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Thermal expansion coefficients of doped and undoped silica prepared by means of PCVD

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The thermal expansion coefficient of silica prepared by means of low-pressure plasma-induced chemical vapour deposition has been investigated in the temperature range 20 to 750° C. Undoped, fluorine-doped (up to 5 wt%), germanium-doped (up to 14 wt%), as well as F/GeO_2-codoped samples were measured and compared to NBS standard silica samples. Fluorine-doped silica shows a lower thermal expansion coefficient than the NBS standard. A surprising hysteresis effect in the measured expansion curves was found. Its concentration dependence and annealing is discussed.

1. Introduction

The low-pressure plasma-induced chemical vapour deposition (PCVD) process [1–3] is well established for the manufacture of high-quality low-loss optical fibres for telecommunication. This process allows the preparation of materials with unusual composition (e.g. silica containing more than 8 wt % fluorine in the solid [4]), resulting in optical fibres with unique features [5, 6]. Despite considerable effort over the past years [7, 8] there is still a lack of knowledge of the basic properties and material characteristics of the doped and undoped silica prepared by means of PCVD. These data are required to predict and fine-tune the optical as well as the mechanical properties of the resulting fibres and to optimize the preparation process. The thermal properties of the materials prepared by means of PCVD may have an impact on the stress in both preforms [9] and fibres [10] drawn from the preforms, thus influencing the mechanical stability and lifetime of both. We therefore investigated the thermal expansion coefficient, its concentration and composition dependence, its temperature dependence and effects of annealing, using undoped, fluorine-doped, germanium-doped and F/GeO_2-codoped glass samples prepared with PCVD.

2. Experimental details

2.1. Sample preparation

The preparation of preforms by means of PCVD is described elsewhere in detail [3]. The preforms obtained are solid glass rods consisting of Heraeus WG substrate tube material on the outside and deposited material as the central part. To obtain bulk PCVD material the substrate tube silica is removed by grinding and polishing (see Fig. 1). A central hole is drilled into the remaining glass cylinders in order to remove the distorted, inhomogeneously doped central regions. The final samples consist exclusively of homogeneously doped or undoped PCVD silica. The tubes have a length of 25 ± 0.05 mm, an outer diameter of approximately 7 mm, and an inner diameter of approximately 1 mm.

2.2. Dilatometer measurements

The samples were measured with a Netzsch differential dilatometer 402 ED equipped with fused silica sample holders and sensing rods. Fused silica NBS 739 was used as a reference sample. The accuracy of the measured thermal expansion was approximately $\pm 0.05\,\mu m$. For positioning, the samples were first heated to 800° C at a rate of $500°\,C\,h^{-1}$ and cooled down to room temperature again. The measurements were then made by heating the samples at a rate of $100°\,C\,h^{-1}$ to 800° C. This end temperature was kept constant for 1 h. Subsequently, the samples were cooled down to room temperature again at a rate of $100°\,C\,h^{-1}$.

3. Results and discussion

3.1. Average thermal expansion coefficient

Up to 500° C the measured thermal expansion of the samples did not show any abnormal characteristics. In Fig. 2 the thermal expansion coefficient, α, averaged over the range 100 to 500° C is given plotted against the dopant-induced relative refractive index difference Δ (%). Δ is defined by

$$\Delta = (n_1 - n_r)/n_r \qquad (1)$$

where n_1 is the refractive index of the material investigated and n_r is the refractive index of the reference, i.e. the index of pure silica. The Δ-scale of Fig. 2 can be transformed into a more common concentration scale using the curve for fluorine given in Fig. 3 [3, 11]. However, the measurement of refractive index differences of the samples was chosen as a measure for the dopant concentration due to the fact that chemical or physical analysis of each sample is both inaccurate and time consuming. Therefore, here the thermal

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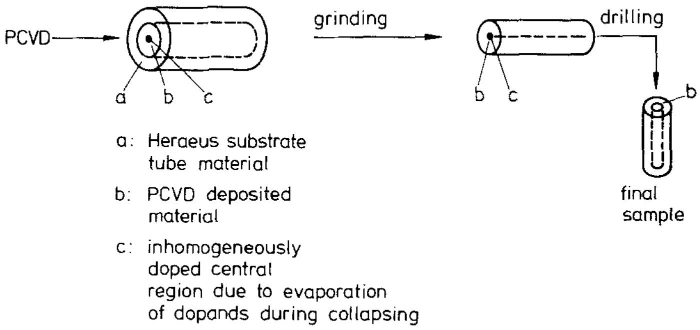


Figure 1 Preparation of the PCVD glass samples.

