

Non-isothermal bleaching of Yb–Li co-doped silica fibers

Miao Li (李淼)^{1,2}, Gui Chen (陈瑰)², Jinyong Leng (冷进勇)¹, Jinbao Chen (陈金宝)^{1,*},
and Jinyan Li (李进延)²

¹College of Advanced Interdisciplinary Studies, National University of Defense Technology, Changsha 410073, China

²Wuhan National Laboratory for Optoelectronics (WNLO), Huazhong University of Science and Technology, Wuhan 430074, China

*Corresponding author: kdchenjinbao@aliyun.com

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In this work, non-isothermal bleaching of Yb–Li co-doped fiber was investigated. The Yb–Li co-doped fiber was beneficial to reduce the photodarkening-induced excess loss and had no bad effect on the temperature of thermal bleaching (TB). Photodarkened fibers were bleached with different temperature ramp rates. The higher the ramp rate, the higher the complete bleaching temperature. The activation energy of the bleaching of Yb/Al/Li fiber was calculated by fitting, which was similar to that of an Yb-doped fiber. These observations are helpful in revealing the relationship between the mechanism of Li ion co-doping and TB.

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Yb-doped fiber lasers (YDFs) have occupied the main market of high power fiber lasers^[1]. The output power of YDFs has been increased year by year. Nowadays, the output power of an Yb-doped single-mode fiber laser has exceeded 20 kW^[2,3]. However, further power improvement of YDFs faces new challenges. The photodarkening (PD) effect has become an important factor influencing the long-term stable operation and high power output of the lasers^[4]. The PD effect can lead to the decrease of output power and efficiency of high power fiber lasers in the case of pump power launching^[5]. The mechanism of PD is still inconclusive, and it is generally believed to be caused by the formation of color centers^[6,7].

In order to suppress and mitigate the PD effect, researchers proposed a variety of methods, such as photo bleaching, thermal bleaching (TB), gas pretreatment, and ion co-doping. The common wavelengths of photo bleaching include 355, 405, 543, 633, 793 nm, etc.^[4,8–10], and short wavelength photons could be used to remove the color centers. The reported gas includes O₂^[11] and H₂^[12], which could suppress the generation of oxygen deficiency centers in the fiber core. Ions commonly utilized in co-doping include Al, P, Ce, alkali metal, etc.^[13–15]. Slight differences existed in how different ions mitigate the PD effect. Generally, ion co-doping could reduce the formation of color centers. Co-doping with alkali metal ions (Na and Li) had satisfactory mitigation effects on PD and did not affect the numerical aperture (NA) and laser efficiency^[15]. Among the methods mentioned above, only TB can completely eliminate the PD-induced excess losses and restore the output power of fiber lasers with strong repeatability.

TB could be divided into isothermal bleaching^[16] and non-isothermal bleaching^[17]. The treatment of isothermal bleaching could experimentally observe the PD rate distinctly grows with temperature. The method of non-isothermal bleaching at different temperature ramp rates

could be used to determine the thermal energy distribution of PD-induced color centers. In our work, non-isothermal bleaching of Yb–Li co-doped fiber was investigated. The TB experiment on Yb–Li co-doped fibers with obvious mitigation effects on PD could not only verify the sensitivity of PD to temperature, but also analyze the thermal energy distribution of color centers. The same non-isothermal bleaching treatment was operated on Yb/Al and Yb/Al/Li fibers, and the effect of co-doped Li ions on the initial recovery and complete bleaching temperatures was studied. Photodarkened fibers were bleached with different temperature ramp rates, and the relation between ramp rate and bleaching temperature was investigated. The bleaching activation energy of the Yb/Al/Li fiber was calculated by fitting the experimental results of different ramp rates. Moreover, the relationship between the mechanism of mitigating PD by Li ion co-doping and TB was discussed.

Single-mode double cladding fibers used in our experiments were fabricated by the conventional modified chemical vapor deposition (MCVD) combined with the solution doping technique. Yb/Al and Yb/Al/Li fibers maintained the same concentration of Yb³⁺ and Al³⁺, and 0.069 wt. % Li⁺ was added in the Yb/Al/Li fiber. The diameters of core and inner cladding were 10 and 130 μm. The measured doping concentration and NAs of the two fibers are listed in Table 1. The NA of two fiber samples was 0.088 and 0.087, respectively. The difference was very slight, which could be considered as the same. Their Yb³⁺ and Al³⁺ concentrations were likewise similar.

