

# Influence of cerium ions on thermal bleaching of photo-darkened ytterbium-doped fibers

Xiaoxia LIU<sup>1</sup>, Chaoping LIU<sup>2</sup>, Gui CHEN<sup>2</sup>, Haiqing LI (✉)<sup>2</sup>

<sup>1</sup> College of Life Science and Chemistry, Wuhan Donghu University, Wuhan 430074, China

<sup>2</sup> Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, China

© Higher Education Press and Springer-Verlag GmbH Germany, part of Springer Nature 2018

**Abstract** We studied the influence of cerium (Ce) ions on photo-darkening (PD) behavior in ytterbium/aluminum (Yb/Al) co-doped silica fibers at room and elevated temperatures. Low levels of PD was observed for Ce co-doped Yb/Al fiber. And the Yb/Al co-doped fiber was completely bleached at ~600°C. The addition of Ce ions as co-dopant can significantly lower the initial recovery and complete bleaching temperatures. The complete recovery temperature is ~450°C and ~400°C for Yb/Al/Ce low fiber and Yb/Al/Ce high fiber respectively. More importantly, Ce co-doping in Yb/Al fiber also decreases the heat-induced loss.

**Keywords** photo-darkening (PD), ytterbium/aluminum (Yb/Al) fiber, cerium (Ce) ions, thermal bleaching

## 1 Introduction

In recent years, ytterbium (Yb)-doped fiber lasers and amplifiers have been rapidly developed and widely applied in many fields, such as military, medication and industry [1]. However, with the increase of laser power, photo-darkening (PD) phenomenon has been demonstrated [2], which reduces the output power and leads to the instability of Yb-doped fiber lasers or amplifiers. Until now, the mechanism of PD is still under discussion. Several theoretical models have been proposed to explain this phenomenon, such as the oxygen deficiency center (ODC) defects [3], a charge transfer (CT) process [4] and energy transfer between Yb<sup>3+</sup> and Tm<sup>3+</sup> [5]. The excess loss induced by PD causes broad spectra absorption ranging from ultraviolet-visible (UV-VIS) to infrared (IR) region,

which increases the loss of pumping and lasing wavelengths. PD has become a main limiting factor for the further development of Yb-doped fiber lasers and amplifiers.

Up to now, several methods have been proposed to completely or partially eliminate PD induced loss, including photo-bleaching (PB), thermal-bleaching (TB), ions co-doping in Yb-doped fibers. The PB wavelengths contain near ultraviolet, visible light and near infrared wavelengths, such as 355, 550 or 793 nm [6–11]. TB is another effective method to decrease PD induced loss. At a certain high temperature, the photo-darkened fibers can be bleached to pristine state. Jasapara et al. [12] demonstrated that photo-darkened fiber returned to its pristine level at 773 K. The PD induced loss can be suppressed by TB, which was demonstrated through isothermal bleaching [13] and non-isothermal bleaching treatments [14]. But the method cannot be put into practice due to the heat damage of fiber coating. The method of ions co-doping is practicable [15–17]. Engholm et al. [15] demonstrated that cerium (Ce) ions co-doping in Yb-doped fibers effectively improved the PD resistance. Zhao et al. [17] showed that Ce co-doping in the ytterbium/aluminum (Yb/Al) co-doped fibers improved the efficiency of PB process. But there is no report about the influence of Ce ions on TB process.

In this paper, we investigated the influence of Ce ions on TB of photo-darkened Yb/Al co-doped fibers. The photo-darkened fibers were annealed by non-isothermal bleaching treatments. The results show that PD induced loss can be thermal bleached at lower temperature by the addition of Ce ions for Yb/Al fibers. Besides, compared to Yb/Al co-doped fiber, the excess loss can also be significantly decreased for the photo-darkened Yb/Al/Ce co-doped fibers at the wavelength of 702 nm by external heating. It is advantageous for the operation of high power fiber lasers. To explain our results, the effects of Ce ions on TB process were also discussed.

