

Refractive Index Properties of Calcined Silica Submicrometer Spheres

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There is no doubt that silica study has had enormous interest for a long time since it is a material easy to obtain with a very inert chemical behavior. Among many relatively modern applications of silica such as optic fibers or its use as electrical isolator in microelectronics, we would like to emphasize its utilization to obtain artificial opals with very interesting optical properties. Submicron spheres of amorphous silica are fabricated by the Stöber-Fink-Bohn¹ (SFB) method; afterward these particles may be arranged by means of several techniques² which will produce a face centered cubic³ (fcc) structure. A few years ago, it was proposed that periodical structures under special conditions could present photonic band gaps⁴ (PBG), that is, energy ranges within which photons would not propagate regardless of the direction in which light is introduced. Unfortunately, artificial opals do not possess all the requirements to present a full PBG. Nevertheless, if opals are used as hosts where a high dielectric material is synthesized and the dielectric constant (ϵ) contrast between the guest material and spheres is high enough⁵ (above 7.85), the conditions to obtain a full PBG are fulfilled, the refractive index of the medium being larger than that of the spheres. This means that the range of available materials is not very large as it must be taken into consideration that the high refractive index (n) material must be transparent in the frequencies where the photonic crystal works. The chances for a material to fulfill the conditions are increased if the opal is inverted⁶ (removing silica spheres with a mild etching process once the opal has been loaded). In this way, the minimum value for the dielectric constant of the adequate guest material can be decreased. In this context, physical characterization of silica is fundamental to explain optical properties of bare opals and also important for optically monitoring the infiltration of opals with a dielectric. To date, silica refractive index⁷ has been often assumed to be 1.45 for Stöber particles. Here it is proven this is the case only for very specific conditions of preparation.

The refractive index of Stöber silica particles is studied, for the first time, to the best of our knowledge, as a function

of calcination temperature. The motivation is that opals usually experience thermal treatments: sintering at 950 °C to strengthen them or guest material synthesis, which often involves high temperatures.

Five samples of spheres of different diameters (379, 575, 800, 870, and 1175 nm) were calcined at 11 temperatures in the following manner: each sample was divided in 11 parts of 100 mg of sample that were heated at 70 °C for 3 h, then the temperature was increased (1 °C/min) up to the desired point and maintained for 3 h, finally it was decreased down to room temperature (10 °C/min). The refractive index of each sample was carefully measured with the Index Matching⁸ (IM) method that consists of measuring the forward scattering intensity for 589 nm wavelength radiation when it hits a dispersion of silica (0.5 vol %) in glycerin and doubly distilled water (DDW). Varying the concentration of glycerin in DDW (by adding DDW) produces a controlled change in the dielectric constant of the solvent. The matching of the (known) refractive index of solvent⁹ and that of the silica spheres takes place when light transmission has a maximum as in Figure 1. To keep the volume concentration constant, the added DDW also contained 0.5 vol % of silica to prevent decreasing intensity by dilution.

Since the behavior is the same for every sample, regardless of sphere diameter, we take the average refractive index for each calcination temperature from all samples as shown in Figure 2 along with its standard deviation. As explained before, several samples of different diameters were used, the smaller of which were synthesized by the classical SFB method. Those with diameters greater than 600 nm (800, 870, and 1175 nm) were grown by means of a modified¹⁰ SFB method in which an overgrowth process on smaller spheres was performed.¹¹ The results of IM characterization did not show any important dependence on synthesis methods and data variations seem to be related to small deviations in sample production.

To characterize water content infrared (IR) reflectance spectra were performed focusing our attention on two principal features: absorption at 3750 cm⁻¹ corresponding to isolated silanol groups¹² and that of water under 3720 cm⁻¹. This was performed with the IFS 66/S Bruker Fourier Transform IR spectrometer and 20 mg of dried sample.

The temperature range was divided into three regions to facilitate discussion of the results.

