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## Photodarkening of Infrared Irradiated Yb<sup>3+</sup>-Doped Alumino-Silicate Glasses: Effect on UV Absorption Bands and Fluorescence Spectra

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**Abstract:** The photodarkening phenomenon in alumino-silicate glass preforms, doped with different ytterbium concentrations, was studied. The UV band, comprised between 180 and 350 nm, was examined before and after irradiation at 976 nm. The non-linear dependence of 240 nm band with concentration after infra-red irradiation was demonstrated and ascribed predominantly to Yb<sup>3+</sup> pair's interaction. The emission spectrum after the excitation in UV spectral region showed increased intensity after photodarkening, probably due to Yb<sup>2+</sup> ions creation. Phenomenological photodarkening model and the possible existence of several defect types are presented.

**Keywords:** photodarkening; Yb-doped fibers; high power lasers

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## 1. Introduction

High power fiber lasers are attracting a lot of interest thanks to their unique combination of high efficiency and beam quality, and low maintenance costs. These characteristics made them the best choice, if compared to traditional gas and solid state lasers, for an increasing number of applications and markets [1]. However, the phenomenon of photodarkening (PD) in optical fibers was found to affect the laser performance by gradually increasing the loss during laser operation [2,3]. Though fibers with minimized photodarkening are nowadays available [4], the continuing race for higher power and the demand of custom glass compositions calls for a thorough understanding of this phenomenon.

In literature, several studies have been devoted to PD dynamics and various mechanisms have been proposed to explain the underlying structural changes occurring under intense pump photons and high power signals [5]. At present, however, none of the proposed mechanisms has been confirmed by commonly accepted experimental evidence.

A crucial role in studying the mechanism of photodarkening is played by the characterization techniques available for determining the structure of the glasses before and after irradiation. Among these ultraviolet (UV) spectroscopy was widely employed to determine the types of defects formed during irradiation [6], since photodarkening is associated to an increase in absorption at predominantly UV–VIS spectral region in Yb-doped silica glasses.

This paper aims at shedding a light into the mechanism of photodarkening by carrying out an investigation of UV absorption peaks induced in optical preforms cores under infrared irradiation. Another experiment was in the domain of fluorescence spectroscopy: the UV absorption band was excited with 230 nm light and an interesting difference in the luminescence band before and after photodarkening was observed.

## 2. Experimental Section

The preforms were prepared by means of modified chemical vapor deposition (MCVD) technique. Cylindrical cores with ~2 mm in diameter were doped with Yb<sup>3+</sup> (0.5, 1, 1.35, 1.8 wt%) and Al<sup>3+</sup> (1.8, 3.4, 3.2, 1.8 wt%) ions, correspondingly. Sliced glass samples were optically polished on both sides to a thickness of ~0.5 mm and then characterized by standard UV-VIS spectroscopy: measurements were made at room temperature for wavelength ranging from 190 to 350 nm using a double beam scanning spectrophotometer (Varian Cary 500). After the first set of absorption measurements of pristine samples, the irradiation with ~200 mW at 976 nm light followed. Each sample core was irradiated by scanning along the whole core area a SMF-28 optical fiber at a distance of about 2 mm in 3–5 days period for a total fluence of about  $3.41 \cdot 10^{23}$  photons/m<sup>2</sup>. The total absorbed energy depends on the Yb concentration and is respectively 1500 J, 3000 J, 4000 J and 5300 J for the four compositions. It was assumed that PD phenomenon reached its final, equilibrium state in each point considering our previous reports [7], *i.e.*, data obtained on the fibers fabricated from the same preforms. During 976 nm irradiation, cooperative luminescence of Yb<sup>3+</sup> was observed in all cases. Afterwards, the second absorption measurements with UV-VIS spectrometer were carried out.

