Deep UV-induced near-infrared photodarkening of Er/Yb-doped and undoped phosphate fibers

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Photodarkening (PD) of Er/Yb-doped and undoped phosphate fibers caused by pulsed 193 nm irradiation from an ArF excimer laser to form Bragg grating mirrors is investigated. Doped and undoped phosphate fibers exhibit the same level of significant UV-induced PD loss, which is associated with the formation of a color center band at 467 nm. The UV-induced absorption extends into the NIR and creates a loss on the order of 1 dB/cm across the C-band. Photo-bleaching by a high-power supercontinuum source, and thermal-bleaching processes are performed on photodarkened samples. Both bleaching processes are found effective to fully erase the UV-induced PD loss.

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Rare-earth-doped phosphate glass (without silica) is a popular medium for high-power amplifiers and compact fiber lasers because of its higher solubility of rare-earth elements, relative to silica glass [1,2]. An additional benefit of this material is the absence of pump-induced photodarkening (PD) at near-infrared (NIR) wavelengths [3]. In this Letter, detailed results are presented about significant NIR PD caused by short wavelength ultraviolet (UV) irradiation at 193 nm, used to form Bragg grating laser mirrors in phosphate fibers, and about ways to eliminate this PD.

The PD effect, referring to light irradiation-induced absorption, has been studied in many kinds of rare-earth-doped optical fibers [4,5], mostly in Yb-doped silica and phospho–silica optical fibers, because the NIR darkening loss induced by high-power pumping severely degrades the output power and long-term reliability of high-power fiber lasers [6–9]. In addition to PD induced by pump light at 980 nm, PD was also observed to occur under irradiation at 193 and 488 nm [10,11]. Although the exact mechanism of the PD in Yb-doped silica fiber is still under debate, light-induced loss is commonly attributed to the formation of color centers by photoionization via either single- or multi-photon absorption processes, depending on the irradiation wavelength [6,11–14]. The peak absorption wavelength observed in different glasses depends on the species of color centers generated and ranges from the visible (VIS) to the UV. Invariably, all color center absorption bands show a long tail extending into the NIR, and hence, a noticeable loss is generated at the pump and signal wavelengths of Yb-doped fiber lasers. In all these silica glasses, however, the absorption decreases gradually further into the NIR spectrum and becomes negligible in the 1550 nm telecommunication window. Hence, the PD effect has not been considered detrimental to Er-doped fiber lasers operating around 1550 nm, even with Yb codopants in the fiber.

For higher power, shorter length fiber lasers made from phosphate glass with integrated Bragg grating mirrors, however, the situation is different. Since phosphate fibers lack photosensitivity in the 244 nm spectral range, commonly used to form fiber Bragg gratings, irradiation with intense 193 nm light from excimer lasers is required [15].

In this Letter, it is shown that such irradiation, even over short lengths of a few centimeters, causes broadband absorption on the order of 1 dB/cm across the whole NIR spectrum up to the C-band. This amount of loss is sufficient to be detrimental to grating-based phosphate fiber laser performance at these wavelengths [16]. Hence, the PD induced by 193 nm light is an important problem to address. The only reported work on the PD effect in phosphate glass fibers is found in Ref. [3]. They found that, even with higher doping concentrations of Yb, the phosphate fiber showed greatly reduced PD loss compared to silica fiber when pumped at 980 nm. Here, however, a significant PD in both Er/Yb-doped and undoped phosphate glass fibers under intense 193 nm irradiation is reported. It is further reported how this PD can be removed completely through both photo- and thermal-bleaching processes.

The PD experiments were performed on three types of fiber samples made from the same base glass composition (a silica-free phosphate glass similar to the one described in [17]): Er/Yb-codoped phosphate fiber, undoped phosphate fiber, and pre-annealed doped phosphate fiber. The parameters of our fiber samples are summarized in Table 1. The pre-annealed fiber is the same fiber as Er/Yb-codoped fiber, but has been annealed at 250 °C for 36 h prior to the PD experiments. This process is aimed at finding out whether the UV-induced PD requires precursors that can be thermally erased in advance. Samples of 5 cm long, phosphate glass fibers are spliced to standard single mode (CORNING SMF 28) silica fibers and side exposed to a high intensity UV beam from a pulsed 193 nm ArF excimer laser (GSI Lumonics PulseMaster 840 series) through a phase mask, in order to have the same irradiation conditions as for writing

Table 1. Phosphate Fibers Parameters

Fiber Type	Core Dopants		Pre-annealed
	Er^{3+}(ions/m^3)	Yb^{3+}(ions/m^3)	
A	1.1×10^{26}	2.15×10^{26}	No
P	None	None	No
AP	1.1×10^{26}	2.15×10^{26}	Yes

Bragg gratings. The laser delivered pulses with durations of ~20 ns at a repetition rate of 100 Hz, and the fluence per pulse at the fiber position is approximately 45 mJ/cm^2. Irradiation lengths of 2 cm are used on the samples, and the resulting UV-induced PD loss over the VIS–NIR spectral bands is measured by using a supercontinuum source with an emission from 500 to 2400 nm (NKT Photonics SuperK Compact) and 2 Optical Spectrum Analyzers (OSA1: Yokogawa AQ 6317B, wavelength range: 600–1750 nm, OSA2: Yokogawa AQ 6373, wavelength range: 350–1200 nm).

