THE BELL SYSTEM TECHNICAL JOURNAL
Vol. 59, No. 8, October 1980
Printed in U.S.A.

B.S.T.J. BRIEF

Reduction of the 1.38-μm Water Peak in Optical Fibers by Deuterium-Hydrogen Exchange

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(Manuscript received September 3, 1980)

I. INTRODUCTION

Absorption due to the 1.38-μm overtone of the OH^- vibration in silica has long been an obstacle to low-loss propagation in optical fibers at wavelengths near the dispersion minimum. The corresponding absorption spectrum of OD^- in silica, however, has a window in this region. A deuterated fiber with OD^- content comparable to that of OH^- in present-day hydrogenated fibers would have a window between 1.0 and 1.65 μm with essentially no added loss due to water.

It is well known that, under certain conditions relatively simple to attain, the hydrogen-deuterium exchange

$$2\,OH^- + D_2\uparrow \leftrightarrow 2\,OD^- + H_2\uparrow$$

takes place in silica as an efficient process[1-5] and that the necessary exchange activation energy may be obtained by heating[1-4] or by irradiation.[5]

We have demonstrated, experimentally, that this exchange can be effected in silica fibers by the simple process of heating the fibers in D_2 at atmospheric pressure and elevated temperatures and, as examples, that the high loss peak at 1.38 μm can be reduced by a factor $\gtrsim$200 in a 100-ppm OH^- silica fiber and $\gtrsim$10 in a 2-ppm OH^- single-mode fiber. We discuss these experiments briefly and suggest ways in which the exchange might be applied more usefully to the fabrication of preforms from which fibers with extremely low losses in the 1.2- to 1.6-μm wavelength region might be made.

II. D ↔ H EXCHANGE IN WET SILICA AT ELEVATED TEMPERATURES

Under appropriate conditions, the OH^- present in ordinary silica can be converted to OD^- with the release of H_2 gas by placing the silica in a deuterium atmosphere at elevated temperatures.[1-4] As the D_2 gas diffuses through the sample, the exchange occurs quickly and efficiently, i.e., the total OD^- need not greatly exceed the original OH^- content, and the evolved hydrogen is eliminated as a gas. The physical and chemical properties of the resultant deuterated fiber should be indistinguishable from those of hydrogenated fibers, and thus the deuterated silica is as stable as the original hydrogenated silica. The reverse exchange process also occurs with approximately equal efficiency.

The rate of gas diffusion into the silica is determined by pressure and temperature; it is appreciable at <200°C and 1 atm, but becomes more rapid as either temperature or pressure increases. The actual $OH^- \leftrightarrow OD^-$ exchange, however, requires elevated temperatures (or irradiation). As an example, we have found experimentally that the exchange is completed in a 110-μm diameter fiber in less than 3 minutes at 1000°C and 1 atm.

III. OH^- AND OD^- SPECTRA

The various spectral absorption peaks due to ordinary water in silica have been ascribed to overtones and combination tones of the hydroxyl radical in the silica network.[6] The OH^- spectrum between 0.9 and 1.5 μm is indicated in Fig. 1, along with the measured relative intensities. The 1.38-μm line is the first overtone of the fundamental OH^- vibration ν_3^1 in SiO_2 at 2.75 μm; the line at 0.95 μm is the second overtone, $3\nu_3^1$; and the line at 1.24 μm is a combination tone, $2\nu_3^1 + \nu_1$, where ν_1 is a vibration frequency of SiO_4. Substitution of D for H in OH^- shifts the wavelength of a particular spectral line to longer wavelengths by approximately the ratio (mass D/mass H)$^{1/2}$. As a consequence, the spectrum of OD^- in silica will appear as shown in the lower part of Fig. 1, where the 1.26-μm and 1.68-μm lines are our own observations, and the 2-μm wavelength is an estimation. Any higher overtones which shift into this spectral region as a result of the exchange will be too weak to observe (the strength of the third overtone is only 0.1 that of the second overtone). Thus, in the region between 1 μm and 1.65 μm, only the second overtone at 1.26 μm will appear with an amplitude as large as 1 dB/km/ppm OD^-, which is only 1/60 that of the 1.38-μm OH^- peak for the same water content.

