](image)
possibility of introducing impurities by drawing the preform directly from a two-layer melt [5] in which pure glass raw material is heated by R.F. induction thereby greatly reducing the transfer of impurities from the crucible into the glass. Fibres have been pulled from the preform as described above and typical results are shown in Fig. 5. The minimum attenuation achieved is 60 dB km\(^{-1}\) near 1.1 \(\mu\)m and again the effect of heat treatment is important. The only distinct absorption peak is that due to OH at 0.97 \(\mu\)m and the rise towards shorter wavelengths may possibly, as indicated above, be due to the tail of the u.v. absorption of the lead-based core glass. Considering the fact that the preform was one of the first prepared by this new method the results are very encouraging and even better results should soon be forthcoming.

4.2. Liquid-core multimode fibres
Using the techniques described in Sections 2 and 3 we have drawn fibre tubes of ME1 glass which have subsequently been filled with hexachlorobuta-1,3-diene. The detailed properties of this combination have been described elsewhere [7] and we are concerned here only with those properties which reflect on the quality of the fibre. By using simple purification techniques the minimum attenuation has now been nearly halved to 5.8 dB km\(^{-1}\) and Fig. 6 shows some small residual absorption peaks which may be attributed to overtones and combinations of C-H and O-H impurity vibrations. Over most of the wavelength range the attenuation follows a \(\lambda^{-4}\) dependence on wavelength as shown and thus may be assumed to arise mainly from Rayleigh scattering. The excess loss for wavelengths in the region 0.85 to 1.15 \(\mu\)m is due to impurities together with a contribution of between 1 and 2 dB km\(^{-1}\) from the lossy cladding (ME1 tubing). By purifying the liquid and using low-loss cladding, such as silica, it should be possible to reduce the loss at, say, 1.06 \(\mu\)m to 4.5 dB km\(^{-1}\) and at 0.9 \(\mu\)m to 8.5 dB km\(^{-1}\).

The interface in these fibres, i.e. the inner surface of the fibre tube, seems to be excellent despite the high pressures (up to 1400 atmospheres) [7] under which they are filled and we have not yet observed any effects which can be attributed to interface
imperfections. Thus the mode conversion (ray scattering) which has been demonstrated [8] seems to be a function only of the bend radius of a fibre and we have observed no limiting amount of mode conversion such as would be expected from scattering or inhomogeneities. This is a valid conclusion to draw despite the fact that the lossy cladding also produces [9] a mode filtering effect (i.e. attenuates preferentially the higher angle rays). A more direct demonstration of this aspect of fibre quality is given in Fig. 7 which shows the far-field distribution of light from a 400 m length where a 'probe' beam of solid semi-angle 0.3° was launched at an angle of 20° (in air) to the axis. Over this length the probe beam makes ~ 10° reflections with the interface but nevertheless the mean angle of the output rays was still 20°. Some mode conversion occurred since the angular width of the ring is greater than 0.3° but this seems to be due to the curvature of the fibre on the supporting drum. The absence of light at small angles to the axis at the output is a clear indication of good fibre quality. For the shorter lengths of glass core (F7) fibre we have been able to measure, a geometric ray analysis also holds [10] indicating good homogeneity in this case as well.

5. Conclusions
We may conclude that the preform technique can be used to draw fibres of high geometric quality and without necessarily introducing any impurities additional to those already present in the preform. In the case of glass-core fibres the transmission loss can sometimes be reduced by appropriate heat treatment.

Acknowledgements
We are indebted to Mr H. Rawson and Dr B. Scott of the Department of Glass Tech-
ology, University of Sheffield, for providing cladded-rod preforms from their special glass melts, to Mr J. P. Dakin for the attenuation measurements on bulk F7 glass and to Mr H. Matsumura for Fig. 7; we have also greatly benefited from discussions with them, and with Mr D. Williams. Grateful acknowledgement is also made to the Ministry of Defence (Procurement Executive) for supporting the work and allowing its publication.

Appendix 1. Filling of liquid-core fibres

Fluid flow in a hollow glass fibre is described by the classical equations for laminar flow in small-bore pipes. The volume rate of flow \( Q \) of liquid in a fibre of internal diameter \( d \) is given by

\[
Q = \frac{\pi(d/2)^2 P}{8l\mu},
\]

where \( P \) is the applied pressure, \( \mu \) is the coefficient of viscosity of the liquid and \( l \) is the length of the fibre containing liquid.

The mean velocity \( v \) of fluid flow is

\[
v = \frac{Q}{\pi(d/2)^2} = \frac{P d^2}{32\mu l}.
\]

It can be seen that the velocity varies inversely with the length of the fibre, so that the liquid movement becomes progressively slower, as expected, as the fibre is filled.

The time \( T \) taken to fill a length of fibre \( L \) is

\[
T = \int_0^L \frac{1}{v} dl = \int_0^L \frac{32\mu l}{P d^2} dl = \frac{16\mu}{P} \left( \frac{L}{d}\right)^3.
\]

In order to reduce the filling time for a given applied pressure the internal fibre diameter \( d \) should be as large as possible. A kilometre of fibre of 100 \( \mu \)m bore could be filled with hexachlorobutadiene (viscosity \( 32 \times 10^{-3} \) poise at 25°C) in 29 h using a pressure of \( 5 \times 10^7 \) N m\(^{-2}\) — approximately 500 atmospheres — whereas a single-mode fibre of 1 \( \mu \)m bore would take \( 10^4 \) times longer.

The maximum applicable pressure is limited by rupture of the fibre. This pressure is given approximately by

\[
P_{\text{max}} = \frac{S(D - d)}{D},
\]

where \( D \) is the overall diameter, and \( S \) is the tensile strength, of the glass. \( S \) has a value of \( 10^8 \) to \( 10^9 \) N m\(^{-2}\), depending on the glass and the surface condition of the fibre. Substitution of \( P_{\text{max}} \) into Equation 3 gives the shortest possible filling time for a fibre of given dimensions.
The preparation of multimode glass-and liquid-core optical fibres

\[ T_{\text{min}} = \frac{16\mu L^3 D}{S d^2 (D - d)} \]  

(5)

However, in practice, the overall diameter of the fibre is limited by flexibility considerations, while the internal diameter may be varied by the fibre-pulling technique outlined earlier. In this case there is an optimum bore diameter for minimum filling time, found by differentiating \([53]\), namely

\[ d = 2D/3. \]

If this requirement is met by suitable choice of pulling conditions, then a pressure equal to one-third of the tensile strength of the glass may be applied before rupture occurs, and the filling time will be given by

\[ T_{\text{opt}} = \frac{108\mu}{S} (L/D)^2. \]

References:

CHAPTER 2
THE DEVELOPMENT OF A LIQUID-CORE FIBRE

2.1 Glass-cladded Fibres based on Hexachlorobuta-1,3-diene (2.1)

Once the fibre-drawing process had been improved, it fast became obvious that the bulk attenuation of the material used for the core of the fibre was the limiting factor in the achievement of lower attenuation. Since the possibilities of commercial glasses had been exhausted and the effort at Sheffield University was hamstrung by the contractors insistence on high numerical aperture, there seemed little prospect for further progress. It was at this time that the use of a liquid core was suggested at the CSIRO in Australia\(^1\) and at Bell Telephone Laboratories\(^2\). They claimed the then lowest recorded attenuation of 15dB/km at 1.06\(\mu\)m with a fibre consisting of a pure silica fibre tube filled with tetrachloroethylene.

Clearly liquid-core fibres provided a means of circumventing the problem of obtaining a glass core of adequate purity, and so it was decided to investigate their properties. Expertise in the production of fibre capillary had already been gained during the experiments on delayed closure of the F7/MEl core/cladding combination. However early trials at Southampton on the filling of fibres made from either MEl or Pyrex with tetrachloroethylene quickly indicated that the index difference between core and cladding was inadequate. A low numerical aperture results in a relatively large proportion of optical power propagating in the cladding. Thus the high optical attenuation of the cladding material was reflected in the measured overall loss and a fibre attenuation no better than 50dB/km could be obtained. (An experimental and theoretical study of this effect may be found in publications P5.1 and P5.3.) The previously-reported silica-cladded fibre had not suffered from this problem, both because the index difference is greater, and because silica has a relatively low loss. We could not produce silica fibres at that time, as the maximum temperature of the fibre-drawing furnace was too low to permit silica drawing. An alternative approach was to find a liquid having a higher refractive index than tetrachloroethylene.

Unfortunately, as with glasses, it transpires that to a certain degree the optical attenuation of a liquid increases with its refractive index. Since the refractive index and the
proximity and intensity of the ultraviolet electronic absorption bands are related through the Kramers-Kronig relationship, this is perhaps not altogether surprising. In addition, it is found that the presence of a hydrogen atom within the molecular structure of the liquid produces an intense absorption band at a wavelength of 3.5μm. Hydrogen has a low atomic weight and when associated with a heavier atom produces both an absorption band sited in the near infra-red and a highly anharmonic vibration. Consequently, absorption overtones are found throughout the visible and near-infra-red. A similar effect is observed when a glass contains the OH radical as an impurity (see publication P3.2).

Further restrictions on the choice of a suitable liquid are set out in P2.1. Numerous liquids are available which satisfy the requirements, but all have a refractive index lower than 1.45. Guidelines for the choice of a suitable liquid are: (a) it must be fully halogen substituted to eliminate the hydrogen from the structure, (b) of the halogen substituting agents only fluorine and chlorine are suitable owing to the absorption produced by the presence of free bromine or iodine and (c) organic compounds containing oxygen or nitrogen are unsuitable owing to the proximity of their IR absorptions. One has little remaining choice but to start with the low molecular weight organic chlorine or fluorine compounds and work up in molecular weight until the refractive index becomes sufficiently large. Unfortunately, the compounds are usually found to be solids before this occurs. However, during the course of the exercise it was noticed that the addition of an ethylenic linkage imparts a higher molar refractivity to the compound, and it was by this means that hexachlorobuta-1,3-diene (HCBD) was discovered. Largely as a result of its two ethylenic linkages, HCBD has a considerably higher refractive index than the only other suitable low-loss liquids known, namely carbon tetrachloride and tetrachloroethylene. One other compound which was unearthed, but which has not yet been tried, is hexachloropropene. It is probably that this liquid will also have low loss, although it does not possess as high an index as HCBD. In addition it is highly poisonous.

A high-pressure (1400 atmospheres) filling machine was designed and built to produce long lengths of HCBD-filled, ME1-clad fibres in as short a time as possible (Fig.2.1). The machine is based upon a constant-torque motor which applies a
regulated force of up to 3000 kg to a piston by means of a screw. The piston moves within a cylinder containing the liquid which is forced into the fibre through a hypodermic needle fixture. A theoretical analysis of the filling process was made (publication P1.2, p306) and this enabled optimisation of both the dimensions of the fibre capillary and the filling time. It was now possible to fill a 1 km length in about 30 hours. A photograph of a typical fibre having an outside diameter of 150 \( \mu \)m and a bore of 100 \( \mu \)m is shown in Fig. 2.2.

2.2 Attenuation Results (P1.2, P2.1)

The combination of ME1 tubing filled with HCBND produced what was then the remarkably low loss of 5.8 dB/km at 1.06 \( \mu \)m. A description of the fibre and details of the attenuation may be found in publications P1.2 and P2.1. The result was all the more significant since commercially-available compound glass tubing, having an attenuation in the region of 1500–3000 dB/km was used, clearly demonstrating the advantage of a large core/cladding index difference. It was estimated\(^3\) that the high loss cladding was contributing only 1-2 dB/km to the overall attenuation, although this depends on the fibre excitation conditions and length (see P5.3). The figure of 5.8 dB/km remains the lowest loss ever reported in a liquid-core optical fibre.

2.3 Discussion

The achievement of low attenuation in kilometre lengths of fibre provided valuable experience in both fibre production technology and particularly in fibre propagation studies, as may be seen from Section II of this thesis. The fibre remains the closest approximation to a perfect homogeneous-core optical waveguide yet produced, and as such may be used to simulate other, less-perfect waveguides by deliberately introducing controlled defects. Expertise in the purification of liquids was acquired, since HCBND of sufficiently high quality could not be obtained commercially. Both vacuum distillation and column chromatographic techniques were used and this knowledge was later put to good use in the development of silica waveguides (Chapter 3). Furthermore, the excellent propagation properties of the waveguides verified the performance of the fibre-drawing machine and indicated a high degree of diameter stability and reproducibility. Numerous ME1/HCBND fibres were produced, both for propagation
studies in our own laboratories and for supply to others at home and abroad. The ability to transmit light over kilometre lengths produced an insatiable demand for fibres, particularly since at the time the HCBD fibre claimed the lowest recorded loss. Furthermore it was the only low-loss guide of any type available in the United Kingdom.

