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Structured blue emission in Bismuth doped fibers

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ABSTRACT

We report an experimental investigation of the photoluminescence (PL) activities detected in as-drawn and γ-ray irradiated samples of a microstructured optical fiber elaborated with a silica-based core doped with Bismuth ions. The presence of several visible emission bands is revealed and characterized under 325 nm laser excitation. In both samples, four narrow emission bands are studied and analyzed. They are similarly bleached by a long UV laser exposure times. In addition, time-resolved luminescence data show that all these bands possess a similar lifetime of ~4 μs Data analysis indicated that the energy levels scheme of the point defects responsible for these bands consists of: one above 5 eV, one at ~3.6 eV, and at least one in the range 2.6–2.8 eV and of the ground one. As a consequence, even if the exact structural model cannot yet be fully identified, we suggest that the bands originate from color centers related to the Bismuth ions.

1. Introduction

Visible and near infrared (NIR) light emitting materials cover a fundamental role in the modern and future technologies [1–6]. As demonstrated by previous studies, the emitting properties of silica-based glasses can be tailored by adding chemical specific elements to the glass matrix [7–11]. Two principal advantages of using silica are i) its abundance in nature and ii) the possibility to produce such materials through different consolidated manufacturing procedures. The final glasses can be functionalized as discrete or distributed sensors [12], light amplifiers [13,14], dosimeters [15], lasers [16], or can be exploited for photovoltaic applications [17]. Among the different studied glasses, the interest for Bismuth doped silica has increased in the recent years as this material has been proposed for the production of red phosphor [3], space-selective emitting materials [2], laser and amplifiers [7,16,18]. All of these investigated applications rely on the various emission activities occurring in the visible and in the NIR spectral ranges in Bi-doped silica.

In details, V. Firstov et al., using excitation wavelengths in the range 400–1600 nm, have observed, at room temperature (RT), emission bands peaking at ~590 nm (broad band), 830 nm and 1430 nm [7]. The red-orange (~600 nm) and the 830 nm emissions were also observed under excitation at 325 nm [19]. For the purpose of the present investigation we remind that if the Bi^{2+} ions have been associated with the broad 600 nm emission band [7], this attribution should be reconsidered taking into account the recent investigation published in Ref. [20], where magnetic circular dichroism experiments were reported. Basing on this data an effective spin zero has been proposed for the ground state (magnetic singlet).

Bi^{3+} ion is considered as responsible for an emission that can be centered, in different materials, within the blue to the yellow domain [2,21–26]. As example, in germanate glass emission bands at ~450 nm and ~510 nm have been attributed to the Bi^{3+} ions [25], in more details, this latter was tentatively attributed to the Jahn-Teller effect on the $^3P_1$.

In the energy level scheme of the Bi^{3+} the $^3P_1$ and $^3P_0$ levels have similar energies. In fact, at room temperature it is possible to detect the emission related to $^3P_1 \rightarrow {}^1S_0$ allowed transition [23,24] and not only the one due to $^3P_0 \rightarrow {}^1S_0$ forbidden transition [23,24]. According to previous studies, at RT, the lifetimes of the emission activities attributed to the Bi^{3+} ions can feature bi-exponential behavior and the obtained values typically from some hundreds of nanoseconds [27,28] to few microseconds (~3 μs [29]) or tens of microseconds [21] depending on their host matrix.

Regarding the Bi^{+} ion, previous investigation [30] provided evidence for the influence of the surrounding host matrix on its energy levels scheme. Indeed, excited states such as the $^3P_2$ and $^3P_1$ can be split by any axial deformation and successively the obtained states can be further separated by Jahn-Teller effect.

All these data demonstrate the variety of the emission activities

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detectable in Bi-doped silica in the visible spectral domain and highlight the difficulty to associate these bands with their corresponding color center structures. To this complexity, we can also add other more general factors. The first one is the possibility to change the emission spectra by using energetic irradiation that modifies the valence state of the Bi ions through the trapping or release of electrons [2,6,22]. The second one concerns the exact nature of defects responsible for the NIR emissions that is still debated. Finally, we also note that the impact of manufacturing techniques or post production treatments on the color center concentration, generation or bleaching kinetics are still poorly explored.

In the present investigation we studied a microstructured optical fiber having a Bi-doped pure-silica core diameter of ~6.4 μm. This fiber has been manufactured by the sol-gel method. Confocal microscopy and time resolved luminescence measurements, performed on as-drawn and γ-ray irradiated samples of this fiber, reveal the existence of four blue emission bands originating from the Bi-doped cores of both samples. The observed bands are bleached by the used probe UV laser (325 nm), they feature very similar characteristics for excitation energy above 2.8 eV and have similar lifetimes. Some hypotheses, on the energy level scheme of the defect type responsible for these emissions, are discussed on the basis of acquired results. More generally, the present investigation illustrates the possibility to tailor the emission spectrum of the Bi doped silica by applying ionizing radiation and/or laser exposures.

2. Materials and methods

The starting ~300 ppm Bi doped silica was obtained by the base-catalysis sol-gel technique [18] and drawn to a microstructured optical fiber by the stack and draw process [31]. The different thermal steps applied to obtain the investigated fiber sample have been previously reported in Ref. [32]. This kind of sample has been employed since the microstructuration allows the light guiding effect in the core without adding other co-dopant.