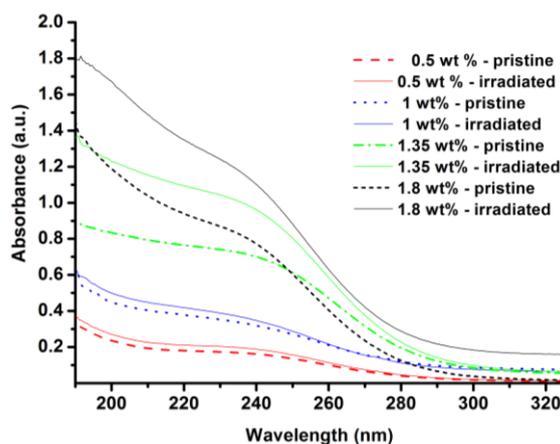
Emission spectra of preform samples were obtained using a Perkin Elmer LS 55 fluorescence spectrometer equipped with a Xenon discharge lamp as excitation, equivalent to 20 kW for 8  $\mu$ s duration. The signal was detected with a red-sensitive R928 photomultiplier. For measurements, excitation and emission wavelengths were set at 230, 350 and 900 nm, respectively. The excitation and emission slit widths were 10 nm. A high passband filter at 290 nm was used to filter out residual UV excitation photons. All measurements were performed at room temperature.

### 3. Results and Discussion

#### 3.1. UV-VIS Absorption Spectra

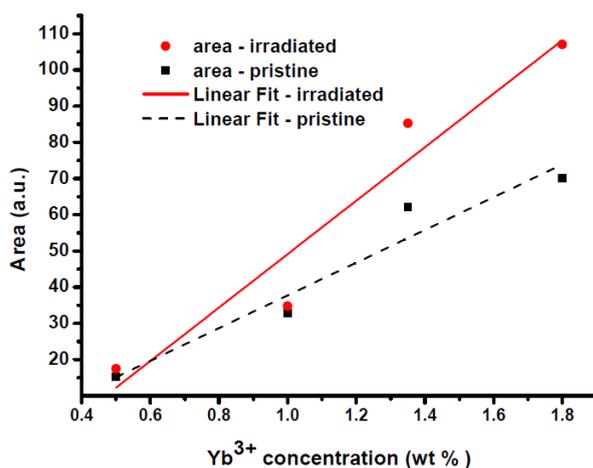
The preform samples showed in the core region wide UV absorption between 180 and 350 nm (Figure 1), characteristic for Yb and Al co-doped silica glasses [8,9].

**Figure 1.** UV absorption spectra of preforms core before and after IR irradiation.



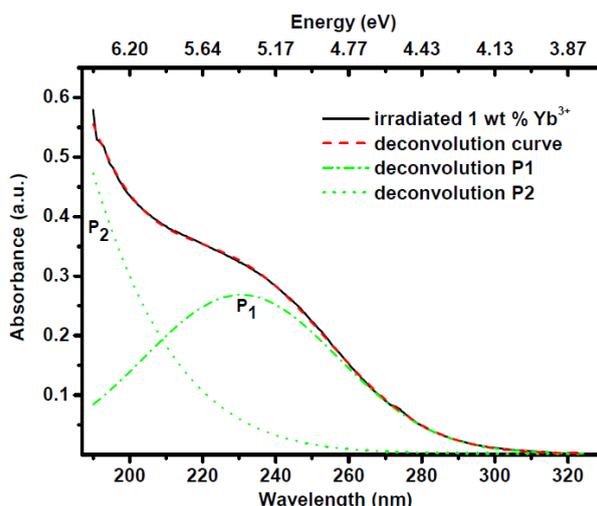
After the exposure to 976 nm irradiation, a significant increase in UV absorption spectra was observed for all samples. In particular, it is evident that the area under UV band linearly increases with increasing the Yb<sup>3+</sup> ion concentration for both, pristine and irradiated glass samples (Figure 2).