To demonstrate the low attenuation of the fibre in more tangible terms and to provide a foretaste of optical fibre communication systems in the future, a simple transmission link was constructed. The equipment captured the imagination of the media and received wide publicity. Although signal transmission over short lengths had been demonstrated before, it was now possible to send a colour television channel over a realistic distance of more than one kilometre using only an inexpensive commercial light-emitting diode transmitter and an avalanche photodiode detector. The experimental link is shown in Fig. 2.3. The equipment was used in January 1973 by the British Broadcasting Corporation to demonstrate the first live television broadcast to be transmitted through 1 km of optical fibre.

References
FIG. 2.1  HIGH-PRESSURE FILLING MACHINE FOR LIQUID-CORE FIBRES
FIG. 2.2 LIQUID-CORE FIBRE END
BORE 90µm, O.D. 140µm
FIG. 2.3

FIBRE OPTICAL TELEVISION LINK – SCHEMATIC DIAGRAM
NEW LOW-LOSS LIQUID-CORE FIBRE WAVEGUIDE

Indexing terms: Fibre optics, Optical waveguides, Glass

Low-loss liquid-core fibre-optical waveguides having a transmission loss of 10 dB/km has been made using commercially available glass tubing. The loss is less than 20 dB/km over a wavelength range of greater than 0.8-1.1 μm, and at the semi-conductor laser wavelength of 0.9 μm, has a value of 14 dB/km. This is the first low-loss fibre to be made using glass.

Introduction: In order to make a cladled fibre suitable for use as a transmission medium for optical communications, it is necessary to select two materials to act as core and cladding which ideally have low attenuation, scattering and dispersion at the wavelength of interest. In addition to the appropriate relative refractive indexes, they should have suitably matched thermal and mechanical properties and be chemically compatible, stable, flexible and strong. A suitable material which satisfies most of these requirements, with one major exception, is glass, but, unfortunately, none is yet available with a sufficiently low absorption coefficient. Using commercial glasses, we have achieved a transmission loss of less than 200 dB/km, which, to our knowledge, is the lowest value yet reported for a multimode cladled-glass fibre, but this is still too high for practical application. In principle, it should be possible to obtain the desired attenuation by reducing the impurities to a sufficiently low level, typically about 1 part in 10⁶ in the bulk glass from which the fibres are made, and, in fact, the loss in selfcore graded-index fibre has been improved to 60 dB/km. A material which is available in very pure form is silica, but its refractive index is too low, and its thermal and mechanical properties are too different from those of glass or similar compounds, to make a low-loss cladled fibre possible. By using silica doped with titania as the core material, and pure silica for the cladding, a single-mode fibre of 200 dB/km has been made, but it has not been commercially available, has a long processing time, and is reputed to be brittle.

Although suitable solid materials which are compatible with silica have not yet been found, there are some liquids of convenient refractive index which are relatively absorption-free. Two groups have independently produced low-loss multimode liquid-core fibres using the combination of tetrachloroethylene in silica tubing. W.J. Ogilvi (CSIRO), using specially selected silica of low water content, has measured a loss of 17.5 dB/km over lengths of several hundred metres, while J. Stone (Bell Telephone Laboratories) reports figures of 20 dB/km or less between 0.84 and 0.88 μm and also between 1.04 and 1.10 μm for a fibre of 75 μm core diameter. In fact, the published curve in the latter paper seems to have a point at 1.10 μm which is near 15 dB/km. We wish to report a new type of liquid-core fibre having an attenuation of 10 dB/km between 1.04 and 1.10 μm and which is below 20 dB/km from 0.8 μm to 1.13 μm. The tubing was made from cheap high-loss glass and we assume that, by purification and filtration of the liquid and by using glass of better quality, the attenuation may be reduced still further.

Method: The fibres were drawn from Chance-Pilkington MEI glass tubing, having a bulk absorption loss in the region of 10000 dB/km, by a precision pulling machine. The tubing was of 14 mm outside diameter and 1.5 mm wall thickness, and was drawn into fibre, typically of 50 μm inner diameter and 27 μm wall thickness, in 5 km lengths, as a single layer on an aluminium drum 1.4 m in circumference. The fibre cross-section was accurately circular and the outer diameter constant to within 1 μm. The refractive index of the glass is 1.457, and, to achieve a guiding stricture, it is essential that the liquid should have a higher index. For a high-loss cladled glass, the liquid should be as high as possible to avoid a significant cladding contribution to the overall fibre attenuation, i.e. the cladding contribution to the fibre attenuation may be reduced by having a large index difference. It is also necessary that the u.v. and i.r. absorption bands of the liquid should be as far removed as possible from the wavelength region of interest (0.7-1.1 μm). This is because strong electronic transition bands in the u.v. may have a significant 'tail' into the region, and, whereas this effect does not show up in normal u.v. spectrocopy where the sensitivity is rarely better than 20000 dB/km, the effect can be significant when considering a path length of 1 km or more. Molecular vibrations in the i.r. have overtones of decreasing intensity at submultiples of the main band. The strong C-H vibration at approximately 3.5 μm is particularly troublesome, eliminating many otherwise suitable liquids, such as methyl salicylate, which we have found to have strong overtones throughout the region of interest, although the peak values of 1000 dB/km would not be expected to show on an infrared spectrometer. In addition, the liquid should have low optical scatter, low toxicity and should be stable and nonvolatile, with low viscosity to assist in fibre filling.

A fully halogen-substituted aliphatic liquid satisfies the above requirements, having no C-H bonding and thus avoiding the 3.5 μm i.r. vibration. The liquid should preferably contain no ethylenic linkages with the associated close u.v. absorption band. We have chosen hexachlorohexa-1,3-diene, which has the following properties:

\[ n_a = 1.5583 \]

melting point = -15°C

boiling point = 212°C

In fact, this liquid has two ethylenic linkages which are conjugated, giving rise to a u.v. spectrum shifted to longer wavelengths and hence nearer the region of interest than would otherwise be the case. The tail of the absorption band dominates the fibre attenuation at wavelengths below 0.6 μm.

The liquid was of normal commercial spectroscopic quality, and was used directly from the bottle. The fibres were filled under a hydrostatic pressure of up to 1400 atmospheres and lengths of 200 m can be reeled on a few bobbins.

Measuring technique: The fibre attenuation was measured using a stabilised quartziodine lamp and chopper disc in conjunction with a p-i-n photodiode and a phase-sensitive detector. The fibre was wound on an 11 cm-diameter drum and the input end was held in a suitable mount. The input beam, after passing through a wavelength-selecting monochromator, was launched into the fibre via a microscope with a <5° objective, corresponding to an input beam semi-angle of 0.4°. Visual observation ensured that the light entered the core centrically. The output end of the fibre was placed perpendicularly on a known spot on the horizontal detector scale in a drop of core liquid. For each measurement, the fibre end was removed and replaced on the detector surface three or four times and recordings made only when successive readings of the output voltage agreed to within 1%. After noting the output at the appropriate wavelengths, the fibre was shortened by a known amount, usually about 200 m, and further readings taken. The estimated accuracy of loss

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1 Matsuoka, K. (private communication)

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Results: The results of the attenuation measurements, given in Fig. 1, show that the loss in the fibre is below 20 dB/km over the rather wide wavelength range 0.8-1.3 μm. The low values of attenuation are repeatable and have been obtained with core diameters ranging from 42 to 72 μm. It is too early to draw any firm conclusions, but preliminary indications are that high quality and uniformity of the internal fibre surface are necessary if the transmission loss is to be low. In the region 0.8-1.1 μm, the loss varies relatively slowly with wavelength. Stone observed a peak of about 85 dB/km at 0.86 μm, which he attributes to the presence of water vapour; our results indicate only a slight rise in attenuation at this wavelength, with a ‘peak’ of between 12 and 13 dB/km, depending on the fibre, and hence semiconductor lasers and gallium-arsenide lasers can be used satisfactorily with these fibres. At the wavelength of the helium-neon laser, 0.633 μm, the attenuation is 75 dB/km, although values as low as 50 dB/km have been measured.

We are in the process of measuring the scattering and light distribution in the fibres, but an upper estimate of the worst case may be obtained by assuming that the entire loss at 0.633 μm is due to scattering and has a Rayleigh dependence. Applying the $\lambda^2$ law, the upper limit of scattering loss at 1 μm is found to be 8 dB/km.

Conclusions: In conclusion, our fibre waveguide has a lower loss over a wider wavelength range than any previously reported. In particular, the peak previously observed covering the region 0.86–1.00 μm is almost absent. The tube material is considerably cheaper than quartz, and may be drawn with high precision at a much lower temperature. In fact, this is the first low-loss fibre of any configuration to be made using glass. The lowest losses so far reported in liquid-filled glass fibres are 130 dB/km² for tetrachloroethylene in Pyrex and 140 dB/km² for bromobenzene in flint-glass tubing.

The importance of liquid-core fibres lies in showing that low attenuations can be achieved, in enabling the development engineer to gain experience in using low-loss fibres and in measuring such parameters as bandwidth over practical lengths of 1 km or so. Our fibres are easily handled, and can be rewound quite simply from the winding drum of the fibre-drawing machine onto other drums for filling, handling, assessment etc. A solid core would be more convenient for practical application in avoiding problems of evaporation, effects of temperature changes and the necessity for having small liquid reservoirs at the fibre terminations. The long-term stability of the liquid has also to be determined. For example, hexachlorobutadiene-1,3-diene comes from a family of organic chemicals which tend to polymerise, and we have observed this effect, with the resulting rise in attenuation due to a shift in the ultraviolet band edge, when the fibres are irradiated with u.v. radiation. An outer covering of black glass can prevent this happening, but other long-term effects may arise.

Another important consequence of these fibres lies in showing that the effect of cladding attenuation on the fibre loss is small. We have not measured accurately the bulk attenuation of ME1, but it is not less than 10 dB/km. The effect of the cladding has been estimated by using a modal analysis, by calculating the loss of each of the modes excited by the 6-9 launching beam and integrating over all modes. Using a value for the bulk cladding loss of 10 dB/km, the contribution of the cladding to the fibre loss is found to be 3-5 dB/km. This is not inconsistent with the upper estimate for the scattering loss of 8 dB/km. Thus, in multimode fibres, the prime need is to reduce the core loss and prevent interdiffusion at the core/cladding interface.

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References

* ROBERTS, C. (Private communication)
CHAPTER 3

THE DEVELOPMENT OF PHOSPHOSILICATE FIBRES

3.1 Silica Fibre Drawing

Whereas liquid-core fibres provided the first demonstration of low attenuation, they suffer from several disadvantages and it was apparent that a solid-core waveguide would furnish a more attractive solution. Although the handling problems experienced with liquid cores are not intractable, they demand careful engineering. For example, it is necessary to provide liquid reservoirs and to permanently pressurise the fibre to avoid 'vapour pockets' which are formed by the action of gravity when a change in ground level is negotiated. In addition the long-term stability of a liquid core is questionable. These effects, coupled with the fact that little further improvement could be expected in the HCBD/ME1 fibre, caused us to institute research into an alternative low-loss waveguide.

Early in the development of optical fibres\(^1\), it was apparent that certain commercially-available, synthetic grades of fused silica exhibit low attenuation. These materials are prepared by vapour deposition techniques utilising oxidation or hydrolysis of volatile silicon compounds such as silicon tetra-chloride or silane. The low observed losses arise in part from the low level of contamination of the silica by the transition metals which can cause considerable absorption loss. These impurities are largely excluded from the silica because the vapour pressure of their chlorides and hydrides are very much lower than that of the corresponding silicon compounds. Therefore when the silicon compounds are vapourised, as part of the preparation process, the potential impurities are left behind and do not become incorporated within the silica. The situation is further improved by the fact that vapour deposition processes do not involve prolonged heating in furnaces - a process which can easily give rise to contamination.

It was thus decided to investigate the drawing of silica fibres from commercial silica rods or tubes. Further incentive for this was given by the earlier reports\(^2\) from Corning Glass Works in the U.S.A. of a 20dB/km single-mode fibre made by blowing a titania-doped silica soot from an oxyhydrogen flame into a

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\(^1\) This refers to the initial stages of fibre technology.

