Silica-based binary glass systems: wavelength dispersive properties and composition in optical fibres

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A composition-dependent single Sellmeier oscillator model, developed for predicting the refractive index against composition behaviour for the three binary glass systems, SiO_2–B_2O_3, SiO_2–P_2O_5 and SiO_2–GeO_2, is extended to a double Sellmeier oscillator model. The inclusion of both composition-dependent u.v. and i.r. terms in the Sellmeier equation has enabled the wavelength dispersive properties of optical glass fibres; refractive index, material dispersion and profile dispersion, to be computed for any composition, in any one of these three binary glasses. Theoretical calculations, for particular compositions, of material and profile dispersions are compared with experimental measurements on fibres of the same compositions, fabricated by chemical vapour deposition.

1. Introduction

In a recent paper by Hammond and Norman [1] refractive index measurements against composition in glass optical fibres are presented for the three most commonly used silica-based binary glass systems: SiO_2–B_2O_3, SiO_2–P_2O_5 and SiO_2–GeO_2. The results are interpreted in terms of a single Sellmeier oscillator of form

$$n^2 - 1 = \frac{E_d E_o}{E_o^2 - E^2} \tag{1}$$

where E_o is the effective oscillator energy (near the fundamental u.v. absorption edge), E the photon energy, and E_d the dispersion energy. The value of Equation 1 results from the widely applicable empirical rules [2] obeyed by E_d and E_o. These allow an interpolation of the refractive index behaviour of a binary glass system, for example $x\,SiO_2$:$1\,B_2O_3$, based on the properties of the end members – glassy SiO_2 and B_2O_3 – through the bond fraction U and cation fraction V [1, 3]. Thus

$$E_o(x) = E_o(B_2O_3) + U[E_o(SiO_2) - E_o(B_2O_3)] \tag{2}$$

and

$$E_d(x) = E_d(B_2O_3) + V[E_d(SiO_2) - E_d(B_2O_3)]. \tag{3}$$

The dispersion energy E_d has been found to obey the empirical rule [2]

$$E_d = \beta N_c Z_a N_e \rho_r \tag{4}$$

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), ρ_r is the ratio of the density of the glassy material to the density of the 'compacted' crystalline structure, and β is 0.28 eV for 'ionic' bonded materials, 0.38 eV for 'covalently' bonded materials [2].

The basis of the method used by Hammond and Norman [1] is to calculate E_d from Equation 4 for each end-member, then using E_d and n_D (D – sodium line, $\lambda = 589.3$ nm) to calculate a corresponding E_o by solving Equation 1. Table I lists the values of E_o, E_d, U and V for the three binary glass systems

TABLE I

Glass system	U	V	u.v. term	i.r. term
$x\,SiO_2:1B_2O_3$	$\dfrac{2x}{2x+3}$	$\dfrac{x}{x+2}$	$E_o(B_2O_3) = 12.63\,eV$	$E'_o(B_2O_3) = 0.17\,eV$
			$E_d(B_2O_3) = 13.00\,eV$	$E'_d(B_2O_3) = 0.11251 - 4 \times 10^{-4}m\,eV$
$x\,SiO_2:1P_2O_5$	$\dfrac{x}{x+2}$	$\dfrac{x}{x+2}$	$E_o(P_2O_5) = 13.84\,eV$	$E'_o(P_2O_5) = 0.155\,eV$
			$E_d(P_2O_5) = 16.49\,eV$	$E'_d(P_2O_5) = 0.11251 - 2 \times 10^{-4}m\,eV$
$x\,SiO_2:1GeO_2$	$\dfrac{x}{x+1}$	$\dfrac{x}{x+1}$	$E_o(GeO_2) = 9.80\,eV$	$E'_o(GeO_2) = 0.113\,eV$
			$E_d(GeO_2) = 15.49\,eV$	$E'_d(GeO_2) = 0.11251 - 1.4 \times 10^{-3}m\,eV$
SiO_2	1	1	$E_o(SiO_2) = 13.38\,eV$	$E'_o(SiO_2) = 0.1254\,eV$
			$E_d(SiO_2) = 14.71\,eV$	$E'_d(SiO_2) = 0.11251\,eV$