The UV-induced PD spectra of six different phosphate fibers after 500 s of exposure are demonstrated in Fig. 1. The transmission spectra are normalized to the transmission of pristine fiber samples before exposure. The spectra from OSA1 and OSA2 overlap in the common spectral range 600–920 nm, and hence, are used together to show spectra over the full range, from VIS to NIR. As seen in Fig. 1, both doped and undoped phosphate fibers, as well as the pre-annealed doped fibers all exhibit almost identical PD responses to UV irradiation. This suggests that the UV-induced PD in phosphate fibers is not due to the presence of the Er and Yb dopants. Also, the pre-annealing process has no impact on the PD, which is therefore not due to pre-existing, thermally erasable defects in phosphate glass (the high energy of 193 nm photons is sufficient to photoionize electrons in such glass). The absorption is much higher than that reported previously for longer wavelength irradiation in various kinds of rare-earth-doped fibers [6,11]. The absorption reaches ~30 dB (i.e., ~15 dB/*cm* of UV-exposed fiber) at 670 nm, and the broadband NIR loss including the C-band is ~2 dB (i.e., ~1 dB/cm). This significant C-band loss has not been observed in PD experiments with VIS or NIR irradiation, but clearly appears under 193 nm [10]. The fact that the transmission at wavelengths shorter than 670 nm falls into the noise is truly due to darkening (and not to insufficient signal of the measurement system), as indicated by the pre- and post-irradiation measurements of a sample of Fiber A, shown in the inset of Fig. 1. It should be noted that the three deep transmission dips in the spectrum of the pristine active sample correspond to the ground state absorption bands of Er ions.

In order to visualize the spectral shape of the darkening loss further in the VIS, the attenuation spectrum of the active fiber sample exposed to only 100 pulses is shown in Fig. 2. The UV-induced absorption band fits perfectly with a single Gaussian function centered at 467 nm.

Right after UV irradiation, the three kinds of photodarkened fiber samples are subjected to a photobleaching process by leaving them connected to the white light source used for the transmission measurement. The average spectral power density launched in the fiber samples is ~4.5 μW/nm. The transmission spectra of the fiber samples are monitored continuously during the process and behave similarly. Figure 3 shows three representative spectra for Fiber A: before (after 9 min), and after 40 min of photo-bleaching by the supercontinuum light. After 40 min, the transmission of the fiber is completely restored at wavelengths longer than 800 nm. In order to highlight the process dynamics, Fig. 4 shows how typical samples of the three kinds of fiber darken and recover under constant UV irradiation followed by constant supercontinuum bleaching. The small difference in the bleaching rates of the samples is caused by changes in the coupled bleaching power into the fibers. We observed that the darkening losses at different wavelengths remain proportional at all times, which points to a PD that would be due to a single species of color center for this particular band. It is important

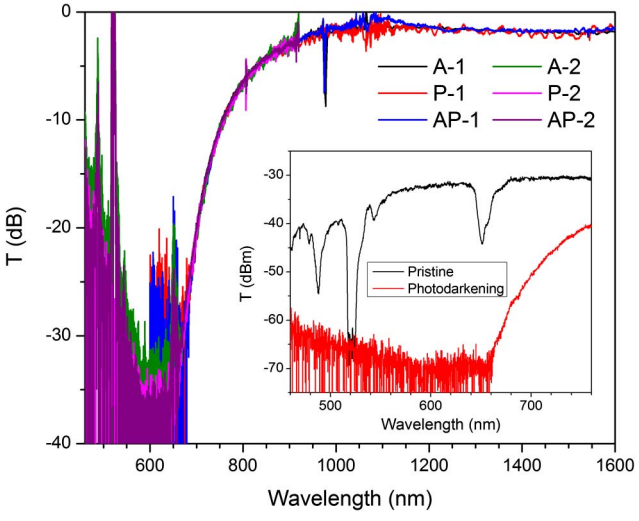

Fig. 1. Transmission spectra of photodarkened phosphate fiber samples after 193 nm irradiation (Samples A-1, P-1, and AP-1 are measured with OSA1, and Samples A-2, P-2, and AP-2 are with OSA2). The inset shows the transmitted intensity spectra of a sample of Fiber A before and after UV irradiation.