expansion data are given plotted against the relative refractive index difference. The left-hand side of Fig. 2 refers to samples containing fluorine as the only dopant thus reducing the refractive index below that of pure silica. The right-hand side of Fig. 2 refers to germanium-doped silica samples with a refractive index higher than that of silica. $\Delta = 0\%$ corresponds to "undoped" PCVD silica. The expansion coefficient of "undoped" PCVD silica is approximately 10% lower than the corresponding value of the NBS reference, which is also included in Fig. 2 (marked with a cross). The measured value of $5.7 \times 10^{-7}\,°\mathrm{C}^{-1}$ for the reference sample proves the accuracy of the measurements and indicates the relevance of the 10% decrease (i.e. $5.1 \times 10^{-7}\,°\mathrm{C}^{-1}$) for the "undoped" PCVD sample. "Undoped" in this context means fused silica with a residual content of chlorine incorporated during the plasma deposition [9]. The incorporation of chlorine during the deposition was found to be correlated with stress effects in preforms [9]. A 10% decrease in the thermal expansion coefficient due to chlorine incorporation in PCVD silica is found to be sufficient to describe the stress difference between natural and deposited silica. This decrease is now confirmed experimentally: chlorine incorporation of approximately 0.4 wt % lowers the thermal expansion coefficient of silica by approximately 10% and increases its refractive index by approximately 0.03% with respect to the values of natural silica.

In agreement with the linear dependence of the thermal expansion coefficient, α, from the refractive index (i.e. from the doping concentration) given by other authors, the right-hand side of Fig. 2 shows the results of our measurement for purely GeO_2-doped silica prepared with PCVD. For comparison, we extracted expansion coefficients from the results given in the literature [12–14]. The data are listed in Table I. Our results are in good agreement with the values given by Aggarwal [14]. The reason for the scatter in the results published by the various authors is not clear to us. Possible explanations are the differences in the methods of preparing the samples, the thermal history of the silica, and the accuracy of the measurements.

Data of the concentration dependence of the thermal expansion coefficient of fluorine-doped silica are scarce. Recently, Takahashi *et al.* [15] published results of fluorine-doped silica also prepared by PCVD. Fig. 4 contains these data together with our own results. For better comparison we restricted the temperature range for averaging our data to 25 to 400° C. The agreement with the results of Takahashi *et al.* [15] is excellent.

The left-hand side of Fig. 2 gives the values of α for 100 to 500° C plotted against the fluorine-induced refractive index of the solid. At $\Delta = -0.7\%$ (corresponding to 2.8 wt % fluorine in the solid, Fig. 3) α is close to its minimum value and, surprisingly, increases again, if the deposit contains more fluorine.

3.2. Temperature dependence of the thermal expansion coefficient

Fig. 2 gives thermal expansion coefficients averaged over the temperature range 100 to 500° C. However, α shows a small variation with temperature in this region and, in addition, shows an increasing temperature dependence above 500° C. Fig. 5, as an example, gives details for purely fluorine-doped silica with a fluorine content of approximately 1.5 wt %, i.e. a refractive index which is 0.38% below the value of pure silica. Up to 450° C, α decreases slightly. Above 450° C, the expansion coefficients measured while heating

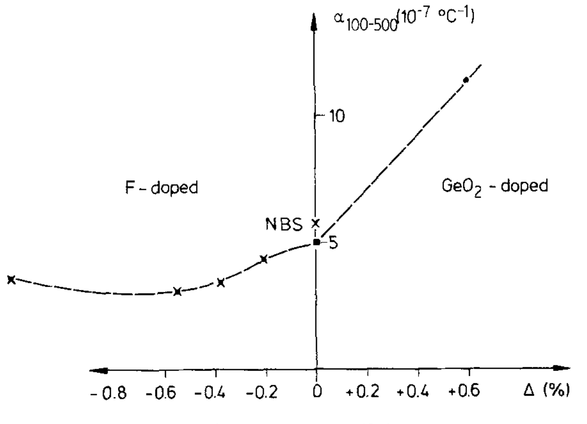


Figure 2 Average thermal expansion coefficient, α plotted against the doping-induced relative refractive difference, Δ.

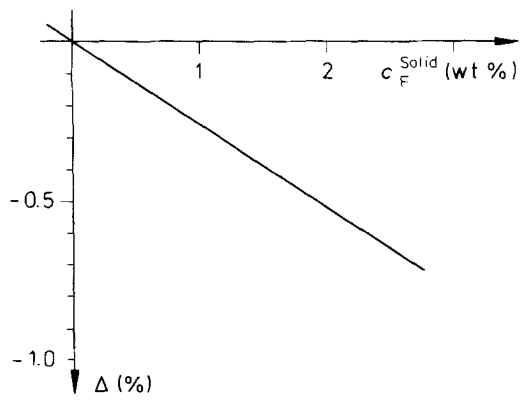


Figure 3 Relative refractive index, Δ, of fluorine-doped silica plotted against the fluorine concentration in the solid.