under consideration. Using these parameters Hammond and Norman obtain theoretical values of core–cladding refractive index differences (above or below silica), which are in good agreement with experimental measurements made at $1.0\,\mu m$ by the near-field scanning technique [4] on optical fibres fabricated by chemical vapour deposition (CVD) [5].

2. Extension of the Sellmeier model

Consideration of Table 1 reveals that in the portion of the spectrum of interest (the visible and near i.r.) $E_o \gg E$, thus in the near i.r., n as defined by Equation 1 is virtually independent of λ. The use of a single Sellmeier oscillator of form defined by Equation 1 when predicting the material dispersion M of a fibre-core glass, where

$$M = \left(-\frac{\lambda}{c}\frac{d^2 n_1}{d\lambda^2} \right) \tag{5}$$

leads to the obviously erroneous result the $M \to 0$ in this wavelength region.

An extension of the Sellmeier model with a second oscillator, in the i.r., is thus required to follow more closely the behaviour of $n(\lambda)$ and $M(\lambda)$, i.e.

$$n^2 - 1 = \frac{E_d E_o}{E_o^2 - E^2} + \frac{E'_d E'_o}{E'^2_o - E^2} \tag{6}$$

where now E'_o and E'_d are respectively the oscillator energy and dispersion energy of this i.r. vibrational term.

For the doping levels commonly used in fabricating fibre-core glasses by CVD (up to 20 mol% dopant in silica) $U \simeq V > 0.8$ so that the binary glass refractive index should still behave closely like that of glassy silica ($U = V = 1$). Consequently, the i.r. term in the three term Sellmeier expression for the refractive index of fused silica due to Malitson [6], forms a good starting point for assigning composition-dependent values to E'_o and E'_d. From Malitson's expression $E'_o = 0.12536\,eV$ and $E'_d = 0.11251\,eV$ after re-writing the Sellmeier equation in the form of Equation 6 above.

The parameter $E'_o = 0.12536\,eV$ is equivalent to a $\lambda'_o = 9.8962\,\mu m$, which is very close to the strong fundamental v_3 vibration of the Si–O bond in the SiO_2 tetrahedron at $8.98\,\mu m$ [7]. So it seems likely that the i.r. oscillators, for the glassy end-members B_2O_3, P_2O_5 and GeO_2, should lie near their respective wavelengths of fundamental vibration at $7.3\,\mu m$, $8.0\,\mu m$ and $11.0\,\mu m$ [7]. In our notation this means that $E'_o(B_2O_3) \simeq 0.17\,eV$, $E'_o(P_2O_5) \simeq 0.155\,eV$ and finally $E'_o(GeO_2) \simeq 0.113\,eV$.

It has been shown that the transmission loss of optical fibres in the near i.r. region is dependent on the positions of the fundamental vibrational absorption wavelengths in the i.r. of the B–O, P–O and Ge–O bonds, in relation to the i.r. vibrational absorption wavelength of the Si–O bond [7]. It is not

unlikely then, that $E'_o(x)$ for a silica-based binary glass depends on $E'_o(SiO_2)$ and $E'_o(B_2O_3)$, for example, through the bond fraction U by the following equation, which is analagous to Equation 2

$$E'_o(x) = E'_o(B_2O_3) + U[E'_o(SiO_2) - E'_o(B_2O_3)]. \qquad (7)$$

However, there seems no theoretical basis for relating $E'_d(x)$ to $E'_d(SiO_2)$ and $E'_d(B_2O_3)$, for example, by an equation analogous to Equation 3.

