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Refractive index of silica glass: influence of fictive temperature

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Abstract

The refractive index (RI) and the peak position of the first overtone of the fundamental SiO_4 -tetrahedron vibration mode, $2\nu_3$, have been studied as a function of fictive temperature. The materials used are synthetic silica glasses of type III (trade names: F310, F300 and F320), which contain mainly hydroxyl, chlorine and fluorine, respectively, and one natural silica glass of type II (trade name: Heraflux-WG). Two main results are presented: (1) The dependence of the RI on the fictive temperature is described for the different types of silica glass; (2) It is shown that the IR-absorption data can be used to determine the fictive temperature of silica glass. In both cases the four silica glasses behave differently because of the different types of dopants and dopant concentrations. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The refractive index (RI) of silica glasses can be adjusted to a certain extent by incorporating different amounts of dopants into the SiO_2 network [1–3]. In addition, the RI can also be modified with different thermal treatments. The heat treatment temperature and the rate of cooling determine the final structure of the silica glass and therefore also the RI. The concept of fictive temperature was proposed by Tool [4], who suggested that, depending on the cooling rate, glass has a frozen-in structure that corresponds to some temperature, called fictive temperature, T_f , of an equilibrium liquid. To obtain silica glass with a certain fictive

temperature, the silica glass samples were annealed at that temperature until structural equilibrium was established. Then it was cooled to room temperature by water quenching.

Spinner and Napolitano [5] measured the RI of silicate glasses with different fictive temperatures and showed that the RI decreases as the fictive temperature increases. In contrast to silicate glasses, silica glass shows an anomalous behaviour in the temperature range between 1000°C and 1500°C, i.e., the RI increases with increasing fictive temperature [6,7].

Silica glasses, which differ in the fictive temperature will also differ in the glass structure. Therefore the peak positions of the fundamental, combination and overtone structural bands will be shifted as the fictive temperature is changed. These vibrational modes can be determined using infrared absorption or Raman scattering measurements [8–10]. Once the correlation between the shift of such vibration modes and the fictive temperature is

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known, it may be used to determine the fictive temperature of silica glass samples [9,10]. There are three fundamental structural bands in the IR absorption spectra at 465, 800 and 1100 cm^{-1} , which have been assigned as the rocking, bending and stretching vibration of the Si–O–Si bridges, respectively [11]. Due to the strong absorption of these fundamental bands, the penetration depth of the incident IR beam is very small. Therefore only surface effects can be studied by monitoring the shift of these bands [9]. Because we want to study bulk effects, we have to use the overtone vibration mode, $2\nu_3$. The peak position of this mode can be obtained by IR-absorption measurements.

In this study, data from commercially available silica glasses are presented to determine the dependence of the RI and the peak position of the first overtone of the fundamental SiO_2 -tetrahedron vibration mode $2\nu_3$ on fictive temperature.

In addition to the commercially available silica glasses, different fluorine-doped silica glass samples with the same fictive temperature were measured in order to determine whether there is an influence of the dopant concentration on $2\nu_3$.

2. Experimental

2.1. Specimen

For this study, tube samples of type II silica glass (Heralux-WG) and of type III silica glasses (F300, F310 and F320) were used. F310 is an undoped synthetic silica glass with a high hydroxyl concentration, whereas F300 and F320 are synthetic silica glasses doped with high chlorine and fluorine concentrations, respectively, and low hydroxyl content. The dopant concentrations of these silica glasses are listed in Table 1. The sam-

ples are 10 mm long tubes with an outer diameter of 15 mm and a wall thickness of 1.6 mm (F300), 1.7 mm (F310) and 1.9 mm (F320, Heralux-WG).

In addition to these four commercially available silica glasses, a set of fluorine-doped silica glasses with concentrations from 2000 to 12,000 ppm were prepared for the IR absorption measurements, in order to determine whether the infrared absorption spectrum is influenced by dopant concentration. To exclude any effects due to different fictive temperatures, all fluorine-doped samples were heat treated at 950°C.

