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REFRACTIVE INDEX AND DENSITY OF FLUORINE DOPED SILICA PREPARED BY THE PCVD PROCESS

H. Wehr and D. Wiechert

Philips GmbH Forschungslaboratorium Aachen, D-5100 Aachen, Germany

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ABSTRACT

Experimental data on the density, the refractive index and the material dispersion derived therefrom are presented for fluorine doped PCVD- (plasma activated chemical vapour deposition-) silica. Both density and refractive index decrease linearly with increasing doping concentration. Comparison of the refractive index depression in PCVD glass and data published for F-doped glasses prepared by other techniques reveal some discrepancies. The influence of small amounts of chlorine in the silica network on the refractive index and on the dispersion is also considered.

MATERIALS INDEX: F-DOPED SILICA, REFRACTIVE INDEX, DENSITY

Introduction

Among the various dopants commonly used for the preparation of silica preforms and fibres for optical communication, fluorine shows some attractive features. In contrast to GeO_2-, P_2O_5-, or Al_2O_3-dopants, which all increase the refractive index n, addition of fluorine heavily decreases n at rather low doping levels. Additional absorption bands at around 1.55 μm, as observed in boron doped silica which also has a lower value of n compared to pure silica, are absent in F-doped glass. Furthermore fluorine doping slightly shifts the wavelength of zero dispersion λ_0 to lower values. Since GeO_2, for example, increases the value of λ_0, variation of the dopant composition GeO_2/F gives the manufacturer the possibility of influencing the dispersion properties of optical fibres in either direction. So far very precise data on the relation between fluorine concentration and refractive index are rather scarce. Fleming and Wood /1/

have determined the refractive index at different wavelengths with fifth decimal place accuracy on two fluorine doped samples, which were prepared at Heraeus Quarzschmelze GmbH by a plasma torch. Data with a lesser precision for samples prepared by flame pyrolysis (i.e. MCVD process) are available at one wavelength from the work of Abe /2/. The incorporation efficiency of fluorine in silica preforms prepared by the low pressure plasma-activated chemical vapour deposition (PCVD) technique as well as the relative refractive index depression at one wavelength have been investigated by Bachmann /3/.

The present work is aimed at extending the measurements of the refractive index of fluorine doped PCVD-glass over a larger wavelength range. The dopant concentrations cover the range typical for optical fibre fabrication to date (i.e. up to about 2.5%(wt) F in the solid). The influence of small amounts of chlorine in the silica network on the refractive index and on the dispersion is also considered. Finally data on the variation of density of PCVD-glass with F-doping are given which so far have not been available.

Experimental

Sample preparation

The glass samples used for the present refractive index and density measurements were cut from the core or cladding regions of optical preforms prepared by the PCVD process. The starting materials for the deposition procedure were $SiCl_4$, O_2 and C_2F_6, in the case of fluorine doping. Further details of the deposition technique are described elsewhere /4/. The collapsing of the internally coated tubes was done by means of an oxygen-hydrogen burner at a temperature of about 2100°C. Subsequently the glass specimens were shaped to prisms with an apex angle of about 30° and faces optically polished to 1/10 wavelength flatness. No additional heat treatment was performed on the samples. The thermal history of the individual samples is thus virtually identical.

Refractive index measurement

Refractive index data were obtained by measuring the deviation of monochromatic light through the prism samples in an autocollimation set-up /5/. Several different light sources were used. The wavelength range from 1064 nm to about 1600 nm was covered by a Nd:YAG-Raman fibre-laser. Due to intensity problems further extension of the measurements into the infrared wavelength range was not possible in the present experiments. Alignment of the set-up and measurements at intermediate wavelengths were performed with the help of a He-Ne laser (632.8 nm) and a Krypton laser (647 nm). Finally the strong lines of a high pressure Hg-Xe lamp were used for the lower and some intermediate wavelengths. The working wavelength of the Nd:YAG-Raman fibre laser and of the Hg-Xe lamp were selected by a grating with 1.5 nm and 2 nm spectral width respectively. During a measurement period the temperature was about 21 ± 1°C. The precision of the rotary prism table was ±1.8 arc sec. The reproducibility of the refractive index measurements was $\pm 5 \times 10^{-5}$.

Density measurement

The density ϱ of some selected PCVD samples relative to its value in natural silica (here: collapsed Heraeus waveguide SiO_2-tube material with about 150 ppm OH) was determined according to the suspension method /6/. The glass pieces were suspended in a liquid mixture of acetone and diiodomethane the composition of which was adjusted to bring its density at about 40°C close to that of the glasses being tested. The temperature of the liquid was adjusted by a thermostat with an accuracy of better than 0.1°C. The final precision in the determination of $\Delta\varrho$ was about 0.0002 g/cm^3.