Examination of the Sellmeier equations fitted to refractive index measurements made on bulk glasses in the GeO_2–SiO_2 and B_2O_3–SiO_2 systems by Fleming [8], indicates that $E'_d(x)$ for these binary glasses is crudely described by:

$$E'_d(m) = A - Bm \qquad (8)$$

where m (mol%) is the level of dopant added to the glassy silica to form the binary glass, and if $m = 0$ mol%, $A = E'_d(SiO_2) = 0.11251$ eV the silica i.r. term value. From Fleming's Sellmeier equations for SiO_2–GeO_2 glasses the average value of B is 1.4×10^{-3}, while for SiO_2–B_2O_3 glasses the average for B is 4×10^{-4}. Whilst no comparable Sellmeier equations exist for SiO_2–P_2O_5 glass, experimental measurements of profile and material dispersion in these laboratories give that $B \simeq 2 \times 10^{-4}$ for P_2O_5 in SiO_2 (see Section 4).

In calculating n from Equation 6 the values of E_o and E_d for silica and the other glassy end-members from Table 1 are retained and the method outlined above followed again, with the addition that now for the i.r. term in Equation 6, $E'_o(x)$ is obtained from Equation 7 for the particular end-member used with silica (see Table 1), and Equation 8 gives $E'_d(m)$.

With the two-term Sellmeier equation for n, it was found that a slightly better fit could be made to the experimentally measured refractive index differences against composition data obtained by Hammond and Norman [1] for the three binary glass systems under consideration.

3. Material and profile dispersion

Although the two-term Sellmeier equation has in effect only been tested by comparison with refractive index measurements at one wavelength, $\lambda = 1.0 \, \mu m$ [1], it has been found to be still accurate in predicting $n(\lambda)$ and more interestingly $M(\lambda)$ and profile dispersion $P(\lambda)$ for the three binary glasses in optical fibres.

Multimode optical fibres with low pulse dispersions are well suited to high data rate applications. These fibres can be fabricated by doping silica by CVD [5] to achieve a refractive index profile characterized by an exponential parameter $\alpha(\lambda)$ that minimizes waveguide (modal) dispersion [9]. For a fibre of binary composition having a silica cladding and doped silica core (or vice versa), the wavelength dependence of the optimum $\alpha(\lambda)$ can be calculated from the core and cladding refractive indices $n_1(\lambda)$ and $n_2(\lambda)$ [10]. Under the condition that $\alpha(\lambda)$ is optimum and minimizes the waveguide dispersion, the pulse dispersion is limited by $M(\lambda)$ the material dispersion (Equation 5) of the core glass.

Olshansky and Keck [10] consider a cylindrically symmetric waveguide with an index profile specified by the equation

$$n^2(r) = n_1^2[1 - 2\Delta(r/a)^\alpha] \qquad (9)$$

where $n(r)$ is the refractive index of the waveguide core as a function of radius r, and n_1 is the index along the fibre axis. At the core–cladding boundary where $r = a$, $n(r) = n_2$, and for $r \geqslant a$ the term $(r/a)^\alpha$ is defined to be unity. Thus from Equation 9 the relative index difference Δ is found to be

$$\Delta = (n_1^2 - n_2^2)/2n_1^2. \qquad (10)$$

According to Olshansky and Keck [10] the optimum α is given by

$$\alpha(\lambda) = 2 - 2P - \Delta \left[\frac{(4 - 2P)(3 - 2P)}{(5 - 4P)} \right] \qquad (11)$$

where the term $P(\lambda)$ in the above, called the profile dispersion is

$$P(\lambda) = \frac{n_1}{N_1}\frac{\lambda\Delta'}{\Delta} \tag{12}$$

Here $N_1 = [n_1 - \lambda dn_1/d\lambda]$ is the material group index and $\Delta' = d\Delta/d\lambda$. Thus from Equations 10 and 12 we may write

$$P(\lambda) = \frac{2\lambda}{(n_1 - dn_1/d\lambda)(n_1^2 - n_2^2)}\left[n_1\left(n_1\frac{dn_1}{d\lambda} - n_2\frac{dn_2}{d\lambda}\right) - (n_1^2 - n_2^2)\frac{dn_1}{d\lambda}\right] \tag{13}$$