\(^2\) This refers to reports from Corning Glass Works indicating their success in manufacturing low-loss fibres.
silica tube where it deposited on the inside walls. The fibre was made by collapsing the tube into a solid rod and pulling. In addition, reports from Bell Telephone Labs described the production of low-loss guiding structures using only fused silica, known as 'single-material fibres. Finally it was felt that it would be instructive to provide the liquid-core fibre with a low-loss silica cladding.

3.2 The Graphite Resistance Furnace (P3.1)

A disadvantage of silica is its high working temperature; it requires a fibre-drawing temperature in excess of 2000°C. In accord with the policy of precision fibre drawing outlined earlier, it was decided to develop a graphite resistance furnace rather than to rely on the poorly-controlled oxyhydrogen flame burner used by other laboratories. Fortunately this rather radical step was rewarded and it proved possible to pull very accurate silica fibres in this way. A full description of the furnace design is given in publication P3.1. Initially some difficulty was experienced in operation of the furnace due to arcing between adjacent segments of the heating element. This was overcome by increasing the clearances and the furnace has operated successfully ever since. The experience gathered in the design of the earlier low-temperature furnace (Chapter 1) permitted a design which is both novel and trouble-free. More recently a commercial design has appeared on the market, but this is believed to be rather less convenient in use as a result of its extended warm-up period. Thus it would appear that despite being the first resistance-heated graphite furnace to be used for optical fibre drawing, the design remains very competitive. It has been successfully reproduced by two industrial concerns, one British and one North American.

With the aid of the new furnace, precision silica fibre drawing proved no more difficult than for compound glass fibres. It was therefore now possible to draw lengths of several kilometres of high quality silica fibre capillary for filling with HCBD. As we had expected, the results obtained with such a fibre represented only a marginal improvement over those obtained with an ME1 glass cladding, even though the loss of the silica cladding is considerably lower. This experiment therefore confirmed that the cladding contributed little to the overall liquid-core fibre attenuation.
Further experiments in silica fibre drawing were conducted in conjunction with C.R. Hammond and S.R. Norman. For example, samples of single-material fibres were fabricated using a silica rod supported on thin glass plates within a silica tube. Losses of 36dB/km were achieved at 0.633μm, although the fibre proved difficult to handle.

3.3 The Homogeneous Chemical Vapour Deposition Process (3.5)

In January 1974 the first experiments were conducted on a new method of silica fibre production, termed, in the Southampton laboratories, the homogeneous (or modified) chemical vapour deposition technique. The earlier reports of the Corning single-mode flame process and later reports from Bell Telephone Labs describing the use of a dilute silane oxidation reaction to deposit a borosilicate cladding for use with a pure silica core, inspired a search for an effective means of exploiting the low-loss properties of synthetically-produced silica.

The chemical vapour deposition (CVD) process, as used by Bell Telephone Laboratories, is familiar in the semiconductor industry where it is used for the production of glassy passivation layers. It suffers from the disadvantage that it requires a homogeneous deposit to be produced on a surface by a heterogeneous reaction of the gas molecules at the surface. This can only occur at low temperatures and with the reactants sufficiently diluted to prevent a homogeneous gas-phase reaction taking place. Such a reaction would produce a dust of fine silica particles and a poor deposit. Because high dilution is required the deposition rate is low, typically less than 0.1μm/min. Furthermore, with hydride starting materials the hydroxyl radical is incorporated into the glass fibre and produces a high overtone absorption at 0.95μm wavelength.

In order to overcome these disadvantages we used concentrated reactants in a modified process operating at high temperatures. The principle results from the observation that a flow of concentrated silicon tetrachloride vapour reacts spontaneously with oxygen at the relatively high temperature of 1400°C to form a fog of fine glass particles. These particles would adhere to the walls of a tube containing the gas, downstream from the hot zone, where they could be subsequently fused to a clear layer.
Thus halides rather than hydrides could be used, and no hydroxyl is involved in the reaction. In addition, such a homogeneous gas-phase reaction is efficient in chemical yield and produces a high deposition rate. A uniform layer of silica can be built up on the inside of a tube by traversing the hot zone back and forth so as to fuse the glass particles as they are formed. A more detailed description of this process is given in publication P3.5, together with the equipment used.

3.4 The Phosphosilicate Glass System (P3.2, P3.3)

Having discovered an efficient and rapid means of depositing silica, it remained to find a suitable additive to increase the refractive index of the deposit so that it might form the core of an optical waveguide with silica as the cladding. Bell Telephone Laboratories had reported a $3\text{SiO}_2\cdot1\text{B}_2\text{O}_3$ glass which had a lower index than silica and might therefore be used as a cladding for a silica waveguide. By now details of a new Corning process had been published whereby a hydrolysed, doped soot was deposited from a flame on the outside of a mandril. The mandril was subsequently removed and the soot fused to give a clear glass. The nature of the dopant however remained a closely-guarded secret, although it is now known to be germania.

As in the case of the choice of a liquid for liquid-core fibres, the field is considerably narrowed by several constraints. Although all oxides with the exception of boric oxide will increase the refractive index of silica, an additive which forms a volatile halide or oxy-halide is required for the homogeneous CVD process. In addition, a spontaneous oxidation temperature close to that of silicon tetrachloride is needed so that the two oxides are deposited simultaneously. The binary glass ultimately formed should be compatible with a silica cladding and be stable up to the pulling temperature of $\sim 2000^\circ\text{C}$. The elements of Groups III, IV and V frequently have volatile halides, examples of which are $\text{AlCl}_3$, $\text{AsCl}_3$, $\text{BCl}_3$, $\text{SiCl}_4$, $\text{GeCl}_4$, $\text{SnCl}_4$, $\text{PbCl}_4$, $\text{SbCl}_5$ and $\text{PCl}_3$ (or $\text{POCl}_3$).

Initial trials using a combination of $\text{SiCl}_4$ and $\text{POCl}_3$ vapours mixed with oxygen and passed through a heated silica tube proved instantly successful. The fibre-drawing machine and graphite furnace were used in these early experiments to provide the traversing hot zone. The silica tube was mounted in the feed
mechanism and driven vertically through the furnace, set to a temperature of \(\approx 1400^\circ\text{C}\). Initially twelve passes were made before radially collapsing the tube to form a rod and pulling into a fibre. Losses of less than 10dB/km in kilometre lengths of step-index fibre immediately resulted, even though poor-quality silica tubes and low-purity chemicals were used as starting materials. The homogeneous CVD technique and the phosphosilicate core material were reported\(^7\) for the first time in March 1974.

Attention now turned towards improvements in the gas-handling equipment and to the production of graded-index fibres. Purification of the starting chemicals and the use of a high-purity synthetic cladding material (Suprasil) resulted shortly afterwards in a loss of 2.7dB/km at 0.83\(\mu\)m. This work was reported in July 1974 (publication P3.2), together with further improvements and a dramatic reduction in hydroxyl content in August 1974 (publication P3.3).

It appears that workers at Bell Telephone Laboratories had been pursuing a similar course for the production of optical fibres. In June 1974 they reported\(^8\) the development of low-loss fibres based on silica doped with either GeO\(_2\) or B\(_2\)O\(_3\). They had discovered an identical process to that described above, but used either GeCl\(_4\) or BCl\(_3\) with SiCl\(_4\) as the starting materials. The incorporation of germania into the core of a waveguide was also reported at the same time by S.T.L.\(^9\), although it is believed that their fabrication method involved the deposition of pure germania within a silica tube and subsequent diffusion into the walls to form a binary GeO\(_2\)/SiO\(_2\) glass.

3.5 Results (P3.4, P3.5)

A period of intense activity followed in which both the new fabrication method and the new phosphosilicate system were characterised and improved. For example it was clear that the optical quality of the silica tube affected the fibre attenuation. To combat this an optical cladding of borosilicate glass was first deposited, and a composite fibre having a borosilicate cladding and a phosphosilicate core was produced. The improved fibre was reported in publication P3.4. It has the dual advantages of (i) a higher numerical aperture and (ii) independence from the quality of the starting tube. The silica tube now acts only as a supporting structure and in fact can be replaced by virtually any tube capable of withstanding the high temperatures
experienced during the deposition stage. An inexpensive 96% silica product known as Vycor has been successfully used.

Phosphosilicate glass as a core material is unique in the apparent ease with which the hydroxyl impurity which plagues other waveguides can be eliminated. It is also free from the oxygen deficiency which produces an increased absorption at shorter wavelengths in germania-doped waveguides. As a consequence of these advantages, the lowest attenuation ever recorded in an optical fibre, 0.47dB/km at 1.23µm, has been achieved in a borosilicate/phosphosilicate fibre. It is difficult to see how this result, announced recently by a Japanese laboratory\textsuperscript{10}, can be improved upon.

Publication P3.5 gives details of the properties of phosphosilicate glasses and of the production of graded-index fibres. An automatic deposition machine has been constructed by C.R. Hammond to replace the earlier method of fabrication. Experiments are continuing to attain closer control of diameter and index profile, together with an investigation of the attractive ternary glass systems based on germania/phosphosilicate and boric oxide/phosphosilicate.

3.6 Single-mode Fibres (3.5)

The homogeneous CVD technique is particularly suited to the production of single-mode fibres. By suitable choice of deposition conditions, the diameter and refractive index of the core may be varied over a wide range. A typical monomode fibre has a core of 4µm and a core/cladding index difference of about 0.3%. This may be provided by a layer of phosphosilicate glass of appropriate composition, deposited in a single pass on the inside of a silica tube. The time taken for manufacture is thus very short compared to that for the 50 or so passes required for a multimode fibre. The attenuation results so far obtained for monomode fibres have not been as low as for multimode fibres, probably because a greater proportion of the optical power propagates in the relatively lossy cladding region. However, a loss of 6.1dB/km at 0.633µm has been achieved. Work is in hand to deposit both the core and the cladding and thus ensure that propagation is confined to regions of low optical attenuation.
3.7 Discussion

It is interesting to speculate on the future of the homogeneous CVD technique. As a result of its simplicity and reproducibility it has now been adopted by all major laboratories engaged in optical communications research. So far the only additive materials extensive used with the process have been germania, boric oxide and phosphorus pentoxide, although limited reports of alumina\textsuperscript{11} and fluorine\textsuperscript{12} doping have been made. The mainstays of the process are the ease with which very low losses may be obtained, the ability to produce accurate refractive-index profiles, and the low capital investment involved. It has however been argued that, as a batch process, it is unsuitable for mass production, although it should be possible to extend the batch size from the current 1-2km to about 7-8km. No doubt the ultimate decision as to the most appropriate fabrication technique will rest on economic arguments and the type of fibre required. Should the telecommunications network demand very low loss (less than 2dB/km) graded-index or single-mode fibres, it is hard to see how other methods of manufacture would be competitive, particularly since they have yet to demonstrate ultra-low attenuation.

References


A Resistance-Heated High Temperature Furnace for Drawing Silica-Based Fibers for Optical Communications

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Currently there is considerable interest in the production of ultra low-loss fibers for optical communications. A suitable material might comprise a compound glass, but it has proved difficult to produce material of the required purity. However, nearly pure silica can be made, and is available commercially, so that various techniques have been developed for making silica-based fibers. Unfortunately, silica has a disadvantage in that it must be heated to \( \approx 2000^\circ \text{C} \) before the viscosity becomes low enough for it to be drawn into fiber, and therefore a furnace is required which will operate up to \( \approx 2200^\circ \text{C} \).

The method generally used in the past has been to heat the silica by burning appropriate gases in a flame furnace but this technique, while being inexpensive, has many disadvantages. 1) It is difficult to control the temperature accurately and to produce a high degree of repeatability. 2) Temperature distribution fluctuates somewhat with the variation in gas flow through the furnace. 3) It is difficult to produce a given, stable, temperature profile along the furnace. 4) It is difficult to produce radially symmetric heating. 5) There is always a possibility of contamination of the fiber from the gases in the flame.

Another method uses a CO\(_2\) laser as a "clean" source of heat, but the process is complex and rather expensive. Induction and rf heating can be applied to glass melting, but they involve the use of expensive, high power rf generating equipment.