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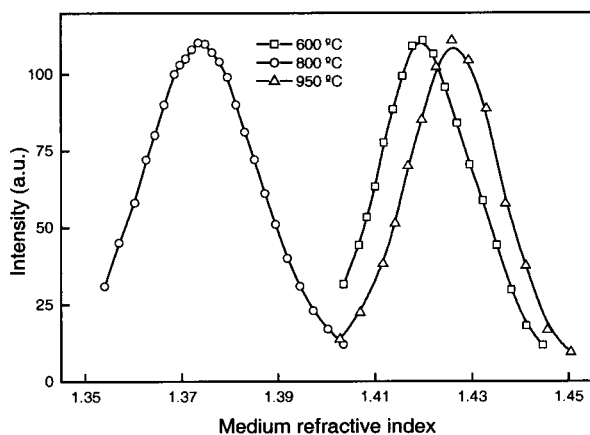


Figure 1. Forward scattering intensity of 589 nm radiation through a dispersion of 870 nm of diameter silica spheres as a function of medium refractive index. When the medium refractive index matches that of the spheres, a maximum of intensity is achieved. Continuous lines are just eye-guides.

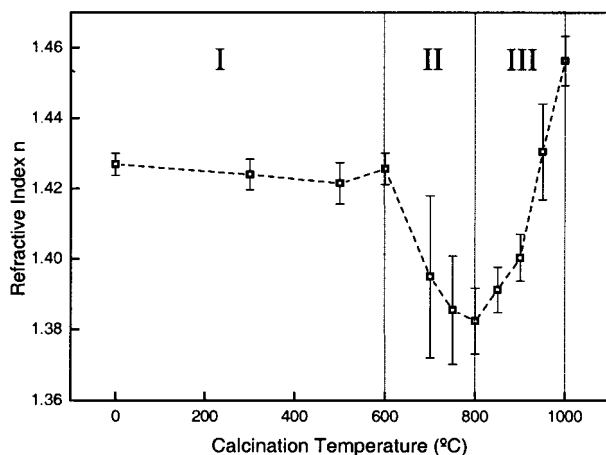


Figure 2. Average refractive index of Stöber SiO_2 samples as a function of calcination temperature. The error bars represent 1 SD with five determinations.

Region I (from room temperature to 600 °C). No significant variation of n demonstrates that no changes have occurred in the internal sphere structure. This inference is consistent with previous work¹³ where it was shown that most of the adsorbed molecules of water are removed under 200 °C. In accordance with IM measurements, the IR spectra in Figure 3 from silica powders show no remarkable variation.

Region II (from 600 to 800 °C). A substantial decrease in n was observed; in some samples the refractive index difference between 600 and 800 °C was as large as $\Delta n = 0.064$. IR spectra show that hydrogen-bonded silanol groups (Si-OH) and bonded water molecules begin to be removed and an absorption band due to stretching vibrations of isolated silanol groups appears at 3750 cm^{-1} . This band becomes clearer as calcination temperature increases. The elimination of internal water would lead to a diminution of the refractive index. However, the estimated amount of eliminated H_2O molecules based on previous thermal gravimetric weight studies^{13,14} cannot explain the observed decrease in refractive index. One possible explanation comes from the combination of water removal and nanopore formation. It has been suggested