Hence for a particular core composition the Sellmeier equation as defined by Equation 6 giving $n_1(\lambda, x)$ may be differentiated to yield $dn_1(\lambda, x)/d\lambda$ and $d^2n_1(\lambda, x)/d\lambda^2$ for the core glass, and by setting $U = V = 1$ $dn_2(\lambda)/d\lambda$ and $d^2n_2(\lambda)/d\lambda^2$ are obtained for the silica cladding. For a SiO_2–B_2O_3 fibre the procedure is reversed since for this geometry the core (n_1) is now silica and the cladding (n_2) the binary SiO_2–B_2O_3 glass. Consequently the parameters $P(\lambda, x)$, $\alpha(\lambda, x)$ and $M(\lambda, x)$ may be calculated at any wavelength, for a fibre waveguide with given core glass composition (on axis) from any of the three binary systems SiO_2–B_2O_3, SiO_2–P_2O_5 or SiO_2–GeO_2.

4. Comparison of theoretical and experimental results

Sladen *et al.* [11, 12] have developed a technique which allows a direct determination of the wavelength dispersive material properties of glasses within a multimode fibre. Their method measures the wavelength dependence of the numerical aperture (NA) directly, thereby yielding the difference in dispersion between core and cladding and hence the profile dispersion P. The total output power from a short length of straight fibre is measured at each wavelength for both apertured and non-apertured excitation, the use of the ratio of the two transmitted powers, which is proportional to $(NA)^2 = 2n_1\Delta n$, provides compensation of the Lambertian source and eliminates the effect of fibre attenuation. The measured
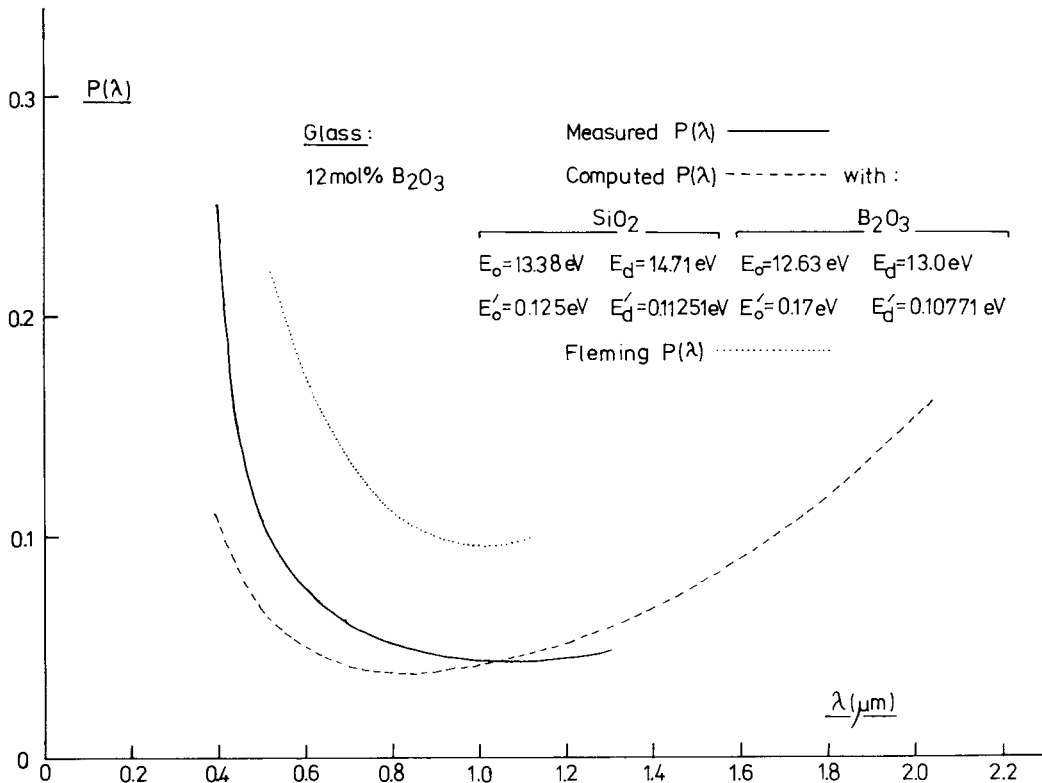

