Silica based binary glass systems - refractive index behaviour and composition in optical fibres

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Received 7 February 1977

Refractive index versus composition data are presented for three silica based binary glass systems SiO₂–B₂O₃, SiO₂–P₂O₅ and SiO₂–GeO₂. Using a near-field scanning method refractive index measurements were made on graded-index optical fibres, of known composition, fabricated by the chemical vapour deposition technique. The experimental data for each glass system is also compared with theoretical predictions of refractive index versus composition made from a single oscillator, Sellmeier model involving an oscillator energy and a dispersion energy term.

1. Introduction
1.1. Optical fibres
In order to fabricate fibre optic waveguides from low-loss synthetic silica a second glass is required which has a different refractive index, but which is also sufficiently mechanically compatible with silica in terms of viscosity and expansion coefficient, to be fabricated into a fibre. The approach generally adopted is to modify the properties of silica by the addition of other glass forming components (usually oxides), producing a silica based binary glass which has a lower or greater refractive index than silica. This has resulted in the development of a number of techniques and materials, amongst them variations of the chemical vapour deposition (CVD) technique to produce phosphosilicate glass [1], germania-silica glass [2, 3] and borosilicate glass [3–5] in fibres.

To operate fibre communications systems at high data rates fibres with low dispersion are required. One means of achieving this is by careful grading of the refractive index profile in the fibre core. By fabricating a nearly-parabolic profile, equalization of the mode transit times is obtained, and waveguide (modal) dispersion is considerably reduced [6]. The ideal profile parameter αₚₐ₉(≈2) depends on the wavelength of operation and on the variation of the refractive index with wavelength [7–11]. In order to fabricate accurately a given profile it is necessary to know how the refractive index of the binary silica glass within the fibre varies with composition.

1.2. Bulk glasses and glasses in fibres
A number of papers give details of refractive index as a function of composition for the binary glasses SiO₂–B₂O₃ [9, 12, 13], SiO₂–GeO₂ [9, 13] and SiO₂–P₂O₅ [13]. However, these are nearly all measurements made on bulk annealed samples of binary glasses prepared by crucible melting of powdered oxides. It is well known that the physical and mechanical properties of glass in the fibre form differ greatly from those of the bulk form of the same glass [14, 15].

In the case of the fibre, where the fibre drawing process imposes severe quenching or chilling of the glass, any attempt at an explanation of measured properties must be based on the thermal history of the glass in the fibre. In our drawing process for these silica based fibres the thermal history includes a quenching from 2100°C to room temperature in less than a second. Generally it can be stated that the physical properties of the fibre formed in the drawing process correspond with the properties of the glass at some elevated temperature (the fictive temperature). Thus the glass in the fibre should differ from the annealed bulk form of the glass by having a lower density and refractive index [14].

Consequently, data relating refractive indices
and refractive index dispersion to glass composition for bulk annealed glass samples cannot really be extended to an analysis of a fibre, fabricated from the same glass system, in terms of pulse dispersion and ideal profile parameter [9]. The most desirable approach is to use refractive index data, for the given glass system, obtained from fibres and hence subjected to the quenching inherent in the drawing process.

1.3. Achievements of this work
This paper reports the measurement of refractive indices against composition, in optical fibres, for the three most commonly used silica-based binary glass systems: SiO$_2$–B$_2$O$_3$, SiO$_2$–P$_2$O$_5$, and SiO$_2$–GeO$_2$. In addition, the results can be interpreted in terms of a Sellmeier dispersion model, which is based on the properties of the end member components of the binary system, and follows the method used by Wemple et al. [12] to explain data from annealed bulk samples of SiO$_2$–B$_2$O$_3$ glass.

2. Experimental procedure
2.1. Chemical vapour deposition of the fibre preforms
Using the chemical vapour deposition technique developed by Gambling et al. [16] a number of glass fibre optical waveguides were fabricated with core glasses from the three silica-based binary systems listed above.

Two fibres were fabricated with cores of phosphosilicate glass (fibres numbered VD/102 and VD/138). During the core deposition the P$_2$O$_5$ concentration in the glass was linearly increased with each layer from zero to a maximum of 16.5 mol % and 18 mol % for VD/138 and VD/102 respectively. After the subsequent collapse to a preform and drawing into a fibre, this should result in a near parabolic distribution of P$_2$O$_5$ (and hence refractive index increase) radially across the fibre core.

