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# Experimental evidence for the formation of divalent ytterbium in the photodarkening process of Yb-doped fiber lasers

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**Abstract:** In this work we present experimental evidence that the valence instability of the ytterbium ion play a key role for the observed photodarkening mechanism in Yb-doped fiber lasers. Luminescence and excitation spectroscopy performed on UV irradiated Yb/Al doped silica glass preforms and near-infrared diode pumped photodarkened fibers show a concentration increase of Yb<sup>2+</sup> ions. A concentration decrease in Yb<sup>3+</sup> could also be observed for the UV irradiated preform. The findings contribute to an increased understanding of the kinetic processes related to photodarkening in Yb-doped high power fiber lasers.

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**OCIS codes:** (160.5690) Rare-earth-doped materials; (260.5210) Photoionization; (140.3615) Lasers, ytterbium; (140.3510) Lasers, fiber.

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## 1. Introduction

Near infrared (NIR) diode laser induced optical losses (photodarkening) in ytterbium (Yb) doped fiber lasers has been under extensive investigation during the last decade. Fiber lasers are commonly used in different industrial applications, where reliability and cost effective solutions are of key importance. Extensive efforts have been made by different research groups to investigate the physical mechanisms related to photodarkening (PD). Several routes to improve the Yb-doped glass material have also been reported including co-doping with phosphorus [1], a combination of phosphorus and aluminum [2] or cerium [3], post processing fibers with hydrogen [4] or oxygen [5]. Still, the physical origin of the pump induced losses is a subject of discussion. So far, essentially two different models have been presented in the literature, which address the fundamental kinetic processes responsible for the pump induced losses. The first model implies that the valence instability of the Yb-ion is the origin of PD where a valence state change is believed to occur through a charge transfer (CT) process [6, 7]. This will result in pair generation of divalent Yb ions together with bound hole centers, which most likely can be assigned to aluminum oxygen hole centers (Al-OHCs) [8]. The second model is related to intrinsic defects such as Oxygen Deficiency Centers (ODCs), which are believed to form during the silica preform and fiber fabrication. The ODCs are believed to act as precursors for the generated hole related color centers [5, 9, 10]. In addition, Liu et al. [11] reported on the existence of an energy transfer between the ODC(II) center and the Yb<sup>3+</sup> ion.

As the physical origin of PD is still an open question, our objective in this paper is to address the issue above concerning the valence instability of the Yb ion versus the ODC model as the primary cause of PD. Jasapara et al. [12] was one of the first to suggest that Yb<sup>2+</sup> ions are part of the PD process. Thermoluminescence measurements made by Mady et al. [13] on photodarkened Yb-doped silica preform samples also implied that Yb<sup>2+</sup> ions play an important role in the PD process. Still, conclusive experimental evidence have so far not been presented for the presence of divalent ytterbium in photodarkened near infrared (NIR) diode pumped Yb/Al doped fibers. We have performed new spectroscopic experiments to investigate the presence of Yb<sup>2+</sup> ions in UV-irradiated Yb/Al doped silica preforms as well as on NIR diode pumped pho-

photodarkened Yb/Al silica fibers. As will be shown the results are in favor for the first model above and we are indeed able to present experimental evidence for generation of divalent ytterbium in the PD process of Yb-doped fiber lasers.

## 2. Experimental

All investigated samples were fabricated by using the standard modified chemical vapor deposition (MCVD) technique as described in [14] and doped with Yb- and Al (0.2 at% / 2.18 at%). Normal (oxidizing) conditions were used during the sintering and the collapse phase of the preform fabrication process. One small piece of the preform was also post processed in a reducing atmosphere (N<sub>2</sub>/H<sub>2</sub>) at 900 °C for 5 hours. The oxidized preform was drawn into a fiber with a 20/150 μm core and cladding diameter and coated with a low index polymer cladding (Luvantix PC-373).