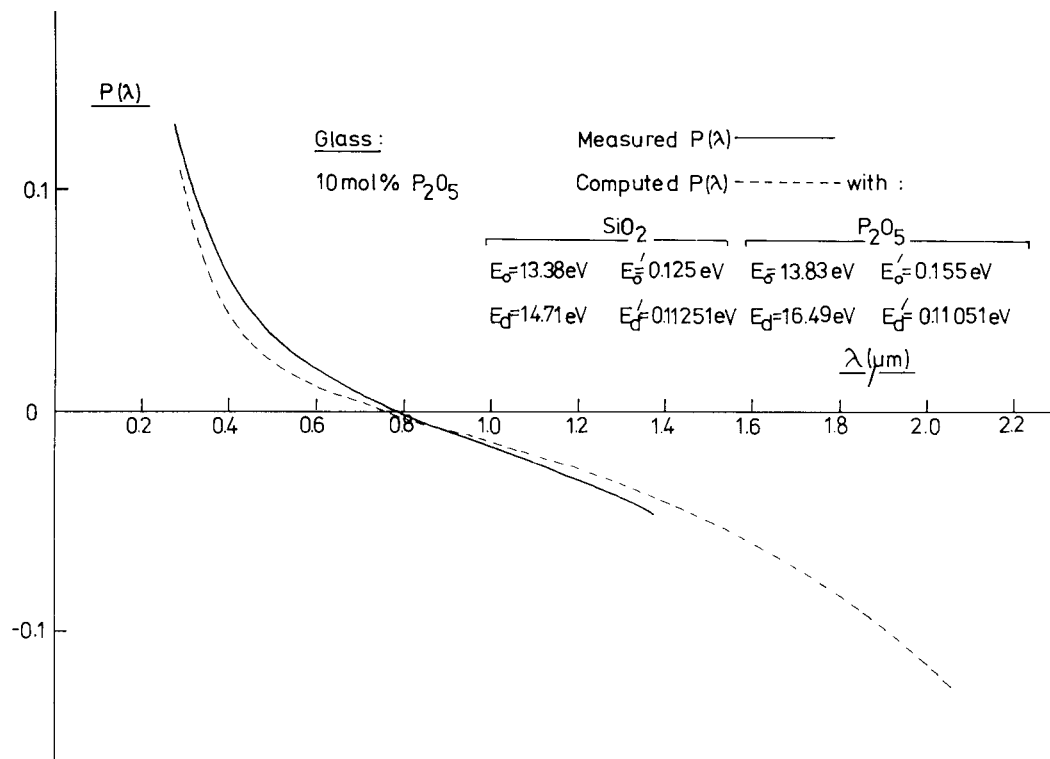*Figure 1* Theoretical and experimental values of $P(\lambda)$ for 12 mol% B_2O_3–SiO_2 glass.

Figure 2 Theoretical and experimental values of $P(\lambda)$ for 10 mol% P_2O_5–SiO_2 glass.

$\Delta n(\lambda)$ is then fitted by the least squares technique to an expanded Sellmeier representation of $\Delta n(\lambda)$ with six physically significant coefficients. From the wavelength dependence of NA, the material dispersion $M(\lambda)$ may also be deduced if the refractive index behaviour of either the core or cladding (usually silica [6]) is known.