Experience with compound glass fibers has indicated the value of precision pulling conditions and especially of an accurate temperature control and profile, since uncontrolled diameter variation can produce higher attenuation, particularly in fibers of low numerical aperture. However, it has been shown it is possible to make fibers of very low cross-sectional variation \((<1 \mu\text{m in } 150 \mu\text{m} \text{ over a length of } 1 \text{ km})\) which produce very low mode conversion. To make silica-based fibers of comparable quality, a precision fiber-drawing furnace, capable of operating at high and accurately controlled temperatures, is required.

Design Criteria

Resistance heating is the simplest and most readily controlled form of heating. Accurate temperature control can be achieved by thermocouple or pyrometric monitoring; power can be regulated by a standard SCR power controller. A further advantage is the hot zone can be closely contained and temperature profiled as desired by adjusting the local resistance of the heating element. In view of these factors and because it is possible to obtain high accuracy at relatively low cost, resistance heating was chosen as the optimum method.

The selection of materials capable of operation at temperatures \(>2000^\circ \text{C}\) is somewhat limited. Most of those available require an inert atmosphere to prevent rapid deterioration by oxidation, and in addition several are brittle and have poor thermal shock resistance. Further difficulties are that different materials in contact at these elevated temperatures tend to react, and problems are caused by their dissimilar thermal expansion coefficients. Another requirement for a fiber-drawing furnace is that the furnace components should be compatible with silica vapor, since silica is relatively volatile at its drawing temperature, and it is not uncommon to have to blow condensed silica dust out of the furnace periodically.

Of the various possibilities, graphite is the most acceptable because of its remarkable combination of thermal and mechanical properties. Also, it is available in pure form, is relatively cheap and can be machined into intricate shapes. A wide variety of graphite products are available, including insulating felt, string, cloth and paper, so that the entire furnace can be constructed from one material thus avoiding the problems caused by having dissimilar materials in contact at high temperature. In addition, graphite has a very high thermal shock resistance, good strength at high temperatures and a high emissivity. The main disadvantage is its high rate of oxidation which makes an inert atmosphere essential. However, since other candidate materials also require an inert atmosphere, it is not a serious drawback.

A description is given of a resistance-heated furnace suitable for drawing silica-based optical fibers with a high degree of precision. The furnace is compact, heats from cold to its operating temperature of \(2000^\circ \text{C} \) in 3 min and has a power consumption of only 1.4 kW. During a fiber pull, the temperature fluctuation is \(< 0.1^\circ \text{C}\).

Design Details

The main body of the furnace is of water-cooled stainless steel and comprises a cylinder to which the base plate assembly is permanently welded. The top plate assembly is removable, complete with the heating element, but is sealed to the main chamber in operation by an O-ring. Inside the body of the furnace there is a graphite felt insulation, a monitoring thermocouple assembly and a graphite tube into which the heating element is inserted. The latter of graphite suitably machined to give the desired resistance prevents deterioration due to atmosphere, air is excluded by a continuous flow of argon which must be smooth, reproducible and accurately defined to ensure high quality of the resulting fiber. Gas enters at both top and bottom of the furnace and exhausts from a single opening at the bottom. The gas flow is so controlled by openings that leakage around the preform and the fiber has a negligible effect.

Details of the construction (Fig. 1) are as follows: The graphite heating element consists of a split cylinder (1) with a flange at one end, to which electrical connections are made, and the hot zone at the other. The two parts of the split cylinder conduct the electric current into and out of the hot zone. The electrical resistance of the latter is increased by machining it into two component meander elements which are in parallel and so arranged as to give radial symmetry. One of the pair of meander elements forming the hot zone can be seen and clearly in the center of Fig. 1 and is so cut as to cause the current to flow in a winding path with the individual elements close and parallel to each other in the longitudinal direction. The thickness of the walls of the split cylinder must be carefully chosen to keep the heat conducted away from the hot zone to a minimum while not producing any appreciable heating due to the current flow. The cross section of the meander element in the hot...
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zone is designed to produce the required temperature when the appropriate value of electric current is passed through it. At the high temperature of operation, arcing between surfaces at different voltages must be avoided; therefore there is a limit on the operating voltages which can be used and adequate clearances must be provided. Allowance must also be made for thermal expansion.

The flange of the heating element is bolted to a ceramic ring (2) which provides support and stability, as well as thermal and electrical insulation. The ceramic supporting ring is, in turn, fastened to the terminal and upper gas flow assembly (3) by electrical terminals which are spring loaded to allow for expansion. Connection to a small stepdown transformer is made by flexible copper cables. The terminal and upper gas flow assembly forms part of the detachable top plate (4) which is water-cooled and is bolted to the body (5) of the furnace through an O-ring vacuum-tight seal. All the metal components are of stainless steel. Incoming gas flows into the rectangular section annular chamber (6) and then, via an annular slot, down the center of the heating element. The gas flow is arranged to pass over the lead-in connectors to provide cooling. Air is excluded from the top of the furnace by a spring loaded iris diaphragm (7) which also locates the incoming silica preform.

The heating element is surrounded by an outer furnace liner (8) consisting of a graphite tube which serves to contain the insulating felt, thus preventing an electrical short circuit. It is fixed to the furnace base plate and has the additional function of providing an exhaust path for the flowing argon. Gas also enters the annular chamber (9) of the lower gas flow assembly and flows through the annular slot up to the heating element. The gas exhausts through the annular channel (10) between the inner and outer furnace liners and the smaller annular chamber (11). At the bottom of the lower gas flow assembly is another iris diaphragm (12) which is normally closed to a diameter of 2–3 mm around the fiber. The insulation (13) is provided by spiral wrapped graphite felt in two sections, between the outer liner and the body of the furnace.

A tungsten/cerium thermocouple (14) is inserted through a hole in the outer furnace wall and a small hole in the furnace lining, with the thermocouple head placed as close as possible to the hot zone. Electrical connections are made to the thermocouple by O-ring seals in the furnace wall.

The furnace is sealed so that when end caps are in position and gas inlet and outlet are closed, the whole structure can be evacuated to remove all traces of oxygen before filling with inert gas. Use of conventional rotary pump, the required evacuation is achieved within ~30 min. However, if the furnace has been exposed to atmosphere for any length of time, then pumping for 24 h is required to completely remove the water vapor absorbed by the graphite. Since the furnace is sealed after use to exclude the atmosphere, the heating elements are not normally necessary.

Performance

The hot zone is 32 mm long with a 22 mm ID, so that a preform to 16 mm OD can be accepted and the furnace operates successfully up to 2200°C.

Externally the furnace is ~280 mm high by 200 mm in diameter. 

Despite its compactness, the outside walls remain at a temperature only a few degrees above ambient. The small temperature difference is a measure of the efficiency of the design in confining the hot zone to a small central region. The overall power consumption is a modest 1.4 kW during a typical fiber pull at 200°C.

Extremely low thermal mass of the furnace, coupled with the low thermal shock resistance of graphite, has enabled the working temperature to be reached ~3 min after switching on from cold.

![Fig. 1. Schematic cross section of furnace. Components are (1) graphite heating element, (2) ceramic ring, (3) terminal and upper gas flow assembly, (4) top plate, (5) stainless steel body, (6) upper gas inlet chamber, (7) lower gas inlet chamber, (8) outer furnace liner, (9) annular outer passage, (10) gas outlet chamber, (11) gas outlet chamber, (12) iris diaphragm, (13) graphite insulation, (14) W-Re thermocouple. End caps shown in detached position.](image)

![Fig. 2. Variation of temperature deviation from set point of 207°C during fiber pull.](image)
there is considerable economy in both time and amount of argon used. Furthermore, the preform can be positioned in the furnace cold, and the operator may then start the fiber pull at his convenience by turning on the furnace power.

Although an argon flow of 10 l/min is required during operation, there is no sacrifice in the accuracy of temperature control. Figure 2 shows the change of temperature deviation from set point during a fiber pull. A temperature of 2070°C was set on the three-term temperature controller and the power turned on. Drawing from a 5 mm diameter silica preform commenced 3 min later. The trace represents the typical temperature stability during a pull and covers some 9 min or 400 m of fiber. The temperature is stable to within 0.06°C of the setpoint, and although this reading represents the furnace stability at the control thermocouple position only, it is unlikely that the deviation will be significantly greater elsewhere.

Figure 3 shows the time response to a step temperature distur-

Fig. 3. Time response of furnace to step temperature change of 7.5°C in controller set point.

bance which was initiated by an abrupt change of 7.5°C in the controller set point. The trace represents the deviation from the new set point during the period of recovery which is complete within 20 s, again demonstrating the advantages of a low thermal mass.

The furnace has now been in use for 18 months and has given eminently satisfactory service. The life of the heating element appears to be dictated largely by the care of the operator in excluding air from the furnace during the preform loading and fiber-starting operations, and it is typically possible to work for months before the element becomes reduced in section by oxidation and requires replacement. The life of the remaining components is considerably longer.

The furnace, shown in operation in Fig. 4, has been used in the fabrication of solid silica fibers, hollow silica for liquid-filled fibers, single material silica fibers, silica cladded fibers with a phosphosilicate glass core and borosilicate-cladded, phosphosilicate core fibers. The latter two have had attenuations of 2 dB/km and 3 dB/km, respectively. The excellent radial uniformity of temperature is reflected in the good circularity of the fibers as shown by the typical cross section in Fig. 5. The boule remaining after a tubular preform has been simultaneously collapsed and drawn into fiber is shown in Fig. 6. The preform consisted of a silica tube with layers of phosphosilicate glass deposited on the inside.

Fig. 6. Boule remaining after tubular preform shown in Fig. 4 has been simultaneously collapsed and drawn into fiber.

Conclusions

A graphite resistance furnace having accurate temperature control and capable of the precision drawing of silica-based fibers at temperatures up to at least 2200°C has been constructed. It is strong and reliable in operation and is suitable for routine production purposes.

Acknowledgment

Grateful acknowledgment is made to E. R. Came for his assistance in the design of the furnace and for its construction.

References

NEW SILICA-BASED LOW-LOSS OPTICAL FIBRE

Indexing terms: Fibre optics, Optical waveguides

A new type of silica-based optical fibre has been made from relatively cheap and abundant materials. The attenuation is very low over the entire range from the near ultraviolet to the gallium-arsenide-laser wavelength. The minimum loss of 2-7 dB/km occurs at 0.83 μm.

Introduction: In many ways, a suitable configuration for an optical-fibre waveguide is a compound glass core surrounded by a compound glass cladding of lower refractive index. Many fibres of this type have been reported, but the best transmissions obtained so far are in the region of 30 to 40 dB/km. The loss is largely due to transition-metal ion impurities, which are difficult to remove completely. A variant of the cladded glass fibre is Selfoc® fibre, in which the core has a parabolic variation of refractive index and a minimum loss of less than 20 dB/km has been obtained.

Silica, on the other hand, is produced commercially in a very pure form having a bulk-transmission loss of the order 2 dB/km at a wavelength of 1.06 μm. However, for it to be incorporated as one component of a claded fibre, a second, compatible material must be found, having a similar softening temperature, expansion coefficient etc., to use as core or cladding, depending on the refractive index. One possibility is to modify the optical properties of silica by the addition of another oxide to form a simple compound glass containing a high proportion of silica. Thus, in 1972, a vapour-deposition technique was used to deposit a titania-silica core glass on the inside of a silica tube, which was subsequently drawn into a fibre. Fibres have also been drawn from rods of silica cladded with a titania-silica-glass layer, and we have successfully repeated this technique. More recently, losses have been announced with a modified silica core material, apparently comprising a mixture of silica and germania. Subsequently, there have been further reports of the successful use of the silica-germania mixture and also of the borosilicate-cladded silica fibre.

Fig. 1 Cross-section of phosphosilicate-core fibre illuminated from far end

Although commonly used in the semiconductor industry, and readily available in pure form, germania is expensive and likely to become more so, since germanium is not an abundant element. An alternative, cheaper and more common material would therefore be preferable, providing that it can be combined with silica to form a suitable low-loss glass. We have tried a number of combinations and find that a phosphosilicate glass core in a pure silica cladding provides a very low-loss fibre. Phosphorus is one of the most common elements and is relatively cheap, and the resulting fibre has a number of interesting properties. The most important wavelength range for optical-fibre communication systems is that of the various semiconductor light sources based on gallium arsenide, namely 0.8 to 0.9 μm, and, although not yet fully developed, the fibre has its minimum loss of 2.7 dB/km in this region. Further, the addition of phosphorus pentoxide to silica to form a binary glass does not appear to increase significantly either the intrinsic material absorption or the scattering.