2.2. Heat treatment time

An important point in this study was the determination of the minimum heat treatment time at a particular temperature (e.g. this time should be longer than the relaxation time, τ_R , of the silica network to ensure that a structural equilibrium has been established). A rough estimation of the relaxation time can be obtained by measuring the change of the RI and the shift of $2\nu_3$ as a function of heat treatment time. For this experiment, silica glass samples with a fictive temperature higher than the heat treatment temperature $T = 1100^\circ\text{C}$ were used. The samples were heat treated for different time intervals and the RI and $2\nu_3$ were measured. With the help of a simple exponential decay fit, effective relaxation times could be determined [8]. These relaxation times represent a lower limit for the heat treatment time to guarantee that a structural equilibrium had been reached at temperatures higher than 1100°C before the samples were water quenched.

It is obvious that the higher the heat treatment temperature, the shorter is the relaxation time [7,8,12–14]. In order to obtain silica glass with high fictive temperatures, high quench rates are neces-

Table 1

Dopant and impurity concentrations of synthetic silica glasses, i.e., F310, F300, F320 and natural silica glass, i.e., Heralux-WG^a

Material	OH	Cl	F	Na	K	Li	Al
F310	233	<50	<50	<0.05	<0.015	<0.02	<0.1
F300	<1	1450	<100	<0.05	<0.015	<0.02	<0.1
F320	<1	150	4850	<0.05	<0.015	<0.02	<0.1
Heralux-WG	153	<50	<50	1.2	0.1	4.5	59

^a Concentrations are reported in ppm, by weight.

sary. Therefore short and thin tubes were used. These were drawn from standard MCVD substrate tubes to the dimensions mentioned above. In addition, a technique was developed for dropping the samples in less than 0.2 s from the furnace into a water bath. The heat treatment periods for temperatures higher than 1200°C were always longer than the relaxation times obtained at 1100°C, therefore structural equilibrium was always achieved. For heat treatment temperatures lower than 1200°C the samples were annealed until no change of either the RI or the peak position $2v_3$ could be observed. Devitrification did not occur in the samples because argon gas was used in the furnace and because every sample was heat treated only once.

2.3. RI measurements

The RI measurements were made at 632.8 nm, relative to the RI of a York reference cell using a Profiler P104 [15]. Due to the algorithm used to calculate the RI from the deflection data of a laser beam, only samples which are of cylindrical geometry, e.g., rods and tubes, can be measured [16,17]. Reproducibility was found to be better than 2×10^{-5} .¹ Fig. 1 shows the relative RI distribution of six samples, which were heat treated at different temperatures and then were water quenched. The outer part shows the RI of the index matching liquid and the inner part represents the RI of the sample. Due to strong temperature dependence of the RI of the index matching liquid the RI will change slightly. But this has no effect on measurement accuracy. At temperatures higher than 1400°C, the homogeneous RI profile changes in such a way that the RI in the inner and outer regions of the tube is higher than in the bulk of the tube. This difference becomes more pronounced at higher temperatures. For this reason, IR-absorption measurements were limited to temperatures below which the RI distribution changes its spatial

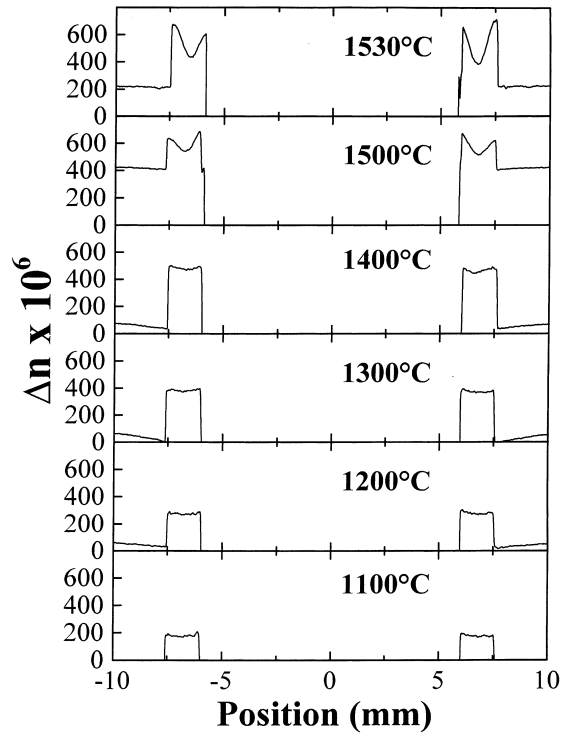


Fig. 1. RI distribution for six F300 samples heat treated at the given temperature until structural equilibrium was obtained. For details see text.

form. Since, at high heat treatment temperatures, the fictive temperature is no longer homogeneous in the sample, IR-absorption measurements would lead to a transmission spectrum, which could not be evaluated by using the technique described below.