Similarly two fibres were fabricated with cores of germania–silica glass, with the GeO$_2$ concentrations increased linearly to 5 mol % and 11 mol % (fibres VD/160 and VD/161 respectively). These fibres also had a small constant amount of P$_2$O$_5$ (3 mol %) included in the core to help fusion of the core layers. This was allowed for in the refractive index difference calculations

\[ \Delta n(3 \text{ mol } \% \text{ P}_2\text{O}_5) \approx 2 \times 10^{-3} \].

Finally a single fibre was fabricated from borosilicate glass (VD/143). As the borosilicate glass system gives refractive indices less than that of pure silica a slightly different technique was adopted. In the first four layers the B$_2$O$_3$ concentration was rapidly increased in steps of 5 mol % to 20 mol %, and then 15 layers were deposited with a constant 20 mol % B$_2$O$_3$ to form a cladding. Finally the B$_2$O$_3$ concentration was linearly reduced from 20 mol % to zero with each core layer deposited and finishing with a layer of pure silica.

2.2. Correction of doping levels in the fibres
The dopant (P$_2$O$_5$, GeO$_2$, or B$_2$O$_3$) level in the silica of each deposited layer is set by controlling carrier gas flows, containing vapours of appropriate volatile halides (POCl$_3$, GeCl$_4$, BBF$_3$ and SiCl$_4$), during the CVD process [16]. There are thus the possibilities that (a) a carrier gas stream after bubbling through its particular liquid halide may carry a smaller amount of vapour than expected due to incomplete vapour saturation, and (b) that the deposited glass composition may not follow that set by the carrier gas streams.

The first problem can easily be overcome with the use of suitable mass–flow controllers for each halide, however as we are limited to bubbling our carrier gases through Dreschel bottles, the vaporization efficiencies of each halide bubbler were measured and corrections applied to find true concentration levels. Consequently during the fibre preform deposition each halide bubbler was weighed before and after to give the actual mass of halide vaporized. Knowing the flow rate and duration of carrier gas flow the theoretical mass loss can be calculated from the halide vapour pressure. The ratio of actual mass loss to theoretical mass loss defined an average vaporization efficiency for that halide bubbler for that deposition. Typically for POCl$_3$ the vaporization efficiency lies between 0.5 and 0.7, depending on halide temperature, carrier gas temperature, liquid height and to a lesser extent carrier flow rate, while the corresponding figure for SiCl$_4$ is more or less constant at 0.9. For a particular dopant–silica combination, it is the ratio of dopant vaporization efficiency to silica vaporization efficiency that is used to give true doping levels.

Microprobe and etch-rate analysis has shown
that for SiO$_2$–P$_2$O$_5$ core fibres the deposited glass composition does closely follow that of the carrier gas streams, for concentrations below about 15 mol % and provided high deposition temperatures are not used. Also French et al. [21] have shown by X-ray analysis that the composition of SiO$_2$–B$_2$O$_3$ glass in fibres closely follows that set by the reactant vapour stream (BCl$_3$ and SiCl$_4$ in O$_2$). Finally microprobe analysis of some of our SiO$_2$–GeO$_2$ fibres has shown that the GeO$_2$ concentrations are only $\sim$ 30% of that set by the vapour reactants during CVD. Consequently microprobe Ge-concentration profiles have been used to determine the true doping levels for each layer in these fibre cores.

2.3. Fibre drawing
The fibre preforms were drawn on a precision fibre drawing machine [16] using a graphite resistance furnace [16, 17] into fibres of between 0.8 and 1 km length. The number of core layers and pulling conditions were adjusted to give fibres of outside diameter 150 $\mu$m and 50 $\mu$m core diameter.

3. Fibre evaluation
3.1. Near field scanning measurements
The near-field scanning technique developed by Sladen et al. [18] provides a simple and rapid method for obtaining detailed refractive index profile measurements of graded-index fibres. A short length of fibre is illuminated with an incoherent source, and the index profile is determined by observation of the light-intensity variations across the fibre output face. To obtain an accurate index profile it is necessary to take into account the presence of tunnelling leaky-modes, which contribute additional power to the observed near-field intensity distribution [18, 19].