Received May 11, 2018; accepted June 21, 2018

E-mail: lhq@hust.edu.cn

Special Issue—Energy Optoelectronics

## 2 Experiment

The experiments were performed with Yb-doped double-cladding fibers fabricated by the modified chemical vapor deposition (MCVD) and solution-doping technique. Table 1 shows the ions concentrations in wt% of oxide for the fiber samples used in our experiments. The chemical compositions were measured on the fibers by electron probe micro analysis technique. Core and cladding diameters of all the fibers are about 10 and 130  $\mu\text{m}$ , respectively.

**Table 1** Chemical core compositions of the fibers are provided. Concentrations are in wt.% of oxide

fiber sample	[Yb]/wt.%	[Al]/wt.%	[Ce]/wt.%
Yb/Al	0.86	1.60	–
Yb/Al/Ce low	0.70	1.64	0.05
Yb/Al/Ce high	0.83	1.58	0.11

The experimental setup for PD and TB is shown in Fig. 1. A white light source (600–1750 nm) of 20 mW was utilized as the probe light. It was free-space coupled by monochromator to ensure probe wavelength light launching into the signal input end of multi-mode combiner. A 915 nm multi-mode laser diode with the diameter of 125  $\mu\text{m}$  and numerical aperture of 0.22 was spliced to the pump input end of combiner. The maximum output power of laser diode was 25 W. A 10 cm double cladding Yb-doped fiber was spliced between the output end of combiner and the cladding pump stripper (CPS). The fiber under test was fixed in a tubular furnace. The hearth temperature was uniform and a temperature sensor was set in the furnace nearby the fiber. The bleaching treatments

were executed through isothermal bleaching. The coating of test fiber inside the furnace was stripped off. The signals were real time monitored without moving the fiber with a detector and a lock-in amplifier controlled by the computer.

## 3 Results and discussion

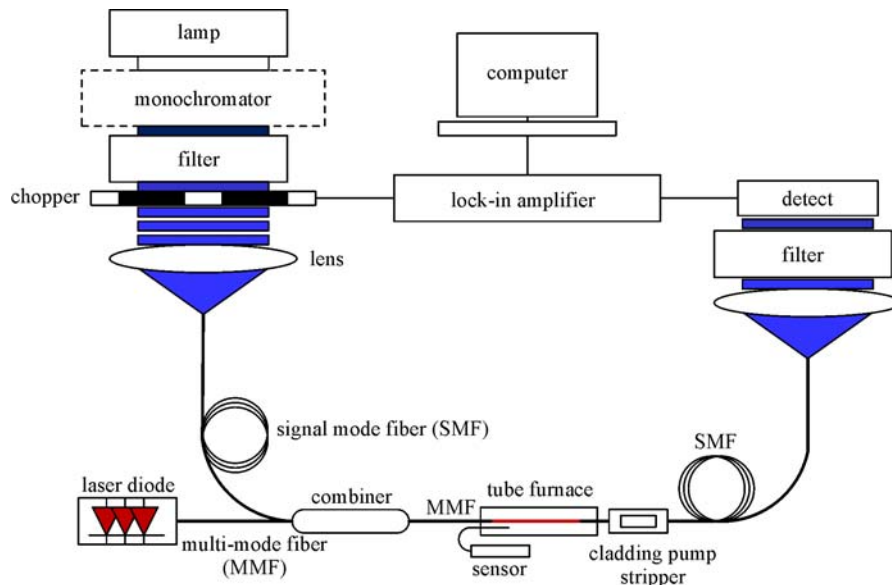
### 3.1 PD induced excess loss

Figure 2(a) shows PD induced absorption spectra between 600 and 860 nm of the three fibers after 420 min pumped by a 915 nm LD. The output power of 915 nm LD was fixed at 8 W, corresponding to a population inversion level of ~55%. It is clear that PD induced loss is larger in visible region than that in near-infrared region for all the fibers. With the increase of Ce concentration, PD induced loss gradually decreases. The variation of PD induced loss is extracted at the wavelength of 702 nm [18,19], as described in Fig. 2(b). The test results are fitted through the stretched exponential function [20] shown as follows:

