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Influence of Ce codoping and H_2 pre-loading on Er/Yb-doped fiber: Radiation response characterized by Confocal Micro-Luminescence

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ABSTRACT

Confocal microscopy luminescence measurements were applied to study the X-ray radiation response of Er/Yb-doped optical fibers in connection with H_2 pre-loading and with the addition of another lanthanide element (Cerium) in the core composition. Laser excitations at 488 nm and 325 nm allow deriving the emission and absorption pattern of Er^{3+}, the latter derived from the dips appearing in a wide luminescence band related to defects in silica. We found that the luminescence spectrum of the X-irradiated Er/Yb-doped core fiber evidences an increase in the emission intensity around 520 and 660 nm; in contrast, no changes are induced by radiation neither after H_2 pre-loading nor when the Cerium is added to the core composition. Both treatments reduce the generation of defects in the Er-doped fibers thus providing hardness in the radiative environment.

1. Introduction

Research interest in Er-doped optical fibers is strongly motivated by their practical importance as an optically-active medium of fiber-lasers and amplifiers [1]. Energetic levels of Er^{3+} embedded in silica provide multi-line luminescence in a wide spectral range, from Infrared (1545 nm) up to Visible [2], commonly used for telecommunication and in energy up-converters, respectively; thus the Er^{3+} ion results to one of the most easily pumped dopants. Co-dopants, such as Yb, are also employed as sensitizers to enhance the Er^{3+}-luminescence efficiency through a transfer process of the excitation energy between the resonant levels of these lanthanide elements [3–5]. One of most critical issues of this type of fibers concerns their characteristic of being very sensitive to ionizing radiation [6]; this contrasts with the requirement to use them in hard environments and, actually, it is at stake for their employment in several application fields (space and nuclear) [1]. The microscopic origin of photodarkening is also currently debated also in connection with the core composition [7]; in particular, it has been hypothesized that Yb plays a crucial role since ionizing radiation may change its valence [8] or induce oxygen deficient centers nearby [9]. The effort to reduce the photodarkening is, so far, centered on external treatments such as O_2 loading [9]; however those experiments remain only qualitatively interpreted.

A comprehensive understanding of mechanisms leading to material degradation is, therefore, mandatory to develop a new generation of fibers with a built-in higher resistance in radiation environments. Consequently, the use of an experimental approach combining microscopic and spectroscopic aspects is crucial to identify the optically-active centers and to assess the changes induced by radiation on the atomistic scale. In this work, we use confocal microscopy luminescence (CML) spectroscopy to investigate the role of the hydrogen pre-loading and the Ce codoping of the fiber and we demonstrate that both treatments may confer stability against ionizing radiation.

2. Experimental

We investigated two different prototypes of Er/Yb-doped optical fibers (fiber 1 and fiber 2), provided by iXFiber SAS [10] and produced by the modified chemical vapor deposition (MCVD) process. The chemical core composition of the two fibers is shown in Table 1: we stress that fiber 2 with the addition of Cerium differs radically from fiber 1. Two cm long samples of each fiber have been irradiated at room temperature with 10 keV X-rays at three different doses (50, 500 and 1000 krad) by using the ARACOR machine at the CEA DIF, France. Samples from the same fibers were H_2-loaded for 48 h at 200 bars and 85 °C; radiation exposure of theses samples was performed after several weeks to allow the H_2 outgassing. Fiber cores have been characterized by CML measurements performed with an Aramis (Jobin-Yvon) spectrometer. Excitation lines were provided by Ar^+ (488 nm) and He–Cd (325 nm) lasers, the photoluminescence (PL)

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Table 1
Core composition parameters of the two Er/Yb-doped fibers.

Sample	P (%wt.)	Er (%wt.)	Yb (%wt.)	Ce (%wt.)
Fiber 1	29.6	0.1	1.9	–
Fiber 2	26.2	0.1	0.8	0.7

spectra were analyzed by a 150 grooves/mm grating and then recorded by an intensified charge coupled device camera. We used a 40× and 50× objectives under 325 nm and 488 nm excitations, respectively; the distribution of the emitting centers along the transverse fiber cross-section was determined with a spatial resolution of about 2 μm.

3. Results

In Fig. 1 we report the emitted luminescence, normalized to maximum amplitude, from the pristine fiber cores 1 and 2 under 488 nm excitation. Both spectra are dominated by the green Er^{3+} emissions from excited levels to the ground state, centered around 490 nm ($^4F_{7/2} \rightarrow {}^4I_{15/2}$), 525 nm ($^2H_{11/2} \rightarrow {}^4I_{15/2}$) and 550 nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$), and a weak red band at 650 nm ($^4F_{9/2} \rightarrow {}^4I_{15/2}$); small relative variations are observed for the peaks at 490 nm and 550 nm: the former more intense in the fiber 2, vice versa for the latter.