TABLE I

References	$\alpha_{25\text{-}200}$ (10^{-7} °C^{-1})	$\alpha_{25\text{-}300}$ (10^{-7} °C^{-1})
This work	13.2	12.8
Huang *et al.* [12]	–	14.2
Schultz [13]	–	13.8
Aggarwal and Randall [14]	13.2	–

Because the measured germanium concentration was 8.6 mol % in our sample, we used this value to deduce α from the reference accordingly.

the sample to higher temperature (——) are different from the values obtained while cooling the sample (– – –) back to room temperature. This hysteresis was found for all fluorine-containing samples. The temperature, T_{hy}, where a significant hysteresis effect can be detected (i.e. 450° C in Fig. 5) depends on the fluorine content, i.e. the refractive index of the sample. Fig. 6 demonstrates the dependence of α on both the temperature and the fluorine content. For the sake of clearness, only the curves obtained while heating the samples are given. Thermal expansion coefficients were measured up to 750° C and a refractive index range of $-1.2 \leqslant \Delta \leqslant 0\%$ is covered. Highly fluorine-doped material shows a sharp increase of α at temperatures as low as 500° C. For undoped silica this effect is not found up to 750° C. The slope of this increase depends on Δ and increases with the fluorine content.

3.3. Hysteresis effects

We investigated the differences in α upon heating (α↑) and cooling (α↓) of fluorine doped samples in more detail. In Fig. 7 the differences

$$\Delta\alpha_{\text{th}} = \alpha\uparrow - \alpha\downarrow \qquad (2)$$

i.e. the values of the hysteresis effect are given plotted against Δ[%] for various temperatures. This figure clearly shows that Δα increases with both the temperature and the fluorine concentration of the solid. The effect is correlated with the use of fluorine as doping material and is not observed for purely GeO_2-doped or undoped silica samples.

The hysteresis effect is of practical importance. Depending on the number of temperature cycles the shape of the sample is changed significantly, resulting in stress. The stress can even exceed the breaking stress of the material, i.e., destroys preforms or fibres. The microscopical reason for this phenomenon needs further detailed investigations.

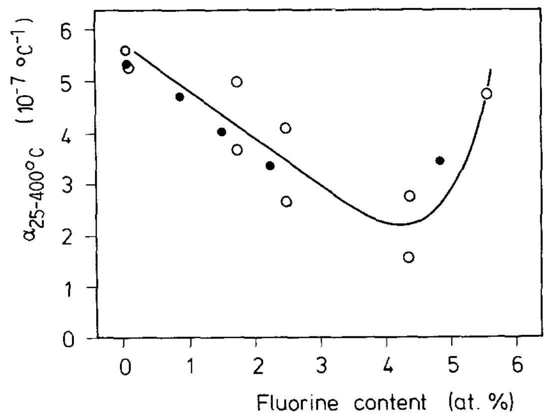


Figure 4 Comparison of the thermal expansion coefficients given (○) by Takahashi *et al.* [15] with the results (●) of the present work.

3.4. Annealing

The thermal expansion coefficient of fluorine-doped silica does not only depend on the fluorine concentration and the temperature, but also on the thermal treatment of the sample. We tempered a sample with $\Delta = -0.55\%$ for 7 h at 1000° C and subsequently cooled it down to room temperature at 100° C h^{-1}. The resulting values of thermal expansion coefficient differ significantly from those without tempering and are given in Fig. 8. This graph also includes the respective data for the same sample after an additional heat treatment at 1200° C for 7 h. The annealing of the hysteresis is clearly visible. However, similar to the hysteresis itself, the reason for the effect of annealing is not yet clear. This subject needs detailed investigation because of its possible impact on both the mechanical and optical properties of optical fibres.