IV. EXPERIMENTAL PROCEDURE

The deuteration experiments were performed on existing fibers. A fiber, stripped bare, was coiled into a 12-cm diameter dish (Pyrex or

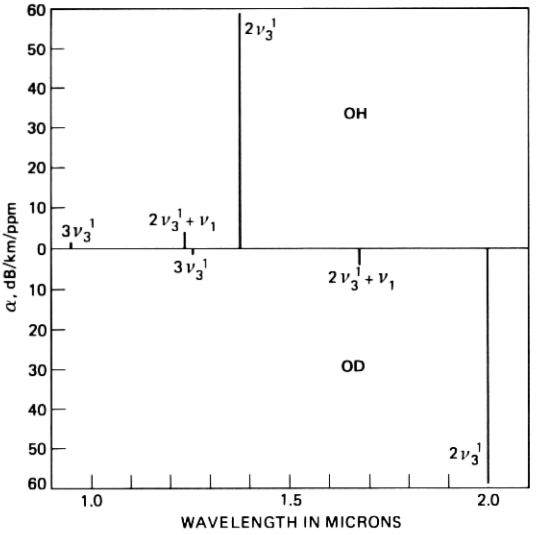

Fig. 1—Position of the significant overtone and combination-tone lines of OH^- and OD^- in silica.

fused quartz, depending on temperature) having a gas inlet tube and a vented cover. After insertion into the furnace, the vessel was flushed, first with dry N_2, then with D_2 (Matheson 99.5% D_2) for the desired time, and finally with N_2 as it was removed from the furnace. The fiber was embrittled by devitrification during this process, and thus became lossy, especially after treatment at the higher temperatures.

The transmission spectra were obtained by passing light from a tungsten-halogen lamp through a monochromator and then through the fiber. The detector was a cooled germanium photodiode. The log of the output was displayed, giving the relative absorption or attenuation coefficients directly. When the water-peak losses were very low, the spectrum was normalized against that of a very short (1-m) length of low-loss reference fiber with negligible water loss, so that the ratio of the two spectra on a log scale yielded the amplitude of the water peaks directly. Amplitudes $\gtrsim 0.1$ dB could be measured in this way. The excess loss due to devitrification, plus handling difficulties, limited the measurements to short lengths of fiber.

V. EXPERIMENTAL RESULTS

5.1 Solid fiber

Fiber of 110-μm diameter was freshly drawn from a silica rod with 100 ppm OH^-, as determined by measurement of the OH^- absorption in the fiber. It was soaked for ~3 min in D_2 at 1000°C and atmospheric

pressure. The normalized loss spectrum of a 3.6-m length of this fiber is shown in Fig. 2, along with the spectrum of the untreated fiber. The slope of the normalized curve indicated a very high scattering loss due to devitrification, but there remained only a suggestion of the OH^- peak at 1.38 μm, corresponding to attenuation $\lesssim 0.03$ dB/m. The untreated fiber had an attenuation of 5.3 dB/m, so that the reduction in loss from deuteration was by a factor $\gtrsim 180$. We believe this corresponds to essentially complete exchange, since the D_2 contained 1 part in 200 of H_2. The expected OD^- peak at 1.26 μm was too small to be seen in this short length.

5.2 TO-8 clad multimode fiber

Three-meter lengths of 110-μm o.d., GeO_2-doped silica-core fiber with TO-8 silica cladding were treated in various ways. The original OH^- content of the core produced a 13-dB/km attentuation peak at 1.38-μm wavelength.

(*i*) Separate samples were heated in air for 2 to 10 min at various temperatures up to 800°C. No measureable change occurred in the spectra.

