# Analysis of frequency-doubling processes in optical fibers using Raman spectroscopy

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We have experimentally found a correlation between the nonlinear characteristics of frequency-doubling optical fibers and a specific modification of their Raman spectra. We propose a tentative interpretation of the physical origin of these phenomena, based on the assumption of the existence of small Si–O rings inside the fiber material. These structures would explain the nonzero value of the second-order nonlinear susceptibility.

For several years, visible-light generation phenomena have been observed in IR-pumped monomode fibers. Most of the experimental results show that third-harmonic generation (THG) processes can often occur when high-power pulses from a 1064-nm Nd:YAG laser are coupled into monomode silica-based optical fibers.[1,2] Moreover, recent experimental observations have suggested that, in the same experimental conditions, frequency-doubling processes could appear as well.[3–6] As second-order nonlinear effects are theoretically forbidden in isotropic media, structural anomalies of the vitreous state are expected to be the basis of such behavior. In order to analyze more thoroughly the development of such phenomena, spectroscopic studies of IR-pumped fibers exhibiting second-harmonic generation (SHG) processes have been undertaken.

In this Letter we report the first attempt to our knowledge at correlating these nonlinear properties (SHG–THG) and discuss some specific features of the spontaneous Raman spectra of two silica-based monomode fibers.

Both THG and SHG processes and stimulated Raman scattering take place simultaneously in several birefringent monomode fibers pumped by a mode-locked and $Q$-switched Nd:YAG laser operating at 1064 nm. A detailed description of the experimental setup can be found in Ref. 2. Figure 1 shows typical results obtained using a 50-m-long sample of a fiber (fiber 1) with a $GeO_2$-doped silica core, having an average radius of 2.3 $\mu$m and 0.6% relative index difference, and a silica cladding. The maximum peak power launched into fiber 1 is about 3 kW.

The upper part (longer wavelengths) of the spectrum of Fig. 1 corresponds to multiple-Stokes-order stimulated Brillouin scattering[7] and extends up to 1700 nm. The lower spectrum includes both THG and three-wave sum-frequency processes[2] (350–550 nm) and three main peaks, A (532 nm), B (590 nm), and C (622 nm), emerging from a complex set of sharp lines extending up to 700 nm. Lines A, B, and C can clearly be assigned to the result of frequency doubling of the pump line (1064 nm), the second-Stokes-order line (1180 nm), and the third-Stokes-order line (1245 nm), respectively. Unlike in the THG spectrum, the relative intensity of lines A–C has been observed to increase with the pumping time until some kind of saturation is reached, as was pointed out in Ref. 5. Moreover, while the THG radiation can be seen in the far-field pattern as a blue ring, the light from lines A–C propagates in the fundamental $LP_{01}$ mode of the fiber. The maximum conversion efficiency has been estimated to be 0.5% (line A).

As the development of the SHG process implies the

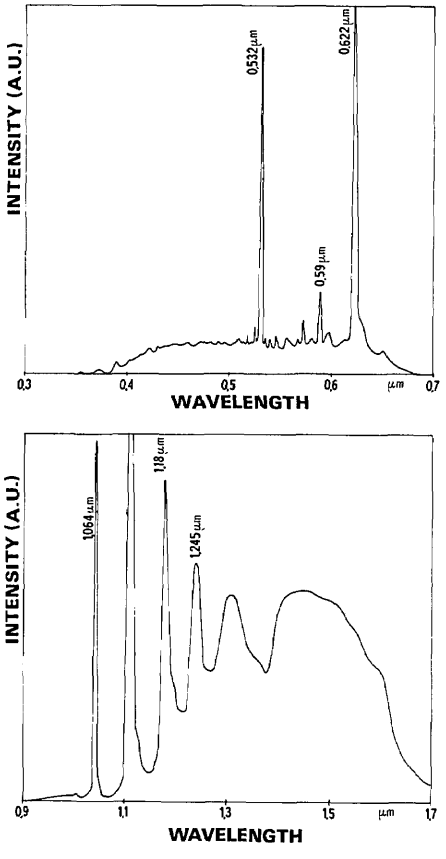


Fig. 1. Visible and infrared light spectra emerging from a 50-m-long sample of fiber 1.