Light-intensity distributions were measured for short lengths ($\approx 0.5$ to $1.0$ m) of fibre taken from the middles of the five fibres described above. In addition as a check on reproducibility of the profiles, light-intensity distributions were also measured on short lengths of fibre taken approximately 200 m from the beginning and end of the five fibres. Fig. 1, solid curve, illustrates the near-field light-intensity distribution for a 1 m length of fibre taken from the middle of the phosphosilicate fibre VD/102.

Although an incoherent light source (a tungsten filament lamp) is used in the near-field scanning system, the convolution of the lamp spectral emission curve and detector response curve indicates that the measurements are effectively made at a wavelength region around 1 $\mu$m.

The numerical aperture (NA) of each of the
short lengths from the five different fibres was also determined with a He–Ne laser by fully exciting the fibre with a high NA launching lens, and measuring the output angle of the far-field radiation pattern.

3.2. Data processing
Finally the near-field intensity distributions were processed using computer programs developed on a Tektronix 4051 graphic systems computer.

Firstly each light-intensity distribution was corrected for the presence of leaky-modes to give a plot now directly related to the true refractive-index profile. The correction factor is a function of radial position in the core \( r \) and depends only on a single normalization parameter involving fibre length \( (z) \), core radius \( (a) \) and normalized frequency \( (\nu) \). The derivation and use of these correction factors are fully explained by [18] and [20]. Fig. 1, dashed curve, illustrates the plot relating directly to the refractive index, obtained after leaky-mode correction of the intensity profile. Using the core radius \( (a) \) and maximum refractive index difference \( \Delta n_n \) defined by the NA \( [NA = \sqrt{2n_2 \Delta n_n}] \) of the fibre, each corrected plot was scaled to give a plot of absolute refractive index difference (above or below the cladding index \( n_2 \)) as a function of core radius: \( \Delta n (r) \). Fig. 2, solid curve, illustrates \( \Delta n (r) \) for the phosphosilicate fibre VD/138.

Secondly, using a curve fitting program, a mathematical expression of the form:

\[
\Delta n(r) = \Delta n - Kr^\alpha
\]

was fitted to the data forming the plot \( \Delta n (r) \).

Although Equation 1 is not the best form of expression to fit the data, because of the insensitivity of \( \Delta n (r) \) to changes in \( \alpha \), it is useful for index-profile analysis as it explicitly contains the maximum index difference \( \Delta n \) and profile parameter \( \alpha \) of the fibre. Fig. 2, dashed curve, illustrates the function \( \Delta n (r) \) with \( \alpha = 2.19 \) and \( n = 10.3 \times 10^{-3} \), fitted to the index-profile (solid curve) of fibre VD/138.

Thirdly, having reduced the index-profile data to a simple mathematical expression \( \Delta n (r) \) and with a knowledge of the number of core layers deposited, it is now possible to define the boundaries of the layers in the core, in a method similar to that used by French et al. [21]. Assigning to each core layer its true concentration of dopant (\( P_2O_5 \), \( GeO_2 \) or \( B_2O_3 \)) in the silica and by weighting the index difference of each layer between its boundary values, a graphical plot (or tabulation) of \( \Delta n (m) \) against true dopant concentration \( (m \text{ mol }\%) \) can be generated. Weighting is used to correct for dopant diffusion between adjacent layers, so that \( \Delta n (m) \) is a monotonic function through the origin.
Figure 3 Solid curve: refractive index difference as a function of mol % B₂O₃ for fibre VD/143. Dashed curve: Sellmeier model of Δn (m) for SiO₂–B₂O₃ glass at λ = 1.06 μm.

Figure 4 Solid curve: refractive index difference as a function of mol % P₂O₅ for fibres VD/102 and VD/138. Dashed curve: Sellmeier model of Δn (m) for SiO₂–P₂O₅ glass at λ = 1.06 μm.
3.3. Results
Fig. 3 shows the variation of refractive index difference with composition $\Delta n(m)$ for the boro-
silicate glass fibre VD/143, Fig. 4 $\Delta n(m)$ for the
two phosphosilicate core fibres VD/102 and
VD/138, and Fig. 5 $\Delta n(m)$ for the two germania-
silicate core fibres VD/160 and VD/161. Included
in Fig. 3 is $\Delta n(m)$ obtained by processing the
refractive-index data (measured interferometrically)
against composition of a graded-index $B_2O_3-SiO_2$
glass fibre presented by French et al. [21–23].
The agreement between these two sets of data for
$\Delta n(m)$ for $B_2O_3-SiO_2$ glass is very good, and
indicates that the near-field scanning technique
gives results as accurate as the more laborious
interferometric technique [23].

