Optical Fiber Technology 30 (2016) 1–7

Contents lists available at ScienceDirect

Optical Fiber Technology

www.elsevier.com/locate/yofte

Regular Article

Observation of temperature dependence of the IR hydroxyl absorption bands in silica optical fiber

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ARTICLE INFO

Article history:
Received 4 May 2015

Keywords:
Fused silica
Glass
Fiber optics
Hydroxyl absorption band

ABSTRACT

This study reports on the temperature dependent behavior of silica based optical fibers upon exposure to high temperatures in hydrogen and ambient air. The hydroxyl absorption bands in the wavelength range of 1000–2500 nm of commercially available multimode fibers with pure silica and germanium doped cores were examined in the temperature range of 20–800 °C. Two hydroxyl-related infrared absorption bands were observed: ~2200 nm assigned to the combination of the vibration mode of Si-OH bending and the fundamental hydroxyl stretching mode, and ~1390 nm assigned to the first overtone of the hydroxyl stretching. The absorption in the 2200 nm band decreased in intensity, while the 1390 nm absorption band shifted to longer wavelengths with an increase in temperature. The observed phenomena were reversible with temperature and suspected to be due, in part, to the conversion of the OH spectral components into each other and structural relaxation.

1. Introduction

Fiber optic sensors have grown in popularity over the past decade as a viable sensing solution for a wide array of applications including pressure and temperature sensing, structural health monitoring, vibration sensing, and bio-sensing [1–5]. The benefits of fiber optic sensing include their inherent small size and footprint, immunity to electromagnetic radiation, and high sensitivity [6,7]. They have particular promise in harsh environments such as corrosive or combustible atmospheres that preclude the use of electronic sensors. Applications of commercially available fused silica based fiber optic sensors are usually limited to environments below 300 °C, but research continues to explore potential applications for these sensors at temperatures in excess of this limitation. One area of exploration is the use of silica glass for fiber optic sensing in environments up to 1000 °C as an alternative to the more expensive, more complex, and less robust sapphire sensing technologies available for high temperature applications [8]. However, thermal exposures can produce undesirable effects, such as coating degradation, increased attenuation, and devitrification [9–11].

The exposure of optical fibers to hydrogen at high temperatures (>300 °C) can dramatically increase the optical loss of transmission fibers and the measurement reliability of fiber optic sensors [9,12,13]. Generally, hydrogen induced attenuation arises from the absorption of light by molecular hydrogen and/or defect sites that have reacted with hydrogen to form absorbing species, such as hydroxyls (OH). Subsequently, the characteristic absorption of the vibrational and rotational modes of hydrogen-related species in silica glass has been well studied in an effort to account for the hydrogen induced losses in optical fibers [14–18]. Nonetheless, little attention has been paid to wavelength regimes much longer than the U (ultra-long wavelengths) band, spanning from 1625 nm to 1675 nm, and there is a lack of detailed information regarding the performance of optical fibers at high temperatures in excess of 300 °C [13,19]. To best assure sensor system reliability and stability, the high temperature performance of fused silica based optical fibers over a wider spectrum must be investigated and understood.

In this paper, we report the changes in the hydroxyl-related absorption bands in the 1000–2500 nm range with varying temperature. In a study to evaluate silica optical fiber performance in

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http://dx.doi.org/10.1016/j.yofte.2016.01.004
1068-5200/

Table 1
Commercial optical fibers tested.

Fiber ID	d_{core} (μm)	d_{clad} (μm)	NA	Relative [OH]
HOH50125	50	125	0.22	High
LOH50125	50	125	0.22	Low
GI50125	50	125	0.22	Low

a hydrogen environment at high temperatures, the attenuation of step index pure silica core and graded index germanium doped core multimode fibers was monitored in situ with temperature and hydrogen exposure. Temperature dependent behavior of the IR absorption bands of the hydroxyl groups around 2200 nm and 1390 nm was observed during the tests. The temperature dependent behavior of hydroxyl absorption around 1390 nm and 2200 nm in silica glass at high temperatures is consistent with other studies [20,21], but to the best of our knowledge, this is the first time that the change around 2200 nm has been reported in optical fiber.

2. Material and methods

The three fibers that were tested in this study are listed in Table 1. The HOH50125 and LOH50125 fibers, purchased from Thorlabs, are step index multimode optical fibers, with a pure silica core and fluorine doped silica cladding. The HOH50125 fiber is designed for UV-to-visible light transmission and contains a high concentration of hydroxyl species. GI50125 fiber, purchased from Berkshire Photonics, is a commercially available graded index telecommunications multimode fiber with a germanium doped core and pure silica cladding. Although a direct comparison of optical fibers with different refractive index profiles is not prudent, the observations of performance variations attributed to glass composition reported here are consistent with previous studies.