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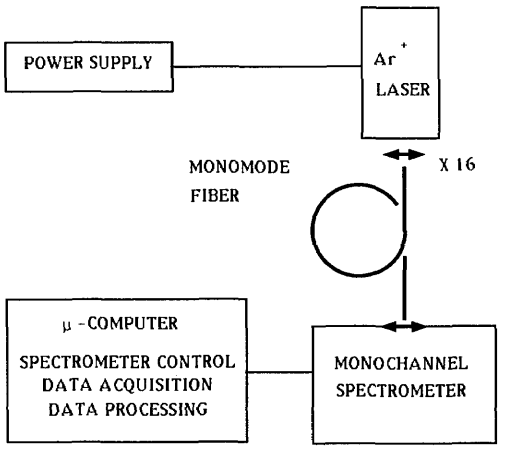


Fig. 2. Experimental setup used to record the Raman spectra of the fiber samples.

existence of a nonzero average second-order susceptibility, we have used Raman spectroscopy as a tool to prove the existence of microscopic structures, with long-range order, inside the core of the fiber.

Figure 2 shows the experimental setup used to record the spontaneous Raman spectrum of the fiber samples before exposing them to high-power radiation of the Nd:YAG laser. The 514.5-nm line of an argon-ion laser acts as pump radiation for the forward-scattering configuration, and the output light of the fiber is focused onto the entrance slit of a DILOR RTI30 triple monochromator. The laser power level was set in the range 30–300 mW; slit widths were 700 $\mu$m, resulting in a resolution of 6 $cm^{-1}$.

In Fig. 3 we compare the spectrum of fiber 1 with the spectrum of a fiber designed for submarine links ($GeO_2$-doped silica core with an average radius of 3 $\mu$m and a 0.57% relative index difference; silica cladding), which we have chosen as our reference spectrum. After the Raman spectra of several identical fibers were recorded, this reference spectrum was found experimentally to be the most representative. Let us consider this spectrum first: the main peak, at about 450 $cm^{-1}$, is commonly attributed to a symmetric stretching motion of the bridging oxygen atoms.[8] The interpretation of the origin of the two peaks at 490 and 600 $cm^{-1}$ is still a matter of controversy.[9,10] However, they are commonly called $D_1$ and $D_2$ defect lines and are related to structural defects in the vitreous state. A qualitative comparison between the reference and fiber 1 spectra clearly shows some major modifications of the defect lines:

- The relative intensities of the 450 $cm^{-1}$ peak and the $D_1$ defect line of fiber 1 are significantly modified.
- The shape of the $D_2$ defect line of fiber 1 is perturbed, extending down to 550 $cm^{-1}$.

Then another fiber (fiber 2) was selected by using the characteristic shape of the $D_1$ and $D_2$ lines of fiber 1 as a spectroscopic criterion. Although the refractive-index profile and the doping level of fiber 2 were different, fiber 2 exhibited a nonlinear behavior similar to that of fiber 1, as is shown in Fig. 4. Here, the A line at 532 nm appears to be the most intense.

As we pointed out above, the development of the SHG process implies the existence of a nonzero second-order susceptibility, at least locally. On the other hand, such an efficiently phase-matched interaction cannot be achieved normally with both the fundamental and harmonic beams overlapping perfectly and propagating in the same guided mode of the fiber. Moreover, if we suppose that the origin of such a phenomenon results from local microscopic structures, such a high conversion rate would imply a long-distance order of these structures. Finally, the time-dependent conversion efficiency clearly indicates an

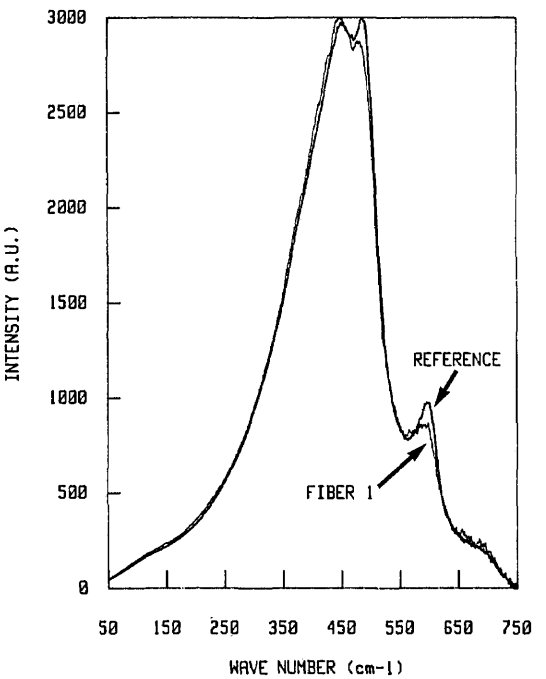


Fig. 3. Comparison between the Raman spectrum of fiber 1 and a reference Raman spectrum.

