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A NEW VISION OF PHOTODARKENING IN Yb³⁺-DOPED FIBERS

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ABSTRACT

Yb³⁺-doped fiber is one of the most promising hosts for high-power fiber lasers [1]. However, in the late 1990s, photodarkening effect, i.e., the creation of color centers induced by light, was observed and reported [2]. Like in other rare-earth-doped materials, a broad visible and near infrared absorption band appears during laser operation, which strongly lowers the laser efficiency. We show how thulium impurities, present at the parts-per-billion weights (ppbw) level in the raw doping material, can induce UV emission, which in turn creates defects responsible for photodarkening in ytterbium-doped continuous-wave fiber lasers [3]. This new vision is not in contradiction with others but it gives for the first time a possible explanation for the creation of UV defects by an infrared beam.

Keywords: photodarkening, Yb-doped fiber, Tm upconversion

1. INTRODUCTION

Ytterbium-doped fiber lasers (YDFL) are currently the preferred gain medium for high-power fiber lasers because of their high efficiency, broad gain bandwidth, and operational wavelength around 1060 nm [1]. Unfortunately, this material suffers from photodarkening (PD) effect, i.e., absorption in the visible and near infrared originating from the creation of color centers in the silica network. This problem is typically overcome by using large-mode-area (LMA) fibers [4]. But even with these fibers photo-induced absorption (PIA) has been observed [5]. Solutions to photobleach the fibers are proposed in this paper to repair the fibers, but it will still be interesting to understand the origin of the creation of these defects. In the last few years, different mechanisms have been proposed to explain the formation of color centers, among them charge transfer bands [6-8] and oxygen-deficient centers [10]. Yb-associated oxygen deficiency centers (ODC), with an absorption peak at 220 nm, were proposed as a precursor to photodarkening in Yb-doped aluminosilicate fibers [10]. Non-bridging oxygen holes [9], and even Yb²⁺-Yb³⁺ pairs [11] have also been suggested. But the question remains: how is it possible to create these defects in the visible with an IR pump? We propose here that the presence of thulium ions, even at very low concentration levels, can lead to UV light, which suggests the need to use Tm-free materials.

2. RESULTS

Two phospho-aluminosilicate fibers (3.3 w% aluminium and 1 w% phosphorus) doped with 1.7 wt.% ytterbium were studied. The usual MCVD technique followed by a soaking method was used to incorporate the ytterbium ions via a high-purity N48 (99.998%) ytterbium chloride solution into the silica matrix. The first sample is doped only with Yb and is referred to as the Yb sample. The second one is co-doped with 0.03 wt.% thulium (Yb-Tm sample). Despite the

high purity of the raw doping material (N48), the presence of impurities even in very small quantities (below 340 ppbw) could still be possible. In fact, in the “pure” Yb sample the Tm impurity has been measured at the level of 210 ppbw by induction coupled plasma spectroscopy.

As we can see in Figure 1, thulium emission bands have been identified in our two samples. Four distinct emission bands are observed across the spectral range; each of these bands is normalized to its maximum in the figure. All bands at 300 nm, 360 nm, 475 nm and 650 nm can be attributed to the presence of Tm^{3+} ions according to the spectroscopy database (see for example [12, 13]). In the literature these emissions are assigned to the $(^1I_6, ^3P_0) \rightarrow ^3H_6$; $^1D_2 \rightarrow ^3H_6$; $^1G_4 \rightarrow ^3H_6$ and $^1G_4 \rightarrow ^3F_4$ transitions, respectively. One emission band (around 520 nm) cannot be assigned to Tm^{3+} emission, but results from a cooperative process involving two Yb^{3+} ions [14]. While exciting the fiber in the IR we have not observed any emission coming from Yb^{2+} ions or from defect centers. These emissions have been seen only under UV excitation for Yb^{2+} [6] or ODC [15]. Note that we have not observed either any emission around 330 nm coming from hypothetical clusters of three Yb^{3+} .