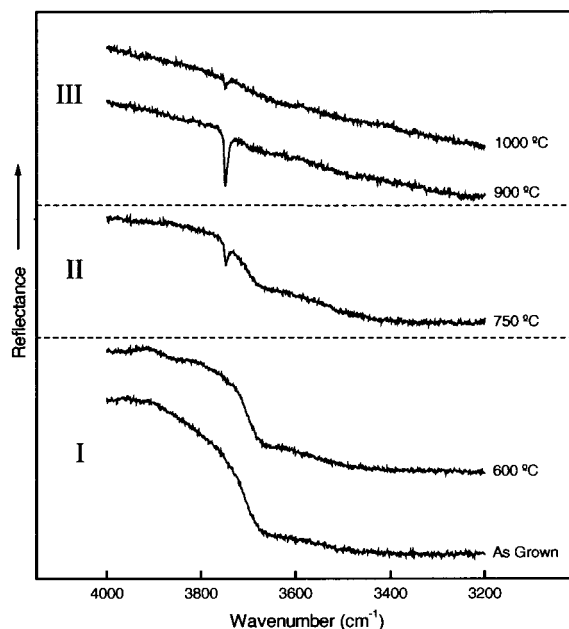


Figure 3. IR spectra from a calcined silica sample with a diameter of 575 nm. See absorption band at 3750 cm^{-1} from isolated silanol groups and the wide absorption band of water onset at 3700 cm^{-1} .

that dehydroxylation often involves nanopore formation;¹⁵ if air porosity is calculated assuming that measured refractive index is the average of air pores ($n = 1.00$) and bulk silica ($n = 1.46$) the resulting particle porosity is around 19% (or even higher for some samples). The specific surface for 870 nm perfect solid spheres is $3.4 \text{ m}^2/\text{g}$, very similar to the value of $11 \text{ m}^2/\text{g}$ obtained using nitrogen porosimetry in our studies of micro and mesopores for spheres of that diameter. This value was constant regardless of calcination temperature, and this small deviation of the experimental value from that of an ideal solid sphere is probably due to surface roughness rather than porosity. Macroporosity was checked as well with mercury porosimetry, but results were also very close to those from a solid sphere. This leads us to believe that surface porosity is very low and most of the pores are inside the sphere and are not accessible. To examine whether internal porosity was present, another experiment was performed; a sample which showed its minimum refractive index when calcined at 750 °C was soaked in DDW for different periods of time before its refractive index was measured. The results displayed in Figure 4 show that water soaks the spheres.

The following equation where the second term is a time dependent exponential decay fits the experimental data:

$$n(t) = n_f - (n_f - n_i)e^{-t/\tau} \quad (1)$$

Here n_f is the final refractive index, that is, the saturating value, n_i is the initial refractive index when no water has entered the sphere, t is the time in hours and τ is the lifetime of the process. The lifetime obtained is 210 h. Such a high value can be understood if we take into consideration that most of the pores are inside the sphere while its outermost volume remains almost poreless.¹⁶

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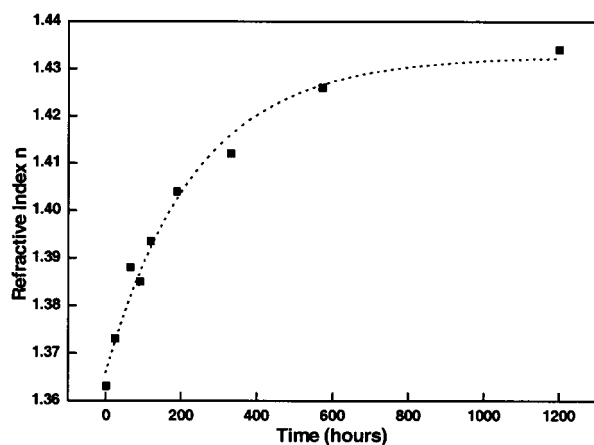


Figure 4. Refractive index variation of a 575 nm diameter sample as a function of time due to water uptake by the pores. Dotted line represents the fit of experimental data to an asymptotic growth.

Refractive indices obtained from this graph lead to porosity of 25%. The possibility of rehydration instead of water filling was discarded since the initial refractive index is recovered by heating the sample again just at 200 °C.