2.4. IR measurements

IR absorption measurements were carried out with an FT-IR spectrometer. The transmission spectra were measured between 2000 and 2500 cm^{-1} , with a resolution of 4 cm^{-1} . The spectra were averaged over 32 scans. Every sample was measured three times perpendicular to the tube axis at three angular positions. Between 2220 and 2300 cm^{-1} the data were fitted to a fifth-order polynomial by using a least square fit procedure and the peak position was determined by the minimum of the fit function. For every sample we have

¹ We have experimentally verified, that when a constant, homogeneous and suitable RI profile of the index matching liquid is obtained, the reproducibility improves by a factor of 2 as compared to the one stated by York Technology.

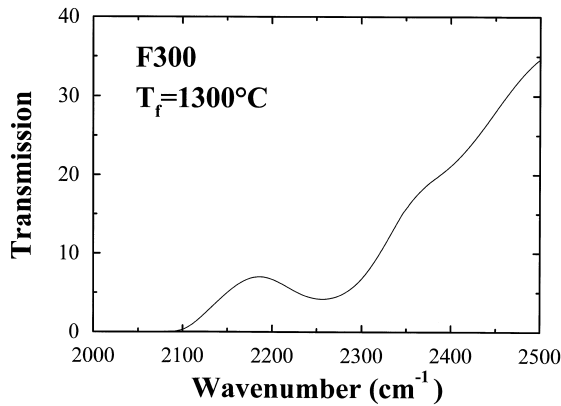


Fig. 2. IR absorption spectrum for F300 heat treated at 1300°C.

nine measurements from which the reproducibility is determined to be better than 0.1 cm^{-1} . In Fig. 2 a typical FT-IR spectrum is shown with a broad absorption band near 2260 cm^{-1} . The observed minimum near 2260 cm^{-1} , i.e. $2\nu_3$, is caused by the first overtone of the fundamental SiO_4 -tetrahedron vibration mode, ν_3 .

The value of RI measurements made with the Profiler P104 lies in the ability to obtain spatially resolved RI profiles, which made it possible to evaluate only the rim region of the tubes. Due to the higher quench rate at the outer surface compared to the inner part of the tube, the silica glass structure at the rim region can still be described by T_f . Therefore the fictive temperature range for the RI measurements can be extended compared to the temperature range for IR-absorption measurements.

3. Results

3.1. RI measurements

The relaxation behaviour of F300, F310, F320, and Heraldux-WG at 1100°C is shown in Fig. 3, where the RI change and the shift of $2\nu_3$ is plotted vs. heat treatment time. For the F320 samples the change of the RI was so small that no relaxation time could be obtained.

The RI decreases as a function of heat treatment time, because the heat treatment tem-