**Figure 2.** Area under UV band as a function of Yb<sup>3+</sup> concentration.



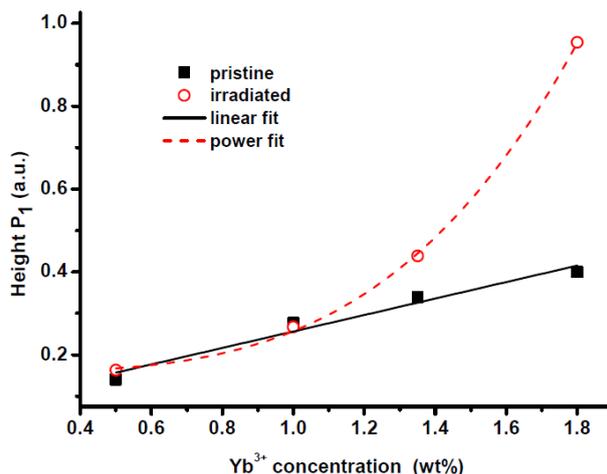
The importance of indicated UV band lays in its correlation with mechanism of PD [6,8–12]. A Gaussian deconvolution curve for irradiated 1 wt% Yb<sup>3+</sup> sample was shown in Figure 3 as an example. It is observed that Gaussian deconvolution provides two bands whose peak wavelength shifts as a function of dopant concentration and host composition. Two characteristic bands of pristine and irradiated samples were observed in the following range: P1 at 231–239 nm (5.4–5.2 eV) and P2 at 93–183 nm (13.3–6.8 eV) which yielded good correspondence with what previously reported in literature [10]. The P2 band could be due to three simultaneously excited ion pairs interaction [10] and its maximum position showed wider spectra of energies in our experiments.

**Figure 3.** Gauss curve deconvolution of UV band for 1 wt% Yb-doped preform core.



In Figure 4 the intensity of the P1 band is shown as a function of dopant concentration for pristine and irradiated samples. Fit curve for pristine set of samples, although based on only four samples, appeared as linear while for the irradiated samples non-linear with a power of 3.6. Considering literature, P1 band is dependent on host composition [9] and ascribed to different origins: simultaneous Yb<sup>3+</sup>-Yb<sup>3+</sup> pairs excitation [10], Yb<sup>3+</sup> ions and oxygen deficiency centers (ODC) [11,12], charge-transfer (CT) absorption band [9]. From Figure 4 it can be noted that P1 band depends on Yb<sup>3+</sup> concentration which is in accordance with [8].