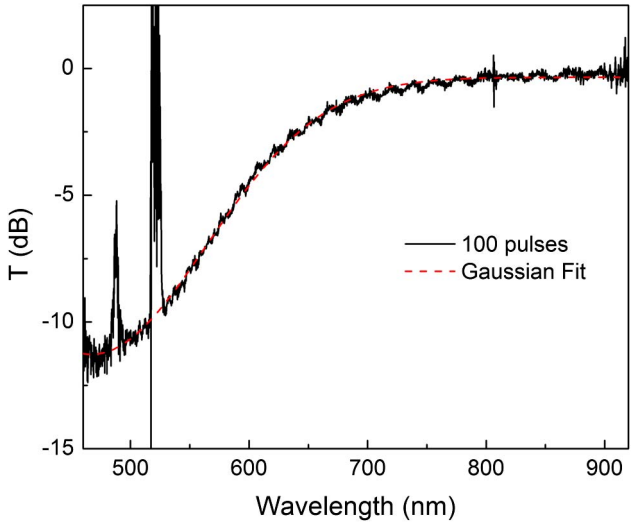

Fig. 2. PD loss spectrum of Fiber A upon 100 pulses exposure, and the Gaussian fitting.

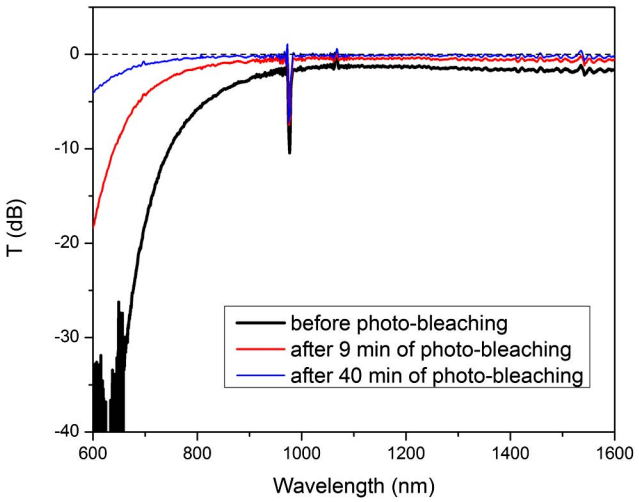

Fig. 3. Transmission spectrum of the photodarkened Fiber A before, during (9 min) and after (40 min) of photo-bleaching.

to note that, without photo-bleaching, we believe that the PD is permanent at room temperature. We measured the PD loss over several days at room temperature and found no decrease apart from some bleaching that occurs every time a spectrum is taken with the supercontinuum source. This photo-bleaching is only due to the VIS part of the supercontinuum; however, separate experiments with the VIS light filtered out by NKT Photonics SuperK SPLIT show that no bleaching occurs when the darkened sample is irradiated only by the NIR light from 1000 to 2400 nm (which includes a strong residual pump light at 1064 nm).

Another investigation concerns thermal bleaching of the PD loss, which is performed on a hot plate. The plate temperature was ramped from room temperature to 200 °C for 1 h (3600 s), after which the heat was turned off to allow the fiber to cool down. In order to avoid corrupting the thermal bleaching by photo-bleaching, only the NIR loss was monitored, using a C-band ASE source and OSA1. As we verified over a period of 4 days of continuous measurement with the ASE source, its power

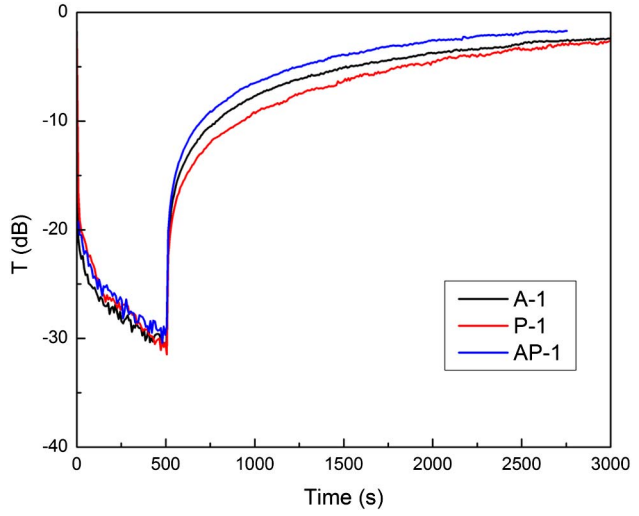

Fig. 4. Evolution of PD loss at 670 nm for phosphate fiber samples during the PD and photo-bleaching processes.

level is too low and its wavelength too long to induce photo-bleaching. The evolution of the NIR darkening losses during the thermal treatment was similar for the three kinds of fibers and a representative result for Fiber A is plotted in Fig. 5. The annealing temperature profile is plotted schematically at the bottom of the figure. The loss in that figure is obtained by averaging the nearly flat spectral response over the whole C-band. The loss completely recovers during the first hour, over which the temperature reached 192 °C. Separate experiments with the supercontinuum source further confirmed that the whole color center absorption band recovers during the process (inset of Fig. 5).