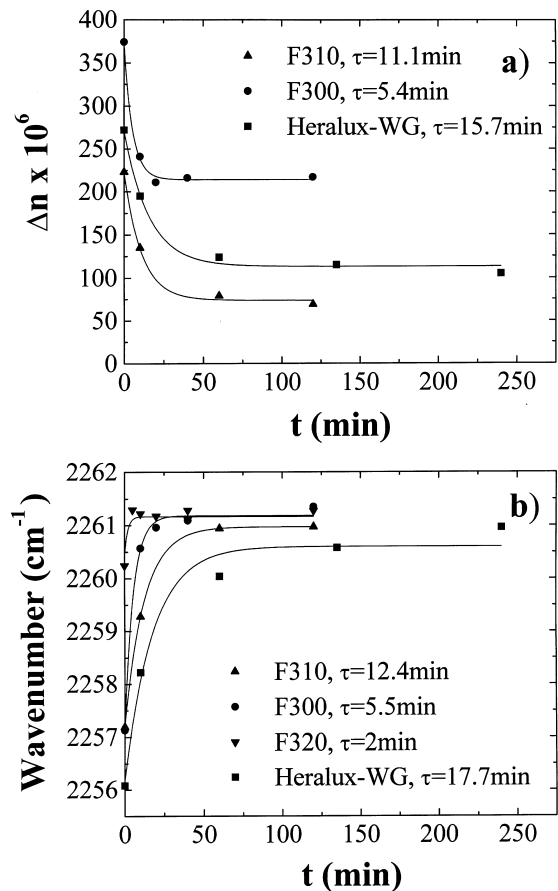


Fig. 3. (a) Change of the peak position $2\nu_3$ and (b) change of RI vs. heat treatment time at 1100°C for F310, F300, F320 and Heraldux-WG. The solid lines are exponential regression fits to the data.

perature is lower than the initial fictive temperature. When structural equilibrium is reached, the RI of F300, F310, F320 and Heraldux-WG are different, as a result of the different types of dopants [18]. The determined relaxation times increase from F300 over F310 to Heraldux-WG (see Table 2). RI measurements vs. T_f are shown in Fig. 4. Measurement results for different silica glass samples, which have the same fictive temperature T_f were averaged and the standard deviation is shown as error bars. In a specific temperature range the data could be fitted to a linear function, by using a least-mean square fit procedure,

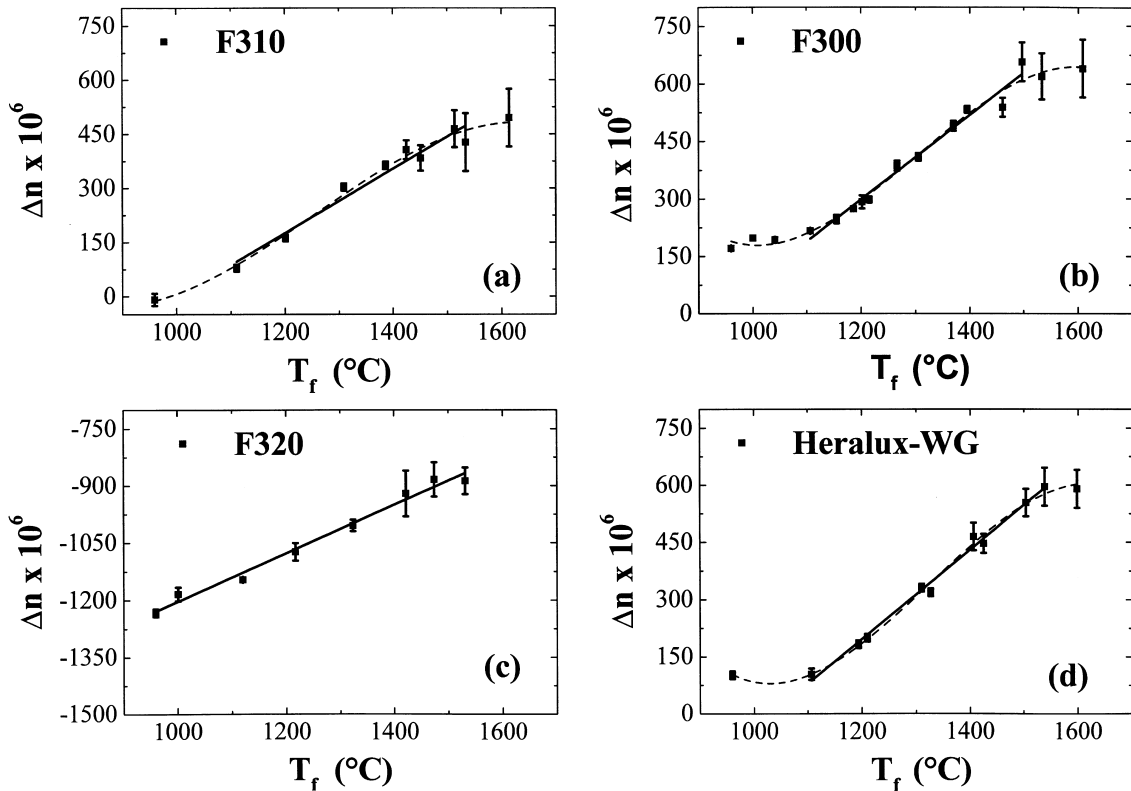


Fig. 4. RI as a function of fictive temperature for: (a) F310; (b) F300; (c) F320 and (d) Heralux-WG glasses.

