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Spectral properties and lifetime of green emission in γ-ray irradiated bismuth-doped silica photonic crystal fibers

A. Alessi[a,*], D. Di Francesca[a], S. Girard[a], A. Morana[a], M. Bouazaoui[b], H. El Hamzaoui[b], G. Bouwmans[b], S. Agnello[c], M. Cannas[c], A. Boukenter[a], Y. Ouerdane[a]

[a] Univ Lyon, UJM-Saint-Etienne, CNRS, Institut d'Optique Graduate School, Laboratoire Hubert Curien UMR 5516, F-42023 Saint-Etienne, France
[b] Univ-Lille, CNRS, UMR 8523 – PhLAM - Physique des Lasers Atomes et Molécules, CERLA, F-59000, Lille, France
[c] Dipartimento di Fisica e Chimica, Università di Palermo, I-90123 Palermo, Italy

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ABSTRACT

We report an experimental investigation focused on the green emission detected in γ-ray irradiated Bismuth-doped photonic crystal fibers. Our photoluminescence spectra, recorded at room temperature, provide evidence for the presence of two emission bands both located at ~530 nm (2.34 eV). One emission is detected only in the Bi-doped core while the other, is detected in the cladding. These two emissions feature different excitation spectra and a fast and a slow decay lifetime. The origin of the fast emission decay, about ten nanoseconds, is tentatively attributed to a silica intrinsic defect, whereas the slow component, having lifetime of about 2 μs and featuring anti-stokes emission, is certainly caused by Bi related defects.

1. Introduction

The presence of near infrared (NIR) emission [1] in Bi-doped silica enhanced the interest on these materials for their use in the production of lasers or amplifiers in the spectral range of telecommunication [2]. In this context, various experimental and theoretical investigations [2–9] have been carried out to improve the understanding of the origin and the properties of different NIR and visible emissions observed in the Bi-doped silica, also because of their potential use in various other applications [10,11]. In particular, in the visible spectral range, a broad emission centered at ~600 nm was usually associated to the Bi^{2+} ion [2,4,10,12–14], anyway recently magnetic circular dichroism results obtained studying Bi-doped silica glass contradict such attribution [15].

This band has been observed in various types of silica materials: optical fibers with different composition, nanoporous thin films, mesoporous samples, nanoporous glass and bulk silica preforms [2,4,10,13,16]. The excitation spectrum of this red emission shows a band centered at ~480 nm [2]. Zhou et al. observed a 590 nm emission with a lifetime of 6.3 μs and showed that the excitation spectrum of this emission exhibits maxima at ~280, 350 and 480 nm [10,13]. Razdobreev et al. detected a broad emission centered at 603 nm, under excitation at 325 nm [16], and an excitation spectrum, having peaks at about 350 and 465 nm, was reported in [15]. In [16] the authors highlighted the presence of another emission around 675 nm under excitation at 532 nm. The time decay of this red emission was approximated by a double exponential fit with time constants of τ_1 ~1.8 μs and τ_2 ~3.8 μs. On the other hand, emission bands in the range 450–530 nm were attributed to Bi^{3+} [4,10,13,17–19]. In details, in nanoporous [13] and mesoporous [10] silica a broad emission band located at ~465 nm with the excitation maximum at ~280 nm was observed and assigned to the Bi^{3+} ions. In nanoporous silica [13] this emission has a lifetime of ~7 μs. Furthermore, in germanate glasses a broad emission band around 450 nm and an additional 530 nm emission band were also tentatively attributed to the Bi^{3+} [17]. In this case, at room temperature, the emission decay features a double exponential profile with a slower component having a time constant lower than 0.5 μs. The assignment of the 530 nm emission to Bi^{3+} has been also suggested in [4]. In this case the 530 nm band was observed without other emissions at shorter wavelengths, but the presence of Bi^{3+} was proposed on the base of XPS experiments. The presence of Bi^{3+}, using XPS data, and of an emission at 530 nm was reported also in crystalline samples [20]. All these results evidence the relevant effects of the surrounding environment on the optical properties of Bi species [20], which in some cases (Bi^{3+}) can be related to Laporte allowed transitions, having decay time in the range 10^{-6}–10^{-8} s [20].

As for the red-orange emission it should be noted that in many cases the attribution to the Bi^{3+} is proposed comparing the emission properties with those observed in other materials. As a consequence, these assignments need further validation. The detection of the Bi^{3+}, for example by XPS, does not strictly imply the relation with an emission,

* Corresponding author.
E-mail address: antonino.alessi@univ-st-etienne.fr (A. Alessi).

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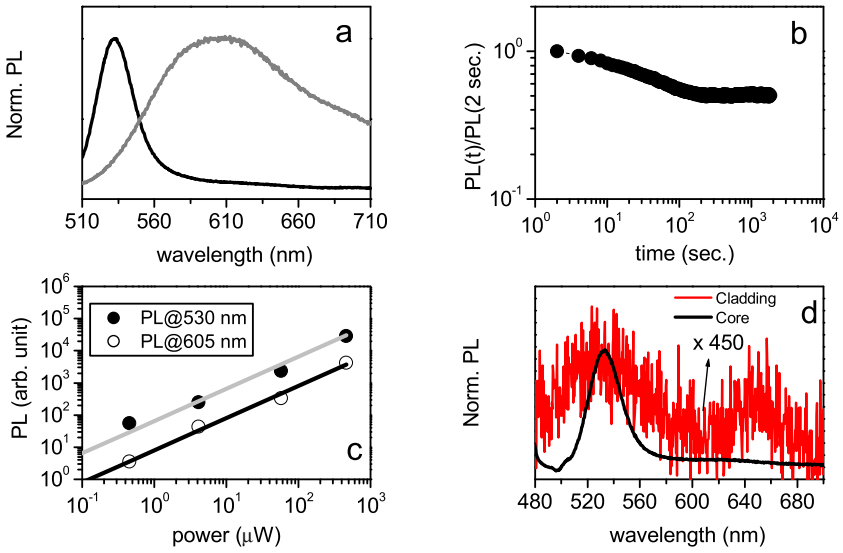