Fig. 2 illustrates the changes induced by X-ray irradiation in the spectra excited at 488 nm for the two analyzed fibers. As shown in the part (a), 500 and 1000 krad X-ray doses induce the relative increase of the peak located at 520 nm, approximately 1.5 times, as well as that at 650 nm, approximately 2.2 times. In contrast, when the Cerium is added to the core composition, fiber 2 in Fig. 2(b), the four main emission bands are weakly influenced by irradiation. We note that the same stabilization effect against the X-irradiation is observed when the fibers, regardless of their core composition, were previously H_2-loaded.

In Fig. 3 are reported the PL spectra of the fiber 1, pristine and after X-irradiation, acquired under 325 nm laser excitation. These spectra evidence a wide band centered at ~390–400 nm, typical of emitting defects in silica based fibers, such as intrinsic or impurity related to Ge or P centers [11,12]. The origin of this band is not central to the purposes of the present work and, hereafter, we focus attention on its lineshape. Regardless of the treatment history (irradiation or H_2 pre-loading) of fiber 1, we observe dips due to the absorption of the emitted light; they are located in correspondence of optical transitions from ground to excited levels of Er^{3+}: 376 nm ($^4I_{15/2} \rightarrow {}^4G_{11/2}$), 406 nm ($^4I_{15/2} \rightarrow {}^2H_{9/2}$), 488 nm ($^4I_{15/2} \rightarrow {}^4F_{7/2}$) and 514 nm ($^4I_{15/2} \rightarrow {}^2H_{11/2}$). Finally, we note that in fiber 2, which is

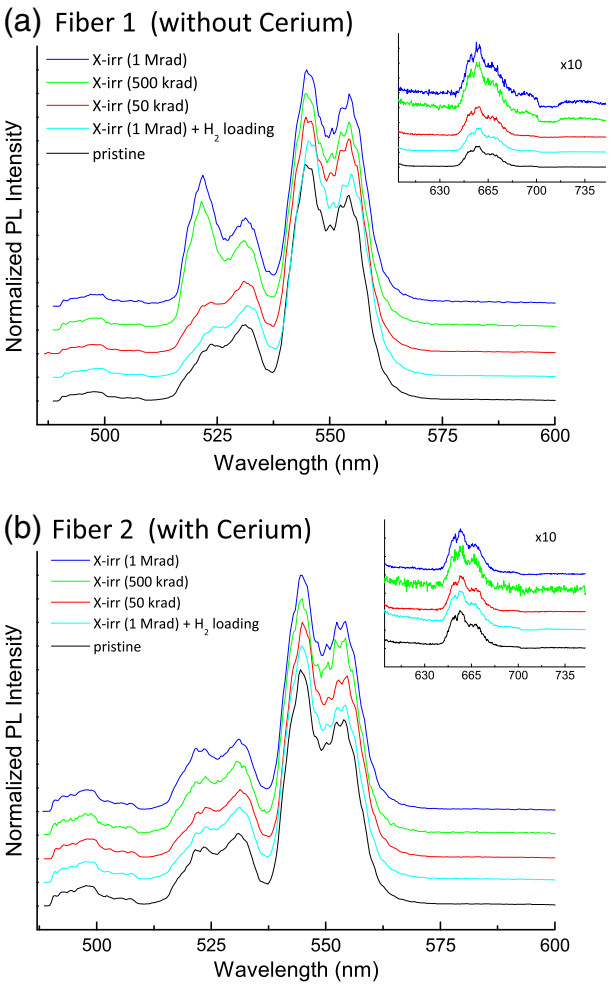

Fig. 2. Normalized CML spectra excited at 488 nm recorded in pristine fiber (black line) and after X-ray irradiation at three doses: (a) Er/Yb-doped core glass (fiber 1); (b) Er/Yb-doped core glass with additional Ce codoping (fiber 2). The inset illustrates the PL contribution at 650 nm. For the sake of clarity, the spectra are arbitrarily shifted.

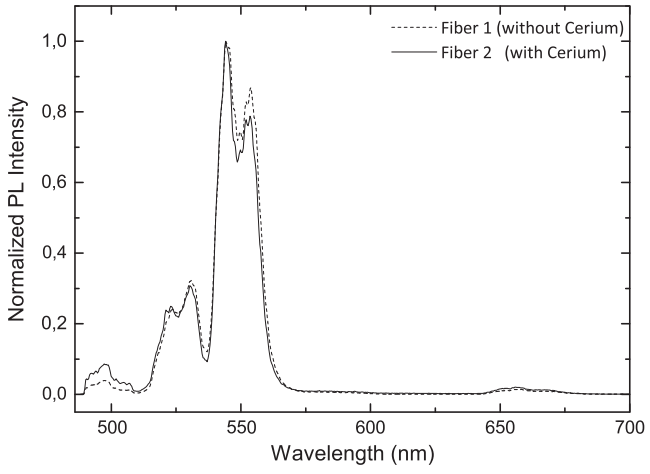

Fig. 1. Normalized CML spectra of pristine fiber cores 1 and 2 under laser light excitation at 488 nm.