4. Sellmeier dispersion model
4.1. Formulation of the Sellmeier model
The refractive-index versus composition analysis
used in the following is based on the theory
developed by Wemple et al. [12] for bulk annealed
samples of $SiO_2-B_2O_3$ glass. Use is made of the
expression for refractive index in terms of a single
Sellmeier oscillator of form:

$$n^2 - 1 = E_oE_a/(E_a^2 - E^2).$$

(2)

$E_0$ is the effective oscillator energy (near the
fundamental UV absorption edge), $E$ the photon
energy, and $E_a$ a dispersion energy (oscillator
strength). The value of Equation 2 is based on the
widely applicable empirical rules [24] obeyed by
$E_a$ and $E_0$. These allow an interpolation of the
refractive index behaviour of the binary glass system, for example xSiO₂ : 1B₂O₃, based on properties of the end members-glassy SiO₂ and B₂O₃. For $E_o(x)$, the assumption is made that the oscillator energy is proportional to the fractional content of Si–O and B–O bonds $U$. Thus

$$E_o(x) = E_o(B_2O_3) + U[E_o(SiO_2) - E_o(B_2O_3)]$$

(3)

where

$$U = 2x/(2x + 3)$$

for $xSiO_2 : 1B_2O_3$. (4)

The dispersion energy $E_d$ has been found to obey the empirical rule [24]

$$E_d = \beta N_c Z_a N_e \rho / \rho_c$$

(5)

where $N_c$ is the cation coordination number, $Z_a$ is the chemical valency of the anion (2 for oxides), $N_e$ is the total number of valence electrons per anion (8 for the oxides considered), $\rho / \rho_c$ is the ratio of the actual density of the glassy material to the density of the 'compacted' crystalline structure, and $\beta = 0.28$ eV for 'ionic' bonded materials and $\beta = 0.38$ eV for 'covalent' bonded materials [24]. Consequently the dispersion energy $E_d(x)$ depends on the fractional content of Si and B cations $V$, rather than the bond fraction $U$. Thus,

$$E_d(x) = E_d(B_2O_3) + V[E_d(SiO_2) - E_d(B_2O_3)]$$

(6)

where

$$V = x/(x + 2)$$

for $xSiO_2 : 1B_2O_3$. (7)

It is also assumed that density and index changes, resulting from quenching are only associated with the B₂O₃ end member, since quenching of vitreous SiO₂ produces relatively small changes in these two parameters (see [12]). Obviously for the other two glasses, $U$ and $V$ will take different forms (see Table I).

The essence of the analysis is to calculate $E_d$ from Equation 5 for each of the end members, then using $E_d$ and $n_D$ (D-sodium line, $\lambda = 0.5893 \mu m$) to calculate a corresponding $E_o$ by solving Equation 2. $E_o$ and $E_d$ for the end members are then substituted into Equations 3 and 6 to yield $E_o(x)$ and $E_d(x)$, and inserting these latter two variables into Equation 2 finally results in $n(x)$. A modification is made in that molar %($m$) is used as the composition variable in place of $x$ where

$$m = 100/(1 + x).$$

(8)

4.2. The dispersion energy and bonding considerations

Now we turn to the calculation of $E_d$ for each of the four oxides. The basic structural building block of glassy SiO₂, P₂O₅ and GeO₂ is the tetrahedron thus $N_c = 4$, whereas for glassy B₂O₃ it is the planar triangle and thus $N_c = 3$ [25] (Table II).