$$n_{\text{type}} = n_{0,\text{type}} + \frac{dn_{\text{type}}}{dT_f} (T_f - 950^\circ\text{C}), \quad (1)$$

where type means the type of silica glass used, i.e., F310, F300, F320 and Heralux-WG; $n_{0,\text{type}}$ is the intercept; dn_{type}/dT_f the slope and n_{type} is the measured RI. For F310, F300, F320 and Heralux-WG the slopes dn_{type}/dT_f are 0.89, 1.10, 0.63 and $1.17 \times 10^{-6} \text{ K}^{-1}$, respectively. The regression coefficients along with the correlation coefficients and the 95% confidence interval are given in Table 3.

3.2. IR measurements

Using the time-dependent shift of $2\nu_3$ at a heat treatment temperature of 1100°C , the relaxation times were determined in a similar way as described above (see Fig. 3(b)). Due to the better reproducibility of the IR absorption measurements the relaxation time for F320 could be determined,

Table 2
Relaxation times of silica glasses determined by RI and IR-absorption measurements at $T = 1100^\circ\text{C}$

Material	Relaxation time at $T = 1100^\circ\text{C}$ (min)	
	RI data	IR data
F310	11.1	12.4
F300	5.4	5.5
F320	–	2
Heralux-WG	15.7	17.7

too. Because the fictive temperature of the samples after the heat treatment is lower than the initial fictive temperature, the position of $2\nu_3$ is shifted to higher values and therefore $2\nu_3$ will increase with heat treatment time [9,10]. The relaxation times are shown in Table 2. It is interesting to see that, despite the different techniques used, the relaxation times agree remarkably well.

The plots of $2\nu_3$ vs. T_f for the silica glasses tested are shown in Fig. 5: The higher the fictive

temperature the lower is $2\nu_3$. The straight lines are least square fits to the data and are described by the following equation:

$$2\nu_{3,\text{type}} = 2\nu_{30,\text{type}} + \frac{d2\nu_{3,\text{type}}}{dT_f}(T_f - 950^\circ\text{C}), \quad (2)$$

where, again, type means the type of the silica glass; $2\nu_{30,\text{type}}$ is the intercept; $d2\nu_{3,\text{type}}/dT_f$ the slope and $2\nu_{3,\text{type}}$ is the measured peak position. The slopes $d2\nu_3/dT_f$ for F310, F300, F320 and

Heralux-WG are 24.5×10^{-3} , 21.8×10^{-3} , 19.9×10^{-3} and $19.9 \text{ cm}^{-1} \text{ K}^{-1}$, respectively.

The regression coefficients of the linear least-mean square fits in Fig. 5 along with the correlation coefficients and the 95% confidence interval for the slope and the intercept at 950°C are also given in Table 4.

In addition to the study of the dependence of the RI and $2\nu_3$ on T_f silica glass samples with different flourine concentrations but the same

Table 3

Regression analysis parameters of the RI vs. T_f data sets shown in Fig. 4^a

Material	Number of points	Temperature range ($^\circ\text{C}$)	Intercept No. (10^{-6})	Slope dn/dT_f (10^{-6} K^{-1})	95% Confidence interval for slope	Correlation coefficient
F310	18	1100–1530	−879.91	0.89	0.5	0.952
F300	28	1100–1500	−965.17	1.10	0.076	0.969
F320	16	960–1530	−1839.03	0.63	0.092	0.970
Heralux-WG	13	1100–1540	−1195.07	1.17	0.1	0.992
Homosil [7]	–	950–1500	–	1.0	–	–

^a95% confidence intervals for the slopes and intercepts were calculated under the assumption of normal regression analysis using the t distribution.