Non-isothermal bleaching was employed in this experiment. The experimental setup is shown in Fig. 1. On the basis of the setup for PD-induced excess loss measurement^[18], a tube furnace was added around the fibers for heating. The coating of the fibers inside the furnace was stripped off completely to prevent the high temperature from damaging the coating material and

Table 1. Parameters of Fiber Samples

Fiber	Yb ³⁺ (wt. %)	Al ³⁺ (wt. %)	Li ⁺ (wt. %)	Core NA
Yb/Al	0.745	0.517	0	0.088
Yb/Al/Li	0.778	0.539	0.069	0.087

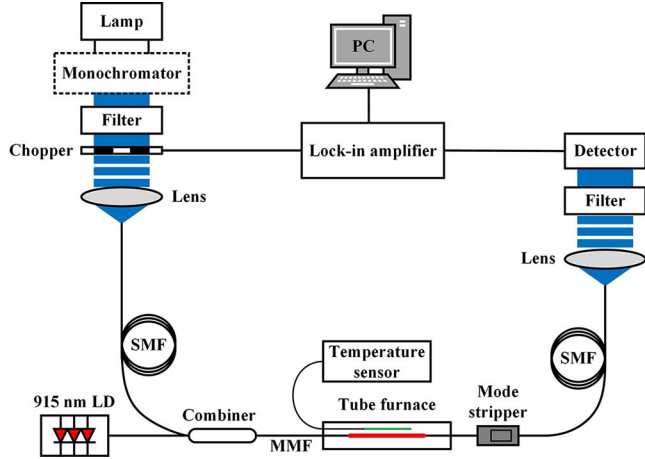


Fig. 1. Experimental setup for spectral measurements of PD and TB.

affecting the measurement results. A temperature sensor was placed in the furnace to accurately show the temperature around the test fiber in the furnace. The length of test fibers was about 10 cm. The pump source is a 915 nm laser diode (LD), and the pump power was kept 5.5 W to provide 45% population inverse.

According to the reports in Ref. [15], the Yb/Al/Li fiber can reduce the PD-induced excess loss by 25%. To make the TB processes comparable, both Yb/Al and Yb/Al/Li fibers need to have the same degree of PD. Therefore, two fibers were pumped at room temperature to produce the same PD-induced excess loss in the range of 650–1100 nm. As shown in Fig. 2, Yb/Al and Yb/Al/Li fibers finally generated the PD-induced excess losses of 71.5 and 72.7 dB/m at 702 nm, respectively. After closing the pump source, the tube furnace to heat the darkened fiber was opened, and the absorption spectrum at a certain temperature interval was measured. PD-induced excess losses could be obtained by subtracting the measured results from the initial results. The tube furnace is turned off and the complete bleaching temperature is recorded until the excess loss at the visible wavelengths decreased to 0 dB/m.

Figure 3 shows the variation of PD-induced excess loss of Yb/Al and Yb/Al/Li fibers by non-isothermal bleaching. The ramp rate adopted in this experiment was 5°C/min. By comparing the bottom x axis of the two curves, it can be observed that the heating process of the two fibers was approximately the same. The PD-induced excess losses presented a process of slowly increasing first, then

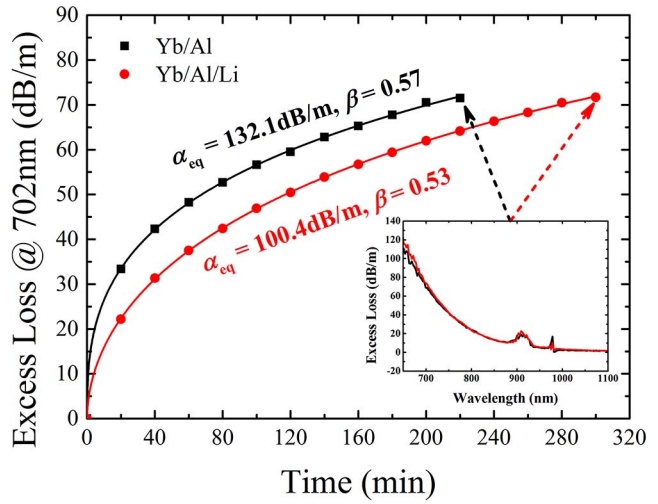


Fig. 2. PD-induced excess loss dependent on time at 702 nm of Yb/Al and Yb/Al/Li fibers. Inset: excess loss spectrum of Yb/Al (at 220 min) and Yb/Al/Li (at 300 min) fibers.