Determination of fluorine and chlorine content

During the PCVD process the efficiency of fluorine incorporation into the deposit depends on the glass deposition conditions and can be below 100% /3/. Therefore the F-concentration in the optical preform usually cannot be identified with the mole fraction of fluorine in the gas stream. We determined the concentration of fluorine and of chlorine, which can always be present in synthetic silica /7, 8, 9/, by wet-chemical analysis (using ion chromatography). The prism samples or equivalent glass pieces taken from the same preform rod were cut into several pieces of about 10 mg weight, which were analysed individually. The standard deviation of the concentration values obtained was about 0.05%(wt) and 0.06%(wt) for fluorine and chlorine respectively and is mostly due to the limited resolution of the chemical analysis. Additional studies of the chlorine concentration profile of the prisms with an electron probe X-ray microanalyzer agreed with the data of the chemical analysis within these error limits.

Results and discussion

Measured refractive index data for six differently doped PCVD-glasses are listed in Table I. The refractive index of the 2.07%- and 2.3%-sample was determined at the He-Ne wavelength only, because of the smallness of the sample size. For comparison the refractive index data of natural silica cut from a collapsed Heraeus waveguide (WG) tube are also presented. The parameters of a three-term Sellmeier dispersion formula, i.e. $n^2 = \sum_{k=1}^{3} A_k \lambda^2/(\lambda^2 - \lambda_k^2) + 1$, adjusted to fit the experimental $n(\lambda)$-data are given in Table II. A graphical representation of the refractive index data and of the material dispersion deduced therefrom is presented in Fig. 1 a,b. Several points are worth noting: the refractive index of the "undoped" PCVD sample is larger than its value in natural silica by about $\Delta n = +4\ 10^{-4}$. From a chemical point of view the main difference between natural silica and the fused PCVD silica sample studied here is the incorporation of 0.6%(wt) Cl in the latter one. It has first been shown by Küppers et al. /7/ that increasing the chlorine content in the deposited glass layers systematically increases the refractive index. It is thus plausible to attribute the refractive index increase Δn observed here equally to Cl doping. For small doping levels one obtains the relationship: $\Delta n \sim + 6\times10^{-4}$ per weight-% Cl. The Cl-concentration however has a negligible effect on the material dispersion as can be seen from the dispersion curve of natural silica and of PCVD silica (without F-doping)

which are identical within the resolution of the experiment. In contrast to the relatively small index increase due to chlorine incorporation, fluorine at a similar doping level causes a large index depression. The wavelength of zero dispersion λ_0 is slightly shifted from 1.275 µm for the 0%F-PCVD sample to about 1.255 µm for the 1.97% F-sample. A more direct determination of the chromatic dispersion of F-doped PCVD optical fibres by pulse-delay measurements yielded values for the shift in λ_0 which are comparable to the present ones /10/.

TABLE I

Wavelength dependence of refractive index for fused PCVD silica at various F-concentrations (weight-%). For comparison the measured data for natural silica (i.e. Heraeus waveguide material) are also shown.

λ [µm]	Heraeus WG-quartz 0% F	0% F 0.6% Cl	0.15% F 0.38% Cl	1.47% F 0.22% Cl	1.97% F 0.54% Cl	2.07% F 0.4% Cl	2.3% F 0.5% Cl
0.404				1.46403			
0.436		1.46757	1.46621	1.46105	1.46021		
0.546	1.46039	1.46090	1.45985	1.45461	1.45372		
0.578	1.45913	1.45957	1.45855	1.45340	1.45248		
0.633	1.45736	1.45782	1.45682	1.45160	1.45070	1.44996	1.44949
0.647	1.45696	1.45736	1.45635	1.45120	1.45018		
0.822	1.45322	1.45363	1.45270		1.44672		
0.879	1.45236	1.45274	1.45177		1.44580		
0.917	1.45187	1.45226	1.45127		1.44532		
1.064	1.44981	1.45028	1.44943	1.44439	1.44325		
1.116	1.44910	1.44957		1.44378	1.44257		
1.123			1.44873				
1.175	1.44842	1.44890		1.44305			
1.180			1.44799				
1.209	1.44803	1.44846					
1.214			1.44760				
1.237				1.44238	1.44119		
1.266	1.44738	1.44781		1.44199	1.44085		
1.271			1.44696				
1.312	1.44687	1.44731		1.44152	1.44041		
1.316			1.44645				
1.357	1.44635	1.44687		1.44106	1.43987		
1.362			1.44593				
1.403	1.44583	1.44624		1.44054	1.43934		
1.407			1.44524				
1.448	1.44530	1.44572		1.44007	1.43881		
1.453			1.44490				
1.494	1.44474	1.44517		1.43952	1.43826		
1.498			1.44437				
1.539	1.44429	1.44472		1.43891	1.43773		
1.544			1.44385				
1.584	1.44368			1.43836	1.43716		
1.630		1.44348					