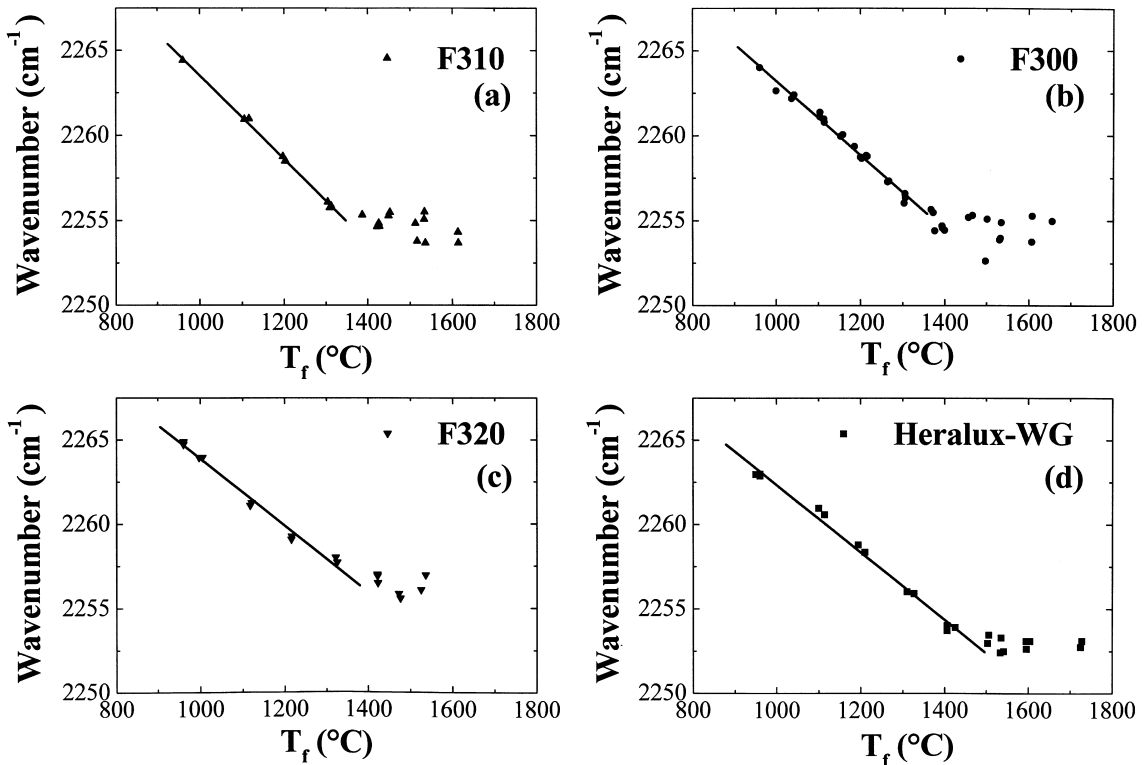


Fig. 5. Equilibrium peak positions of 2260 cm^{-1} band vs. fictive temperature for: (a) F310; (b) F300; (c) F320 and (d) Heraldux-WG.

Table 4
Regression analysis parameters of wavenumber vs. T_f data sets shown in Fig. 5^a

Material	Number of points	Temperature range (°C)	Intercept $2\nu_{3,0}$ at 950°C (cm ⁻¹)	95% Confidence interval for $2\nu_{3,0}$ (cm ⁻¹)	Slope $d2\nu_3/dT_f$ (10 ⁻³ cm ⁻¹ K ⁻¹)	95% Confidence interval for slope (10 ⁻³ cm ⁻¹ K ⁻¹)	Correlation coefficient
F310	10	960–1310	2264.7336	0.1980	-24.5	0.79	0.998
F300	24	960–1310	2264.3004	0.2425	-21.8	0.99	0.989
F320	11	960–1325	2264.8745	0.3445	-19.9	1.64	0.988
Heralux-WG	13	960–1425	2263.3235	0.3507	-19.9	1.22	0.991
different types [9]	–	960–1320	2263.826	–	-22.4	–	–

^a 95% Confidence intervals for the slopes and intercepts at 950°C were calculated under the assumption of normal regression analysis using the t distribution.