Manufacture: The phosphosilicate glass is made by a controlled chemical-vapour-deposition technique. The starting materials are purified silicon tetrachloride and phosphorus oxychloride, which are vapourised, mixed with oxygen and passed through a tube of silica cladding glass. This tube containing the flowing gas mixture is traversed through a fibre-pulling furnace, which is operated at an appropriate temperature. Simultaneous oxidation and fusion occurs so that a clear phosphosilicate glass is deposited on the inner surface. A suitable thickness is obtained in about 1 h. The composite tube is then simultaneously collapsed and drawn into a fibre, or the operation can be carried out in two separate stages. We use a graphite resistance-heated furnace, which has been developed in these laboratories. The operating temperature, which can be in excess of 2200 °C, is monitored by a thermocouple to allow accurate control and repeatability.

Fig. 2a shows a typical fibre cross-section, illuminated from the far end. There is a dark spot in the centre, presumably due to some volatilisation of phosphorus pentoxide from the inner surface of the deposited layer at the temperature (> 2000 °C) required for fibre drawings. The fibres typically have a core diameter of 50 μm, an overall diameter of 150 μm and are drawn in lengths of about 1.2 km. The numerical aperture can be varied up to 0.18 or more as desired by control of the relative concentration of phosphorus pentoxide in the core.

Fibre attenuation: The loss in pure bulk silica is mainly by Rayleigh scattering, but with a small absorption component from the intrinsic ultraviolet absorption edge. There may also be impurity bands superimposed on this due to hydroxyl ions. The addition of a second oxide in making a high-silica-content glass for use as core material is expected to introduce an additional component of scattering due to compositional fluctuation. The intrinsic absorption may also be increased, depending on the proximity of the ultraviolet-absorption edge of the additive.

Fig. 2a shows the spectral absorption curve of the SiO2/PO45+ core in Suprasil cladding. The main features are as follows:

(a) Most striking, perhaps, is the smoothness of the curve over the short-wavelength portion, where, as indicated by Fig. 2a, the loss is below that of pure silica, showing that the addition of phosphorus pentoxide to silica does not increase either the scattering or the absorption. In addition, there is no evidence of the drawing-induced colour centres at 0.6 μm, which have been observed elsewhere. The minimum attenuation measured at 0.83 μm is 2.7 dB/km. The total loss at 0.633 μm is 5.8 dB/km, compared with the Pinnow et al. prediction of 7 dB/km, of which 4.8 dB/km is due to scattering. This implies that our intrinsic absorption is only
1 dB/km and is therefore less than the expected value of \( \approx 2 \text{ dB/km} \). Also, at 0.45 \( \mu \text{m} \), again assuming the scatter loss to be that of silica, i.e. 19 dB/km, our intrinsic absorption is 7 dB/km, compared with a predicted value for silica of 10 dB/km. Further, the total scattering in the fibre at 0.633 \( \mu \text{m} \) has also been measured directly by an integrating sphere, and the loss of 5-8 dB/km obtained is greater than that of silica, thus implying an even smaller intrinsic absorption. It would appear that the intrinsic absorption is less than that predicted.7 If this is correct, the ultimate loss at 0.85 \( \mu \text{m} \) could be less than 2 dB/km. To determine the true limit of intrinsic absorption, the loss measurements must be extended to wavelengths below 0.4 \( \mu \text{m} \).

(b) The effect of the OH impurity can be clearly seen, particularly the peak at 0.95 \( \mu \text{m} \) rising to 40 dB/km. We believe that the OH bands are not characteristic of the phosphosilicate core material, but are due entirely to the high hydroxyl content of the Suprasil cladding, which has a bulk loss of 1000 dB/km at this wavelength. The normalised frequency of the fibre represented in Fig. 2a is \( V = 20 \), and hence of the order of 10\% of the power is carried by the cladding, so that the loss contribution of the latter at 0.95 \( \mu \text{m} \) will be significant. This has been confirmed by making further fibres with

Conclusion: A new type of silica-based fibre has been made from relatively cheap and abundant materials and having an attenuation which is

(a) exceptionally low over the full range from the gallium-arsenide-laser wavelength to the near ultraviolet

(b) somewhat lower than has been predicted for pure silica.

The minimum attenuation is 2.7 dB/km and occurs at 0.83 \( \mu \text{m} \). By controlling the phosphorus-pentoxide concentration in the core, the numerical aperture can be varied up to 0.18 or more as desired. The intrinsic loss of phosphosilicate glass appears to be no greater than that of pure silica.

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References

4 Schultze, F. C.: 'Preparation of very low-loss optical waveguides', Presented at the American Ceramic Society meeting, Cincinnati, Ohio, USA, 1973

* After this letter was accepted for publication, the attenuation, as measured in a length of 1.2 km, has been reduced appreciably at all wavelengths above 0.85 \( \mu \text{m} \), and is now 2-4 dB/km at 1 \( \mu \text{m} \). The OH bands have also been virtually eliminated, and peaks of less than 1 dB/km at 0.95 \( \mu \text{m} \) have been obtained.
PREPARATION OF WATER-FREE SILICA-BASED OPTICAL-FIBRE WAVEGUIDE

Indexing terms: Fibre optics, Light absorption, Losses, Optical waveguides

A technique is described whereby the hydroxyl absorption bands of the new phosphosilicate-core optical-fibre waveguide, which arise from impurities in the cladding, can be largely eliminated. The resulting fibre has ultralow loss over the entire wavelength range 0.4-1.1 μm.

Introduction: A problem commonly encountered in the preparation silica-based optical fibres is the presence of OH absorption bands at a number of wavelengths, particularly at 0.95 μm. We have observed the same effect in a new type of fibre comprising a phosphosilicate glass core in a silica cladding. These fibres are made by an accurately controlled chemical-vapour-deposition technique in which silicon tetra-chloride and phosphorus oxychloride are simultaneously oxidised and fused into a clear layer of phosphosilicate glass on the inside of a silica tube that is subsequently drawn into a fibre.

It is found that, when the silica tube used is of a synthetic high hydroxyl content (1200 parts in 10^6), such as Suprasil, the minimum attenuation is between 2 and 3 dB/km, and the OH band at 0.95 μm rises to a peak of about 40 dB/km. On the other hand, with Heraflux tubing, in which the water concentration is only one-tenth that in Suprasil, but the level of other impurities is higher, the minimum loss rises to 6 dB/km, but the peak at 0.95 μm falls to 15 dB/km. This is a strong indication that the cladding has an appreciable effect on the transmission loss, which is to be expected, since, at the normalised frequency of the fibre of V = 20, it carries approximately 10% of the propagating power. We conclude, therefore, that the OH impurity giving rise to the absorption bands is present mainly in the cladding and not in the vapour-deposited core. It follows that, if the relative amount of optical power propagating in the impure cladding can be decreased, the hydroxyl bands can be correspondingly reduced.

Results and discussion: A typical fibre cross-section (Fig. 1) clearly shows the Suprasil cladding and the three layers of increasing refractive index. The overall diameter is 145 μm and the numerical aperture of this particular fibre is 0.16. The spectral attenuation has been measured over the entire drawn length of 1.2 km and the resulting curve (Fig. 2) is remarkably smooth. As predicted, the broad iron absorption band in the vicinity of 1 μm has been largely removed by some fairly straightforward improvements in fabrication techniques. Further, the intermediate layers have almost eliminated all the OH bands. The only one remaining is at 0.95 μm, but its height has been reduced to 2 dB/km. In fact, in some other samples, the magnitude is only 0.8 dB/km and the effect of the wings of the band at the semiconductor-laser wavelength is negligible. As a result of these modifications, the attenuation is very low over the entire wavelength range and is below 5 dB/km between 0.7 μm and the highest wavelength measured (1.1 μm) with a minimum of 2.4 dB/km. Even at 0.45 μm, the loss is less than 20 dB/km and transmission in the near ultraviolet, in particular, is considerably better than has previously been reported for conventional u.v.-transmitting fibres. It should be noted that extrapolated absorption and scatter measurements suggest that, at least from 0.4 to 1.1 μm, the intrinsic loss of phosphosilicate glass is similar to that of pure silica. This indicates that, with further improvements, it should be possible to obtain an attenuation of less than 2 dB/km in the regime (from 0.85 to 0.9 μm) of gallium-arsenide devices, and still lower values at longer wavelengths. Measurements on some preliminary 1 km lengths of graded-refractive-index fibres show that they have a slightly higher overall attenuation, but similarly small hydroxyl peaks. Again, it is expected that further improvements are possible.

Conclusion: The phosphosilicate glass produced by vapour deposition has ultralow loss over the entire wavelength range so far investigated (0.4 to 1.1 μm). When used as the core material in an optical fibre, the effect of impurities in a silica cladding of commercial quality can be greatly reduced by adopting the technique of (a) a buffer layer surrounding the core, (b) a graded-refractive-index distribution or (c) a stepped approximation to a graded refractive index. The resulting fibre has an attenuation comparable with that of the core.

Fig. 1 Cross-section of stepped-refractive-index fibre

Showing the Suprasil cladding and three successive core layers of increasing refractive index. The overall diameter is 145 μm.

Method: One method of doing this during the preparation of the phosphosilicate-core fibre would be to deposit initially a silica layer of low hydroxyl content on the inside of the commercial silica supporting tube. This can be done, but, to produce simultaneous oxidation and fusion to a clear glassy layer, the deposition rate must be kept low. Thus the time taken to build up the required thickness of this layer is unnecessarily long. However, if, instead, a layer of phosphosilicate glass having a suitably small proportion of P2O5 is deposited, the deposition rate can be increased appreciably, and the refractive index is not changed greatly from that of silica.

An alternative approach is to use the fact that a graded-refractive-index core effectively restricts the optical power to a region closer to the fibre axis than in a normal cladded fibre. Reflections at the core-cladding interface do not occur, except for those rays propagating near the critical angle, and hence the amount of power contained in the cladding is reduced. With our method of vapour deposition, the fabrication technique for a graded-refractive-index fibre is a simple one and involves introducing only successive changes in the relative concentration of the reacting gases. The first layer may now, as before, contain a suitably small proportion of P2O5 and may be deposited at a much higher rate than the silica. The second, and subsequent, layers contain increasing concentrations. The total deposition time for the entire core is about 1 h. However, we have found that a stepped approximation to a graded-refractive-index core, in which the refractive index increases in three successive steps, is equally effective in confining the optical power to the core region. We have fabricated fibres of all three types, but present here the results obtained only for the latter version.

Fig. 2 Spectral attenuation curve of 1.2 km length of phosphosilicate-core silica-cladded fibre shown in Fig. 1

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References

3 SCHWARTZ, P. C.: Preparation of very low-loss optical waveguides. Presented at the 1973 American Ceramic Society meeting, Cincinnati Ohio, USA.
A BOROSILICATE-CLADDED PHOSPHOSILICATE-CORE OPTICAL FIBRE

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A new type of optical fibre waveguide is described having a graded phosphosilicate core in a borosilicate cladding. The attenuation, which is independent of the supporting jacket made from commercial silica, is consistently low over the wide wavelength range 0.75 to 1.25 μm and the numerical aperture is 0.23. The pulse dispersion is 1.3 ns/km.

1. Introduction

A convenient method of making a low-loss optical waveguide is to deposit a suitable glassy material of high silica content on the inside of a silica tube which is subsequently drawn into a fibre. The deposited layer then becomes the core of the fibre and is contained in the silica cladding. Unfortunately most commercial silica tubing contains impurities and in particular the presence of OH radicals can prove to be troublesome, causing a number of peaks in the absorption curve of the fibre, including one at 0.95 μm. This arises because some of the guided energy is present in the cladding, especially in a simple stepped-index configuration, to a degree dependent on the normalized frequency, and cladding impurities therefore contribute to the total fibre attenuation. However, a technique was recently described [1] for making the transmission properties independent of the silica supporting tube and was applied to the phosphosilicate glass fibre. It involves the incorporation of a buffer layer of low P₂O₅ content immediately adjacent to the core with the result that propagation is controlled entirely by the deposited layers and is independent of the silica tube. The latter now acts only as a supporting structure so that relatively low-quality commercial tubing can be used instead of the ultra-pure, and therefore expensive, variety.

An alternative method of isolating the propagating fields from the supporting tube is to increase gradually the P₂O₅ concentration in successive layers [1] so that, after drawing the preform into fibre, a graded refractive index is produced across the core.