3.5. Binary codoping systems

The binary codoping systems $GeO_2/F/SiO_2$ is of practical importance for the large-scale manufacture of optical fibres by means of PCVD. This material system allows the preparation of fibres with low Rayleigh scattering terms and low OH-excess loss [5, 16]. We therefore investigated a sample containing fluorine ($\Delta_F = -0.63\%$) and a small codope of GeO_2 ($\Delta GeO_2 = +0.1\%$; approximately 0.1 mol % GeO_2). The results show, that

(a) for temperatures < 500° C the temperature dependence of α of GeO_2/F-codoped silica is similar to the purely fluorine-doped or GeO_2-doped samples;

(b) measured hysteresis effects agree quantitatively with the results obtained from samples with the same amount of fluorine, i.e. the germanium in the solid does not change this effect. Fluorine seems to be exclusively responsible for the hysteresis;

(c) the thermal expansion coefficient of GeO_2/F-doped samples is higher than for the respectively purely fluorine-doped material. GeO_2 increases α in the binary codoping system. The results indicated that in the expansion coefficient of such a sample is merely the mean value of the respective coefficients of purely fluorine- or GeO_2-doped silica with the same doping concentration.

3.6. Thermal expansion

The thermal expansion given by

$$\theta = \int_{T_1}^{T_2} \alpha \, \mathrm{d}T \qquad (3)$$

is responsible for the development of thermal stress in multicomponent silica samples like preforms and fibres. In cylindrical samples the axial stress is proportional to the differences of θ. Fig. 9 gives θ for differently doped silica as a function of the temperature, assuming T_1 = room temperature and $T_2 = T$ in Equation 3. The data are obtained by integration of α↑. The difference of 10% between the NBS reference and undoped PCVD silica is also valid for the integral

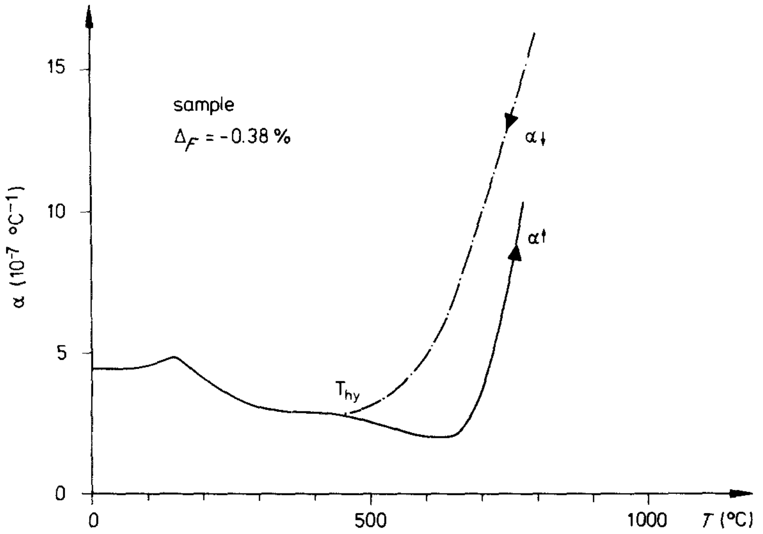
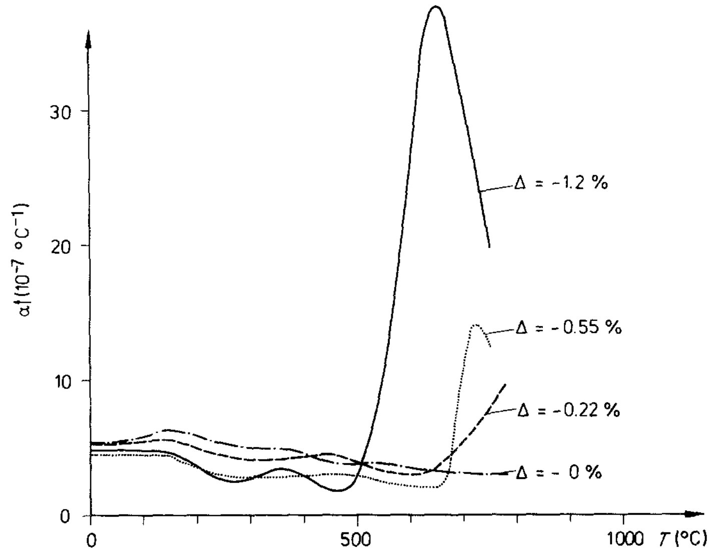


Figure 5 Temperature dependence of α of a fluorine-doped sample ($\Delta_F = -0.38\%$).

Figure 6 Concentration and temperature dependence of α of fluorine-doped silica (only α↑ is shown).