It is clear from our results that Er and Yb dopants are not responsible for PD under 193 nm irradiation in these phosphate glasses. Over the wavelength range that we can measure, a single band of nearly Gaussian shape and peak wavelength (467 nm) was observed, in close agreement to the only previous report of PD in bulk Yb-doped phosphate glasses induced by 266 nm irradiation (peak darkening at 490 nm) [3]. The choice of a Gaussian curve to fit the observed PD was just made for convenience (and good fit), allowing us to pinpoint the band center but without implication on the physical origin of the defect band. Because of the similarity of the position of the absorption band, we tentatively conclude that the mechanism proposed in Ref. [3] is the same here; namely, the color centers arise from UV photons that ionize existing precursors in the fibre host material and generate free holes and electrons, which are trapped at the defects in the glass matrix. This mechanism is also supported by the fact that shorter wavelength photons induce a much stronger defect band. Without further corroborative evidence from other diagnostic techniques, we cannot assign a particular defect state to the observed induced optical absorption band. However, the position of this absorption band is reminiscent of a phosphorus–oxygen hole center (POHC) associated group of bands

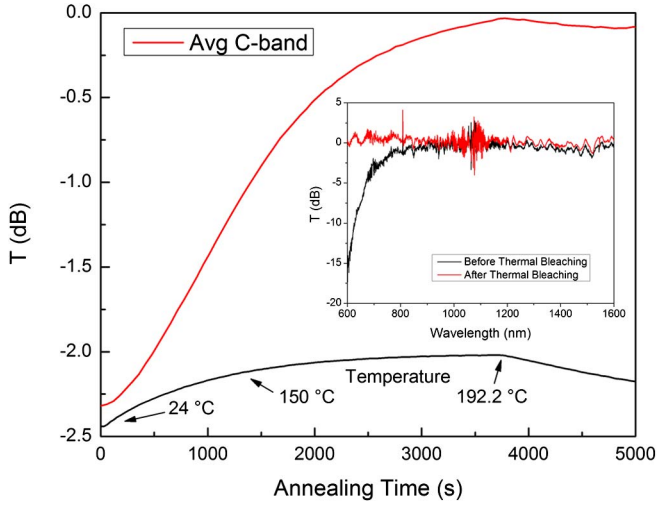

Fig. 5. Evolution of the average PD loss across the C-band of Fiber A during the thermal bleaching. The inset shows the VIS–NIR transmission spectra (normalized by the transmission of the pristine sample) of a fiber sample before and after thermal bleaching. The actual temperature profile is also shown.

that is often observed in other kinds of glasses containing large amounts of phosphorus [18,19].

Fortunately, this significant PD loss is shown to be fully erased by photo or thermal bleaching processes. What is particularly useful from a practical point of view is that, for the thermal bleaching process temperatures and durations used here, the reflectivity of FBGs written in these fibers, using the exact same irradiation conditions, actually gets stronger, as demonstrated previously [15]. This clearly indicates that the PD and the majority of the photo-induced refractive index change have different physical origins and that removing PD does not simultaneously diminish the reflectivity of FBGs. While PD and its bleaching must be accompanied by refractive index changes (through the Kramers–Kronig relations), these changes appear negligible relative to the index change (a sinusoidal refractive index variation with amplitude of 0.0001) associated with the Bragg mirrors under similar irradiation conditions, according to our observation. It is also interesting to note that somewhat similar results (thermal annealing completely erases the UV-induced PD but does not affect the reflectivity of UV-induced FBGs) were obtained recently in the alumino–silicate glass system, although for different irradiation and thermal regimes [20]. It is also worth pointing out that the presence of supercontinuum light in the fibers during the UV irradiation is not thought to have a significant increasing or decreasing impact on the PD itself, because earlier Bragg grating writing experiments (not reported here for lack of space) had similar PD without the presence of monitoring light in the fiber.

In conclusion, a significant PD effect has been observed in Er/Yb-doped and undoped phosphate fibers after 193 nm irradiation. A color center absorption band was measured with a peak near 467 nm and a long tail into the NIR that creates loss on the order of 1 dB/cm across the C-band. Fortunately the PD is quite unstable and both photo- and thermal-bleaching processes have been demonstrated to be effective in erasing the darkening loss under conditions where the grating strength of the UV-induced FBG is not diminished.

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