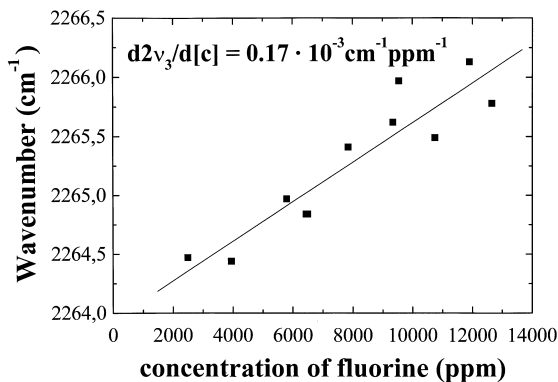


Fig. 6. Equilibrium peak positions of $2\nu_3$ vs. fluorine concentration. The samples were heat treated at 950°C before the measurement.

fictive temperature were prepared, in order to see whether $2\nu_3$ is influenced by dopant concentration. Fig. 6 shows that the concentration of dopants has an influence on $2\nu_3$. A linear regression results in a slope of $0.17 \times 10^{-3} \text{ cm}^{-1} \text{ ppm}^{-1}$. This behaviour is in contrast to Duma et al. [19] who noted that the frequency positions of the structural bands were not influenced by fluorine concentration.

4. Discussion

4.1. Specimen

A comparison of dopant concentration for F300, F310, F320 and Heraldux-WG reveals that only Heraldux-WG consists of a combination of different dopants. The synthetic materials, how-

ever, i.e. F300, F310 and F320, contain only one principal dopant, which lowers the viscosity. Therefore differences in the correlation of RI and $2\nu_3$ against the fictive temperature for the synthetic materials can be attributed to the dopant and also to its concentration. In contrast Heraldux-WG, a natural silica glass, consists of a combination of different dopants, some of which lower the viscosity like hydroxyl and chlorine and some of which increase the viscosity like aluminium [20]. For this reason Heraldux-WG will be excluded in the following comparison of material differences.

4.2. RI and IR measurements

The dependences of RI on T_f are shown in Fig. 4 as broken lines. Instead of the maximum around 1500°C, that Brückner has found, the curves show a saturation behaviour, which can be explained as follows [7]. For example, silica glass samples with high fictive temperatures require a sufficiently high quench rate, $\Delta T/\Delta t_q$. The time interval necessary to quench the sample from the heat treatment temperature to a temperature, at which the relaxation time is long compared with the experimental time period, is given by Δt_q . The difference between this temperature and the heat treatment temperature is ΔT . For low heat treatment temperatures T , the relaxation time is longer than Δt_q . Thus silica glass with fictive temperatures $T_f = T$ can easily be obtained. As the heat treatment temperature increases, the relaxation time becomes shorter and at a specific temperature the relaxation time is always shorter than Δt_q . This leads to an

upper limit in fictive temperature and therefore this accounts for the saturation behaviour of the RI and partly for the equilibrium peak position $2\nu_3$. The quench rate in the study of Brückner et al. [21] was nearly 10 times smaller. This could explain the fact, that in our study we could not resolve this maximum. At low fictive temperatures only the anomalous behaviour of the fictive temperature can explain the non-linear dependence of the RI on T_f for F300, F310 and Heralux-WG.

In addition to the saturation effect at high temperatures mentioned above, IR measurement results are also influenced by an inhomogeneous RI distribution. The RI measurements reveal that the higher the fictive temperature the more pronounced is the non-homogeneous spatial RI distribution (see Fig. 1). So both effects lead to an upper temperature limit for the determination of fictive temperature using Eq. (2).

4.3. Influence of material composition

Comparing the data of RI and $2\nu_3$ in the temperature range of the least square fits it can be noticed that the slopes dn_{type}/dT_f for the synthetic materials differ significantly. The same is valid for $d2\nu_{3,\text{type}}/dT_f$ and for the intercept $2\nu_{3,0,\text{type}}$ at 950°C . In general, the higher the dopant concentration, i.e., the amount of network interrupting dopants, the less the influence of the fictive temperature on RI and $2\nu_3$ is: F320 with the highest concentration of dopants shows the weakest dependence of RI and $2\nu_3$ on the fictive temperature. This is followed by F300 and F310. However, F310 behaves differently with respect to the slope dn_{type}/dT_f and the intercept $2\nu_{3,0,\text{type}}$ because the slope dn_{type}/dT_f is smaller and the intercept $2\nu_{3,0,\text{type}}$ is larger than it is for F300. Due to its smallest principal dopant concentration, compared with F300 and F320, the opposite behaviour for F310 was expected. This may be explained if hydroxyl has a different strength in modifying the silica glass structure, compared with chlorine and fluorine. A large variation of the dopant concentration will influence the viscosity and the relaxation time. As the concentration of the network interrupting dopants, i.e., hydroxyl, chlorine or fluorine

increases in the order from F310, F300 to F320, the relaxation time at 1100°C decreases. This result agrees with Mikkelsen et al. [14] who said that the viscosity and the relaxation time decrease as the concentration of network interrupting dopants increases.