(*ii*) Separate samples were heated in D_2 at 800°C for times ranging from 30 seconds to 64 minutes. The amplitudes of the 1.38-μm OH^- peak and those of the 1.26-μm OD^- peak are shown in Fig. 3. The OH^- peak initially increased to 7.3 dB/m (120 ppm OH^-) after 8 min and then decreased, and the OD^- peak increased to a saturation value of

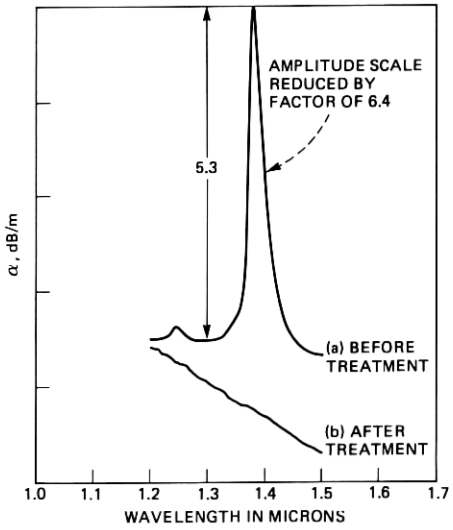

Fig. 2—Absorption spectra of a solid silica fiber, initially 100 ppm OH^-, (a) untreated, (b) after deuteration. The curves are displaced vertically.

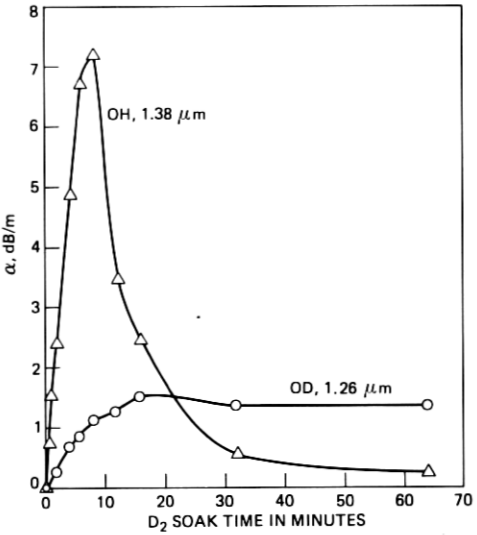

Fig. 3—Attenuation coefficient of the OH^- peak at 1.38 μm and the OD^- peak at 1.26 μm in a TO-8 clad multimode fiber, as a function of soak time in D_2 at 800°C.

1.7 dB/m (1700 ppm OD^-) after about 20 min. These results indicate that, as the D_2 gas diffused into the high-OH^- cladding, exchange occurred and H_2 diffused into the core forming additional OH^- and raising the absorption. At the same time D_2 was reaching the core, exchanging and creating an OD^- absorption at 1.26 μm, but this exchange effect was masked at 1.38 μm by the rapid infusion of H_2 (released from the cladding) which increased the OH^- level drastically. As the cladding exchange saturated, the exchange in the core became dominant, and the OH^- content decreased (and still was decreasing after 64 minutes). For this material, the number of OD^- sites exceeded the original number of OH^- sites.

(*iii*) A sample was heat-treated in D_2 at 200°C for 20 min. to absorb D_2, with no resultant change in the spectrum. It then was heated in air at 800°C for 20 sec. The OH^- peak at 1.38 μm increased to 65 dB/km (from 15 dB/km), and a 9-dB/km OD^- peak appeared at 1.26 μm. Further heating, up to 20 min, did not produce additional changes in the spectrum. These results, in combination with those described in item (*i*) above, confirm that diffusion can occur at low temperatures, but that exchange requires higher temperatures and that the diffusion and exchange processes can be controlled independently.