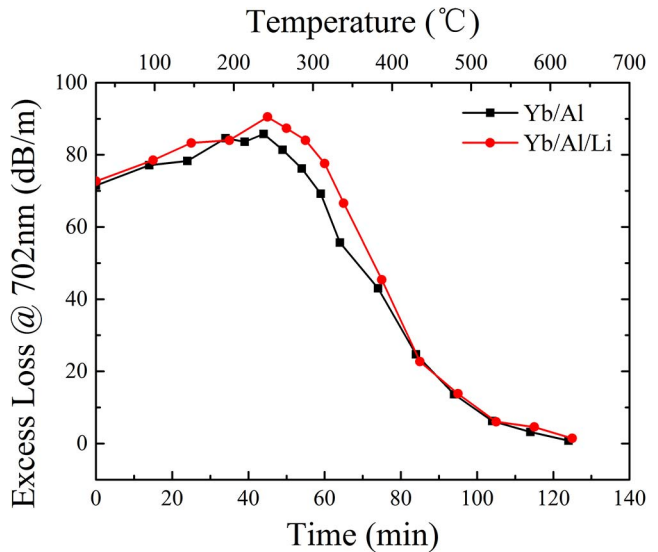


Fig. 3. Variation of PD-induced excess loss by TB at 702 nm for Yb/Al and Yb/Al/Li fibers.

rapidly decreasing, and finally reaching 0 dB/m. It was shown that increasing the temperature of a darkened fiber first resulted in a loss of enhancement resulting from a thermal activation of additional color centers^[19] and the growth of the absorption cross section of the color centers^[20] before TB dominates. When the temperature rose to a certain value, TB came into play, and the darkened fibers were completely bleached. For the Yb/Al fiber, the initial recovery temperature was 242°C, and the complete bleaching temperature was 631°C. Two characteristic temperatures of Yb/Al/Li fibers were 245°C and 614°C, respectively. Due to the low accuracy of the temperature control module of the tubular furnace, there was a certain gap between the actual heating process and the set ramp rate. Therefore, the measured temperature had

an error of $\pm 5^\circ\text{C}$. The characteristic temperatures of Yb/Al and Yb/Al/Li fibers could be considered the same. The results indicated that the Yb–Li co-doped fiber was not only useful for mitigating PD, but also had no bad effect on the temperature of TB.

Figure 4 shows the absorption spectrum of the pristine, photodarkened, thermal bleached at 614°C , and cooled to room temperature Yb/Al/Li fibers. From 650 to 850 nm, the absorption spectrum of the darkened fiber was significantly increased. When the optical fiber was heated to 614°C , the absorption spectrum decreased obviously and basically returned to the pristine fiber level. The absorption spectrum between 850 and 1100 nm in the Yb ion absorption band showed a strong temperature correlation. As reported, induced color center losses exhibited temperature-dependent spectral broadening, which might distort the absorption decay curves recorded in the course of PD measurements^[19]. Therefore, the absorption spectrum at high temperature showed a significant difference. By enhancing the temperature, the PD-induced excess loss of the Yb–Li co-doped fiber was reduced at short wavelengths (from 650 to 850 nm), while the influence of high temperature on 850–1100 nm was significantly greater than that of PD-induced excess loss.

In order to avoid the influence of high temperature on the measurement process of PD and TB, the Yb/Al/Li fiber was naturally cooled to room temperature after TB. At this time, the absorption spectrum was measured again to verify whether the PD-induced excess loss in the range of 850–1100 nm was completely bleached. As shown in the purple line in Fig. 4, not only the visible wavelength was restored to the original level, but also the near-infrared wavelength was basically coincident with the pristine fiber. It indicates that the PD-induced excess loss at the near-infrared wavelength under TB has also been bleached effectively.

Based on the above experimental results, it can be speculated that the mitigations of PD by Li ion co-doping and TB were two distinct mechanisms. The mitigation

mechanism of Li ion co-doping was to introduce more non-bridged oxygen (NBO) into the fiber core. The NBO might be captured by trivalent Yb ions to prevent the formation of ill-valenced bonds^[15]. Thus, the formation of the oxygen defect center (ODC) could be effectively reduced, thereby mitigating the PD effect. The mechanism of TB was that the bleaching activation energy produced by high temperature could eliminate the PD-induced color centers. The peak center and FWHM of the bleaching activation energy were determined by the color center. Our observations show that the ability of Li ions to introduce NBO was independent of temperature or had little effect on temperature. The co-doping of Li ions effectively reduced the formation of color centers like ODC. However, at this time, the high energy state of color centers still did not decline, indicating that there were other types of color centers existing. Therefore, the initial recovery and complete bleaching temperatures of Li-free and Yb–Li co-doped fibers were approximately the same.