However, in both the buffered and graded-index cores the numerical aperture of the fibres is limited by the maximum concentration of P₂O₅, which it is possible to combine with SiO₂ while still retaining a compatible temperature coefficient of expansion with the silica supporting tube. So far we have achieved a value of 0.18 in a core having a diameter of 50 μm; the loss has a minimum value of 2.0 dB/km and is low over a wide range of wavelengths. In order to increase the efficiency of coupling for incident radiation from a light-emitting diode a higher value of numerical aperture is desirable and can be brought about in two ways. The first is to increase the refractive index of the core and the second is to reduce that of the cladding. We have chosen the second alternative and have replaced the buffer layer by one of a borosilicate glass [2] having a refractive index lower than that of silica. The fabrication technique is similar to that for phosphosilicate glass which is described briefly below.

2. Fibre fabrication

The manufacturing process comprises the three stages of (i) chemical vapour deposition of the appropriate glassy layers in a silica tube, (ii) collapse of the tube and layers into a solid rod composite preform and (iii) drawing the preform into a fibre. The starting materials for the deposition process are volatile chlorides of the required constituents, namely SiCl₄, POCl₃ and BCl₃. The phosphorous oxychloride is normally distilled in the laboratory in order to improve the purity. To produce a phosphosilicate glass oxychloride is bubbled through separate containers of SiCl₄ and POCl₃ as in fig. 1a, the two vapour-carrying gas
streams are combined, diluted with further oxygen, and passed through the silica supporting tube. As shown schematically in fig. 1b a short furnace is traversed along the tube and oxidation of the chlorides to produce the relevant oxides takes place.

Chemical vapour deposition of glasses is not new and has been used for the production of synthetic silica for some years. Oxidation of silicon tetrachloride is achieved either by flame hydrolysis or by high-temperature plasma-torch pyrolysis. Low-loss optical waveguides have been made by a similar process at the Corning Glass Works. Furthermore in the semiconductor industry thin films of glass have been deposited onto a substrate by means of a low-temperature surface oxidation reaction but the deposition rate is very low. However, the method described here differs from these because we have found [3] that the oxidation reaction of the chlorides of silicon and phosphorus occurs spontaneously in the gas phase at the relatively low temperature of 1300°C to form a dense fog of small glass particles. In addition, provided the viscosity of the glass is substantially lowered by the incorpora-

tion of sufficient phosphorus pentoxide (or other suitable component) then the glass particles fuse on the walls of the container to form a clear, uniform, homogeneous layer of phosphosilicate glass. Thus a high deposition rate can be obtained since no gas dilu-

tants are required to slow the reaction and the glass deposition may occur directly on the walls of a silica tube which, because of the comparatively low temperature, suffers no deformation. This technique was also developed independently at Bell Telephone Laboratories [4] although the details of our method are somewhat different and so are the materials.

Typical operating conditions are as follows. For a silica tube with a bore of 10 mm the flow rates of oxygen and silicon tetrachloride vapour are kept constant at 600 and 35 ml/min, respectively, while that of the phosphorous oxychloride vapour is varied over the range 1 to 13 ml/min. With a furnace temperature between 1300 and 1450°C the phosphosilicate glass layer is deposited on the inner wall as the tube is passed through. (In practice it is more convenient to keep the furnace fixed in position and to traverse the silica tube.)

The deposition time of each layer is 8 minutes for a typical length of 50 cm and the P₂O₅ concentration is between 2 and 15 at. up depending on the flow rate of the phosphorous oxychloride. With these flow rates and temperatures the amount of downstream soot formation is small. The refractive index of successive layers, each about 12 μm thick, can be accurately controlled and a wide range of profiles, from a uniform to a graded-index, can be produced.

With the present fibre the cladding layers of borosili-

cate glass are produced by a system similar to that in fig. 1a but with an additional input for boron trichlo-

gas. The flow rates of BCl₃ and SiCl₄ are 8 and 35 ml/min, respectively, together with 450 ml/min of oxygen. A cross-section of a portion of a typical series of depositions is shown in fig. 2a. The first 3 layers are of constant composition while the next 3 are formed by reducing the BCl₃ flow rate to zero in stages. The amount of POC1₃ is then increased gradually from 0 to 9 ml/min over the next 14 layers, giving a total of 20. The successive depositions of phosphosilicate in particular stand out clearly in fig. 2a but diffusion takes place during the subsequent tube-collapsing and fibre-drawing stages producing some smoothing out of the concentration gradient. A fibre having a graded-index core in a borosilicate cladding is thereby
The preform is drawn into fibre with a precision fibre-drawing machine [5] having a speed control and stability to better than 0.1%. The furnace is of novel design and uses resistance-heating so that operating temperatures up to 2200°C can be stabilized to ±0.05°C. The hot zone is small, giving a short response time, and the temperature distribution is carefully profiled. For experimental purposes a fibre length of 1.2 km is normally drawn from a 50 cm preform although there is no reason why this length should not be considerably greater.

3. Results

Fig. 2b is a photograph of the end of a typical fibre. The graded core of phosphosilicate glass is surrounded by the cladding of borosilicate glass which shows up as a dark ring. The outer annular ring of intermediate brightness is the silica supporting tube. The measured numerical aperture of 0.23 is 40% larger than that of the conventional phosphosilicate fibre and the core diameter is 66 μm. Thus the numerical aperture and core diameter are comparable with those of many multi-component glass fibres.

The attenuation, fig. 3, has been measured over the wide wavelength range of 0.44 μm to 1.65 μm, using a silicon detector below 1.1 μm and a lead sulphide detector at longer wavelengths. It may be seen that there is a broad “window” from 0.75 to 1.25 μm where the loss is low and nearly constant. The minimum value of 3 dB/km is small but would have been lower but for the poor quality of BCl₃ available. The
phosphosilicate glass core a low-loss fibre of increased numerical aperture has been produced. The core diameter is quite large thus easing the problem of efficient coupling from light-emitting diodes, as well as facilitating jointing and handling generally. As with phosphosilicate fibres the technique of chemical vapour deposition is used which is flexible and allows a range of refractive index profiles to be easily selected. The raw materials are inexpensive compared with those required for "soft" glass fibres and the low loss of 3 dB/km has been obtained despite the poor quality of the boron trichloride. The region of low attenuation extends out to 1.25 μm where, as we show elsewhere, the material dispersion falls to zero. Consideration should therefore be given to the operation of optical fibre communication systems at these longer wavelengths since a moderately wide bandwidth might be attainable using light-emitting diodes thus obviating the need for lasers which are still not available with adequate lifetimes.

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References

Optical fibres based on phosphosilicate glass


Indexing terms: Fibre optics, Glass, Vapour deposition

Abstract

The homogeneous chemical vapour-deposition technique, developed for the preparation of phosphosilicate glass fibres, is described. The properties of the binary phosphosilicate glass are outlined and details of preform fabrication and fibre drawing are given. Multimode graded-index fibres have been produced in lengths up to 4 km, with numerical apertures up to 0.25, attenuations as low as 2 dB/km and with pulse dispersions of below 1 ns/km depending on the source used. Single-mode fibres have also been made with attenuations close to that of pure bulk silica at the design wavelength and with a pulse dispersion of less than 0.1 ns/km.

1 Introduction

When, in their classic paper 1 of 1966, Kao and Hockham proposed the use of cladded optical fibres as long-distance transmission lines only one material was known to have a sufficiently high transmission. Thus, synthetically produced silica, obtained commercially by flame hydrolysis or plasma-arc oxidation of silicon tetrachloride, is a liquid which is easily purified by conventional techniques such as fractional distillation and the associated compounds of the principal contaminants (mainly transition-metal elements) of conventional glasses, being relatively low volatility, may therefore be removed. Secondly the glass is formed directly and requires no further processing in containers which may introduce impurities.

However, to form a convenient type of guiding structure a second material is required which has a different refractive index and is sufficiently compatible with silica to be drawn into a composite fibre. It is, not to make ultra-low-loss fibres by conventional methods and an alternative approach is to modify the properties of silica by the addition of a second component to increase or decrease the refractive index from that of pure silica. This high-silica glass might then be used with silica to produce a core and cladding combination. Several methods and materials have been used successfully. Thus, a silica/titania glass produced by flame hydrolysis 2 resulted in the first low-loss fibre, having an attenuation of 20 dB/km. Another combination, having a refractive index lower than that of silica and hence suitable for use as a cladding, is a borosilicate glass initially made 3 by the oxidation of silane and boron trichloride. A new variation of the chemical vapour-deposition technique, involving the simultaneous oxidation and fusion of the components, produced phosphosilicate glass 4 fibres and germania-doped 5 silica fibres; there have also been reports of the doping of silica with alumina 6 and fluorine 7.

The present paper describes both the properties of fibres based on phosphosilicate-core fibres and the method, developed in the Southampton laboratories, for their manufacture. The technique involves a homogeneous gas-phase reaction and produces a high deposition rate of pure phosphosilicate glass on the inside of a tube which is subsequently collapsed and drawn into fibre.

The starting materials, volatile chlorides, are vapourised, diluted with excess oxygen and passed through a silica supporting tube which is traversed by a short hot zone at a temperature of about 1 500°C. Within the hot zone, simultaneous oxidation and fusion of the chlorides occurs to produce a layer of glass, typically 10–15 mm thick, on the inside walls.

2 Phosphosilicate glasses

The addition of another oxide component to silica to form a binary glass by homogeneous chemical vapour-deposition requires (a) that a volatile halide of the proposed additive exists which is preferably a liquid at room temperature and (b) that this halide reacts spontaneously with oxygen at an elevated temperature, which is below that of the softening point of the silica substrate (~1 500°C). These two requirements restrict the choice of glass system considerably but we have found that P2O5 is suitable, producing very low-loss fibres although, as will be shown, the technique is applicable to other oxides, either separately or in combinations with that of phosphorus.

The P2O5/ SiO2 glass system has not been extensively studied as it is difficult to make by conventional means because of the volatility of phosphorus pentoxide. Furthermore, P2O5 is not an obvious choice as a component which can be added to silica since it sublimes at 300°C, is hygroscopic and has an expansion coefficient some 25 times larger. However, in combination with silica it forms a stable glass having an expansion coefficient compatible with that of pure silica at least for concentrations up to about 25 mol%. The resultant glass shows no tendency either to phase separation or to devitrification and preliminary measurements indicate a good resistance to attack by water.

The variation of the refractive index of the deposited phosphosilicate glass is shown in Fig. 1 as a function of the equivalent proportion of P2O5 in the gas stream. The experimental points were obtained from measurements of the numerical aperture of a series of fibres fabricated using different gas phase ratios of POCl3 to SiCl4. Microprobe analysis and separate tests have shown that, at least for P2O5 contents below 10 mol%, the deposited glass has a similar composition to that expected from the ratio of the reactants in the vapour. Thus, the data for the lower P2O5 concentrations fits fairly closely to the dashed curve which is drawn assuming a pure additive and linear relationship between the refractive indices of silica (1.458) and pure phosphorus pentoxide (1.52). However, the departure at higher concentrations may either represent inherent nonadditivity in the P2O5/SiO2 system, or, more probably, it may indicate that the deposited-glass composition no longer reflects that in the reacting gases.

It may also be seen from the figure that at a P2O5 concentration of 24 mol% the refractive index differs from that of silica by 0.5% corresponding to a numerical aperture of 0.19. At this concentration, corresponding to a weight ratio of 43% P2O5, there is also a difference in the expansion coefficient and the viscosity compared with silica. The expansion coefficients of P2O5 and SiO2 are, respectively, 140 × 10−6°C−1 and 5.5 × 10−6°C−1 and the composite phosphosilicate glass will therefore have an increasing expansion coefficient with P2O5 content. This fact ultimately limits the amount of P2O5 which can be incorporated into the fibre, as the stress resulting from the expansion mismatch between the deposited layers and the silica substrate eventually causes spontaneous phase formation.

The maximum concentration of germanium (60 × 10−6°C−1) and boron oxide (150 × 10−6°C−1) which can be incorporated into silica is ultimately limited in a similar way.

A particular advantage of the phosphosilicate combination is that even small admixtures of P2O5 lower the viscosity of silica appreciably, enabling the soft formers in the gas-phase reaction to fuse into a clear glass layer at a temperature well below that at which the silica tube deforms. At a high P2O5 content, however, the viscosity becomes so low that care must be taken to prevent deformation of the core during the preform collapse stage.