Wemple and DiDomenico [24] state that all the six-coordinated oxides take the 'ionic' value of $\beta = 0.28$ eV, while the four-coordinated oxides seem to be either 'ionic' or 'covalent'. Consideration of the Allred–Rochow electronegativity differences [26] between O and Si, B, P and Ge is also useful in ascertaining the bond type of the four oxides. The electronegativity differences obtained (1.44 to 1.76) indicate that the bonds in the four oxides should have strong ionic characteristics [26]. Certainly for SiO₂ it has been shown experimentally that $\beta$ does indeed take the 'ionic' value of $\beta = 0.28$ eV [12]. On the other hand Wemple et al. [12] have shown experimentally

<table>
<thead>
<tr>
<th>Material</th>
<th>$N_c$</th>
<th>$\beta$(eV)</th>
<th>$\rho$(g/cm³)</th>
<th>$\rho_o$(g/cm³)</th>
<th>$n_D$</th>
<th>$E_d$(eV)</th>
<th>$E_o$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>4</td>
<td>0.28</td>
<td>2.212</td>
<td>2.65</td>
<td>1.4578</td>
<td>14.71</td>
<td>13.38</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>3</td>
<td>0.38</td>
<td>1.804</td>
<td>2.56</td>
<td>1.4355</td>
<td>13.00</td>
<td>12.63</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>4</td>
<td>0.28</td>
<td>2.176</td>
<td>2.365</td>
<td>1.490</td>
<td>16.49</td>
<td>13.84</td>
</tr>
<tr>
<td>GeO₂</td>
<td>4</td>
<td>0.28</td>
<td>3.651</td>
<td>4.228</td>
<td>1.610</td>
<td>15.49</td>
<td>9.80</td>
</tr>
</tbody>
</table>

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that $B_2O_3$ takes the 'covalent' value of
$\beta = 0.38 \text{ eV}$. $GeO_2$ can be six-coordinated [25]
and phosphorus can be 5- or 6-coordinated [26],
and because of the appreciable degree of ionic
character of the bonds in $GeO_2$ and $P_2O_5$ [26],
these two oxides were assigned the 'ionic' value
of $\beta = 0.28 \text{ eV}$. Table II summarizes the values of $\beta$
assigned to the four oxides.

Finally it is necessary to assign appropriate
values to the density ratio $\rho/\rho_e$ in Equation 5
which is one of the key factors in predicting the
refractive index behaviour of these quenched
glasses.

4.3. Density and refractive index values for
the model
The values of $n_D$ and $e$ for vitreous silica, and $\rho_e$ for $SiO_2$ are well documented in the literature
(see [12]). Density and refractive index data for
the other three oxides in the glass form are less
readily available, and some judgement has been
exercised in selecting values appropriate to the
highly quenched glass form.

For instance Vedam and Schneider [27] give
$\rho = 1.833 \text{ g/cm}^3$ and $n_D = 1.447$ for low-density
(quenched) glassy $B_2O_3$, while Shelby [28] gives
$\rho = 1.804 \text{ g/cm}^3$ and $n_D = 1.458$. Scaling the
value of $n_D = 1.447$ by the square root of the
ratio of the densities ($n \propto \sqrt{\rho}$) gives that $n_D$
should be $\approx 1.436$ for $\rho$ equal to 1.804 $\text{g/cm}^3$. Thus
presumably Shelby's value of $n_D$ is somewhat on the
high side. The values $\rho = 1.804 \text{ g/cm}^3$ and
$n_D = 1.436$ were thus selected for computations
on glassy $B_2O_3$ (see Table II) as being the most
appropriate to the quenched glass form.

Few data are available for glassy $P_2O_5$, but
Cormia et al. [29] give refractive index data for
glassy and crystalline $P_2O_5$, and a relationship
between temperature ($^oC$) and the density of
crystalline $P_2O_5$ :

$$\rho = 2.372 - 3.38 \times 10^{-4} \text{ T(g/cm}^3).$$

Eq (9)

Assuming that quenched, glassy $P_2O_5$ would take
the density of the melt at the melting temperature of
$580^oC$ [14] we estimate $\rho = 2.176 \text{ g/cm}^3$ from
Equation 9. Also from Cormia et al. [29] $n_D = 1.490$ was judged to be the most appropriate
refractive index for quenched vitreous $P_2O_5$.

Finally for glassy $GeO_2$ the most appropriate
density and refractive index that could be found
were $\rho = 3.651 \text{ g/cm}^3$ and $n_D = 1.630$ from
Morey [30] and Shelby [28]. Unfortunately no
thermal history is given for the material used by
Morey, and the specimens used by Shelby were
well annealed.