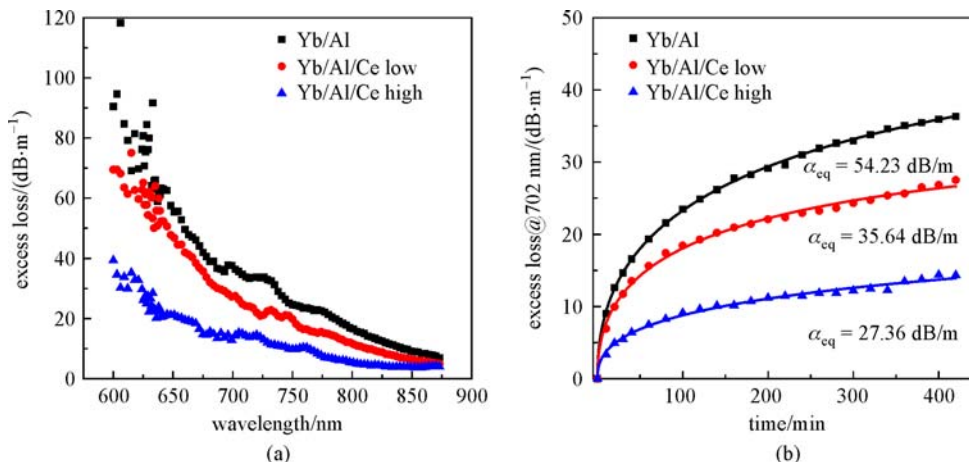
$$\alpha(t) = \alpha_{\text{eq}}[1 - \exp(-(t/\tau)^\beta)],$$

where  $\alpha_{\text{eq}}$  is the excess loss at the final equilibrium state,  $\tau$  is the time constant and  $\beta$  is the stretching parameter. The adjusted  $R$ -square  $R$  is greater than 0.99.

From the fitting results in Fig. 2(b), PD induced loss at equilibrium state is 54.23, 35.64 and 27.36 dB/m at 702 nm for Yb/Al, Yb/Al/Ce low and Yb/Al/Ce high fibers, respectively. The excess losses of appropriate 34% and 49.5% are suppressed by Ce co-doping, compared with Yb/Al fiber. Therefore, the PD resistivity in Yb/Al-doped fibers can be greatly improved by adding Ce to the core glass composition. Based on our experiments, it is



**Fig. 1** Schematic of the experimental setup



**Fig. 2** (a) PD induced fiber absorption spectra after 420 min illumination; (b) PD induced loss as a function of exposure time at 702 nm and adjustment by stretched exponentials ( $\alpha_{eq}$  equilibrium value of the induced loss)

observed that the PD resistivity can be improved even further as the Ce ions increased. It has been found both valence states (3+ and 4+) of the Ce-ion exist in Yb/Al doped silica glass prepared under normal oxidizing condition. Depending on the fraction of Ce ions in each valence state, Ce ion can reduce the number of color center by capturing both hole- and electron-related color centers [20,21]. Though high concentration Ce co-doped could further improve the PD performance by a less level formation probability of color center, the slope efficiency may be decreased.

### 3.2 Temperature effect and TB process

A 915 nm LD was utilized to pump the three fibers to generate the same excess loss 10.5 dB/m at 702 nm. Then, after switching off the pump source, the darkened fibers were heated by a tube furnace from the ambient temperature 30°C to high temperature until fiber is completely bleached.

