Optical Fiber Technology 46 (2018) 141–146

Contents lists available at ScienceDirect

Optical Fiber Technology

journal homepage: www.elsevier.com/locate/yofte

Effects of thermal treatment on photoluminescence properties of bismuth/erbium co-doped optical fibers

Jianan Hao[a], Yushi Chu[a,b], Zhanyu Ma[a], Quan Chai[a], Jing Ren[a,*], Yanlei Liu[a], Yanhua Luo[b], Jun Yang[a], Zhihai Liu[a], Jianzhong Zhang[a,*], Libo Yuan[a], Gangding Peng[b]

[a] Key Lab of In-Fiber Integrated Optics, Ministry Education of China, Harbin Engineering University, Harbin 150001, China
[b] Photonics & Optical Communications, School of Electrical Engineering & Telecommunications, University of New South Wales, Sydney 2052, NSW, Australia

ABSTRACT

The effects of thermal annealing on the photoluminescence (PL) properties of bismuth/erbium co-doped multicomponent optical fiber (BEDFs) in a temperature range of from room temperature (RT) up to 1100 °C are clarified by PL, Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD) measurements. When pumped by an 830 nm laser diode, the fiber exhibits a broad near-infrared (NIR) emission band consisting of three distinctive peaks at the wavelengths of 1100, 1420 and 1530 nm, originating from different luminescence centers, viz., Al-related, Si-related bismuth active centers (BACs) and Er^{3+}, respectively. The relative emission intensities of the BACs and Er^{3+} vary in distinctively different manners with thermal treatment temperature are comprehensively studied. Three temperature regions, i.e., RT ~ 300 °C, 300–800 °C, and 800–1100 °C can be distinguished accordingly. The instability of the BACs, formation of non-luminous bismuth centers and crystallization of the fiber are proposed to account for the thermal effects on the PL behaviors of the different luminescent centers in the fiber. A first-ever piece of information is also given concerning the PL reversibility of the various luminescence centers in the BEDFs.

1. Introduction

since Fujimoto et al. first demonstrated the feasibility of bismuth (Bi) doped aluminosilicate glasses luminescing in the 1000–1600 nm near-infrared (NIR) wavelength region covering the whole low-loss window of silica fiber [1], a series of Bi doped glasses (BDGs) have been investigated owning to their unprecedented ultrabroadband photoluminescence (PL) properties and potential development of broadband fiber amplifiers and ultra-short pulsed fiber lasers [2–12]. The PL properties of BDGs are different from rare earth ions (REs) activated counterparts in that their spectroscopic features are closely associated with the chemical state and surrounding ligand field of Bi active centers (BACs), the amount of which can be altered by post thermal treatment and topological engineering of the glass structure for example. So far, some experiments have been made to study the thermal effect on the PL properties of BACs in BDGs. It has been demonstrated that the thermal quenching of the NIR PL was reversible when the thermal treatment temperature was not too high, however, the emission quenched gradually and vanished totally at higher temperatures (e.g., up to 750 °C). The cause has been suggested to be related to the conversion of BACs to non-luminous centers, of which the exact mechanism is not clarified yet [13,14]. Similar thermal quenching effects were also observed in bismuthate glasses, which was considered to be the main cause for the strong background losses and represents one of the most important energy dissipative sources [15,16].

The conventional fiber-drawing method inevitably subjects Bi doped glass fiber perform to an intense thermal heating process, which in turn may strongly influence the chemical state of Bi centers in as-prepared optical fibers. Several distinctive BACs have been identified in Bi-doped fibers (BDFs) such as Al-related (BAC-Al), P-related (BAC-P) and Si-related (BAC-Si) centers differing in the emission peak wavelengths at 1100, 1300 and 1420 nm, respectively [17]. It was found that the NIR PL of the BAC-Al increased when fibers were heated in a temperature range of 25–700 °C due to the increasing content of BACs formed [18,19], whereas the NIR emission of the BAC-Si was firstly enhanced with the heating temperature and then dropped sharply at higher annealing temperatures [20,21]. The previous studies are focused on the thermal quenching of a single type of BACs. However, since a multiple of BACs are likely to be formed in BDFs especially in multi-component fibers, a detailed investigation on the thermal effects on the PL properties of the various possible BACs in fibers is called upon for a better understanding and thus controllable synthesis of BDFs [9]. Moreover, because the emission efficiency of BACs generally falls sharply towards the long wavelength side (e.g., C and L bands), Er^{3+} has been applied as an useful codopant to enrich the emission intensity at the longer wavelengths and thus further broaden the amplification window of fiber amplifiers, for example, the authors of this article have previously demonstrated an ultrabroadband PL across O-, E-, S-, C-, and