Table II lists the values of $n_D, \rho$ and $\rho_e$ used to
determine $E_a$ and $E_0$ for the end members, and
their values for each vitreous material. Then using
a computer program with the appropriate values of
$E_a$ and $E_0$ (Table II), and $U$ and $V$ (Table I)
for the end members, refractive index against
composition $n(m)$ is obtained using Equations 3,
6 and 2. It is customary in fibre optics to use
index differences rather than absolute indices, so
Figs. 3-5 (dashed curves) give $\Delta n(m)$, calculated
at $\lambda = 1.06 \mu m$ for the three binary glass systems
under consideration. For pure $SiO_2$, $U = V = 1$ to
give $n(silica) = 1.4518$ (at 1.06 $\mu m$), so that
$\Delta n(m)$ equals $n(m) - 1.4518$ for each binary glass.

5. Discussion
5.1. $SiO_2-B_2O_3$ and $SiO_2-P_2O_5$ glasses
Quenched $SiO_2-B_2O_3$ glass has refractive indices
less than those of vitreous silica and hence its
common use as a cladding glass for optical fibres.
Fig. 3 shows that good agreement is obtained
between the measured values of $\Delta n(m)$ (solid
curve) and the values calculated from the Sellmeier
model (dashed curve), over the composition range
considered - up to 20 mol % $B_2O_3$. At this
concentration the measured value of $\Delta n(m)/n(SiO_2)$ is
0.65%, which agrees with the figure of 0.6%
measured by Wemple et al. [12] for a quenched
25 mol % $B_2O_3$ sample, see Fig. 3. More generally
the shape of our $\Delta n(m)$ curve, for both measured
and theoretical values, is consistent with that
obtained by Wemple et al. [12] for low density
$SiO_2-B_2O_3$ glass. The severe quenching inherent
in the fibre drawing process here greatly increases
the value of $\Delta n$ obtained from a given composition
by considerably lowering $n(m)$ with respect to
$n(SiO_2)$. As an illustration of this, Fig. 3 also
contains data points obtained from measurements
made by Fleming [9] on two bulk samples of
$SiO_2-B_2O_3$ glass - points G and H. Thus quench-
ing in this system is very advantageous when using
these glasses as claddings for optical fibres. Finally
measurements on other fibres fabricated in these
laboratories indicate that even greater values of
$\Delta n(m)$ can be obtained for $B_2O_3$ levels above
20 mol%, before the limit imposed by expansion coefficient considerations is reached.

Also agreement between experimental values and theoretical calculations for quenched SiO$_2$-P$_2$O$_5$ glass is extremely good for compositions up to 20 mol% P$_2$O$_5$, Fig. 4. Results from other fibres fabricated in these laboratories indicate that 25 mol% is the maximum amount of P$_2$O$_5$ that can be incorporated in this glass system, because of expansion coefficient mismatch. At this composition $\Delta n(m)/n$ (SiO$_2$) is equal to 0.9%. Quenching in this glass system has the effect of decreasing the value of $\Delta n(m)$ obtained from a given composition by lowering $m$ (m) with respect to $n$ (SiO$_2$), which is to some extent a disadvantage when using SiO$_2$-P$_2$O$_5$ glass for a fibre core. Fig. 4 also indicates some departure of the glass composition away from the vapour-phase composition at high P$_2$O$_5$ concentrations (> 15 mol% P$_2$O$_5$).

5.2. SiO$_2$-GeO$_2$ glasses

Initially little agreement was found between the measured refractive index differences as a function of gas-phase composition, and calculations made from the Sellmeier model for quenched SiO$_2$-GeO$_2$ glass. However, fairly good agreement was obtained between the Sellmeier model and refractive index measurements made by Fleming [9], on bulk samples of SiO$_2$-GeO$_2$ glass prepared by r.f. plasma fusion (see Fig. 5). This lack of consistency between fibre core glass measurements and bulk glass measurements suggested that the SiO$_2$-GeO$_2$ core glass composition was greatly different from that set by the vapour streams in this particular CVD process.