UV absorption was measured on a thin piece of Yb/Al silica preform by using a deuterium light source and an Ocean Optics Maya Pro spectrometer. UV irradiation experiments were performed by focusing the output of a laser driven light source (LDLS) from Energetiq and monochromator set to 210 nm with an irradiation intensity of ~0.11mW/mm<sup>2</sup>. The LDLS was also used as an excitation source in the luminescence and excitation experiments, where the emission from the preform samples was collected at right angles by using a 115 μm core optical fiber connected to an Ocean Optics USB2000+ spectrometer. Excitation spectra were measured by scanning the excitation wavelength and measuring the intensity of the emission from the preform sample by using the lock-in technique. Luminescence experiments on photodarkened fibers were made by using a single mode (SM) fiber coupled (1 mW, 405 nm) laser diode as an excitation source. The oxidized Yb/Al fiber was cladding pumped for several hours until PD saturation was reached by using a 20 W, 920nm, laser diode from Oclaro (MU20-915). A short piece of the photodarkened fiber was stripped, carefully cleaned and spliced to the SM fiber. The emission was measured perpendicular to the Yb/Al fiber by using a 115 μm core optical fiber connected to the Ocean Optics USB2000+ spectrometer.

## 3. Results and discussion

The strong absorption band observed near 240nm in Yb/Al doped silica glass, see Fig. 1 has earlier been shown to consist of several sub-bands [14] assigned to CT transitions between the Yb<sup>3+</sup> ion and the oxygen ligands. It was further shown that excitation to the first (lowest in energy) CT sub-band results in characteristic Yb<sup>3+</sup> luminescence near 1 μm, whereas excitation to the second (higher in energy) sub-band produce permanent color centers with an associated broad absorption band extending from the UV- to the NIR spectral range. A CT transition involves an interaction between the Yb<sup>3+</sup> ion and the host lattice and corresponds to the transfer of an electron from a nearby oxygen ligand to the Yb ion according to the relation:



$h\nu_{CT}$  represents the excitation energy to the different CT states and  $h_{temp/bound}$  corresponds to a temporarily formed or a bound hole, which is left behind on the oxygen ligand. A possible interpretation of the previous reported observations is that excitation to the first (lowest in energy) CT-state result in a temporal (non-stable) Yb<sup>2+</sup> ion and a localized hole ( $h_{temp}$ ) on a nearby oxygen ligand whereas excitation to the second (higher in energy) CT sub-band corresponds to the formation of a permanent (stable) Yb<sup>2+</sup> ion and a bound hole ( $h_{bound}$ ). The nature of the bound hole is most likely an Al-OHCs situated in the vicinity of the Yb ion, which has previously been identified by Arai et al. [8] in photodarkened preform and fiber samples by performing Electron Spin Resonance (ESR) measurements. Now, for a permanent Al-OHC to

form in the PD process a charge compensating (electron related) trap also need to form. Arai et al. was unable to detect any Yb-related defects in their ESR measurements and only a minor concentration increase was observed for the electron related color centers Si-E' and Si(H)-E'. Hence, the nature of the electron trap that charge compensate the Al-OHCs in photodarkened fibers is still unclear.

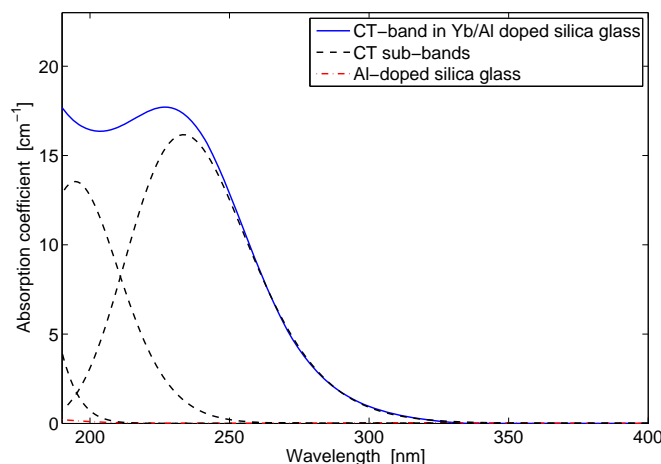


Fig. 1. CT absorption band of the 0.2 at% Yb/Al doped silica glass preform (blue solid line). The black dashed lines show a Gaussian deconvolution of CT absorption band and the red dashed-dotted line shows the absorption spectrum of a non-Yb-doped reference preform.