* Corresponding authors.
E-mail addresses: ren.jing@hrbeu.edu.cn (J. Ren), zhangjianzhong@hrbeu.edu.cn (J. Zhang).

https://doi.org/10.1016/j.yofte.2018.10.010
Received 26 January 2018; Received in revised form 5 September 2018; Accepted 8 October 2018

L-bands from the bismuth and erbium codoped optical fibers (BEDFs) [9]. However, detailed comparison of thermal effects on the PL properties especially the PL reversibility of the different PL centers (e.g., BACs and Er^{3+}) in BEDFs is extremely rare in literature.

In this work, a comprehensive study is made of the influences of thermal treatment temperature (from RT to 1100 °C) and time (up to 120 min.) on the PL properties of BEDFs which possess three different PL centers, viz., BAC-Si, BAC-Al and Er^{3+}. Different mechanisms, the instability of BAC-Si, formation of non-luminous Bi centers and crystallization of fibers are put forward to account for the PL behaviors at different temperature ranges, viz., RT ~ 300 °C. 300–800 °C and 800–1100 °C, respectively. The results presented in this article are expected to provide some tests of thermal stability of the fibers essential to future practical lasing as well as sensing applications.

2. Experiment

The BEDFs were made by modified chemical vapor deposition (MCVD) and in situ doping method with composition of [SiO_2] ~ 85, [GeO_2] ~ 12.9, [P_2O_5] ~ 0.94, [Al_2O_3] ~ 0.15, [Er_2O_3] ~ 0.01 and [Bi_2O_3] ~ 0.16 in mol% [22]. The characteristics are as following: core diameter ~4.4 μm, core refractive index ~1.47, cladding diameter ~112 μm, cladding refractive index ~1.46, cut-off wavelength ~1.05 μm, back-ground loss ~1.71 dB/m at 1 μm, numerical aperture ~0.18, and mode field diameter ~6.98 μm at 1.55 μm. The EDFs and SMFs were commercially available from YOFC Company in China, the parameters are following: For EDFs: cladding diameter ~125 μm, cut-off wavelength ~1.3 μm, back-ground loss ~6 dB/m at 1.1–1.3 μm, numerical aperture ~0.23, and mode field diameter ~5.4 μm at 1.55 μm. For SMFs: cladding diameter ~125 μm, cut-off wavelength ~1.53 μm, back-ground loss ~0.19 dB/km at 1.55 μm, numerical aperture ~0.12, and mode field diameter ~9.3 μm at 1.55 μm.

The set-ups studying the influence of the thermal treatment on the PL properties of the BEDFs are shown in Fig. 1. An 830 nm LD was used as the pump source and PL spectra were recorded by an optical spectrum analyzer (OSA). The BEDFs with a length of 10 cm were used for the measurement. Both the influences of thermal treatment temperature and time on the emission spectra were examined, i.e., (a) The BEDFs were heated from RT to 1100 °C with a heating rate 10 °C/min, and the emission spectra were recorded for every 100 °C increment in temperature; (b) The BEDFs were kept at 100, 200, 300, …, 1000, 1100 °C, respectively, and the emission spectra were recorded for every 5 mins up to 120 mins. After the thermal treatment, the fibers were taken from the furnace, cooled down and the emission spectra were recorded again. For comparison, emission spectra of a commercially available erbium doped optical fiber (EDF) pumped by an 830 nm LD were measured. Besides, transmission spectra of a single mode optical fiber (SMF) using an amplified spontaneous emission (ASE) as the source were also measured to confirm the reliability of the designed experiment.

X-ray diffraction (XRD) patterns of the powdered fiber samples with the cladding removed were recorded under the same measurement conditions using an X-ray diffractometer (D/MAX 2550VB/PC, Rigaku Corporation, Japan) with Cu Kα as the incident radiation source. The microstructure of fiber samples was studied using transmission electron microscopy operating at an accelerating voltage of 200 kV (TEM, JEM-2100F) and equipped with an Energy Dispersive X-ray detector (EDX). TEM specimen was prepared by partially removing the cladding using a 40 vol% HF solution, and then finely grinding the residual fibers to powders, finally drying a drop of a dilute ethanol dispersion solution of fiber pieces on the surface of a carbon coated copper grid. It is noted that the fiber samples used for the XRD and TEM examinations had undergone exactly the same course of thermal treatment as for the PL measurement (regarding the temperature and time), thus the XRD and TEM results should reflect the real-time variations of the fibers as those during the PL measurements.