Fig. 1. a) Normalized (to the maximum) CML spectra recorded with a laser excitation (325 nm) power of 460 μW in the Bi-doped core of the pristine (—) and 1 MGy irradiated fiber with laser exposure of 2 s (▬); b) PL evolution at 533 nm as a function of the laser exposure time, c) PL amplitude recorded in cores of the irradiated (●) and pristine (○) fibers as a function of the laser power (laser exposure of 1 s), the (—) and (▬) lines indicate two linear dependences; d) CML spectra recorded in the Bi doped core (▬) and cladding (▬) of the 1 MGy irradiated fiber, the spectrum of the cladding was multiplied by the factor 450. The spectra were acquired with 1 s of laser exposure. The error on the amplitude of the CML spectra is of about ± 6%.

since this latter could be originated by a small amount of defects. A simple and well known example of this is constituted by germanate glasses where Ge atoms are substitutional to the Si but the emission bands are related to the Germanium Lone Pair Center (two fold-coordinated Ge atom) [21], which represents a small amount of the Ge.

It is worth to consider that the emission properties of the Bi-doped materials can be modified by applying thermal treatments or irradiation as showed for Bi-doped mesoporous silica under irradiation with a femtosecond laser [10], and for the Bi-doped α-BaB_2O crystal under γ-rays irradiation or thermal treatments [22]. These effects were explained by the change in the valence state of the Bi atoms as a consequence of the trapping of holes or electrons.

In the present investigation, we report evidence for the γ-rays induced modification of the emission properties of Bi-doped photonic crystal fibers and we study the properties of the Bi related green emission to better understand how the features of such emission are affected by the electron-phonon coupling due to the surrounding matrix.

In details, in the core of the pristine fiber we observe a red-orange emission, whereas in the core of the irradiated fibers we evidenced the presence of an emission centered at ~530 nm, at similar wavelengths a second emission is detected in the pure cladding part. These emissions feature different full width at half maximum (FWHM), lifetimes and excitation spectra. Based on our results, we propose the energy levels schemes of the defects which are the origin of these emission activities. Furthermore, we provide evidence for anti-stokes component to the Bi-related green emission.

2. Materials and methods

The Bismuth-doped silica optical fiber investigated in the present study is a photonic crystal fiber having a core diameter of ~6.4 μm [23]. The starting high-purity Bi-doped silica glass, used as core material, was produced by sol-gel technique [24] with a Bi content of ~300 ppm, evaluated by EPMA (electron probe micro-analysis). The microstructured fiber was fabricated by stack and draw process [25]. Further details regarding the different steps of the fiber production are available in [23,24].

We performed room temperature confocal microscopy luminescence (CML) measurements using a LabRamAramis (Jobin-Yvon) equipped with a He−Cd (325 nm) excitation laser, a CCD camera and micro-translation stages. The spectra were recorded employing a 40 × UV objective and a 150 grooves/mm grating in a back-reflected geometry. The measurements were performed with a spatial resolution of about 5 μm, allowing the separate investigation of the doped core and of the cladding. The error on the amplitude of the CML spectra has been estimated to be about ± 6% by the repeatability of the measurements.

We carried out room temperature time resolved luminescence (TRL) experiments in a 90° geometry. The third harmonic of a Nd:YAG laser was employed to pump an optical parametric oscillator, having a second harmonic generation nonlinear crystal, to generate the excitation laser pulse. The pulse width and the repetition rate were of 5 ns and 10 Hz, respectively. The light emitted by the sample was spectrally resolved by 300 grooves/mm grating. The spectral resolution was of ~5 nm. The spectra were acquired by a gated intensified CCD camera using different delay times (t_d) from the laser pulse and various acquisition time widths (t_w). Differing from CML data, in this case the recorded signals arrived from the core and the cladding, since both regions were illuminated by the laser. The error on the obtained results has been evaluated by using the measurements repeatability and applying the error propagation according with the performed analysis for the area estimation and the evaluation of excitation spectra and time decay kinetics. In the following, if not visible the error bar is smaller than or comparable with the sizes of the employed symbols.

The fiber samples were γ-rays irradiated up to the dose of 10 MGy (SiO_2) with 1.2 MeV photons at room temperature using the Brigitte facility at SCK-CEN (Belgium).

3. Results

In Fig. 1a, we report the CML spectra recorded under excitation at 325 nm in the core of the pristine and of the 1 MGy irradiated fiber. The two spectra exhibit very different features in the range 510–710 nm. In fact, the spectrum of the pristine fiber is dominated by a very broad band (FWHM of ~100 nm) located at ~605 nm (~2.05 eV), whereas the one of the irradiated fiber is dominated by a narrower green emission centered at ~530 nm (2.33 eV) having a FWHM of ~30 nm. It is worth to note that this green emission is observed also at higher γ-irradiation doses (up to 10 MGy(SiO_2)). Fig. 1b shows the dependence of the intensity of the green PL on the exposure time of the irradiated sample to the excitation laser. We observed that the amplitude decreases by a factor 2 after ~150 s and then it reaches a plateau. We also noticed a small shift of the peak position from 532 to 534 nm (not shown). By contrast, the amplitude and the lineshape of the 605 nm emission, detected in the pristine fiber, do not show any change by laser exposure. As reported in Fig. 1c the amplitude of the 530 nm emission (before long laser exposure) linearly increases with the laser power, without any lineshape modification. Similar results were observed for