

UV luminescence in Gd-doped silica and phosphosilicate optical fibers

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Abstract—Gd-doped silica and phosphosilicate fibers were pulled from preforms fabricated using the rod-in-tube technique and the solution doping technique, respectively. Ultraviolet (UV)-B luminescence from trivalent Gd at around 312 nm given by transition from first excited state to ground state were observed under deep UV excitations.

Keywords—gadolinium; photoluminescence; ultraviolet; fiber

I. INTRODUCTION

Optical fiber laser sources exhibit unsurpassed beam quality and power handling capabilities. Silica fibers are the favorite hosts for lasing ions as they tend to have high temporal stability and mechanical strength as well as strong chemical and radiation resistance. They are compatible with existing silica-based optical fiber components and can be transparent in the ultraviolet (UV) [1]. Up to date numerous fiber lasers operating in the near infrared and visible have been demonstrated, based on rare earths such as Yb³⁺, Er³⁺, Ce³⁺ and Tm³⁺. Short wavelengths have been generated through up-conversion process, such as LiYF₄:Er operating at 551 nm [2], Ho³⁺ fluorozirconate fiber laser emitting between 540 and 553 nm [3], Pr³⁺/Yb³⁺ codoped ZBLAN fiber lasers tunable in the red, orange, green, and blue wavelength range [4], and LiYF₄:Tm fluorescing near 350 nm and 450 nm and weaker features at wavelengths down to 288 nm under avalanche pumping [5]. Extension to the UV would benefit medical and industrial applications, where, at present, gas lasers, lamps, diodes or sources based on nonlinear harmonic generations are mostly used [6]-[9]. Here, we investigated the UV-B luminescence emissions from silica fibers single doped with trivalent gadolinium ions, Gd³⁺, with an energy gap of ~32000 cm⁻¹ between the ground state (⁸S_{7/2}) and the first excited level (⁶P_{7/2}) (Fig.1).

II. SAMPLE PREPARATION

Two types of fiber core host materials, i.e., phosphosilicate and pure silica, were investigated. The phosphosilicate sample had a pure silica cladding and a Gd doped phosphosilicate core fabricated using the modified chemical vapor technique (MCVD), with vapor-phase SiCl₄ and POCl₃ precursors, and the solution doping technique [12], with GdCl₃·6H₂O in a methanol solution. The dip at the center of fiber index profile (Fig.2, black) has been attributed to the evaporation of P₂O₅

during soot consolidation and tube collapse. The average Gd³⁺ concentration in the core, measured using energy-dispersive X-ray spectroscopy (EDX), was ~1170 ppm. The preform was pulled into a fiber at temperature above 2000 °C. The fiber cladding and core diameters were 5.8 μm and 125 μm, respectively.

The Gd³⁺ doped silica sample had a silica core fabricated by sol-gel [13] and a fluorosilicate cladding added via rod-in-tube technique. The fiber sample has a top-hat index profile (Fig.2 blue). Characterization of the sol-gel rod had been previously presented elsewhere [14]. The rod without the cladding was pulled into fiber canes for the PL measurements.

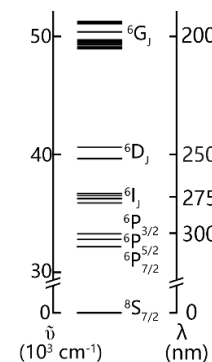


Fig. 1. Schematic of the Gd³⁺ energy levels (adapted from reference [10] and [11]). $\tilde{\nu}$ and λ are the wavenumbers and wavelengths of the photons emitted in the transitions to the ground level.

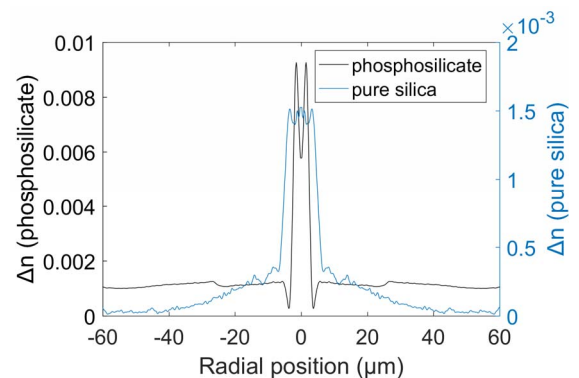


Fig. 2. Refractive index profiles of the Gd-doped optical fibers with phosphosilicate and pure silica cores.

III. UV ABSORPTION SPECTRA

Absorption associated to Gd^{3+} doping in the phosphosilicate fiber (Fig. 3) was investigated by pumping it with a broadband deuterium lamp source (BDS130, BWTEK). The propagation loss measured via the cutback method shows relatively narrow peaks at the wavelengths $\lambda=301.4$ nm, 306.3 nm and 311.9 nm, attributed to the Gd^{3+} transitions from the fundamental ($^8S_{7/2}$) to the 6P_J multiplet levels. High losses at short wavelengths are mostly related to defects [15] and to the small phosphosilicate electronic bandgap [16]. Since luminescence from oxygen-deficient centers (ODCs) was observed in a previous work [17], an attempt to reduce loss by reducing the concentration of ODCs was carried out by placing phosphosilicate optical fiber samples in an oxygen loading cell at 200 bar and 60°C for one month. To avoid overlaps with the Gd absorptions associated to the $^8S_{7/2} \rightarrow ^6D_J$ transition, changes in the absorption related to oxygen loading were monitored by measuring the propagation loss at $\lambda=260$ nm. The cut-back measurements are presented in Fig. 4 and show a 50% reduction from 0.5 dB/cm to 0.23 dB/cm. Additionally, non-bridging oxygen hole center (NBOHC), another type of defect, with its absorption band centered at 258 nm [18], was investigated by detecting its red luminescence using a spectrofluorometer (Fluorolog-3, Horiba), and it turned out to be negligible in both Gd-doped phosphosilicate and pure silica fiber samples. Further investigation and minimization of loss at short wavelengths would be required for future work.