**Figure 4.** Height of the P1 peak *versus* Yb<sup>3+</sup> ions concentration.

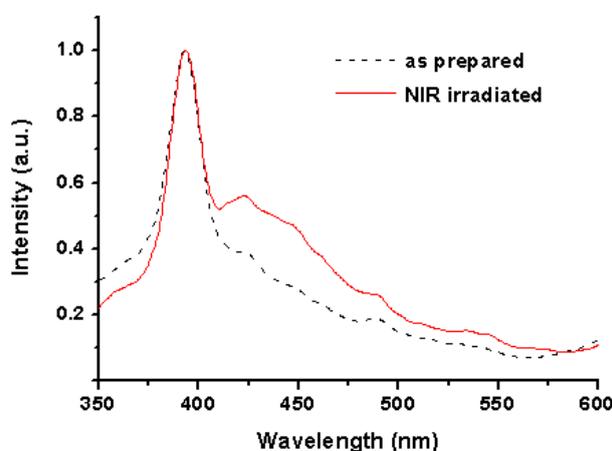


In order to explain the behavior of the P1 band, *i.e.*, difference between the linear and non-linear curves obtained before and after PD, we could suppose two different interaction regimes. In the first one, characteristic for low  $\text{Yb}^{3+}$  concentrations (0.5 and 1 wt%), the interaction among the active ions is weak and minimized by surrounding  $\text{Al}^{3+}$  ions. At higher  $\text{Yb}^{3+}$  content (samples with an  $\text{Yb}^{3+}$  content of 1.35 and 1.8 wt%), the non-linear behavior could be ascribed to one or more of the following reasons: increase of the  $\text{Yb}^{3+}$ - $\text{Yb}^{3+}$  pairs interaction [10],  $\text{Yb}^{3+}$ -neighbor interaction *i.e.*, ODC creation [13], activation of different color centers (CC) types [14] or increased phonon-electron coupling [15]. However, in Figure 4 there seems to exist a critical concentration of around 1 wt% of  $\text{Yb}^{3+}$  ions above which the non linear growth is observed for the irradiated samples: thus the nonlinear growth of P1 after the irradiation should be mainly related to the  $\text{Yb}^{3+}$ - $\text{Yb}^{3+}$  pairs interaction influenced by UV light. The increase of dopant concentration enhances cooperative luminescence (CL) which is probably one of the paths in which PD can occur [10]. CL should be involved in PD mechanism especially for higher dopant concentrations and additionally accelerate the process causing nonlinear effects [10,16]. The extension of the claim can include the change in local environment around  $\text{Yb}^{3+}$  ions. Ytterbium concentration increase can also linearly increase the number of ODC [13] or enhance the electron-phonon coupling [15] contributing to non-linear behavior as the consequence. However, exact behavior of P1 band for different dopant concentration should remain an open question since it can be strongly influenced by  $\text{Al}^{3+}$  ions content which in our case has similar, but not exact value in all samples.

### 3.2. Photoluminescence Spectroscopy upon Excitation at 230 nm

Figure 5 shows emission spectra for UV excitation at the wavelength of 230 nm of the 1 wt%  $\text{Yb}^{3+}$  doped preform slice before and after irradiation at 976 nm.

**Figure 5.** Emission spectra of pristine and IR irradiated preforms for an excitation wavelength of 230 nm. Both emission spectra are normalized to the peak at 392 nm.



The effect of irradiation consists of an increase of emission in a broad band ranging from 420 to 580 nm. Trivalent state *i.e.*,  $\text{Yb}^{3+}$  ions is energetically preferred state in oxides and fluorides [17], rather than  $\text{Yb}^{2+}$ . The charge transfer (CT) model proposed in [18] explains the PD by a CT mechanism which involves the formation of an  $\text{Yb}^{2+}$  ion and a hole polaron. Due to that, the

percentage of  $\text{Yb}^{2+}$  ions increases as PD progresses, however the number or percentage of  $\text{Yb}^{2+}$  ions is hard to predict. The CC type linked to the formation of  $\text{Yb}^{2+}$  ions could be either: AlOHC [19], NBOHC [12],  $\text{E}'$  centers and ODC [20]. Based on the literature, the increase of visible fluorescence in the range between 420 and 580 nm observed in the irradiated samples could be generated by  $\text{Yb}^{2+}$  ions. The 392 nm (3.2 eV) band which appears in pristine and photodarkened sample may be due to emission from charge transfer band to  ${}^2\text{F}_{7/2}$  level [21,22]. Another opinion present in the literature attributes the same peak to ODC [12] or ODCs influenced by glass modifiers [23] which could be created by fabrication process. The 392 nm band is also attributed to aluminum-oxygen hole centers (Al-OHCs) [10], but in this last case the presence of such defects should be supposed in the pristine samples, which in general do not show paramagnetic defects of that kind [19]. A similar emission spectrum is reported in [24] where a preform slice was irradiated with a deuterium light (characterized by a broad emission spectrum in the UV region between 180 and 370 nm, and with an intensity of about  $200 \mu\text{W}/\text{mm}^2$ ) and recently under UV irradiation [18].