Measurements made with a JEOL microprobe analyser (JXA-50A) by counting the $K_{\alpha}$, X-ray emission from the Ge in a fibre core against that from a pure Ge reference sample, supported the above supposition. For instance fibre VD/160 fabricated to have a maximum of 15 mol% GeO$_2$ in the gas-phase was found actually to have a maximum core doping of only 5 mol% GeO$_2$. Fibre VD/161 with a gas-phase maximum of 24 mol% GeO$_2$ was found to have a maximum GeO$_2$ concentration in the core of ~11 mol%. Consequently the microprobe analyser was used to obtain Ge concentration profiles of the fibre cores, and from these the true doping level of GeO$_2$ for each deposited core layer was determined. Fig. 6 illustrates how the actual concentration of GeO$_2$ in the core glass (m) varies as a
function of the set gas-phase concentration ($m'$) for VD/161. Here for $m > 2$ mol % GeO$_2$ the curve is described by the relation

$$m = 0.275(m')^{1.55}.$$  (10)

The exact relationship between $m$ and $m'$ varies from fibre to fibre and is obviously dependent on the deposition conditions, particularly the deposition temperature. It has been found experimentally that the higher the deposition temperature the lower is the amount of GeO$_2$ incorporated in the core glass from the gas-phase. For the deposition temperatures we use for GeO$_2$ ($\sim 1500^\circ$ C) a good approximation is that $m \approx 0.3m'$. Similar observations on SiO$_2$–GeO$_2$ glass have been made by Ito [31].

Fig. 5, solid curve, shows the measured variation of refractive index with actual GeO$_2$ concentration $\Delta n(m)$ for the two fibres VD/160 and VD/161. Agreement between the experimental measurements and the theoretical calculations for SiO$_2$–GeO$_2$ glass from the Sellmeier model (dashed curve) is again extremely good. Again the effect of quenching on the SiO$_2$–GeO$_2$ glass system has been to lower the values of $\Delta n(m)$ obtained, by about $2 \times 10^{-3}$ below the data points obtained from Fleming’s measurements on bulk samples B, C and D [9].

At the maximum GeO$_2$ concentration obtained here, i.e. 11 mol % GeO$_2$, $\Delta n(m)/n$(SiO$_2$) is about 1%, thus the refractive index differences for the SiO$_2$–GeO$_2$ glass system are about three times that obtained for the same doping levels in the SiO$_2$–P$_2$O$_5$ glass system. However, the reduction in GeO$_2$ concentration by about one third between the gas-phase and the glass in CVD, means that for equivalent gas-phase compositions the refractive index differences obtained are roughly the same for each glass system, i.e. 25 mol % P$_2$O$_5$ yields $\Delta n = 13 \times 10^{-3}$ while 11 mol % GeO$_2$ yields $\Delta n = 14 \times 10^{-3}$.

6. Conclusion

Analysis of the refractive index behaviour of the binary glasses: SiO$_2$–B$_2$O$_3$, SiO$_2$–P$_2$O$_5$ and SiO$_2$–GeO$_2$ in the quenched condition present in fibres, has shown that the observed dependence on composition can be explained in terms of properties of the end-member glasses. Provided that in the Sellmeier model the effects of quenching on the properties of the end-members B$_2$O$_3$, P$_2$O$_5$ and GeO$_2$ are considered, and that the true fibre dopant concentrations, particularly for GeO$_2$, are used in the model. It should be mentioned that an alternative analysis based on the molar-refractivity concept [32] has not been attempted, since preliminary calculations based on this model gave only rather qualitative results for these three glass systems.

The Sellmeier model has also been used to determine doping programmes to fabricate fibres with profiles having given alpha values [33]. An extension to the model has been made with the addition of a second infra-red Sellmeier oscillator term having a second pair of composition dependent energies $\epsilon'_c$ and $\epsilon'_d$. This refinement has enabled calculations to be made of pulse broadening, profile dispersion and optimum alpha value [7] as a function of wavelength for these three glass systems [33].

7. Acknowledgements

The authors wish to thank F. M. E. Sladen and M. R. L. Power for near-field scanning measurements of the fibres, and E. J. Heath for microwave measurements. Grateful acknowledgement is made to the UK Science Research Council, the UK Ministry of Defence, and the Pirelli General Cable Co., for financial support. Discussions with Professor W. A. Gambling over the manuscript were also very constructive and useful.

References

33. C. R. HAMMOND, (to be published).