We have recently performed UV-irradiation experiments on Yb:YAG single crystals and could experimentally verify relation (1) above [15]. Characteristic Yb<sup>2+</sup> absorption bands are observed in UV-irradiated Yb:YAG single crystals in addition to a superimposed absorption band centered near 300 nm attributed to bound hole polarons. In the case of Yb/Al doped silica glass, on the other hand no characteristic Yb<sup>2+</sup> absorption bands, see e.g. [6] has to the best of our knowledge been observed in UV irradiated preforms or NIR diode pumped fibers. One explanation for this could be that the Yb<sup>2+</sup> related absorption bands in the UV spectral range are obscured by the broad absorption bands associated with Al-OHCs. An alternative way to possibly detect the presence of Yb<sup>2+</sup> ions in UV-irradiated Yb/Al doped silica glass or NIR diode pumped Yb/Al fibers would be through photoluminescence. Characteristic Yb<sup>2+</sup> luminescence originating from  $5d - 4f$  transitions has earlier been reported around 520 nm in Yb/Al-doped silica preforms prepared under reducing conditions when excited in the 200 - 450 nm range [16, 6]. Kirchof et al. [17] have previously observed a luminescence in the 300 - 800 nm range when exciting Yb/Al doped silica preforms with a deuterium light source. Especially, they observed an increased emission in the 450 - 800 nm range after the Yb/Al doped sample was irradiated with the deuterium light source. A good correlation with a typical Yb<sup>2+</sup> emission spectrum could, however not be identified. An emission band centered around 350 nm was also observed under UV excitation, which only marginally changed after UV irradiation. The origin of the 350 nm band was not revealed, but its existence may have hampered their interpretation of the increased emission in the 450 - 800 nm range.

To measure the potential occurrence of Yb<sup>2+</sup> ions through photoluminescence on UV irradiated samples is challenging. The fraction of Yb<sup>3+</sup> ions that will change its valency by UV

irradiation is expected to be low. Hence, the  $\text{Yb}^{2+}$  emission is weak and difficult to measure. The fraction of  $\text{Yb}^{3+}$  ions that will change its valency in a NIR diode pumped fiber is expected to be even less, making the luminescence even more challenging to measure. Still, by careful optimization of the experimental setup and by using long integration times, we could detect the presence of  $\text{Yb}^{2+}$  through emission.

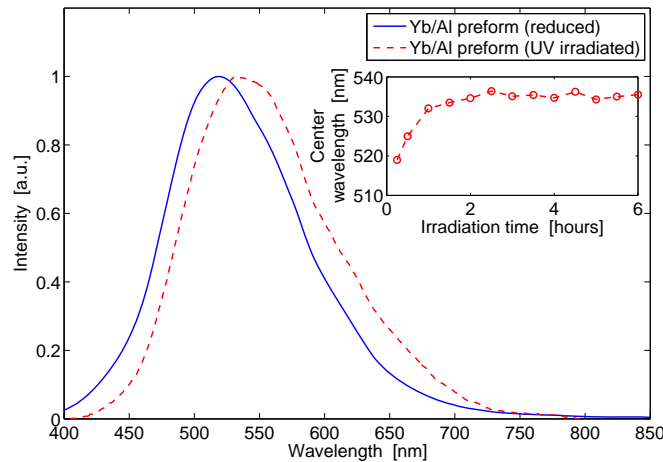


Fig. 2. Normalized luminescence from the reduced Yb/Al preform (blue solid line) and the oxidized Yb/Al preform irradiated at 210 nm for 6 hours (red dashed line). The excitation wavelength is 300 nm for both samples. The center wavelength as a function of irradiation time is shown in the inset.

Figure 2 shows a normalized luminescence spectra for the reduced Yb/Al preform sample and the oxidized Yb/Al preform sample irradiated for 6 hours at 210 nm. Although they are not identical, there is a strong similarity between the characteristic  $\text{Yb}^{2+}$  luminescence observed for the post-processed Yb/Al preform and the UV irradiated oxidized preform. The most apparent discrepancy is a small shift to longer wavelengths for the emission band of the 210 nm irradiated preform sample. The origin of this shift is most likely related to a slightly different local environment for the irradiation induced  $\text{Yb}^{2+}$  ions compared to the  $\text{Yb}^{2+}$  ions in the post-processed (heat treated) Yb/Al preform. A different local environment will change the crystal field, which in turn affects the energy level structure for the  $\text{Yb}^{2+}$  ion. Hence, a minor discrepancy, e.g. shift of the emission band between the irradiated and post-processed Yb/Al samples is not unexpected. Further investigations revealed that the center wavelength of the emission band is actually shifting to longer wavelengths during irradiation, see inset of Fig. 2. The greatest change of the center wavelength occurs during the first hour after which the center wavelength appears to stabilize around 534 nm. Figure 3 displays the integrated intensity for the  $\text{Yb}^{2+}$  luminescence as function of irradiation time. As observed in the inset of Fig. 3 a small decrease is also observed for the characteristic  $\text{Yb}^{3+}$  emission indicating a decrease in  $\text{Yb}^{3+}$  concentration, which is consistent with relation (1).