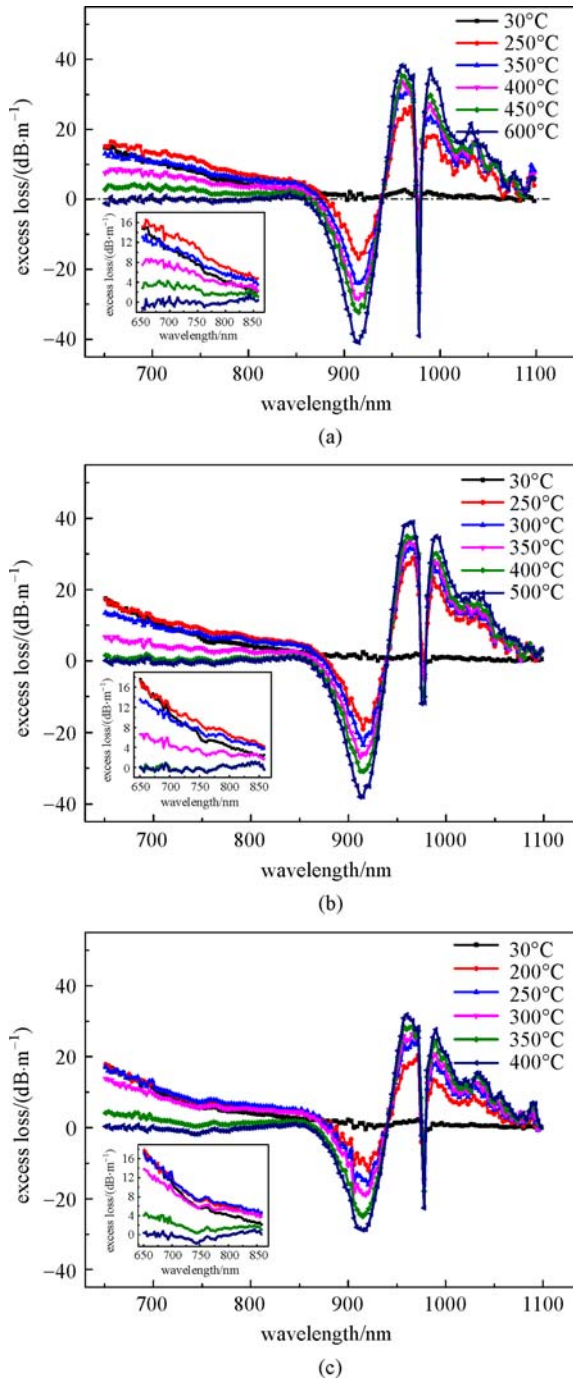
From the insets of Figs. 3(a), 3(b) and 3(c), it is found that the excess loss induced by PD can be decreased with the increase of temperature at a certain high temperature and completely bleached ultimately for three fibers at the wavelengths of 650 to 850 nm. For different fibers, the starting temperature and completely bleaching temperature are different. When the temperature is up to ~600°C, the Yb/Al co-doped fiber is completely recovered to pristine state. However, there is no need for the Ce co-doped fiber to be heated to beyond 500°C. For the Yb/Al co-doped fiber, when temperature below ~300°C, the higher temperature, the larger excess loss at the wavelengths of 650 to 700 nm. But it is almost no significantly increase for Yb/Al/Ce low fiber and no observable influence for Yb/Al/Ce high fiber.

For the excess loss in the range of 850 to 1100 nm, it is strongly temperature-dependent, as shown in Fig. 3. That

is because the test results are markedly influenced by the absorption of Yb doped fiber core while small PD induced excess loss. Since the absorption and emission cross sections of Yb ions change with the increase of temperature [22]. Absorption spectrums of Yb/Al/Ce co-doped fiber at different temperature are shown in Fig. 4. The results indicated that absorption intensity at 976 nm is almost not influenced by temperature, but the absorption width is broadened with increasing temperature. Conversely, the absorption at wavelengths from 860 to 940 nm is significantly decreased due to rising temperatures. Thus, the excess losses become smaller and smaller in this region. This way, not pay attention to the data between 850 to 1100 nm because temperature-dependent Yb absorption distorts the loss spectrum.