Based on our previous reports [13,16] and the present study, the following phenomenological model of PD could be proposed. The 3–4 photon absorption gives adequate energy to break the connection between an  $\text{Yb}^{3+}$  ions and its neighbor and the released electron drifts to nearby available sites. The phenomenon should be taken as a cumulative effect and not individual electron picture. It means that the released electrons are synchronized with other drifted electrons (related with the number of active ions) which define currently PD rate, and the number of “available sites” given by glass matrices. The hole centers (NBOHC, ODC, Al-OHC,  $\text{E}'$  *etc.*) [15,16] can be recognized as potential sites for color center creation. These optical traps have continuous energy spectra rather than narrow, specific energy level, divided by gaps from different CC types. The relative amounts of particular types of defects depend mostly on dopant concentrations, but also on pump power and pump wavelength. The PD is strongly related to the number of dopant ions and of course, the number of CC. The “number of CC” includes all types of defects. We would suppose that an arbitrary CC type can be transformed to a different CC type and vice versa *i.e.*, number of specific defects type is time dependent although the total number of CCs can remain the same. Each type can have different impact on PD. As the consequence, it is possible that the last part of the stretched exponential curve (much longer than characteristic time “ $\tau$ ”) shows smaller PD rate since defects of a different type were created. These defects can be on higher energy level as suggested by limited bleaching at 633 nm [14] and have lower impact on PD being the absorption tail blue-shifted. In addition, the total PD loss can increase due to increase of specific CC type although the total number of CC remains the same due to CC type conversion.

The assumption of minimum two different CC in aluminosilicate fibers can be supported by the two band deconvolution of the UV band in the present study as well as with our previous study [14]. In [18] these two bands were attributed to two different CT bands. The previous assumption of continuous CC energy range can be supported with the observed shift of the  $\text{P}_1$  and  $\text{P}_2$  bands for different dopant concentrations. Furthermore,  $\text{P}_2$  band has wider energy range dependent on dopant concentration and it is related with larger number of  $\text{Yb}^{3+}$  pairs in interaction than in the case of  $\text{P}_1$  band. The reversible phenomenon to PD *i.e.*, photobleaching [13] can support the peculiar dynamics of these CC types and its evolution in time described above. Furthermore, cooperative luminescence

certainly plays a role in PD mechanism and more than one Yb-Yb pair should be involved as assumed in [10,14].

The wide emission band between 420 and 580 nm supports the picture given in the previous section where simultaneous pairs interaction is supposed. In our opinion it occurs not only due to  $\text{Yb}^{2+}$  creation, but also due to clustering of  $\text{Yb}^{2+}$  and  $\text{Yb}^{3+}$  ions. The  $\text{Yb}^{2+}$  number and the surrounding oxygen linked defects are influenced by PD phenomenon induced by 976 nm irradiation. These observations may be an evidence of the fact that PD is due to a rigid silica matrix incapable to host a large amount of RE ions and the multi-valence ytterbium nature.

#### 4. Conclusions

This paper showed characteristics of the UV spectra of aluminosilicate preforms, before and after irradiation at 976 nm. Deconvolution of the 190–320 nm UV band gave two different bands supporting the assumption of different color center types involved in photodarkening. It is demonstrated that the 240 nm band is strongly related with  $\text{Yb}^{3+}$  content and has a different nature after IR irradiation. The increase of dopant concentration also increases the number of oxygen deficiency centers. The 240 nm band showed non-linear height change with the increase of  $\text{Yb}^{3+}$  concentration after the photodarkening was induced. That could be a first evidence of a possible involvement of several  $\text{Yb}^{3+}$  pairs in PD mechanism.

In the second experiment, the emission spectrum after the excitation in UV spectral region showed increased intensity after photodarkening, probably due to  $\text{Yb}^{2+}$  ions creation and is related to  $\text{Yb}^{2+}$  and  $\text{Yb}^{3+}$  ions coexistence, *i.e.*,  $\text{Yb}^{2+}$ - $\text{Yb}^{2+}$  and  $\text{Yb}^{3+}$ - $\text{Yb}^{2+}$  ion pairs interaction. A phenomenological picture of photodarkening phenomenon was presented.

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#### Conflicts of Interest

The authors declare no conflict of interest.

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