In order to obtain the effect of an Yb–Li co-doped fiber on the bleaching activation energy, we conducted TB of the fibers with different temperature ramp rates. Firstly, the fiber sample (about 10 cm) was fused to the experimental system in Fig. 1. The 915 nm LD for pumping was turned on, and the PD effect in the Yb/Al fiber was induced. After darkening to a certain extent, the pump source was closed, and the PD-induced excess loss at that time was recorded. Then, the tube furnace was opened, and the ramp rate was set at $5^\circ\text{C}/\text{min}$. The temperature was gradually increased from room temperature to a certain temperature so that the PD-induced excess loss was almost eliminated. Secondly, after the whole system was cooled to room temperature, the fiber sample in the system was not changed, and the pump-induced PD effect was conducted again. After darkening to the same level, the pump source was closed, the tube furnace was opened, the heating rate was set at $10^\circ\text{C}/\text{min}$, and the above process was repeated.

Unfortunately, the precision of the heating control of the tube furnace used in the experiment is not high. When the ramp rate is set at $10^\circ\text{C}/\text{min}$, a severe mismatch between the setting temperature and the actual temperature has occurred, and the difference between the two can reach $\pm 10^\circ\text{C}$. Therefore, non-isothermal bleaching experiments for higher ramp rates (such as $15^\circ\text{C}/\text{min}$ and $20^\circ\text{C}/\text{min}$) were not carried out.

The curves of variation of PD-induced excess loss with temperature under the two ramp rates are shown in Fig. 5. The curves of the slight increase stage of the loss almost coincide, indicating that the thermal activation of additional color centers was independent of the ramp rate and only related to the temperature. For the Yb/Al fiber, the initial recovery temperature was 242°C when ramp rate $r = 5^\circ\text{C}/\text{min}$ and 251°C when $r = 10^\circ\text{C}/\text{min}$. For the Yb/Al/Li fiber, the initial recovery temperature was 245°C when ramp rate $r = 5^\circ\text{C}/\text{min}$ and 237°C when $r = 10^\circ\text{C}/\text{min}$. Within the error range, it can be

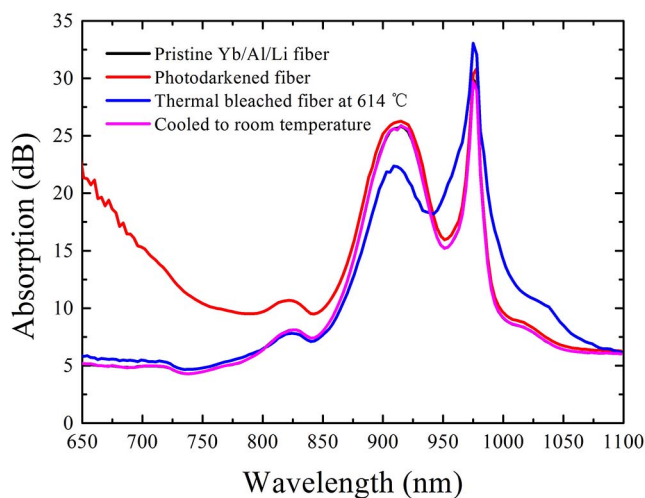


Fig. 4. Absorption spectra of Yb/Al/Li fiber.