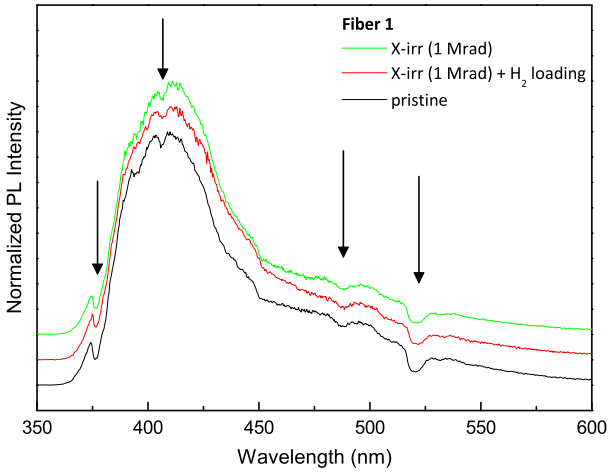

Fig. 3. PL spectra of the pristine and treated Er/Yb-doped fibers under laser light excitation at 325 nm. Arrows indicate the dips related to the absorption of the Er^{3+} ion. For the sake of clarity, the spectra are arbitrarily shifted.

co-doped with Cerium, we observe a similar PL spectrum with a much higher intensity.

4. Discussion

The above reported results indicate that the core composition of rare earth doped fibers designed for telecommunication influences their response to ionizing radiation as well as their optical properties in the visible. CML spectra of Er/Yb-doped fibers, shown in Fig. 2(a), result from an intra-center (Er^{3+}) optical process starting with the 488 nm excitation ($^4I_{15/2} \rightarrow {}^4F_{7/2}$) and evidence an amplitude change of the peaks at 520 and 650 nm after 500 krad X-ray irradiation. Such a result agrees with previous works [13] and could be interpreted as due to a variation of emission efficiency from $^2H_{11/2}$ and $^4F_{9/2}$ levels of Er^{3+}, respectively. It is worth noting that this radiation induced effect is considered relevant for its connection with the photodarkening that induce losses in the telecommunication IR region [7]. With regards to its origin, we rule out the direct interaction between the ionizing radiation and the electronic structure associated with Er^{3+}, because it should influence the whole emission spectrum to the same extent. On the other side, the spectra of Fig. 3 provide the complementary absorption features of Er^{3+} and evidence that irradiation does not affect the radiative transition from ground to excited states. Also Yb does not play a direct role since 488 nm excitation falls out of its absorption bands, both in the trivalent form in the pristine fiber and in a different valence after irradiation [14]. Then, we can assume that the local modifications of the glass structure induced by X-ray radiation (point defect generation and/or conversion) around the Er^{3+} ion favor the activation of non-radiative relaxation channels thus modifying the PL quantum efficiency from specific excited levels, such as those emitting at 520 and 650 nm. The addition of Ce to the core composition causes a hardening effect almost equivalent to that induced by H_2 pre-loading. In the latter case, it is well known that point defects generated in the silica matrix by irradiation (intrinsic such as E′ centers, nonbridging oxygen hole centers or impurity related defects) are stabilized by their reaction with mobile H_2 [15–17], thus restoring the fiber optical properties, at least in the Visible and NIR region. We observe that in the present work the radiation exposure is performed without free H_2 in the fiber core. However, hydrogen could be made available by the radiolysis of Si–H and O–H groups [16–18], most of them being formed by H_2 loading. The action of the addition of Ce is expected to be completely different from that of H_2, due to its immobility, and could be related to its multivalent state in silica glass, acting as a reducing or oxidizing element. So, as suggested by Engholm et al. [14], the formation of permanent defects in glasses is reduced because electrons or holes are easily captured at the site of these ions before they are involved in radiolysis processes.

5. Conclusions

Confocal luminescence microscopy has been successful in measuring the visible absorption/emission pattern of Er^{3+} ion in doped fibers designed to IR transmission and their response to X-ray exposure. Post-manufacturing fiber treatments, such as H_2 preloading or Cerium addition in the core composition, inhibit any changes induced by X-irradiation on optical spectra. The hardness achieved is microscopically related to the reduction of induced defects: i) by their reaction to mobile hydrogen; and ii) by the multivalence state of the Ce that acts as a capture site of electrons or holes.

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