To further support the argument that the observed emission in the UV irradiated preform is related to  $\text{Yb}^{2+}$  we also measured the excitation spectrum monitored at 530 nm after the sample was irradiated for 6 hours. Figure 4 shows the excitation spectra for both the reduced and the UV irradiated Yb/Al samples in the 300 - 480 nm spectral range. The characteristic  $\text{Yb}^{2+}$  absorption bands are also included for comparison. As observed there is strong resemblance between the two excitation spectra and the characteristic  $\text{Yb}^{2+}$  absorption bands. A small shift

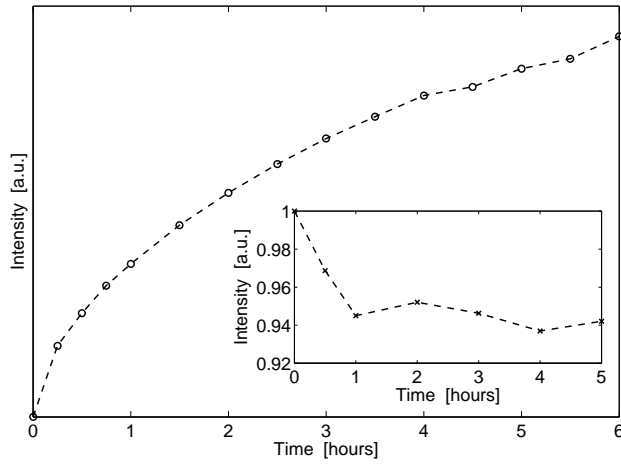


Fig. 3. Integrated intensity in the 400 - 800 nm range as a function of time for the  $\text{Yb}^{2+}$  luminescence. The integrated intensity for the  $\text{Yb}^{3+}$  emission near  $1 \mu\text{m}$  is displayed in the inset.

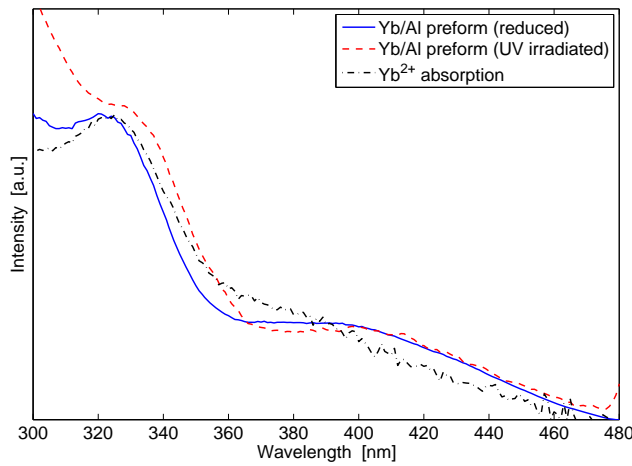


Fig. 4. Excitation spectra for the reduced Yb/Al preform (blue solid line) and UV irradiated Yb/Al preform (red dashed line) monitored at 530 nm. The characteristic  $\text{Yb}^{2+}$  absorption spectrum is also shown for comparison (black dash-dotted line).



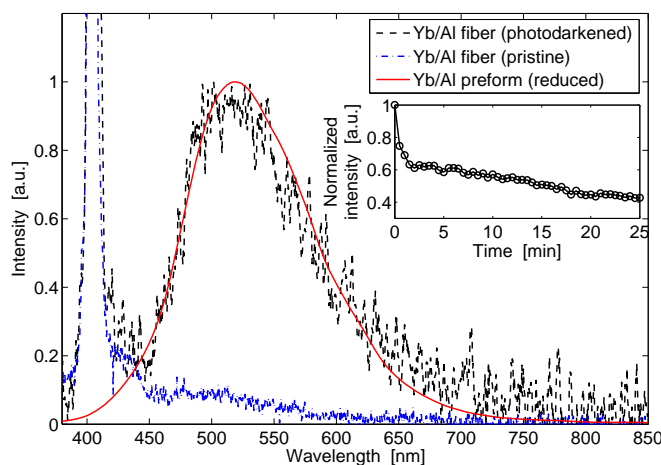


Fig. 5. Normalized luminescence from the NIR diode pumped photodarkened Yb/Al fiber excited by a 405 nm SM fiber coupled laser (black dash-dotted line) and the pristine Yb/Al fiber (blue dashed-dotted line). The reduced Yb/Al preform excited by 300 nm is shown for comparison (red solid line). The inset shows the decrease in intensity as a function of time.