TABLE II

Sellmeier parameters for the glasses investigated.

	A_1	λ_1	A_2	λ_2	A_3	λ_3
0% F 0.6% Cl	0.69913	0.08793	0.40697	0.09344	1.06869	10.61535
0.15% F 0.38% Cl	0.69788	0.08823	0.40575	0.09044	1.01796	10.42423
1.47% F 0.22% Cl	0.68943	0.06196	0.39965	0.12067	0.90574	9.96621
1.97% F 0.54% Cl	0.68908	0.07148	0.39717	0.11326	0.95894	10.06590
0% F Heraeus-WG quartz	0.69750	0.09169	0.40743	0.08666	1.66008	13.16405

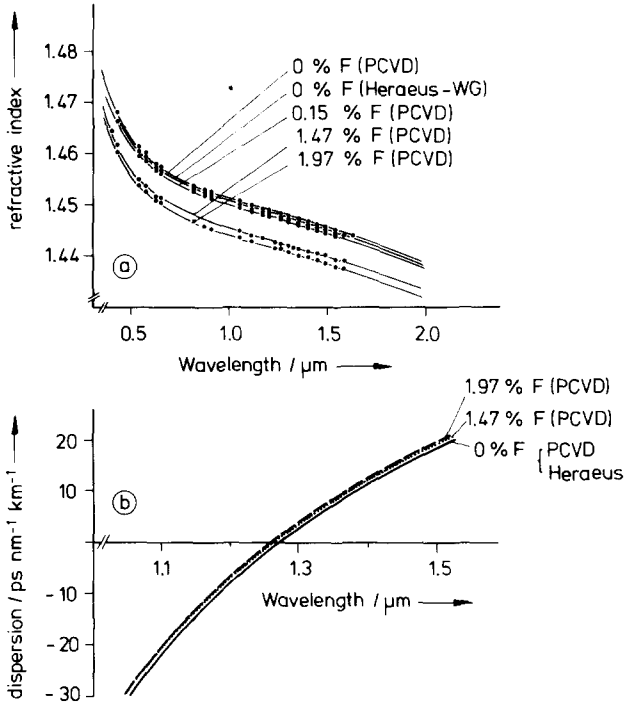

FIG. 1

a) Refractive index vs wavelength for fused PCVD silica at various F-concentrations and for natural silica (i.e. Heraeus WG material)

b) Material dispersion vs wavelength derived from a three-term Sellmeier formula fitted to the experimental refractive index data.

The variation of refractive index with fluorine concentration for λ = 633 nm is depicted in Fig. 2. In this plot the refractive index data of the present experiments (dots) were corrected for the Cl-contribution, which slightly varied in the individual samples (see also Table I). Additional data for PCVD-glass extracted from Bachmann's work /3/ (triangles) as well as data from Fleming et al. /1/ (stars) and data published by Abe /2/ (circles) (after correction to match the wavelength λ = 633 nm) are also shown. In all experiments the refractive index decreases virtually linearly with fluorine doping. However the slope of the curve measured by Fleming differs markedly from that observed in the present experiments, which in turn shows a better agreement with Bachmann's and Abe's data.

Since fibre design based on bulk measurements is convenient an important question is, how much the fibre drawing process changes the refractive index from its value in the preform. Using the refracted nearfield technique (RFN) for the refractive index measurement on fibres /11/ we could not resolve discrepancies between PCVD bulk and fibre results within the error limits $\Delta n \sim 2 \times 10^{-4}$ of the (RFN) set-up.