3 The homogeneous chemical vapour-deposition technique for phosphosilicate fibres

Chemical vapour deposition of glasses is not new, it has been used for some time in the semiconductor industry to deposit thin films of glass on substrates for use as passivation layers or diffusion sources. For this application, heat formation is avoided by employing a heterogeneous (surface) reaction at low temperatures and low reactant concentrations with the result that the deposition rate is also low. To increase the deposition rate we have developed a technique...
which utilizes the homogeneous (gas-phase) reaction at high temperature and with high reactant concentrations. A dense dispersion of small glass particles is produced and is fused onto the walls of the supporting tube at temperatures of approximately 1400°C, the precise value depending on the composition. The reaction does not involve the presence of hydrogen so that glass of very low OH content is obtained.

Silica and phosphorus pentoxide are derived by direct oxidation of silicon tetrachloride and phosphorus oxychloride vapours according to the following equations:

\[
\text{SiCl}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{Cl}_2
\]

\[
4\text{POCl}_3 + 3\text{O}_2 \rightarrow 2\text{P}_2\text{O}_5 + 6\text{Cl}_2
\]

After fusion the oxides form a binary phosphosilicate glass in which the concentration of phosphorus pentoxide is always equal to the vapour phase. The oxides are collected by bubbling oxygen streams through temperature-controlled Dreschel bottles containing the liquid chlorides, Fig. 2A. It would be possible to use phosphorus trichloride instead of the oxychloride but an inert carrier gas would be necessary as PCl₃ oxidizes to POCl₃ in the presence of oxygen with an accompanying rise in temperature. This would cause a temperature, and thus a vapour pressure, fluctuation in the flask and a temperature rise is more convenient requiring, as it does, only one carrier gas. The ratio of the oxygen flow rate through the phosphorus oxychloride to that through the silicic tetrachloride is related to the molar fraction \( M \) of phosphorus pentoxide in the vapour phase by

\[
R = K \left( \frac{M}{1-M} \right)
\]

where \( K \) is a constant which depends on the vapour pressures of the liquid chlorides. It is assumed that the oxygen streams are fully saturated with vapour. At 20°C the vapour pressure of silicon tetrachloride is 193 torr, that of phosphorus oxychloride is 28 torr so that \( K = 173 \). Thus, \( R \) lies between 0·17 and 4·45 for \( M \) ranging from 1 m/o to 20 m/o. In practice, \( M \) is most easily controlled by holding the oxygen flow rate through the silicon tetrachloride constant and varying the oxygen flow through the phosphorus oxychloride. The rate of glass deposition has been studied for the above conditions and for our particular tube dimensions and equipment in which the hot-zone length is about 5 cm. A typical result is given by Fig. 3 which shows the variation in deposited layer thickness, produced in a single pass of the hot zone, as a function of traverse speed and reactant concentration expressed as the flow rate of SiCl₄ for a given P₂O₅/SiCl₄ ratio of 10 m/o. It can be seen, first that for any given traverse speed the layer thickness may be increased by increasing the reactant concentrations. Secondly, the thickness of an individual layer may be increased by reducing the traverse speed; but, on the other hand, fewer traverses can then be made in a given period of time. Thus, while the traverse speed affects the individual layer thickness it has little effect on the overall deposition rate of the multilayer structure which is controlled mainly by the reactant concentrations. The best flow rates and traverse speeds have been determined experimentally and typical values of 100 ml/min for the oxygen flow through the silicon tetrachloride and 120 ml/min respectively, give a very adequate deposition rate of a 10μm thick phosphosilicate-glass layer per traverse. Under these conditions the yield of the process is in the range 40–60% by weight of vapour deposited as glass.

Excess oxygen is added to the two vapour-carrying oxygen streams, Fig. 2A, to control the deposition conditions, particularly the formation of the glass-particle dispersion downstream from the hot zone. With little or no excess oxygen, the glass particles tend to flocculate and stick to the colder tube walls in large feathery conglomerations which cause nonuniformities in the deposited layer after fusing by the traversing hot zone. An additional oxygen flow of between 300 and 500 ml/min seems to cure this problem by increasing the gas velocity through the tube and preventing soot flocculation.

The hot zone is provided by either a silicon-carbide resistance furnace or a surface-mix oxypropane gas burner. A burner is convenient for rapid experimentation but for more controlled deposition conditions a silicon-carbide furnace is preferable. The description which follows relates to the use of a gas burner but a similar procedure is followed to the case of a furnace. As the burner moves along the tube the hot-zone temperature is a function of both the flame temperature and its traverse speed. The latter is usually kept constant at a value giving a reasonably thick phosphosilicate-glass layer (~10μm), and the hot-zone temperature is changed by
varying the oxygen flow to the burner. The temperature at which the deposited materials fuse into a clear homogeneous glass layer lies between 1400°C and 1550°C and is a function of phosphorus-pentoxide content, falling slightly with increasing concentration.

Provided the ratio of phosphorus-pentoxide present is less than 20 m/o and the hot-zone temperature is below about 1600°C, then the resulting fused-glass composition is largely independent of the hot-zone temperature. This is certainly not the case for germania-silica glass, where the germania concentration in the glass is found to be a strong function of deposition temperature.

![Graph showing variation in thickness of a single deposited phosphosilicate layer as a function of traverse speed of the hot zone and of reactant concentration.](image)

To simplify fibre fabrication an automated machine has been developed to carry out the chemical vapour-deposition process, Fig. 2B. The vertical silica support tube is held at each end by coaxial chucks that are rotated at the same speed, about 50 rev/min, so that there is no relative motion between them. The gas mixture from the gas distribution system of Fig. 2A is fed into the top of the silica tube via a rotary swivel joint, and the reaction by-products and excess reactants are extracted at the bottom. The oxy propane burner is moved by a d.c. motor and gearing so that the 50 mm long hot-zone travels down the tube at a controlled constant speed of up to 350 mm/min. At the end of the downward pass the burner is driven rapidly back to the top of the tube, at a reduced temperature to prevent deposition, and the cycle repeats itself. The extent of travel of the burner is limited by microswitches which also provide control signals for a programmer linked to the mass-flow controller, Fig. 2A, to control the flow of phosphorous oxychloride. This enables the phosphorus pentoxide concentration of each layer to be accurately pre-set, and thus a step approximation to any required concentration profile can be produced. During the subsequent preform-collaps and fibre-drawing stages some diffusion occurs between adjacent layers so that in the core of the fibre the concentration gradient, and thus the refractive index profile, becomes smoothed over distances comparable with the layer thickness; the stepped structure is not observed.

In addition to the binary phosphosilicate glass we have applied the chemical vapour-deposition technique to other combinations. For example, the borosilicate glass consisting of boron oxide and silica, has been used as a cladding glass with fibres having a phosphosilicate core. The glass is formed in the same way by simultaneous oxidation and fusion of boron trichloride or boron tribromide and silicon tetrachloride within the silica tube. Boron tribromide is a liquid at 20°C and may be introduced into one of the Dreschel bottles in the gas distribution system of Fig. 2. On the other hand boron trichloride is a gas, so there is no need for an oxygen bubbler.

It has been found that the addition of fluorine to silica also lowers its refractive index, and we have fabricated phosphosilicate fibres with fluorine-doped silica claddings. The fluorine is obtained by dissociating sulphur hexafluoride or a fluorocarbon, which is fed at an appropriate flow rate into the silicon tetrachloride and excess oxygen stream before it enters the silica tube. Fibres have also been made having cores of the ternary glass system formed by phosphorus pentoxide, germania and silica. The addition of phosphorus pentoxide to germania-silica glass considerably reduces the viscosity, and helps prevent bubble formation within the fibre core layers.

4 Tube collapse

The second stage in fibre fabrication is the collapse of the composite tube and deposition layers into a solid preform. It has been found that, while the quality of the cladding is governed by the deposition process, the circularity of the final preform and concentricity of the core and cladding are mainly controlled by the collapsing process so that great care is therefore required during this stage.

To effect collapse, one end of the silica tube is heated to approximately 1900°C with an oxy-hydrogen burner. At this temperature the viscosity of the glass is sufficiently low for surface tension forces to initiate tube collapse. The hot-zone, which is about 20 mm long, is then slowly traversed along the rotating tube to produce a uniform partial collapse. Depending on the traverse speed, between two and four passes are normally sufficient to cause total collapse of the tube into a symmetrical cylindrical preform in a time of about 20 min.

When fibres having a high concentration of Pr2O3 in the core are being manufactured there is an increased tendency for the tube to form an elliptical cross-section during the collapsing process. This may be counteracted by applying a slight positive pressure (approximately 1 millibar) to the inside of the tube during collapse and by using a controlled high-pressure air-stream to quench the preform shortly after its closure into a rod and immediately after the traverse of the burner.

One problem which has not been completely overcome, however, is the volatilisation of Pr2O3 from the innermost phosphosilicate layer during the high-temperature collapse. This effect is commonly observed in fibres having binary glass cores in which one component is more volatile than the other and causes a characteristic dip in the refractive index profile at the centre of the core region, Fig. 5. It can be minimised by (i) increasing the total deposition thickness (ii) increasing the concentration of the more volatile component in the final layer and (iii) substituting, or adding, a less volatile component to the last layer.
Fibre drawing

The preform is drawn into a fibre on a precision fibre-drawing machine consisting of a crosshead drive to feed the preform into a furnace, from which the fibre is drawn onto a winding drum. To maintain constant fibre diameter over the entire pull, the preform feed rate and the fibre-pulling rate are interlocked and have a stability greater than 0.1%.

Conventional oxyhydrogen-flame furnaces are unsuitable for precision fibre-drawing purposes because of their lack of controllability and repectility. A novel graphite resistance furnace has therefore been developed specifically for drawing fibres of high silica content. Furnace-temperature control is achieved by use of an optical pyrometer (also developed in these laboratories) and a standard s.c.r. power controller. To prevent oxidation of the graphite at the high temperatures required, the furnace is operated with a flow of argon through it. There are several notable features about the design and performance of the furnace. First, it can operate at temperatures up to 2200°C, and having reached set temperature, it is stable to within 0.06 deg C. Secondly, the low thermal mass and efficient insulation of the furnace hot zone results in a power consumption of 1.4 kW at an operating temperature of 2000°C. Thirdly, the high thermal-shock resistance of graphite allows the furnace to be raised from cold to working temperature in approximately 3 min. Fourthly, because of the low thermal mass and high stability of the furnace the response time to a temperature disturbance is very short — typically the furnace will fully respond to a 7.5 deg C temperature step in less than 20 s. Finally, the furnace hot zone has excellent radial and longitudinal temperature uniformity enabling the circularity of the preform to be retained during its transformation to a fibre. The temperature is monitored either with a tungsten-rhenium thermocouple placed close to the hot zone or by an optical pyrometer looking into the hot zone.

Fibre drawing is usually carried out at a temperature of approximately 2040°C, and at pulling speeds in the range 0.75–1.5 m/s. Over lengths in excess of 1 km the fibre diameter variation is less than ±2 µm in 150 µm and is generally due to taper in the preform.

Fibre lengths of up to 4 km, with core and overall diameters of 50 µm and 140 µm respectively, can be fabricated from a 1 m length of preform 9 mm in diameter. However, for experimental purposes fibres are fabricated in lengths of approximately 2 km from somewhat shorter preforms.

6 Properties of phosphosilicate fibres

6.1 Numerical aperture

As indicated in earlier sections the maximum numerical aperture which has so far been achieved in fibres having a pure phosphosilicate core and a silica cladding is limited to 0.19 by the change in expansion coefficient with increasing P2O5 concentration. On the other hand in a composite structure consisting of a phosphosilicate core in a borosilicate cladding an increase in numerical aperture by 30% to 0.25 has been obtained. The cross-section of such a fibre is shown in Fig. 6. The graded core is surrounded by a borosilicate glass cladding which shows up as a dark ring. The outer annular ring of intermediate brightness is the silica supporting tube. In this particular case the core diameter is 66 µm, overall diameter 140 µm, and the numerical aperture is 0.23. The values of numerical aperture quoted here were determined experimentally from the far-field output pattern for fibres fully excited at the input. Preliminary work in these laboratories with fluorine-doped silica has shown that an increase in numerical aperture can be obtained but the value achieved so far is not as high as that with a borosilicate cladding.