Fig. 1 (solid curve) shows the profile dispersion parameter $P(\lambda)$ obtained by Sladen [13] for a step-index CVD-multimode fibre with silica core and a cladding of 12 mol% B_2O_3 in SiO_2, measurements being made over the range 0.35 μm to 1.30 μm. Also shown in Fig. 1 (dashed curve) is the computed variation of $P(\lambda)$ for a fibre with 12 mol% B_2O_3–SiO_2 cladding and silica core using the parameters $E_o = 12.63$ eV, $E_d = 13.0$ eV, $E'_o = 0.17$ eV and $E'_d = 0.10771$ eV for the glassy B_2O_3 end-member. Here agreement with the experimental values of $P(\lambda)$ is reasonably good particularly in the near i.r. region. These results may also be compared with those obtained by Fleming [8] from measurements of $n(\lambda)$ on a bulk unquenched sample of 13.5 mol% B_2O_3–SiO_2 glass (shown dotted). The higher values of $P(\lambda)$ obtained by Fleming probably arise from the unquenched bulk nature of his sample, whereas Sladen's measurement is on a highly quenched fibre.

Sladen [13] has also measured $P(\lambda)$ over the same wavelength range for a step-index CVD-multimode phosphosilicate glass core fibre with 10 mol% P_2O_5 (Fig. 2 – solid curve). The computed variation of $P(\lambda)$ for a 10 mol% P_2O_5–SiO_2 core fibre with parameters $E_o = 13.38$ eV, $E_d = 16.49$ eV, $E'_o = 0.155$ eV and $E'_d = 0.11051$ eV for glassy P_2O_5 is also shown by the dashed curve. For P_2O_5, $E'_d(m)$ was given the value $0.11251 - 2 \times 10^{-4}m$ eV as this produced the best fit to the experimental variation of $P(\lambda)$ for this and other phosphosilicate core fibre measurements.

The measured and computed variations of $M(\lambda)$ have been compared for both the borosilicate fibre and phosphosilicate fibre described above. Both measurement and computation agree very well and lie very close to that of $M(\lambda)$ for pure silica, calculated from Malitson's three term Sellmeier equation.
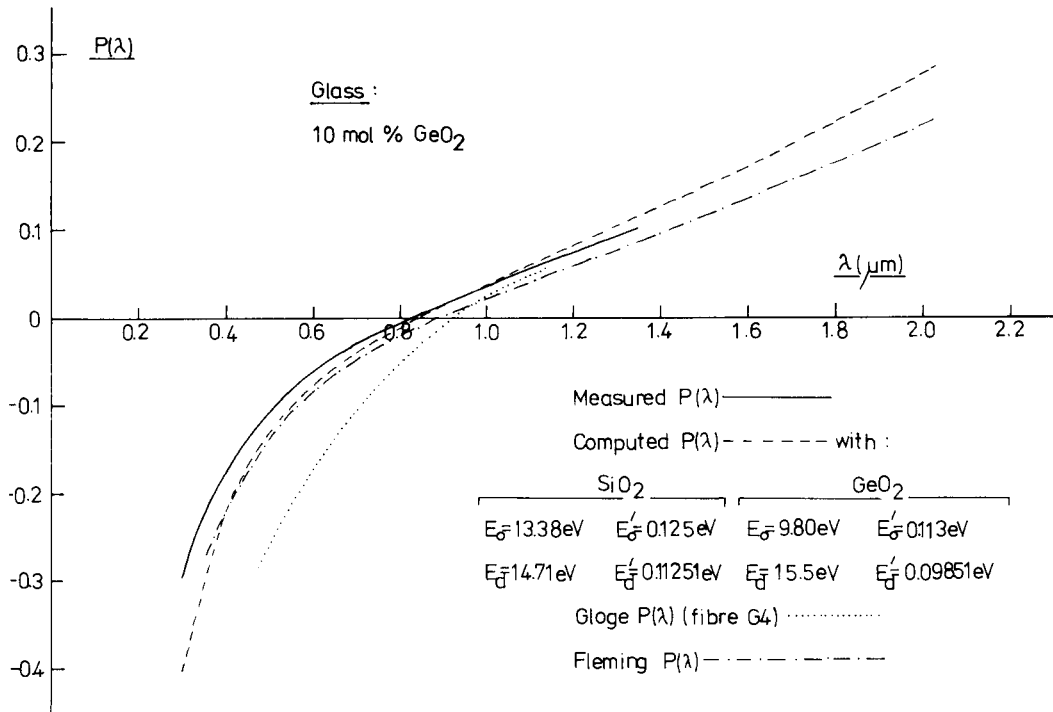
Figure 3 Theoretical and experimental values of $P(\lambda)$ for 10 mol% GeO_2–SiO_2 glass.