The optical fibers were heated to a maximum temperature of 800 °C and cooled to room temperature in a MTI GSL-1500X furnace for several cycles; acrylate fiber coating was burned off during the first cycle. The length of the heating region of the furnace is 15 cm. Optical spectra were collected in-situ throughout the entire temperature profile. The spectra wavelength ranged from 1000 nm to 2500 nm and data was recorded using a Thorlabs OSA203 – Fourier Transform Optical Spectrum Analyzer every 5 min with an Ocean Optics HL-2000 White Light Source. Hydrogen exposure was implemented by exposing fibers to a continuous 95% N_2/5% H_2 gas mixture throughout each thermal cycle at a flow rate of 50 sccm inside the furnace. The specialty gas mixture was purchased from AirGas. Schematic diagram of the system is shown in Fig. 1.

The optical spectrum of the "as received" LOH50125 fiber was selected as the baseline for all the analysis. As this spectrum best represents the intrinsic silica absorption, all test spectra were subtracted from the "as received" LOH50125 spectrum. Furthermore, the calculated loss (dB/cm) neglects any loss due to the low tem-

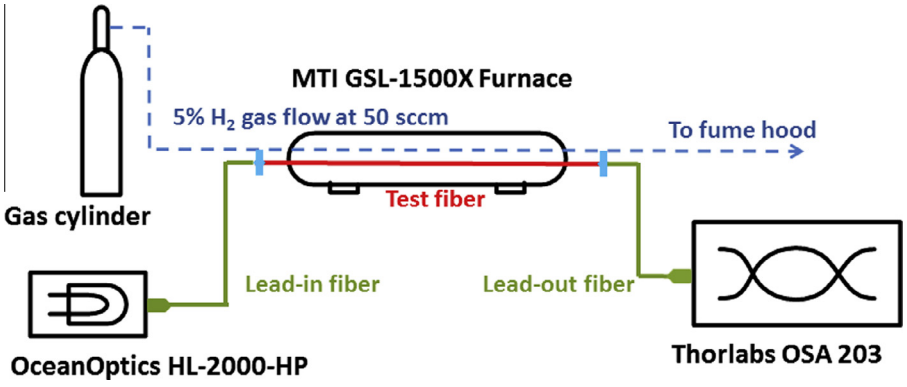

Fig. 1. Schematic diagram of the system where fibers were heated with hydrogen exposure.

Table 2
OH, H_2O and their combination vibrations in fused silica glass.

Assignment	Wave number (cm^{-1})	Wavelength (nm)	Description	Refs.
$\nu_1(OH) + \nu_4(SiO_4)$	4100	2439	Combination of fundamental OH stretching and fundamental SiO_4 vibrations	[23,24]
$\nu_1(OH) + \nu_1(SiO_4)$/ $\nu_{comb,2}(OH)$	4450	2247	Combination of fundamental OH stretching and fundamental SiO_4 vibrations/asymmetric distribution of silanol vibration due to hydrogen-bond	[23,24]
$\nu_4(OH) + \nu_3(SiO_4)$/ $\nu_S(SiOH) + \nu_B(SiOH)$	4520	2212	Combination of fundamental OH stretching and fundamental SiO_4 vibrations/combination fundamental OH stretching and SiOH bending	[23–26]
$\nu_B(H_2O)_I + \nu_{SS}(H_2O)_I$	5102	1960	Possibly, combination of bending and symmetric stretching band of Type I molecular water	[24]
$\nu_B(H_2O)_I + \nu_{AS}(H_2O)_I$	5249	1905	Combination of bending and stretching of molecular water, or more specifically, bending and asymmetric stretching of Type I molecular water	[24]
$\nu_S(GeOH)$	7042	1420	OH stretching vibration bonded to Ge site	[18]
$2\nu_3(OH)$	7100	1408	First overtone OH stretching	[23]
$2\nu_2(OH)$	7220	1385	First overtone OH stretching	[18, [23–25]
$2\nu_1(OH)$	7260	1377	First overtone of OH stretching	[23–25]
$2\nu_3(OH) + \nu_2(SiO_4)$	7380	1355	Combination first overtone OH stretching and fundamental SiO_4 vibration	[23]
$2\nu_3(OH) + \nu_1(SiO_4)$	7920	1263	Combination first overtone OH stretching and fundamental SiO_4 vibration	[23]
$2\nu_1(OH) + \nu_1(SiO_4)$	8065, 8130	1230, 1240	Combination first overtone OH stretching and fundamental SiO_4 vibration	[23,25]
$2\nu(OH) + 2\nu(SiO_4)$	8889	1125	Combination first overtone OH stretching and first overtone SiO_4 vibration	[25]

Bands at same the wavelength are listed in one row when they were interpreted differently in references.