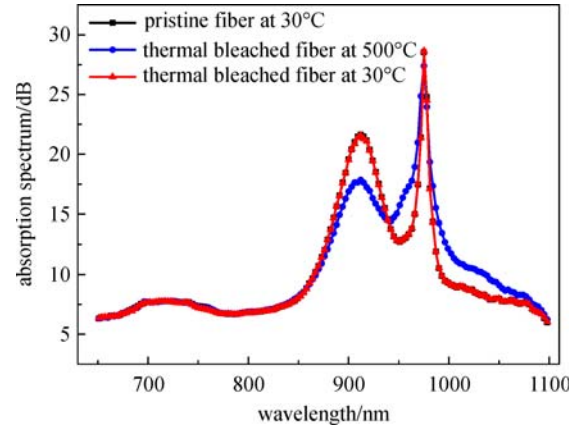
To intuitively display the variation of excess loss as the time, the excess losses at 702 nm are given for the three fibers, as shown in Fig. 5. The results show that the excess loss gradually increases from 30°C to 250°C and reaches the maximum value at 250°C for Yb/Al fiber, about 2.84 dB/m of excess loss increased. Then, the excess loss begins to decrease and is completely bleached at 575°C for Yb/Al co-doped fiber. However, the maximum heat-induced loss is 1.31 and 0.85 dB/m, and completely bleached temperature is 420°C and 400°C, for Yb/Al/Ce low fiber and Yb/Al/Ce high fiber respectively. Therefore, with the increase of Ce concentration in Yb/Al co-doped fiber, the completely bleaching temperature and the heat-induced loss have gradually decreased.

On the basis of our bleaching experiments, it clearly shows that PD induced loss is a balanced dynamically. This is a kind of spontaneous relaxation processes, involving hole and electron centers. After the 915 nm LD switched off, the color centers formation gets the advantage within certain temperature range. Under action of heat activation, the precursor species transform to color centers, leading to heat-induced excess loss. It is similar to the results

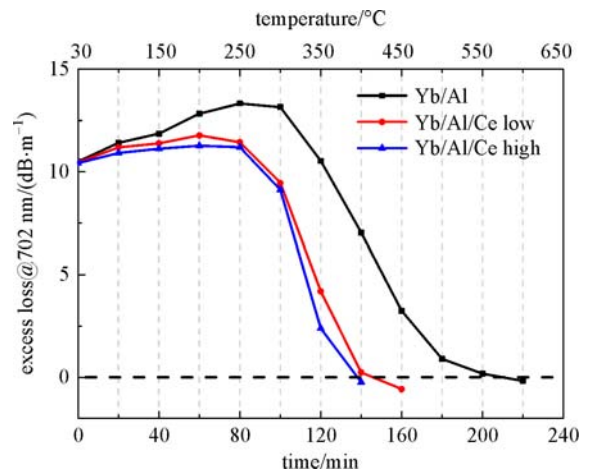


**Fig. 3** Absorption spectra at different temperatures for (a) Yb/Al fiber, (b) Yb/Al/Ce low fiber, (c) Yb/Al/Ce high fiber. The insets of (a), (b), (c) display an increase of excess loss between 650 and 850 nm

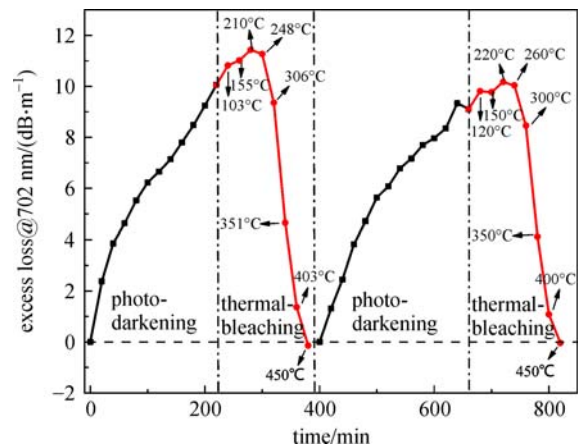
obtained in Ref. [23]. Ce ions have the potential to trap a hole or electron inhibiting the color center generation [24,25], and lower competitive edge of the formation of color centers. Consequently, the maximum excess loss enhanced by external heating is lower in Yb/Al/Ce co-doped fiber compared with Yb/Al co-doped fiber. When