In order to judge the influence of material composition on the determination of the fictive temperature from the values given in Table 3, the peak positions $2\nu_3$ of F310 and F320 at $T_f = 1300^\circ\text{C}$ are compared: The difference $\Delta\nu$ is nearly 1.7 cm^{-1} , which results in a difference in the determination of the fictive temperature of 100°K , when using a value for $d2\nu_{3,\text{type}}/dT_f$ of $17 \times 10^{-3}\text{ cm}^{-1}\text{ K}^{-1}$. Therefore, in order to determine T_f accurately by measuring $2\nu_3$ composition effects have to be included.

It is also possible to use the dependence of RI on T_f to determine the fictive temperature. This requires an accurate knowledge of the dopant concentration, because 100 ppm of chlorine will increase the RI by about 1×10^{-5} for example. Therefore the calculation of the fictive temperature using Eq. (1) will give a fictive temperature, that differs by roughly 10°K . In return, if the fictive temperature is known, RI measurements will allow a determination of the dopant concentration of silica glasses which contain only one principal dopant.

The influence of dopant concentration on $2\nu_3$ can also be estimated by comparing material properties of F300 with F320 at fictive temperature of 950°C . The difference in peak shift $\Delta\nu$ and principal dopant concentration Δc are 0.57 cm^{-1} and 3400 ppm, respectively.² Therefore 100 ppm would shift the peak position by roughly

² Here we assume that a change in chlorine concentration (wt%) will have a similar effect on the shift of $2\nu_3$ as it is the case for fluorine. One can imagine that the concentration (mol%) as well as the ionic radius of the dopants will have an influence on $2\nu_3$. Therefore, it is understandable that the same concentration (wt%) of chlorine, compared with fluorine, will shift $2\nu_3$ at nearly the same amount: The higher molar mass of chlorine, indicates a smaller number of network interrupting dopants compared to fluorine. But this will be compensated by the larger ionic radius of chlorine. Also it is important, that both belong to the same periodic group.

0.017 cm^{-1} , which is equivalent to change in fictive temperature of roughly 1 K. Note that the same relation was obtained for the different fluorine-doped samples (see Fig. 6). Therefore Eq. (2) seems to be less sensitive to a variation in the principal dopant concentration.

The results of the RI and IR-absorption measurements show that the material with the highest concentration of network interrupting dopants has the weakest dependence of RI and $2\nu_3$ on fictive temperature. This can be explained by comparing structural and optical properties of silica with those of silicate glasses. One main difference is the concentration of alkali oxides in silicate glasses, which is responsible for their low viscosity. Hydroxyl, chlorine and fluorine also reduce viscosity, but the concentration of these dopants in the corresponding synthetic silica glasses is low compared to the concentration of alkali oxides in silicate glasses. The optical properties of silica and silicate glasses are quite different: For silica glasses, the RI increases with the fictive temperature, whereas for silicate glasses the RI decreases. For $2\nu_3$ the opposite relations hold [5,22,23].

From this result one could conclude that very high concentrations of hydroxyl, chlorine and fluorine would alter the optical properties of silica and make them more similar to silicate glass. F320 may be considered to be an indication of this effect. A similar discussion is reported by Brückner [7], who investigated optical properties of silica glass with different hydroxyl contents. To confirm this trend, it would be helpful to use silica glasses, doped with several percent dopants.

5. Conclusion

We measured the dependence of the RI and the dependence of the first overtone of the fundamental SiO_4 -vibration mode, $2\nu_3$, on the fictive temperature for commercially available silica glasses. We observed that the dependence of the peak position of the $2\nu_3$ -band on the fictive temperature depends on the type of the silica glass as well as on the concentration of dopants.

For F300, F310, F320 and Heralux-WG we showed that the fictive temperature can be determined by IR-absorption measurements. Once the fictive temperature is known, one can estimate the dopant concentration by measuring the RI. However, it is necessary that only one principal type of dopant is present in silica glasses.

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