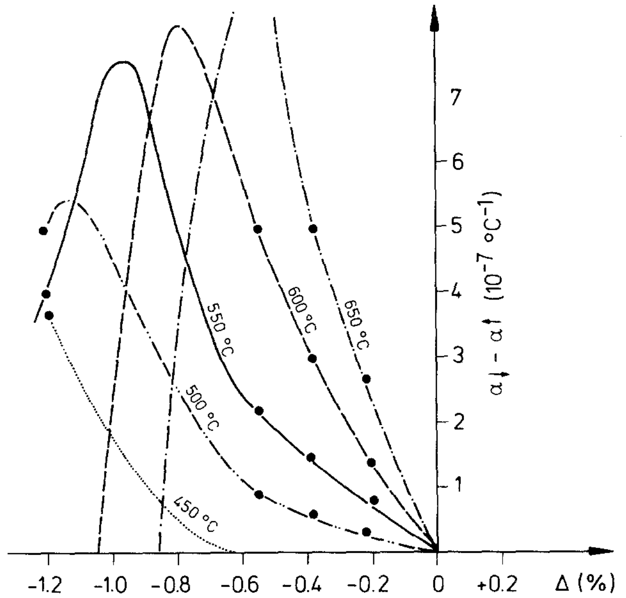


Figure 7 Concentration and temperature dependence of the hysteresis effect of α in fluorine-doped silica.

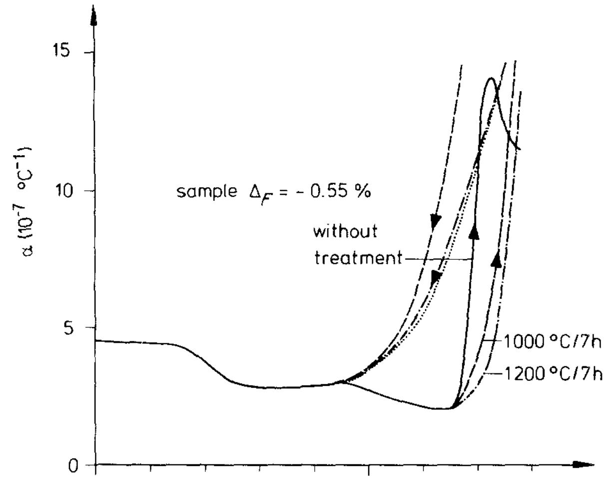


Figure 8 Annealing of the α-hysteresis.

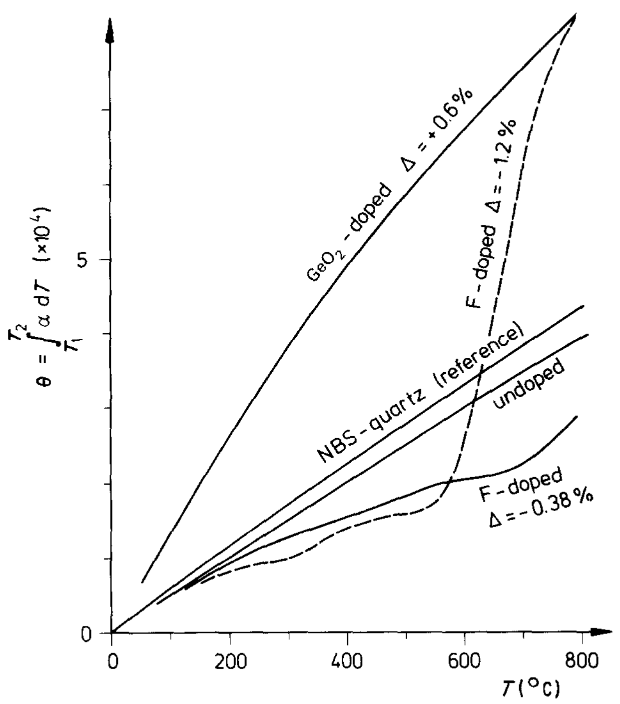


Figure 9 Thermal expansion, θ, plotted against the temperature for differently doped silica samples.

value of θ. For a quantitative correlation of and stress effects the setting point temperature and θ data up to the setting point temperature of the material are required [9]. Extrapolation of the θ curves for the undoped and the GeO_2-doped sample to approximately 1000° C, however allows a rough estimation of the stress difference (using the E-modulus and Poisson ratio given in [9]). The results differ less than 10% from the measured stress differences published in [9].

4. Conclusion

We investigated in detail the thermal expansion coefficients of undoped, fluorine-doped, germanium-doped and F/GeO_2-codoped silica prepared by means of the low-pressure plasma CVD process. Doping ranges common in optical fibre preparation are covered.

The thermal properties are collected up to 750° C. In addition to the basic knowledge on material properties which are closely correlated with stress effects in preforms and fibres and thus are at least relevant with respect to the mechanical stability of both, we found a surprising hysteresis effect. This effect exists in all samples doped or co-doped with fluorine, is dependent on the thermal history of the glass, and can be partly reduced by annealing.

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