Region III (from 800 to 1000 °C). The refractive index rapidly increases reaching the bulk silica value in some cases. IR spectra indicate that water molecules have been almost completely eliminated at 850 °C. It is also observed (Figure 3) that the absorption at 3750 cm^{-1} is maximum at 900 °C and then begins to diminish. The increase of refractive index due to the formation of crystalline phases was discarded as a possible reason since X-ray diffraction (XRD) experiments did not show their presence in SiO_2 powders calcined at temperatures as high as 1050 °C.^{13,14} It can be deduced then, that refractive index rise may be due to sphere size compaction caused by internal chemical changes and volume reduction. To demonstrate that size reduction actually happens, we performed scanning electron microscopy image analysis of samples prior and after being calcined at two different temperatures: 750 and 950 °C. The analysis was done identifying the very same spheres before and after calcination to avoid errors due to spheres diameter dispersion. Results revealed that diameter reduction was hardly observable at 750 °C but very clear (about 13%) when calcined at 950 °C.

In a previously published experiment,¹⁷ transmission measurements at normal incidence with respect to the growth direction were studied for opals calcined at different temperatures (Figure 5). Bragg's law predicts a diffraction peak at the wavelength $\lambda_c = 2d(\epsilon_{\text{av}})^{1/2}$, where ϵ_{av} is the average dielectric constant of the structure and d is the distance between the crystalline planes responsible for that reflection; as opal growth is produced in the (111) direction, this distance is $(2/3)^{1/2} \cdot \phi$, where ϕ is the sphere diameter. The results obtained for temperatures above 600 °C can now be revisited in light of the new refractive index data. At 600 °C a drastic change in the diffraction peak position is observed; this effect was not satisfactorily

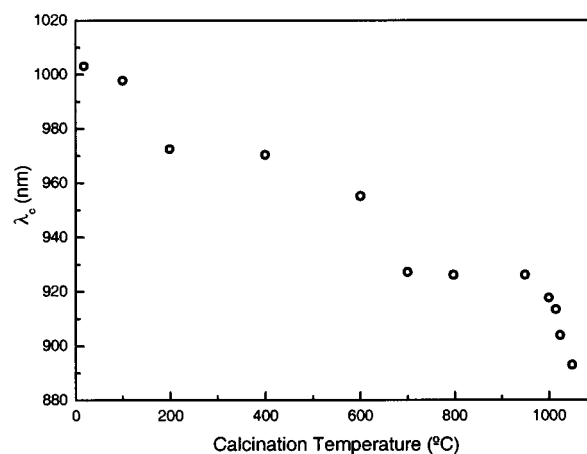


Figure 5. (111) Bragg reflection maximum wavelength, λ_c , plotted against the calcination temperature of an opal made of silica spheres of diameter 415 nm. Taken from reference (12).

explained at first but can be now described in terms of the refractive index variations shown in Figure 2. Because an increase in refractive index was clearly observed, the stable λ_c values from 750 to 950 appear to contradict our refractive index results. However, the results can be explained if the diameter reduction is taken into account because the effects of sphere shrinkage. This equilibrium is broken at 950 °C when the opal is sintered producing a lattice parameter decrease with a corresponding diminution of λ_c .

The results obtained are useful not just to explain Bragg peaks but also to give crucial information about opals processing. For instance, it can be deduced that a good temperature for silica sintering is 950 °C, although refractive index is not very stable around this temperature. Here the filling fraction of the structure corresponds to that of a fcc structure and the interpenetration of spheres is enough to harden the sample without deforming it. Another interesting consideration is that sintered silica will not suffer any additional modification when reheated under 800 °C. This is very important when filled opals are optically characterized since variations are definitively attributed to the infiltrated material.

In summary, the refractive index behavior of different diameter silica spheres with calcination temperature from room temperature to 1000 °C has been characterized. A strong dependence was observed between 600 and 1000 °C that can be assigned to pore formation and water removal. Although nitrogen and mercury porosimetry have not shown the presence of pores, their existence has been demonstrated by filling the silica spheres with DDW and by checking their compaction when calcined above 750 °C.

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