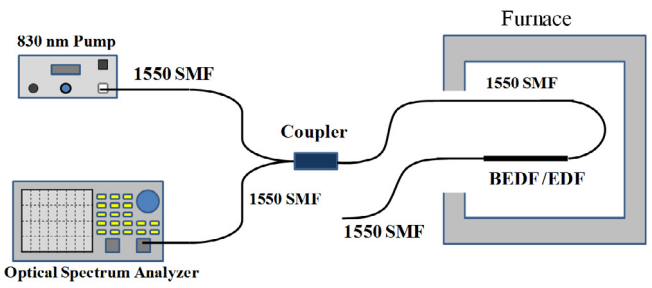

Fig. 1. Schematic of experimental set-ups for photoluminescence spectra measurement.

3. Results and discussion

Previously we have examined the different pumping schemes [9], and found that the PL spectra of the fibers differ drastically when pumped at different wavelengths. For example, the PL spectrum when pumped at 830 nm is much broader than at 808 nm, e.g., the 1100 nm PL peak corresponding to BAC-Al is much stronger in the case of the 830 nm pumping. Since the present study aims to explore the influence of thermal treatment on as many different BACs as possible, the 830 nm pumping is obvious a more rational option. On the other hand, for potential applications in fiber amplifiers, broader PL spectra are highly needed, and from this point of view, the 830 nm pumping is also a better choice [23].

Fig. 2(a) shows emission spectra of BEDFs and EDF (the inset) samples thermally treated at different temperatures upon the 830 nm excitation. The spectra of the BEDFs samples are composed of typical emission bands attributed to the BAC-Al (~1100 nm), BAC-Si (~1420 nm) and Er^{3+} (~1530 nm), respectively [24]. The valley at 1380 nm is due to the absorption of OH overtones. The spectra of the EDF samples only exhibit the typical Er^{3+} emission band at 1530 nm. The emissions from the BAC-Ge (~900 and 1600 nm) and BAC-P (~1300 nm) centers related to P_2O_5 and GeO_2, respectively, are difficult to be identified because their characteristic emission bands are severely overshadowed by those of the other BACs and especially the strong emission of Er^{3+}. It is nearly impossible to quantify the exact amount of the different BACs, because the nature of BACs is still unknown, given many hypotheses have been put forward, e.g., Bi-clusters, Bi^{+}, BiO, dimer ions Bi_2, Bi_2^{-} and Bi_2^{2-}, Bi^{0}, molecular orbital models or even point defects [25]. All of these centers are likely to present in the studied multicomponent fibers. The absorption spectra of the BEDFs have been published elsewhere [23]. Distinct absorption bands can be observed at 717, 812, 1050 and 1400 nm due to various BACs such as BAC-Al and BAC-Si etc. in the BEDFs.

The variations of the emission intensities of the various BACs and Er^{3+} in BEDFs (denoted by BEDF-Er) and EDF (denoted by EDF-Er) are plotted against thermal treatment temperature as shown in Fig. 2(b). The emission intensities are normalized with respect to the transmitted 1550 nm signal recorded from a SMF at RT. The signal transmitted from the SMF barely fluctuates during the course of thermal treatment, indicative of a negligible thermally induced optical loss of the standard silica fiber used and the reliability of our designed experiment. It is obvious that the variations of the emissions of the BACs and Er^{3+} follow quite different trends with thermal treatment temperature, and can be tentatively divided into three regions, viz, I, where EDF-Er, BEDF-Er and BAC-Al increase, while BAC-Si slightly decreases with temperature; II, 300 °C to 800 °C, where BEDF-Er, BAC-Al and BAC-Si sharply decrease, and III, 800 °C to 1100 °C, where the emissions of all the PL centers are strongly quenched. Hereafter, the variations of the emission intensities in there different temperature regions will be discussed separately.

I. In a temperature range of RT ~ 300 °C. The PL intensity of BAC-Si