**Fig. 4** Absorption spectra of Yb/Al/Ce low fiber



**Fig. 5** Variation of PD induced loss by thermal bleaching at 702 nm for Yb/Al fiber, Yb/Al/Ce low fiber and Yb/Al/Ce high fiber



**Fig. 6** Evolution of PD induced loss by the illumination of 915 nm LD and thermal bleaching at 702 nm for Yb/Al/Ce low fiber

the temperature reaches a certain value, a new balance has been emerging. With temperatures rising further, the action

of thermal bleach have started to appear. We observed that the initial and complete bleaching temperature are lower for Yb/Al/Ce co-doped fiber than for Yb/Al co-doped fiber, and the span of temperature is narrower. Thus, we speculate, the addition of Ce ion may reduce the mean value and the full width at half maximum of a Gaussian distribution thermal activation energy of PD induced color centers.

Then, the Yb/Al/Ce low fiber was photo-darkened and thermal-bleached alternately. Figure 6 depicts the changing process of excess loss at 702 nm. Repeatable processes of PD and thermal bleaching have been observed. It is obvious that the PD induced loss can be completely bleached by TB process repeatedly. We conclude that Ce ion could be a good co-dopant of Yb/Al fibers for high power fiber lasers and amplifiers, considering their thermal characteristics of PD.

## 4 Conclusion

We have measured and analyzed PD thermal characteristics of two Ce concentrations Yb/Al/Ce fibers in comparison with an Yb/Al fiber, including their spectroscopic properties and loss characteristics. First, PD induced loss significantly decreases at the equilibrium state with the increase of Ce concentration in Yb-doped fibers. Secondly, as Ce content increases, PD induced loss is initially and completely bleached at lower temperature in Yb/Al/Ce co-doped fibers. Thirdly, the heat-induced loss vividly decreases from 2.84 dB/m in Yb/Al co-doped fiber to 0.85 dB/m in Yb/Al/Ce low co-doped fiber at the wavelength of 702 nm. The experiment results may indicate that Ce ions can promote the transformations from color centers and darkening precursor species to defect precursors. The detailed theoretical explanation needs to be further researched, which is valuable to interpret similar phenomena. The addition of Ce ions in Yb/Al fiber reduces the difficulty of TB process and maximum excess loss enhanced by external heating, making it could be a really attractive option for PD reduction to apply in high power fiber lasers.

**Acknowledgements** This work was financially supported by the National Natural Science Foundation of China (Grant No. 61735007), and The Youth Fund of Wuhan Donghu University (No. 2017dhzk009).