to longer wavelengths is also observed in the excitation spectrum for the UV irradiated Yb/Al sample, consistent with the luminescence spectrum.

From the results above it can be concluded that  $\text{Yb}^{2+}$  ions are formed in Yb/Al doped silica glass through a CT process according to relation (1). A major question still remain: are  $\text{Yb}^{2+}$  ions also formed in the PD process of NIR diode pumped Yb/Al doped fibers? To investigate this, a short piece of the oxidized Yb/Al doped fiber was photodarkened to reach saturation by using a 920 nm, 20 W laser diode as a pump source. Due to the small dimension of the fiber core we were unsuccessful in using the LDLS as the excitation source. Instead, we used a SM fiber coupled 405 nm laser diode for these excitation experiments. According to the excitation spectrum in Fig. 4, the  $\text{Yb}^{2+}$  ions can be excited at this wavelength although it will be more experimentally challenging. UV- and visible pump sources have earlier been reported to cause photobleaching [18, 19], which means that any possible presence of  $\text{Yb}^{2+}$  in the photodarkened fiber rapidly decreases when the fiber is exposed to UV- or visible radiation. Hence, special care has to be taken in selecting the excitation power of the 405 nm laser diode in relation to the integration time of the spectrometer. Figure 5 shows the 405 nm excited luminescence from the photodarkened fiber (black dashed line). No emission was detected from the pristine oxidized Yb/Al fiber (blue dash-dotted line). As observed there is a very good correlation between the NIR diode pumped Yb/Al fiber and the reduced Yb/Al preform, which provides evidence for the formation of  $\text{Yb}^{2+}$  in the PD process. A rapid decrease in intensity is observed due to the photobleaching effect, see the inset of Fig. 5. Unlike the case of the UV irradiated preform, no shift of the emission band is observed for the NIR diode pumped Yb/Al fiber. We interpret this result as only a small fraction of the  $\text{Yb}^{3+}$  ions are converted into  $\text{Yb}^{2+}$  in the photodarkened NIR diode pumped Yb/Al fiber as compared to the UV irradiated preform.

Our results provides evidence that  $\text{Yb}^{2+}$  ions are formed in photodarkened Yb/Al doped silica fibers through a CT process. Yet a few more questions need to be considered for a comprehensive understanding of the PD phenomenon. In particular, what is the transfer route of the low energy NIR photons to the CT absorption band in the UV spectral range? It appears now that



there is common acceptance that NIR photons are transferred to higher energy states (CT-band) through some still unidentified excitation channel. Peretti et al. [20, 21] have recently observed that small impurity levels of thulium ( $\text{Tm}^{3+}$ ) constitute a path to the color center generating CT bands. In contrast, Jetschke et al. [22] implied that  $\text{Tm}^{3+}$  impurities below 1 mol-ppm should not influence the typical PD behavior in Yb/Al doped fibers. Yet another possible transfer route could be excited state absorption (ESA) from the  $^2\text{F}_{5/2}$  level [23]. The onset of a strong ESA in the visible range was observed in Yb/Al doped silica fibers with an inversion dependent absorption of several tens of dB per meter. Surely, more investigations are needed to identify the energy transfer route from the NIR range to the color center generating CT absorption bands and for a complete understanding of the PD mechanisms.

#### 4. Conclusions

To conclude, we have shown that  $\text{Yb}^{2+}$  ions are formed in a 210 nm irradiated Yb/Al doped silica preform and a NIR diode pumped Yb/Al doped silica fiber through a CT process. The presented results show a strong support for the model that the valence stability of the Yb ion play a key role for the PD kinetics in Yb-doped fiber lasers. Furthermore, the  $\text{Yb}^{2+}$  ions can act as electron traps, which can charge compensate the Al-OHCs that has earlier been identified to be responsible for the induced absorption bands in the visible- and NIR range [8].

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