It is interesting to note that cooperative emission of pairs of Yb^{3+} associated to 1.7 wt.% of ytterbium has the same intensity as the $^1G_4 \rightarrow ^3H_6$ emission of 210 ppbw of Tm^{3+} . This effect has been also observed by Goldner et al. [16]. The cooperative emission efficiency is very low, around $10^{-8} \text{ cm}^2/\text{W}$ [17] even if this emission is plainly visible to the naked eyes.

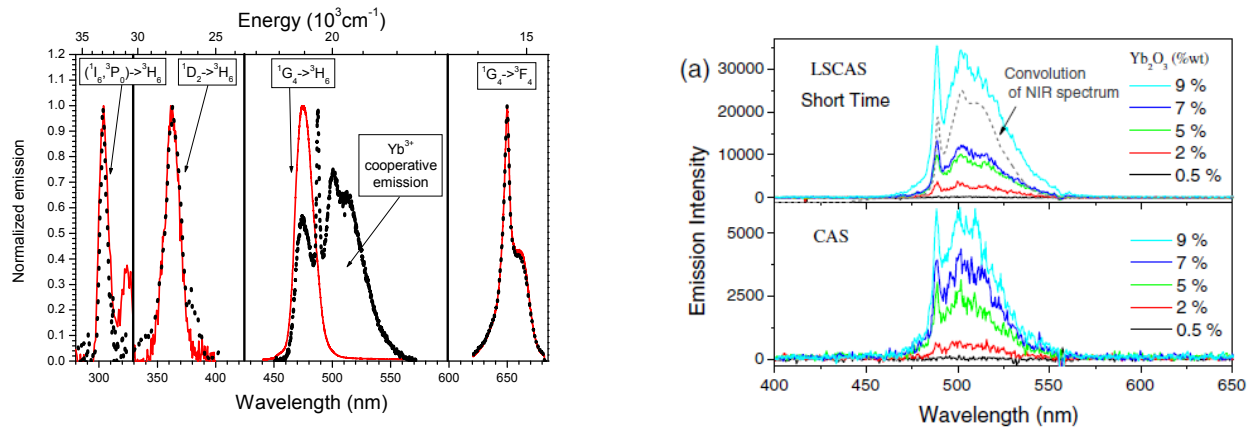


Figure 1: a) UV and visible normalized emissions of the Yb-doped sample (black dotted lines) and Yb-Tm-codoped sample (red solid lines) with 200-mW cw excitation at 976 nm; b) from [13], cooperative luminescence spectrum of the Yb in two different calcium aluminosilicate glasses.

Despite the high purity of the raw doping material (N48) used to manufacture the Yb sample, the presence of thulium contamination even in very small quantities (210 ppbw) still produces a significant light emission. The blue emission has also been attributed to thulium by Jetschke et al. [18] and it can be also clearly identified in [19-20]. The emission at 375 nm was observed in Tm-doped silica fibers by Hanna et al. [21]. But, to our knowledge, this is the first time that a UV emission around 300 nm is measured in silica glass. Nevertheless, this emission band has already been seen in polycrystalline AlF_3 particles doped with 0.2% Tm^{3+} , 10% Yb^{3+} [22] and in Tm^{3+}/Yb^{3+} codoped YF_3 nanocrystals [23]. In a Tm^{3+} -doped ZBLAN fiber El-Agmy [24] obtained a continuous-wave laser of $42 \mu\text{W}$ at 284 nm pumped with 590 mW from a Nd:YAG laser operated at $1.064 \mu\text{m}$.

Figure 2 shows a schematic energy level diagram of Tm^{3+} and Yb^{3+} ions. Depending on the Tm concentration, two different mechanisms have been proposed to excite Tm^{3+} ions up to the 1I_6 level [22-24]. For high Tm concentrations a cross relaxation (CR) process can be observed between Tm ions in addition to Yb-Tm energy transfer (ET), whereas for low Tm concentrations a 5 steps Yb-Tm ET was suggested [25], leading to the successive population of the 3H_5 , 3F_2 , 1G_4 , 1D_2 and finally the $^3P_0 \rightarrow ^1I_6$ energy levels. In addition, it was shown in [24] how increasing the ratio of Yb^{3+} to Tm^{3+}

concentrations leads to an increase in the populations of the 1I_6 and 1D_2 levels, and therefore an enhanced emission in the UV.