## References

- Richardson D J, Nilsson J, Clarkson W A. High power fiber lasers: current status and future perspectives. *Journal of the Optical Society of America B, Optical Physics*, 2010, 27(11): B63
- Paschotta R, Nilsson J, Barber P R, Caplen J E, Tropper A C, Hanna D C. Lifetime quenching in Yb-doped fibres. *Optics Communications*, 1997, 136(5–6): 375–378
- Yoo S, Basu C, Boyland A J, Sones C, Nilsson J, Sahu J K, Payne D. Photodarkening in Yb-doped aluminosilicate fibers induced by 488 nm irradiation. *Optics Letters*, 2007, 32(12): 1626–1628
- Engholm M, Norin L, Åberg D. Strong UV absorption and visible luminescence in ytterbium-doped aluminosilicate glass under UV excitation. *Optics Letters*, 2007, 32(22): 3352–3354
- Peretti R, Jurdyc A M, Jacquier B, Gonnet C, Pastouret A, Burov E, Cavani O. How do traces of thulium can explain photodarkening in Yb doped fibers? *Optics Express*, 2010, 18: 20455–20460
- Manek-Hönninger I, Bouillet J, Cardinal T, Guillen F, Ermeux S, Podgorski M, Bello Doua R, Salin F. Photodarkening and photobleaching of an ytterbium-doped silica double-clad LMA fiber. *Optics Express*, 2007, 15(4): 1606–1611
- Piccoli R, Gebavi H, Lablonde L, Cadier B, Robin T, Monteville A, Goffic O L, Landais D, Méchin D, Milanese D, Brand T, Taccheo S. Evidence of photodarkening mitigation in Yb-doped fiber lasers by low power 405 nm radiation. *IEEE Photonics Technology Letters*, 2014, 26(1): 50–53
- Guzman Chávez A D, Kir'yanov A V, Barmenkov Y O, Il'ichev N N. Reversible photo-darkening and resonant photo-bleaching of ytterbium-doped silica fiber at in-core 977-nm and 543-nm irradiation. *Laser Physics Letters*, 2007, 4(10): 734
- Piccoli R, Robin T, Brand T, Klotzbach U, Taccheo S. Effective photodarkening suppression in Yb-doped fiber lasers by visible light injection. *Optics Express*, 2014, 22(7): 7638–7643
- Gebavi H, Taccheo S, Tregoaat D, Monteville A, Robin T. Photobleaching of photodarkening in ytterbium doped aluminosilicate fibers with 633 nm irradiation. *Optical Materials Express*, 2012, 2(9): 1286
- Zhao N, Xing Y B, Li J M, Liao L, Wang Y B, Peng J G, Yang L Y, Dai N L, Li H Q, Li J Y. 793 nm pump induced photo-bleaching of photo-darkened Yb<sup>3+</sup>-doped fibers. *Optics Express*, 2015, 23(19): 25272–25278
- Jasapara J, Andrejco M, DiGiovanni D, Windeler R. Effect of heat and H<sub>2</sub> gas on the photo-darkening of Yb<sup>3+</sup> fibers. In: *Proceedings of Conference on Lasers and Electro-Optics/Quantum Electronics and Laser Science Conference and Photonic Applications Systems Technologies*. Long Beach, CA, USA: IEEE, 2006, CTuQ5
- Leich M, Jetschke S, Unger S, Kirchoff J. Temperature influence on the photodarkening kinetics in Yb-doped silica fibers. *Journal of the Optical Society of America. B, Optical Physics*, 2011, 28(1): 65
- Leich M, Röpke U, Jetschke S, Unger S, Reichel V, Kirchoff J. Non-isothermal bleaching of photodarkened Yb-doped fibers. *Optics Express*, 2009, 17(15): 12588–12593
- Engholm M, Jelger P, Laurell F, Norin L. Improved photodarkening resistivity in ytterbium-doped fiber lasers by cerium codoping. *Optics Letters*, 2009, 34(8): 1285–1287
- Sakaguchi Y, Fujimoto Y, Masuda M, Miyanaga N, Nakano H. Suppression of photo-darkening effect in Yb-doped silica glass fiber by co-doping of group 2 element. *Journal of Non-Crystalline Solids*, 2016, 440: 85–89
- Zhao N, Wang Y B, Li J M, Liu C P, Peng J G, Li H q, Dai N L, Yang L Y, Li J Y. Investigation of cerium influence on photodarkening and photo-bleaching in Yb-doped fibers. *Applied Physics A*, 2016, 122(2): 75