6.2 Attenuation

A characteristic attenuation result for a phosphosilicate fibre of core-diameter 50 µm and numerical aperture 0.16 is shown in Fig. 7. The variation of attenuation with wavelength, obtained with all modes excited and over a length of 1.2 km, is very smooth and has three main features. First the loss is low, particularly at the shorter wavelengths where it is slightly below that predicted for pure
silica\(^9\), showing that the addition of phosphorous pentoxide to pure silica does not greatly increase either absorption or scattering. The loss of the fibre illustrated in Fig.7 has a minimum value of 2-7 \(\text{dB/km}\) at 1-1 \(\mu\text{m}\) although values as low as 2 \(\text{dB/km}\) have been obtained. Additional measurements\(^8\) show that it is below 5 \(\text{dB/km}\) over the considerable wavelength range of 0-7 \(\mu\text{m}\) to 1-25 \(\mu\text{m}\). Even at 0-45 \(\mu\text{m}\) it is less than 20 \(\text{dB/km}\) and is considerably better than has been reported for u.v. transmitting fibres. The low loss at short wavelengths indicates the absence of the nonstoichiometry or oxygen deficiency which has been observed when germania or some other oxides are used as a dopant.

The second feature is the small increase in attenuation of 2 \(\text{dB/km}\) at 0.95 \(\mu\text{m}\) due almost entirely to the OH impurities in the silica cladding. In fact in other samples of phosphosilicate-cored fibres\(^8\) where cladding is formed by borosilicate glass this peak is as low as 0.5 \(\text{dB/km}\) and measurement of the height of the corresponding peak at 1.39 \(\mu\text{m}\) indicates an \(\text{OH}\) impurity level of as little as 0.5 parts in 106. It is thought that this exceptionally low \(\text{OH}\) content is due to the hygroscopic nature of \(\text{P}_{2}\text{O}_{5}\) which converts any residual water in the deposition equipment, on contact, to nonvolatile phosphoric acid and is not carried into the deposition zone.

A further characteristic of phosphosilicate glass is its sensitivity to ferrous-ion absorption in the region of 1 \(\mu\text{m}\). Iron can produce appreciable absorption even when present in very small concentrations and the effect might be expected to be greater in phosphosilicate glasses which tend to reduce this particular impurity mainly to the more sensitive ferrous (Fe\(^2+\)) rather than the ferric (Fe\(^3+\)) state. To achieve good results it is essential to exclude iron impurities from both the materials used and the deposition system.

The fact that the loss in the region of 1 \(\mu\text{m}\) exceeds that of silica may well be due to the presence of some residual ferrous iron. The upper curve in Fig. 3 was obtained for a fibre which was made while there was a slightly corroded stainless-steel valve in the gas distribution system and illustrates the sensitivity to iron. The large broad absorption of 60 \(\text{dB/km}\) centred on 1 \(\mu\text{m}\) is consistent with the presence of ferrous iron but the blue loss is largely unaffected indicating that there is little iron present in the ferric state.

The above results show that at least at shorter wavelengths the total loss of phosphosilicate glass, at the concentrations applicable in fibres, is comparable with that of silica. Scattering measurements have been made in an integrating sphere for fibres with cores of varying relative concentrations, using a helium-neon laser operating at a wavelength of 0.632 \(\mu\text{m}\). The laser is focussed so as to partially excite the fibre, thus ensuring that only Rayleigh scattering within the core is measured, and no waveguide leakage effects are included. The results, shown in Fig. 8, indicate that the amount of scattering increases linearly with change in refractive index. The curve extrapolates to the value reported for Rayleigh scattering in pure silica and it may be concluded that the addition of \(\text{P}_{2}\text{O}_{5}\) to silica causes a small amount of excess scattering presumably arising from concentration fluctuations. However, the effect on the total attenuation is small and amounts to 1-6 \(\text{dB/km}\) at 0.9 \(\mu\text{m}\) and 0-8 \(\text{dB/km}\) at 1.1 \(\mu\text{m}\).

6.3 Material dispersion

In stepped-index multimode fibres the pulse dispersion, and thus the bandwidth, is limited largely by the spread in mode-transit times. This group delay dispersion can, however, be greatly reduced by introducing an appropriate radial variation of refractive index so that material dispersion then becomes the dominant factor particularly when an i.e.d. is used. A technique has been devised for the measurement of material dispersion\(^1\) involving the measurement only of the propagation times of pulses of different wavelengths. To ensure time coincidence of the 25 ps input pulses the output of a modelocked ruby laser was split into two beams, the wavelength of one was shifted by means of a Babinet cell, and they were then combined before being launched into a fibre. The results of the measurements, Fig.9, show that the material dispersion (defined here in terms of the second derivative of refractive index \(n\) with respect to wavelength \(\lambda\), namely \((-\lambda^2c^2 \Delta n/d\lambda)^2\)) is the same as that of pure silica for wavelengths from 0.7 to 0.95 \(\mu\text{m}\) and is independent of \(\text{P}_{2}\text{O}_{5}\) concentration over the range measured, corresponding to fibre numerical apertures from 0.1 to 0.18. This is in contrast to the case of germania-silica fibres which have a material dispersion larger\(^2\) than that of silica. The low material dispersion of phosphosilicate glass is consistent with the low transmission loss in the blue region of the spectrum\(^1\). Silica has a low material dispersion compared with most other optical glasses and it follows that the bandwidth limitation due to material dispersion alone is smaller in phosphosilicate fibres than in most others except for those having a silica core. The magnitude of this limitation is such that for an i.e.d. of 40nm linewidth at a wavelength of 0.9 \(\mu\text{m}\) the material dispersion of 69 ps \(\text{nm}^{-2}\) \(\text{km}^{-1}\) would correspond to a pulse broadening of 2.8 ps/km.

On the other hand, this contribution to pulse broadening could be very greatly reduced by operation at longer wavelengths. Calculations\(^3\) from the published refractive-index data\(^4\) indicate that the material dispersion of silica (as defined above) goes through zero at a wavelength of 1.27 \(\mu\text{m}\) and there is strong reason to assume, from the close correspondence over the range 0.7 to 0.95 \(\mu\text{m}\), that the phosphosilicate glass will behave similarly. Thus, for a fibre in which the transit-times between modes has been minimised by the appropriate choice of refractive index profile\(^5\) a considerable increase in bandwidth (e.g. by a factor of \(\approx 10\) for an i.e.d. with a line spread of 40nm) could be achieved by operation at 1.27 \(\mu\text{m}\). The attenuation of the phosphosilicate fibre is less than 5 \(\text{dB/km}\) at 1.27 \(\mu\text{m}\) but no suitable source is yet available. However, GaInAs light-emitting diodes of high radiance (15W/sr/cm\(^2\)/100mA) and capable of being modulated at high rates (3dB bandwidth of 150MHz) with an emission wavelength of 1.06 \(\mu\text{m}\) have already been reported\(^7\) as well as devices\(^8\) of GaAs, InAs, InGaAs, InP operating at 1.15 \(\mu\text{m}\).

6.4 Pulse dispersion

In stepped-index fibres the pulse dispersion is dominated by group delay between modes and, for full excitation, values of \(\sim 37 \text{ns/km}\) are predicted for a typical phosphosilicate fibre of 0.18 numerical aperture. Measurements with a semiconductor laser \(\text{Er}\) doped in \(\text{P}_{2}\text{O}_{5}\) for fibres of \(\sim 5 \text{ns/km}\) probably because most of the power is launched into the lower-order modes. If the optimum refractive-index profile could be achieved then a reduction to values in the region of 0.1 ns/km.

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**Fig. 8**

Scattering loss in a phosphosilicate fibre as a function of the percentage difference in the refractive index compared with silica at a wavelength of 0.633 \(\mu\text{m}\)

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**Fig. 9**

Material dispersion \(d^2n/d\lambda^2\) as a function of wavelength

The solid curve is calculated for silica from the data of Stalliton\(^*\) and the points have been measured in a fibre having a phosphosilicate-glass core in the wavelength region for GaAs devices.

\(a\) is the wavelength region of negligible material dispersion

\(b\) is the wavelength region of minimal material dispersion

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might be expected despite complete mode excitation but such perfection is difficult to attain. Nevertheless, a considerable improvement is possible even when the profile is far from the ideal one. For example, the profile in Fig. 3 was measured on a phosphosilicate core fibre using a simple technique involving a scan of the near-field intensity pattern of a short (~1m) length of fibre when excited by a Lambertian source. Except for points near the axis the profile correlates to that described by \( \alpha = 2.5 \) but at the centre the depletion process described in section 4 causes a dip. Nevertheless, the pulse dispersion, measured over a length of 0.65km with a semiconductor laser operating at 0.9nm, was 1ns/km. A similar measurement with a helium/neon laser producing a smaller degree of excitation and using the same (Gaussian beam) launching conditions that are required for efficient launching into a single-mode fibre gave a dispersion of 0.2ns/km. It would appear, therefore, that a graded-index phosphosilicate fibre produced by the techniques described above is capable of a bandwidth comparable with that of a single-mode fibre, at least when equivalent launching conditions are used and over this length.

The effect of the dip in the refractive-index profile on the dispersion when the fibre is fully excited has still to be determined.

Fig. 10
Remaining preform after a fibre has been drawn

6.5 Single-mode phosphosilicate-core fibres

The flexibility in fibre-preform production which vapour deposition allows, particularly in the selection of core diameter, is such that single-mode fibres can be made very simply and quickly. For example a Suprasil tube was placed in the deposition machine and a single pass of the hot zone made to volatilise the impurities from the inner surface. This was followed by a single deposition pass at greater speed than normal, giving a single thin phosphosilicate-glass layer. The tube was collapsed and drawn in the normal way so as to produce a fibre having a core of about 8µm diameter, with the result that single-mode operation was obtained at the 0.633µm wavelength of the helium/neon laser. The transmission loss of 6.1 dB/km is close to the fundamental attenuation limit of silica at this wavelength. The guidance property of the fibre is good as the low attenuation was measured with a fibre wound on a 20cm radius drum. In addition calculations and experiment show that the bend loss is negligible down to a bend radius of 100mm. At larger wavelengths the loss increases because the core-diameter/wavelength ratio is smaller and the fields penetrate further into the somewhat lossy cladding. If the core diameter were to be increased, but still kept within the limitation of single-mode operation, the attenuation in the infrared would be less owing to closer confinement of the mode to the core region.

The pulse dispersion was measured with a mode-locked helium/neon laser over a length of 0.4 km. No detectable pulse broadening could be observed indicating that the dispersion is less than the resolution of the apparatus, or 0.1 ns/km, thus confirming experimentally the very large bandwidth predicted theoretically for single-mode fibres. This value of dispersion is the lowest reported for any type of fibre.

7 Conclusions

A technique has been described for the deposition of glass layers involving a homogeneous (gas-phase) reaction at high temperatures and high reactant concentrations. The deposition rate is much higher than is obtained with the heterogeneous (surface) reaction used earlier. The glass layers are deposited in a supporting tube which is subsequently drawn into a fibre. Various types of fibre based on a phosphosilicate glass are now available having very low loss over a wide wavelength range with a minimum of 2 dB/km, numerical apertures up to 0.25 and with values of material dispersion equal to those of silica. The fabrication method is comparatively straightforward and has been made largely automatic, producing fibres up to 4km length and ~50µm core diameter. The starting materials are cheap and abundant and clean-room conditions are not necessary.

A range of refractive index profiles can be obtained and may be pre-programmed on the controller of the deposition machine. As commonly observed in fibres made by the c.v.d. process, there is a small dip in refractive index at the centre of the core. Although the optimum profile has not yet been achieved pulse dispersions as low as 1 ns/km with a semiconductor laser and 0.1 ns/km with a helium/neon laser have been measured in graded-index multimode fibres. The same fabrication technique can be used to produce single-mode fibres which have an attenuation at the design wavelength of 0.633µm close to that of bulk silica and a pulse dispersion of less than 0.1 ns/km.

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9 References

6 BLACK, F.W., IRVEN, J., BYRON, K., FEW, I.S., and WORTHINGTON, R.: 'Measurements on waveguide properties of GeO₂-SiO₂-core optical fibres', ibid., 1974, 10, pp. 239-240


17 NUDE, C.J., and OLSH, G.H.: 'Room-temperature heterostructure laser diodes of InₓGaₓAs/InₓGaᵧAs, with emission wavelength between 0.9 and 1.5μm', *Appl. Phys. Lett.* 1975, 26, pp. 528–530