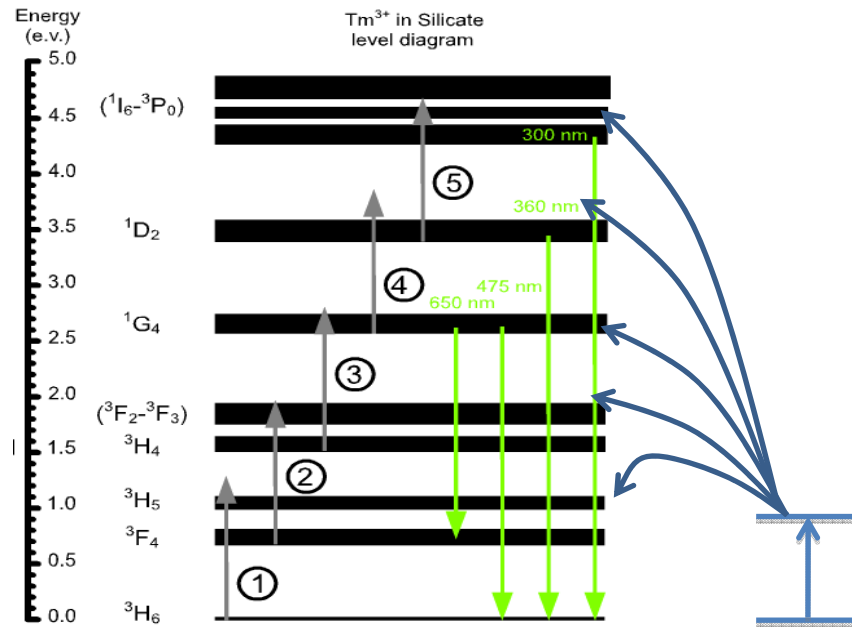


Figure 2: Schematic of the Tm^{3+} and Yb^{3+} energy levels with the different emissions observed.

UV photons are thus easily generated in a fiber thanks to Tm^{3+} ions, even at very low concentration; it is in fact possible to create defects in an optical fiber only with a UV lamp [26]. If the sample is “free” from Tm^{3+} one has to come up with another process to create UV absorption. In Figure 3, we represent schematically the commonly cited mechanism involving cooperative excitation between three Yb^{3+} ions (Figure 3a), a mechanism we deem would have an extremely low probability of occurrence, and suggest in Figure 3b a possible cooperative sensitization process. The efficiency of this second phenomenon is around 2 orders of magnitude higher than the cooperative emission [17].

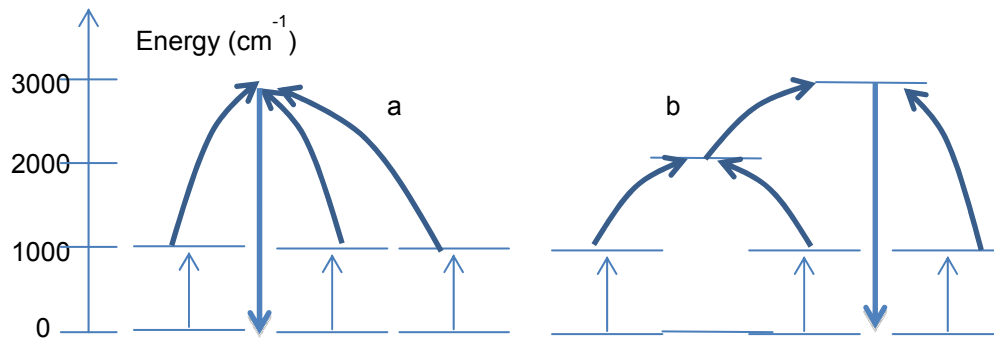


Figure 3: Mechanisms to reach the UV levels in Tm-free samples: a) cooperative emission between three Yb^{3+} ions, b) and cooperative sensitization.