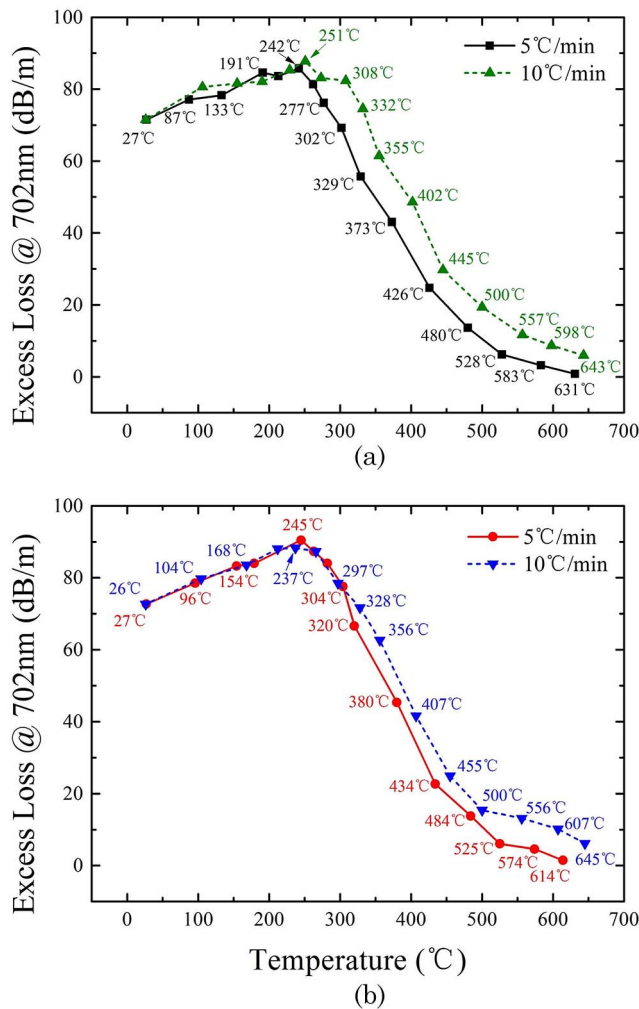


Fig. 5. Development of the PD-induced excess loss during TB with different ramp rates in (a) Yb/Al and (b) Yb/Al/Li fibers.

considered that the initial recovery temperatures were almost equal and did not vary with the ramp rate.

After the TB began, the excess loss of PD realized a rapid decline, and the decline rate was related to the ramp rate. When the Yb/Al fiber with $r = 5^\circ\text{C}/\text{min}$ reached the initial recovery temperature, the PD-induced excess loss decreased rapidly. However, the fiber with $r = 10^\circ\text{C}/\text{min}$ decreased slowly first, and the PD-induced excess loss declined rapidly after exceeding 308°C . Finally, it can be seen that the complete bleaching temperature of fiber with $r = 10^\circ\text{C}/\text{min}$ was higher than that of fiber with $r = 5^\circ\text{C}/\text{min}$.

The maximum temperature of our tubular furnace is 700°C . To ensure the safety of the experiment, the upper limit of the temperature set in the experiment was 650°C . Therefore, the Yb/Al and Yb/Al/Li fibers were not completely bleached, even when reaching the upper limit of temperature in the $r = 10^\circ\text{C}/\text{min}$ experiments. Although the experiments only measured non-isothermal bleaching at $5^\circ\text{C}/\text{min}$ and $10^\circ\text{C}/\text{min}$, the results were highly consistent with the simulation results in Ref. [17]. Due to the lack of data of $15^\circ\text{C}/\text{min}$ and $20^\circ\text{C}/\text{min}$, only $5^\circ\text{C}/\text{min}$

and $10^\circ\text{C}/\text{min}$ were selected for fitting. The activation energy of the bleaching E_A of the Yb/Al/Li fiber was calculated to be 1.262 eV by using the model in Ref. [17], which was similar to that of 1.27 eV Yb-doped fiber, indicating that the addition of Li ions did not change the activation energy required for bleaching color centers. Therefore, the Yb–Li co-doped fiber had no significant reduction effect on the complete bleaching temperature. The results further proved that the co-doping of Li ions could only reduce the color centers of ODC. However, there were still other types of color centers, so the bleaching activation energy remained unchanged, and the complete bleaching temperature did not decrease.

In conclusion, non-isothermal bleaching of an Yb–Li co-doped fiber was studied in this Letter. The same non-isothermal bleaching treatment was operated on the Yb/Al and Yb/Al/Li fibers with the same doping concentration. PD-induced excess losses presented a process of slowly increasing first, then rapidly decreasing, and finally reaching 0 dB/m. The initial recovery and complete bleaching temperatures of Yb/Al and Yb/Al/Li fibers were almost the same. The Yb–Li co-doped fiber was not only useful for mitigating PD, but also had no bad effect on the temperature of TB. Photodarkened fibers were thermally bleached with different temperature ramp rates. The higher the ramp rate, the higher the complete bleaching temperature. However, initial recovery temperatures were almost equal and did not vary with the ramp rate. The bleaching activation energy of the Yb/Al/Li fiber was calculated by fitting, which was similar to that of the Yb-doped fiber. Based on these observations, we conclude that the mechanism of mitigating PD by Li co-doping was different from that of TB. The ability of Li ions to introduce NBO was independent of temperature or had little effect on temperature. The co-doping of Li ions could reduce the color centers of ODC, but there were still other types of color centers, so the activation energy required for bleaching color centers remained unchanged.

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