18. Koponen J, Laurila M, Söderlund M, Ponsoda J J M I, Iho A. Benchmarking and measuring photodarkening in Yb doped fibers. In: Proceedings of SPIE 7195, Fiber Lasers VI: Technology, Systems, and Applications. San Jose, California, USA: SPIE, 2009, 71950R
19. Chen G, Xie L, Wang Y B, Zhao N, Li H Q, Jiang Z W, Peng J G, Yang L Y, Dai N L, Li J Y. Photodarkening-induced absorption and fluorescence changes in Yb fibers. Chinese Physics Letters, 2013, 30 (10): 104208
20. Cicconi M R, Neuville D R, Blanc W, Lupi J F, Vermillac M, de Ligny D. Cerium/aluminum correlation in aluminosilicate glasses and optical silica fiber preforms. Journal of Non-Crystalline Solids, 2017, 475: 85–95
21. Lupi J F, Vermillac M, Blanc W, Mady F, Benabdesselam M, Dussardier B, Neuville D R. Steady photodarkening of thulium aluminosilicate fibers pumped at 1.07  $\mu\text{m}$ : quantitative effect of lanthanum, cerium, and thulium. Optics Express, 2017, 41(12): 2771
22. Jetschke S, Unger S, Röpke U, Kirchof J. Photodarkening in Yb doped fibers: experimental evidence of equilibrium states depending on the pump power. Optics Express, 2007, 15(22): 14838–14843
23. Peng X, Dong L. Temperature dependence of ytterbium-doped fiber amplifiers. Journal of the Optical Society of America B, Optical Physics, 2008, 25(1): 126
24. Söderlund M J, Montiel i Ponsoda J J, Koplów J P, Honkanen S. Heat-induced darkening and spectral broadening in photodarkened ytterbium-doped fiber under thermal cycling. Optics Express, 2009, 17(12): 9940–9946
25. Sylvia J, Sonja U, Anka S, Martin L, Matthias J. Role of Ce in Yb/Al laser fibers: prevention of photodarkening and thermal effects. Optics Express, 2016, 24(12): 13009



**Xiaoxia Liu**, associate professor of Wuhan Donghu University, received the Master's degree in Materials Science from Wuhan University of Technology, Wuhan, China, in 2004. In the post-graduate stage, she mainly studied the transmission of ultraviolet laser hollow-core fiber system. From 2004 to 2005, she was engaged in the Research and Development department of Shenzhen Jinke special materials Co., Ltd. In 2006, she moved to Wuhan Donghu University. Her research interest includes the

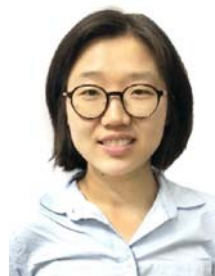
research and development of photoelectric materials and active fiber. Prof. Liu authored and co-authored more than 15 journal and conference papers. She has participated in more than 5 research projects.

Email: [xiaxiaoliu@126.com](mailto:xiaxiaoliu@126.com)



**Chaoping Liu** received her Master's degree from Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, China, in 2017. Her research interests include rare earth doped fiber.

Email: [849736882@qq.com](mailto:849736882@qq.com)



**Gui Chen** received her Ph.D. degree from Wuhan National Laboratory for Optoelectronics (WNLO), Huazhong University of Science and Technology, China, in 2014. Now she works toward Postdoctor in WNLO. Her research interests include rare earth doped fiber, design optimization and high power fiber laser system.

Email: [Chen\\_Gui@hust.edu.cn](mailto:Chen_Gui@hust.edu.cn)



**Haiqing Li**, optical engineer of Wuhan Optoelectronic National Laboratory, received the Master's degree in Optical Engineering from Huazhong University of Science and Technology, Wuhan, China, in 2013. From 2001 to 2008, she was engaged in the Research and Development department of optical fiber technology and new optical fiber products at Fiberhome Telecommunication Technologies Co., Ltd. In 2008, she was recruited as engineer by Huazhong University of Science and Technology. Her research interest includes high power fiber lasers, active fiber and large mode area optical fibers.

Email: [lhq@hust.edu.cn](mailto:lhq@hust.edu.cn)