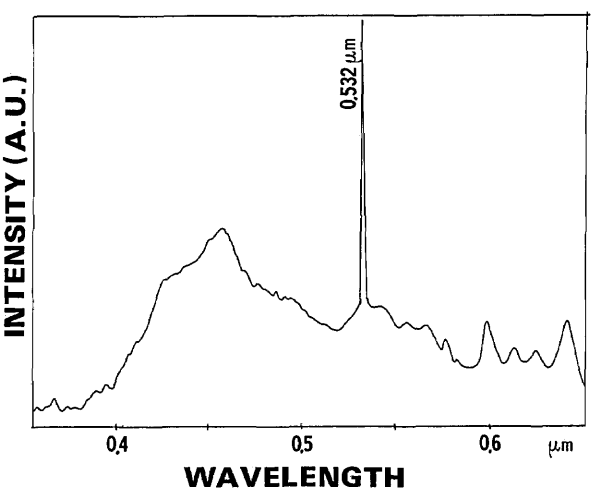


Fig. 4. Visible-light spectrum emerging from a 50-m-long sample of fiber 2.

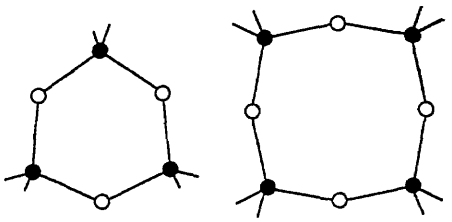

Fig. 5. Schematic representation of planar conformations of threefold and fourfold Si–O rings: filled circles, Si; open circles, O.

irreversible structural modification under the influence of the pumping radiation.

The $D_1$ and $D_2$ defect lines have been attributed by several authors to fourfold and threefold rings,[11] involving the Si–O basic unit (Fig. 5). Although Galeener favors a planar conformation of these rings,[11] it must be noticed that these structures are quite similar to those of cycloalkanes with a large number of possible conformations. In addition, it is well known that these defect lines are valuable probes of the thermal and mechanical history of the glass. In our opinion, the fiber-drawing parameters (tensile stress, furnace temperature, . . .) may greatly influence the number, the relative orientations, and the shapes of such structures. In Ref. 12, Donnadieu has shown that the thermal and mechanical parameters of the vitrification process can modify the ring statistics.

From these observations, we can now develop three main hypotheses that would explain the basic features of the nonlinear properties of frequency-doubling optical fibers.

First, we think that a large number of specific defects with specific orientations are created inside the fiber glass during the drawing process. As any possible conformation of threefold rings does not exhibit an inversion center, these specific structures are thought to be responsible for the nonzero average value of the second-order nonlinear susceptibility.

Next, we attribute the time dependence of the nonlinear coefficients to a structural transformation under the influence of the irradiation with a strong beam, which would induce an increase of the local density of ring defects. The threshold value of the pump peak power, reported in Ref. 6, remains unexplained.

Finally, the development of such structures implies the existence of microscopic stresses between them. We have experimentally observed that the mechanical strength of the fiber is dramatically lowered by a long irradiation (the mean tensile rupture strength value dropped from 2 daN to 0.5 daN). Furthermore, the fiber often breaks out during the pumping stage.

Up to this point, this set of hypotheses has been suggested by tentative conclusions drawn from our experimental observations and has to be confirmed by further experimentations. We also observed the SHG process in one phosphorous-doped fiber without any noticeably different behavior.

We have reported the first attempt to our knowledge to correlate the specific nonlinear characteristics of frequency-doubling fibers and have discussed some specific features of their Raman spectra. In order to determine the physical origin of these phenomena, we have proposed a set of hypotheses based on the existence and the development of specific defects inside the bulk of the fiber. We have noticed that threefold Si–O rings, with long-range order, would explain the nonzero value of the second-order nonlinear susceptibility. Further studies are needed, however, to explain the dynamics of the microscopic process.

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