This fact for P_2O_5–SiO_2 glass has also been observed by Luther-Davies *et al.* [14] and Katsuyama *et al.* [15].

Finally Fig. 3 illustrates the measured [13] and computed variation of $P(\lambda)$ over the same wavelengths for a step-index CVD-multimode fibre with a core glass of 10 mol% GeO_2–SiO_2. $P(\lambda)$ was computed using the values of $E_o = 9.80$ eV, $E_d = 15.5$ eV, $E_o' = 0.113$ eV and $E_d' = 0.09851$ eV for the vitreous GeO_2 end-member. Also shown for comparison are measurements of $P(\lambda)$ made by Gloge *et al.* [16] on a graded-index SiO_2–GeO_2 glass core fibre with $\Delta = 0.02$ (fibre G4), and values of $P(\lambda)$ obtained by Fleming [8] from measurements of $n(\lambda)$ on a bulk glass sample of 13.5 mol% GeO_2–SiO_2. Agreement between the three curves of $P(\lambda)$ obtained by measurement [13], computation and Fleming is very good, but Gloge's measurements show considerable departure from the other data towards the u.v. region. However $P(\lambda)$ obtained by Gloge [16] for three other GeO_2–SiO_2 fibres shows a considerable spread in value; ± 0.05 over his wavelength measurement region (0.5–1.1 μm).

The measured and computed dispersion $M(\lambda)$ for the same GeO_2–SiO_2 glass core fibre are present in Fig. 4. At 900 nm the measured value of $M(\lambda)$ is 10% greater than $M(\lambda)$ for SiO_2, while the computed value of $M(\lambda)$ is 25% greater than $M(\lambda)$ for SiO_2. A measurement by Gloge [17] using two GaAs lasers operating at slightly different wavelengths gives a value of $M(\lambda)$ 20% greater than $M(\lambda)$ for SiO_2 which is in good agreement.

Measurements on $n(\lambda)$, $P(\lambda)$ and $M(\lambda)$ have also been made on a number of glass systems in fibres, amongst them SiO_2–B_2O_3, SiO_2–P_2O_5 and SiO_2–GeO_2 by Presby and Kaminow [18]. They use an interference method [16] with thin ($\sim 50\,\mu$m) sections of multimode fibre to obtain $\Delta n(\lambda)$. A least-squares fit is used to obtain a polynomial representation of $\Delta n(\lambda)$ and derivations of $\Delta n(\lambda)$. Using $n(\lambda)$ for silica [6] they then calculate $P(\lambda)$ and $M(\lambda)$ from the polynomials.