We have shown [3] that photon-induced absorption (PIA) as a function of time is higher and its establishment faster in the Yb-Tm sample than in the Yb sample. The same result has been observed in figure 3b of reference [18]. In that figure, it is difficult to conclude whether there is any difference between the samples containing 0.04 and 0.08 mole ppm of Tm_2O_3 . But one can clearly see an increase in the PIA between the 0.08 and 7 mole ppm samples. Although there

is no additional measurement between samples contaminated with 0.04 and 0.08 mole ppm, the authors speculate that the thulium should not have any effect below 1 mole ppm but it can be **kept** below 0.1 mole ppm anyway.

We have used the classical stretched exponential function below to fit our data [27]:

$$\alpha(t) = \alpha_{st} \left[1 - \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right) \right]$$

where $\alpha(t)$ represents the loss induced at a time t after the pump is switched on, α_{eq} is the loss at the final equilibrium state, τ a time scale, and β the stretching parameter, respectively. Note that, as shown in [28], β corresponds to the distribution of τ among the phenomenon (or the phenomena) leading to PD.

We can see Figure 4 the different fits we have done on our data. PIA versus time is fitted with the stretched exponential function with either β free or assigning to it a fixed values namely 0.5 or 0.7 for the Yb fiber and 0.6 and 1 for the Yb-Tm fiber. It can be observed that all the fits are good.

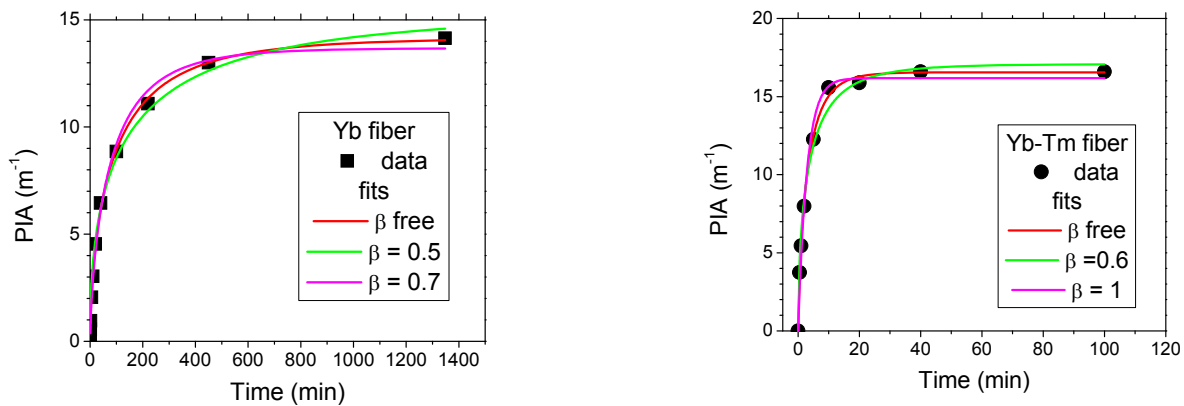


Figure 4: Different fittings of the PIA variation with time for the Yb fiber (left) and the Yb-Tm fiber (right).

Table 1: Fitting parameters for the Yb-sample.

	Value	Error	Value	Error	Value	Error
α_{st}	14.1	0.2	13.7	0.3	15.4	0.6
β	0.62	0.02	0.7	Fixed	0.5	fixed
τ	100	8	86	7	152	26

Table 2: Fitting parameters for the Yb-Tm sample

	Value	Error	Value	Error	Value	Error
α_{st}	16.5	0.2	17	0.5	16	0.4
β	0.78	0.04	0.6	Fixed	1	fixed
τ	3.3	0.2	3.8	0.5	2.9	0.3

Although we have made careful measurements to ensure equal and uniform inversion just as in [27], our stretching parameters β is not constant. Actually, adding Tm can modify the PD phenomenon not only quantitatively but

qualitatively (UV emission spectra or dynamics, for example); as a result, the τ distribution will change and so will β . This is why we think that it is really difficult to extract comparable parameters for α_{st} and τ . We can only verify in Table 1 and Table 2 that the τ factor is much higher in the Yb-Tm fiber, confirming that the PIA is faster in the codoped sample.