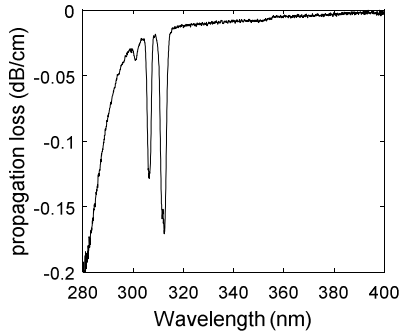


Fig. 3. Propagation loss of the phosphosilicate optical fiber.

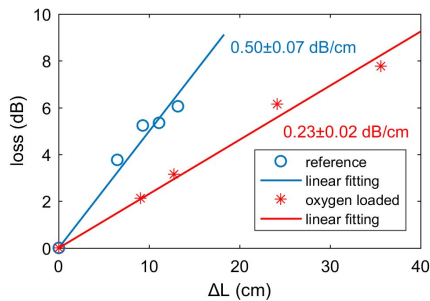


Fig. 4. Cut-back measurements used to determine the propagation loss at $\lambda=260$ nm before and after oxygen loading.

IV. PHOTOLUMINESCENCE

A Horiba Fluorolog-3 spectrofluorometer equipped with a Xenon excitation lamp were used to record the

photoluminescence (PL) and the photoluminescence excitation (PLE) spectra of a disk cut from the phosphosilicate preform, a bundle of phosphosilicate fibers and a stack of silica fiber canes. To improve the signal-to-noise ratio (S/N), light was incident on the sample sides, which have the highest core to cladding aspect ratio.

UV-B emission originating from the $Gd^{3+} \ ^6P_{7/2} \rightarrow ^8S_{7/2}$ transition was observed at $\lambda=311.7$ nm from the phosphosilicate preform disk. PLE peaks were recorded at $\lambda_{ex}=243.7$ nm, 245.7 nm and 251.9 nm, when pumping into the 6D_J levels; at $\lambda_{ex}=272.6$ nm, 275.2 nm and 278.3 nm, when pumping into the 6I_J levels; and at $\lambda_{ex}=304.0$ nm, when pumping into the $^6P_{5/2}$ levels, respectively (Fig. 5, red).

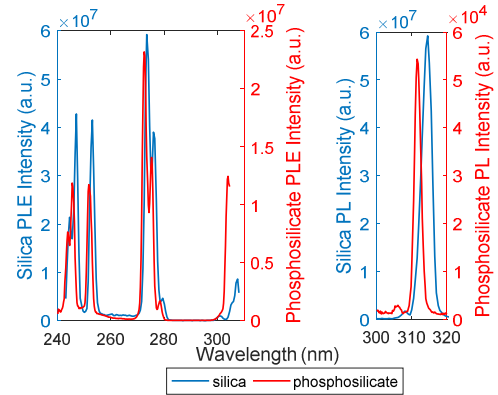


Fig. 5. PL and PLE spectra of Gd-doped samples with pure silica ($\lambda_{ex}\sim 274$ nm, $\lambda_{em}\sim 314$ nm) and phosphosilicate ($\lambda_{ex}\sim 272.5$ nm, $\lambda_{em}\sim 312$ nm) cores.

These transitions feature a spin change and show linewidths of the order of $\Delta\lambda\sim 2.5$ nm (FWHM) in the PL spectrum. Fig. 6 presents a comparison of the PL and PLE spectra recorded from the Gd^{3+} -doped phosphosilicate optical fiber and from the fiber preform used to fabricate it: a comparison suggests that the thermal treatment during the fiber pulling process did not affect the position of the PLE peak wavelengths.

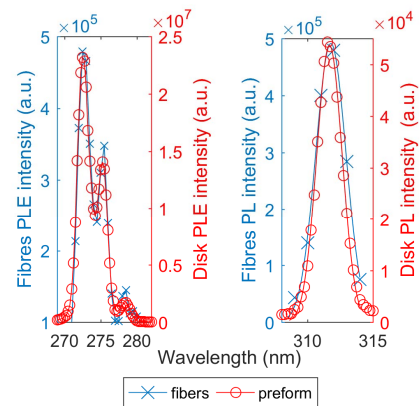


Fig. 6. PL ($\lambda_{em}\sim 272.5$ nm) and PLE ($\lambda_{em}\sim 312$ nm) spectra of phosphosilicate preform disk and fibers.

Similar results were recorded from the Gd^{3+} -doped silica fiber cane, with a wavelength shift of $\Delta\lambda\sim 1.5$ nm with respect

to the phosphosilicate samples (Fig. 5, blue): the peak emission wavelength (314 nm) was unchanged when the preform rod was pulled into an optical fiber [14].

V. CONCLUSION

UV-B PL emissions at $\lambda=311.7$ nm and 314 nm were recorded in Gd³⁺-doped phosphosilicate and silica fibers, respectively. The absorption and emission wavelengths were not affected by thermal treatments during fiber pulling at a high temperature. A spectral shift of $\Delta\lambda\sim 1.5$ nm caused by the difference in the host materials was recorded. Absorption at short wavelengths was reduced via oxygen loading process. To work towards laser operation, in addition to a high power pump source, future work will need 1) to perform a quantitative measurement of absorption cross-sections, 2) to manufacture the laser cavity possibly by writing mirrors directly into the active fiber core using femtosecond laser irradiation and 3) to further improve the material transparency in order to achieve a large gain at the Gd fluorescence wavelengths.

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