The investigated fiber has an external size diameter of 125 μm and an inner core diameter of 6.4 μm defined as the distance between two diametrically opposed holes. The pitch of the periodic cladding, Λ, and the diameter of the air holes, d, are 4.0 μm and 1.6 μm, respectively as illustrated in Fig. 1a.

The irradiations were performed at RT with γ-rays up to the dose of ~10 MGy(SiO_2) (which corresponds also to ~10 MGy(Si)) using the Brigitte facility at SCK-CEN (Belgium). The samples were irradiated at the same time and the different doses were obtained by changing the distance from the source, which implies different dose rates, for the 10 MGy the dose rate was of ~12 kGy/h and for 1 MGy of ~1.2 kGy/h.

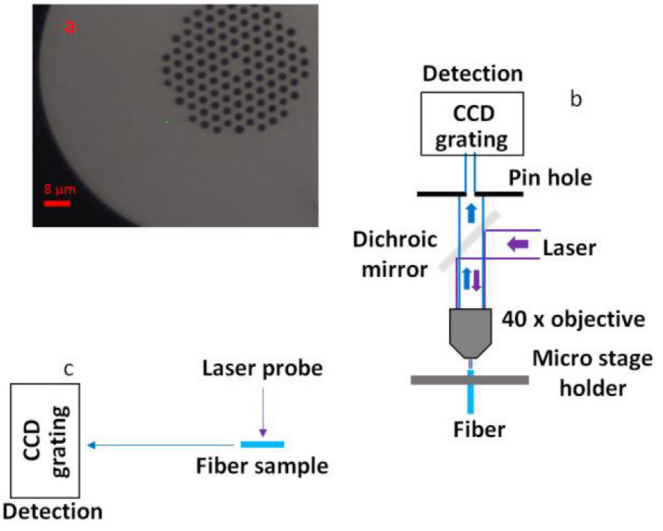

Fig. 1. a) image of the studied fiber recorded with a 50 × objective; b) simplified scheme of the CML set-up; c) simplified scheme of the TRL and PLE set-up.

Confocal microscopy luminescence (CML) measurements were acquired at RT in back-reflected geometry with an Aramis (Jobin-Yvon) spectrometer equipped with a He–Cd (325 nm) laser excitation line, a CCD camera (Synapse Horiba cooled at −70 °C) and micro-translation stages, which allowed to record spectra each 1 μm. The spectra have been recorded focusing the laser on cleaved fiber using 150 and 600 grooves/mm gratings employing a 40 × UV objective and a pinhole assuring a maximal confocal lateral resolution of 2 μm. Fig. 1b illustrates a simplified scheme of the CML set-up.

Time-resolved luminescence (TRL) spectra were recorded at RT in a 90° geometry. The excitation laser pulse was supplied by an optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser, having pulse duration width of 5 ns and repetition rate of 10 Hz. The light emitted by the fiber has been spectrally resolved by 300 grooves/mm grating. The employed spectral resolution was of about 5 nm. The detection was carried out by a gated intensified CCD camera (PI-MAX3 from Princeton Instruments) at different delay times (t_d) from the end of the laser pulse using acquisition time widths (t_w) of 0.5 μs or of 1 μs.

Photoluminescence excitation (PLE) spectra were measured by tuning the same laser equipment at different excitation energies. The reported data have been recorded using t_w of 20 μs t_d and of 0.4 μs. The signal recorded at each excitation wavelength has been divided for the laser power. Fig. 1c illustrates a simplified scheme of the set-up used for TRL and PLE measurements.

Differing from the CML measurements the recorded signals are related to the whole fiber since the laser is not focused on a specific part of the fiber cross section and it has to pass through the cladding to reach the Bi-doped core.

3. Results

The CML spectrum (*inset of* Fig. 2) recorded in the core of the as-drawn fiber under 325 nm excitation features the presence of two narrow intense emission bands peaked at ~2.67and ~2.61 eV as well as the presence of two other weaker narrow bands located at ~2.52 and ~2.47eV. Finally, another broad band peaking at ~2 eV represents the main PL contribution in terms of amplitude.

After irradiation, as illustrated in Fig. 2, the CML spectrum of the 1 MGy irradiated fiber core is mainly constituted by emission bands peaking at ~2.67, ~2.61, ~2.52, ~2.47 and ~2.33 eV. This latter band, studied in Ref. [33] cannot be clearly detected in the non-irradiated fiber. The bands peaking at 2.67, 2.61, 2.52, and 2.47 eV are labeled as E1, E2, E3 and E4 (Ei emissions). We remark that the Ei

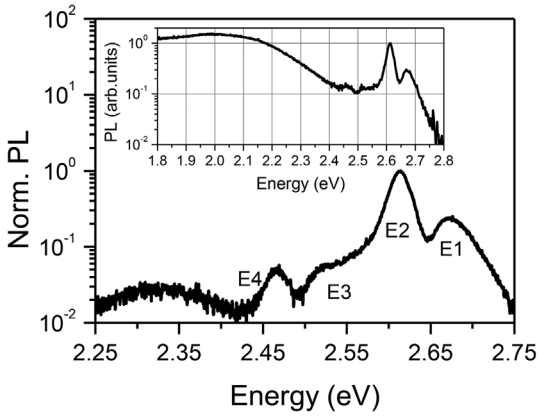

Fig. 2. Normalized PL spectrum recorded under 325 nm excitation in the core of the Bi-doped fiber irradiated at 1 MGy. The inset gives PL spectrum recorded under the same conditions for the non-irradiated fiber.