Unfortunately the polynomial representation of $\Delta n(\lambda)$ apparently causes serious errors in the computation of $P(\lambda)$ and $M(\lambda)$. For instance in the u.v. and visible region, the values of $M(\lambda)$ for silica
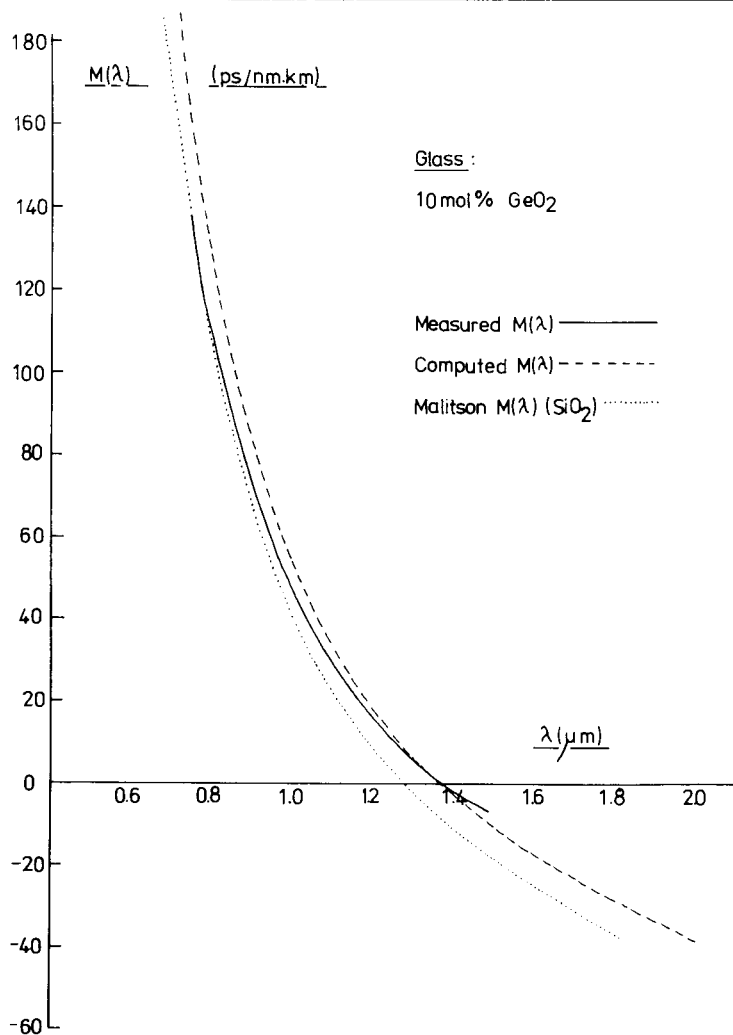
Figure 4 Theoretical and experimental values of $M(\lambda)$ for 10 mol% GeO_2–SiO_2 glass.

presented by Presby and Kaminow [18] are at least 40% greater than the normally accepted values calculated from Malitson's Sellmeier equation for silica. More generally their values of $P(\lambda)$ and $M(\lambda)$ for the various binary glasses considered are at variance with other known measurements [8, 11, 12, 15, 16].

5. Conclusions

A two-term composition-dependent Sellmeier model has been developed for predicting the wavelength dispersive properties of the core glass of an optical multimode fibre fabricated from a SiO_2–B_2O_3, SiO_2–P_2O_5 or SiO_2–GeO_2 binary glass system. The Sellmeier model has been tested by comparing computations of refractive index $n(\lambda)$, profile dispersion $P(\lambda)$ and material dispersion $M(\lambda)$ with measured values obtained from multimode fibres from the three glass systems of known compositions. Reasonably good and accurate agreement with the measurements was obtained.

The Sellmeier model has also shown, as suggested by Gloge [16] that to a first order $P(\lambda)$ is independent of composition, and is only a function of the constituents of the binary glass. Calculations to determine pulse broadening, profile dispersion and optimum alpha for a large number of fibres of differing compositions from the three glass system have also been made with success [19].

Finally an extension of the Sellmeier model to predict the wavelength dispersive properties of the

core glasses of optical multimode fibres fabricated from silica-based ternary glass systems is possible, which is the subject of further study [19].

Acknowledgements

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