Another difficulty to interpret the photodarkening origins is that PIA depends on the wavelength. As we can see in Figure 5, the increase in absorption varies with wavelength.

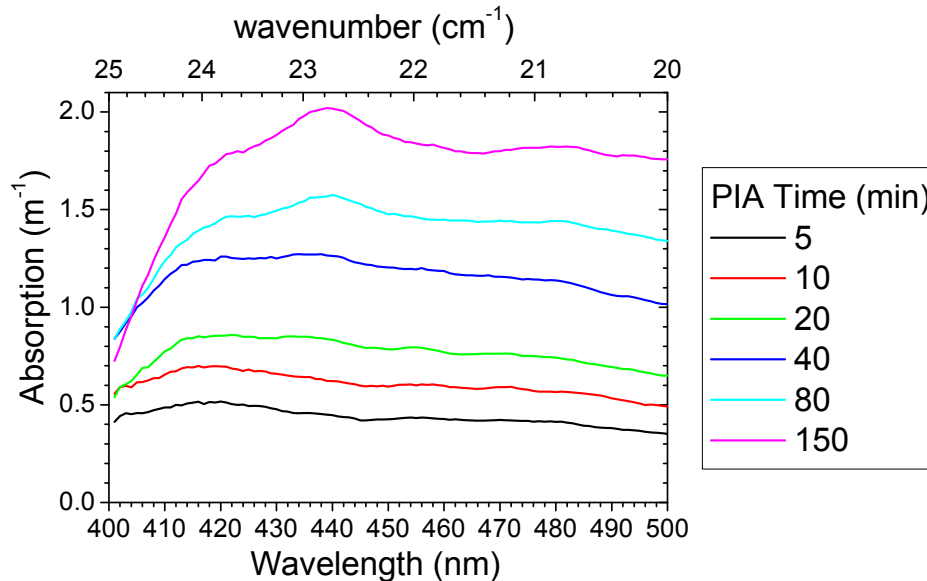


Figure 5: Absorption as a function of wavelength versus time in Yb sample

PIA is usually measured at a single probe wavelength; moving to another wavelength will change the shape of the PIA and its interpretation. In Figure 5 we can clearly see a different dynamic of evolution at 440 nm compared to 490 nm, showing for example that new defects are growing over time. We did not push this study further, but it is clear that a band appears around 440 nm, which can be attributed to the creation of ODC. Regarding the mechanism we proposed in Figure 3b, two Yb^{3+} can sensitize an ODC in the visible, then a new transfer can help reach UV levels, for example in ODC centers [10, 15].

3. CONCLUSION

Photodarkening in Yb^{3+} -doped fiber is explained by the creation of defects that absorb visible or UV light. The presence of UV photons is necessary to generate these defects. Mechanisms leading to UV photons emission are not yet fully understood. A cooperative process involving three Yb^{3+} to reach UV absorption is **highly unlikely because of the very weak efficiency of this process**. The presence of Yb^{2+} ions or silica defects such as ODC could be a part of the explanation, but these hypotheses are not easy to confirm experimentally. A cooperative sensitization of two Yb^{3+} ions using a real intermediate state in the gap could also be possible. In our samples, we have identified the UV emission of Tm^{3+} ions traces (210 ppbw). Jetschke et al. showed also the effect of Tm^{3+} ions on the photodarkening process [18] and tried to define a lower limit to the effect of trace impurities of Tm. They estimated that below 1 mole ppm, corresponding to ~ 65 ppbw, there is no detectable impact of Tm^{3+} . We think that more experiments still have to be carried out to accurately define this limit and clarify the PD dependence on Yb^{3+} concentration, on the sample composition and preparation, on the pump and signal wavelength and power, etc. Nevertheless, it is obvious that the presence of thulium helps excite UV absorption bands and accelerates the creation of defects. In a recent article, [29] we have shown how this observed impact of thulium ions is reinforced by published results, and how it can be an explanation for

discrepancies in literature. Care has to be taken to suppress thulium ions in order to reduce PD in Yb-doped fibers by using 5 or even 6N raw materials.

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