5.3 Single-mode fiber

This fiber, with an o.d. of 170 μm, was composed of a TO-8 silica outer cladding, a deposited borosilicate cladding (75 μm diam.), and a

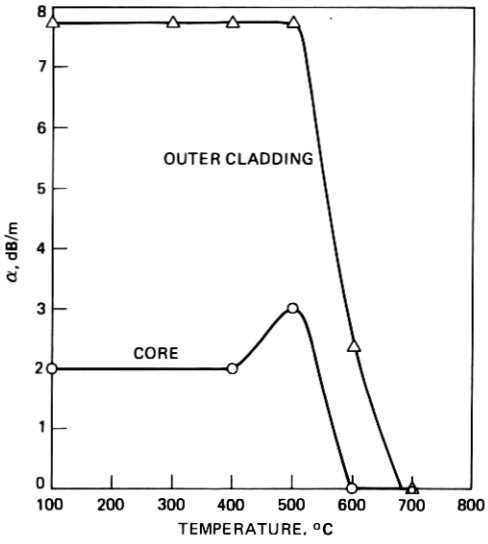

Fig. 4—Attenuation coefficients of the core and outer-cladding OH^- peaks in a single-mode fiber with a TO-8 outer cladding, a borosilicate-deposited cladding, and a pure silica core. The plot is against treatment temperature and the treatment time was 10 min.

pure silica core (<10 μm diam.). The initial OH^- loss at 1.38 μm was 8 dB/m for the outer cladding and 2 dB/m for the core. Short lengths (1 to 3 m) were heated in D_2 for 10 minutes at various temperatures. The results are plotted in Fig. 4. The OH^- peak in the outer cladding decreased above 400°C and was not measurable after the 700°C treatment. The core OH^- absorption remained unchanged to 400°C, increased slightly at 500°C (indicating a contribution from H_2 released by exchange in the outer cladding), then decreased to a value less than 0.2 dB/m at 600°C. The OD^- peak of both core and cladding was too small to measure. These results, taken with those of item (*ii*) above, suggest that the exact composition of the host glass affects the OH^- behavior.

VI. DISCUSSION AND CONCLUSION

The results of numerous experiments, summarized here only briefly, clearly indicate that fiber losses in the 1 – 1.65 μm region, due to OH^- in the silica network, can be reduced greatly or eliminated by isotopic exchange of OD^- for OH^-. The absorption spectrum then is that of OD^-, which has absorption bands in silica primarily at wavelengths outside the range of interest for present lightwave transmission. The only OD^- absorption in the band, at 1.26 μm, has an amplitude of

1 dB/km/ppm OD^-, only 1/60th that of the primary OH^- absorption in the band at 1.38 μm.

Deuteration of fiber preforms would appear to be simpler than deuteration of finished fibers. The simplest process probably would be deuteration of a porous, unconsolidated deposited preform such as that which exists at one stage of the OVD[7] and VAD[8] processes. It might most profitably be used in combination with a chemical drying process. In combination with the Cl_2 drying process,[9] for example, deuteration would reduce the OH^- content and a following chlorination would reduce both the residual OH^- and also the added OD^- absorptions. Use of deuteration would add only one short and inexpensive step to the manufacturing process, and the drying requirements would be much less stringent than those for OH^- alone.

Deuteration might be applied to the MCVD process[10] in several ways. For example, the inside of the present silica support tube (100 ppm OH^-) might be deuterated at high pressure and temperature before deposition of the core material. After finishing the preform in the usual way, exchange in *hydrogen* gas could create $OD^- \rightarrow OH^-$ exchange in the deuterated cladding, releasing D_2 to diffuse into the core and create the desired $OH^- \rightarrow OD^-$ exchange there. Deuterium might also be introduced into the gas flow during the layer-by-layer application and/or consolidation of the deposited cladding. Variations of the process could be used for both single-mode and multimode fibers.

Finally, we point out that, because this exchange process can eliminate detrimental effects due to the initial presence of OH^-, fiber fabrication techniques which have been considered unacceptable because they introduce additional water now might be reconsidered.

VIII. ACKNOWLEDGMENT

We are indebted to D. L. Bisbee for drawing the solid-silica fibers especially for these experiments.

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