Finally we considered the variation of density upon fluorine doping. The difference in density between F-doped PCVD glass and Heraeus WG quartz is listed in Table III and plotted in Fig. 3. The absolute density of the Heraeus WG-sample was determined independently with the help of a pycnometer to be: ϱ = 2.23 ± 0.01 g/cm^3 at 21°C. Fluorine doping systematically decreases the density by 0.0115 g cm^{-3} in going from the 0%-F-sample to the 2.07%F-sample. The difference in density of -0.0015 g cm^{-3} between the 0%-F PCVD sample and the Heraeus WG-quartz sample is presumably also due to the presence of chlorine in the latter specimen. Inspection by light microscopy did not reveal any bubbles or irregularities inside the samples. It is therefore believed that the reduction in density is an intrinsic property of the fluorine and/or chlorine doped silica network. Theoretically one might regard fluorine doped silica as a binary mixture of SiO_2 and SiF_4. Consequently ϱ is expected to vary linearly with composition, as it is observed, for example, for synthesized SiO_2-GeO_2 glass /12/. However this behaviour cannot be observed experimentally over a larger composition range in SiO_2-SiF_4 since SiF_4 is known as a gas only.
Inserting the values of ϱ and n into the well-known Lorenz-Lorentz formula, one can infer the value of the molecular electronic polarisability. At λ = 633 nm these values are 2.91 Å^3, 2.86 Å^3 and 2.84 Å^3 for the 0%F-, 1.47%F- and 2.07%F-sample respectively. For comparison, in the SiO_2-GeO_2 system the polarisability increases by about 0.02 Å^3 and 0.03 Å^3 in going from the 0% GeO_2- to the 1.47% GeO_2- and 2.07% GeO_2-sample respectively (as deduced from the data of Ref. /12/.)

TABLE III

The difference in density between synthetic PCVD silica and natural silica for different F-concentrations.

	0% F 0.6% Cl	1.47% F 0.22% Cl	2.07% F 0.4% Cl
$\Delta\varrho$ [gcm^{-3}]	-0.0015	-0.0086	-0.0130

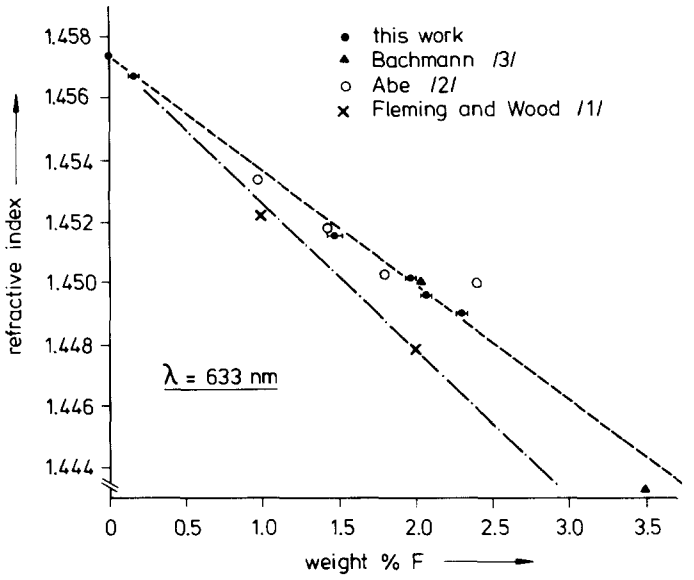

FIG. 2

Refractive index at 633 nm vs fluorine concentration in fused silica.

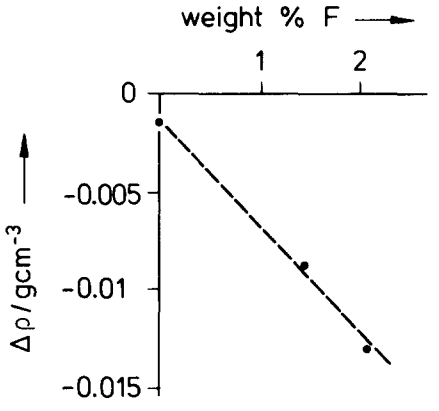

FIG. 3

Difference in density $\Delta\varrho$ between fused PCVD silica and natural silica for different F-concentrations.

Summary

Refractive index and density decrease almost linearly with the F-content in PCVD fused silica within the fluorine dopant concentration range typical for optical fibre fabrication to date (i.e. up to some %(wt)-F in the solid). In contrast to fluorine doping chlorine incorporation during the deposition process (some tenths of a %(wt) Cl) slightly increases the value of the refractive index which is established by a comparison of the values found for synthetic PCVD silica and natural silica. A Cl-induced variation of the material dispersion could not be resolved. The slight decrease in density of the PCVD SiO_2-sample when compared to natural silica is also attributed to the presence of chlorine. Finally agreement between bulk and fibre refractive index data was obtained within the experimental error limits of 2×10^{-4}.

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